

# Effect of Temperature Variation on the Copper Slag Flotation at Aurubis-Bulgaria

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**ABSTRACT:** A laboratory-scale study investigating the effect of pulp temperature on copper recovery during slag reprocessing by flotation operated at the Aurubis-Pirdop copper smelter in Bulgaria was conducted.

Temperature variations in the range of 15 to 35 °C have been investigated to follow up grade and recovery of copper and iron during rougher and scavenger stages without modifying the reagent suite as used at the plant. In parallel to the laboratory tests, plant survey has been realized to trace pulp physicochemical parameters (DOD, Eh, pH, conductivity). The data collected during the plant survey have been compared to the one registered during the laboratory tests.

Kinetics and grade-recovery curves for the Cu-bearing phases (metallic and sulphide Cu) and iron have been drawn as function of the various temperatures. Automated mineralogy analysis has been realized on copper, iron, and gangue minerals (fayalite, quartz) to find out the liberation degree of the copper bearing phases, their morphology and composition.

Ultimately, it has been established that elevated temperatures (35 °C) favor both higher grade and recovery of Cu-phases when compared to the rest temperature conditions being tested (15, 20, 25 °C). The reasons for occasional copper losses in the tailings during the winter periods are discussed on that basis.

**Keywords:** copper slag, flotation, quantitative mineralogy, grade-recovery, temperature variation

## INTRODUCTION

While copper production relies in majority on flotation of sulfide-bearing polymetallic ores, slags from the subsequent pyrometallurgical process could serve as additional source for copper recovery (Sibanda et al., 2020). During the

pyrometallurgical processing of valuable metals like copper, byproduct notably known as slag is generated. Sustainable metallurgy focuses on recovering, reusing, and recycling valuable materials from waste residues, including slags. Research findings indicate various valorization options

for slags, such as utilization in civil engineering, fertilizer production, road construction, and landfilling, contributing to environmentally responsible metal production (Shamsuddin, 2021). Slags from copper refining contain a relatively high amount of copper in metallic form, but also as oxides and sulphides, with other non-ferrous metals being likewise present.

The copper smelter in Pirdop, Bulgaria, operated by Aurubis Bulgaria AD, valorizes the generated copper slags using flotation as main process aiming at maximizing copper recovery and utilization. Despite extensive research on the influence of pulp chemistry during sulphide ores flotation (Adam et al., 1984; Bruckward et al., 2011; Gonçalves et al., 2003; Greet et al., 2004; Huang & Grano, 2005a and b; Grano, 2009; Ekmekçi et al., 2005), the role of temperature variation in flotation of copper slags remains poorly documented.

Previous observations (Pashkevich, Li, & Waters, 2022) suggested that temperature fluctuations affect grade, recovery and selectivity in flotation. However, there is a lack of comprehensive documentation on the temperature effects when copper slag flotation is concerned. While temperature fluctuations and their impact on the flotation of pyrite have been intensively studied (O'Connor & al., 1984; O'Connor & Mills, 1990), the broader scope of driving mechanisms affecting flotation has not been adequately explored. The main objective of the present work is to investigate the influence of temperature variation on the flotation of the copper slags generated at Pirdop smelter. This study aims to fill the existing literature gap by providing an added support on the influence of temperature variation during the flotation of copper slags, thus contributing with insights into the cross-border aspects of mineral processing and metallurgy of non-ferrous metals.

## **AURUBIS BULGARIA COPPER SMELTER, PIRDOP**

The pyrometallurgical process at Aurubis plant in Bulgaria commences with blending and drying copper concentrates before entering the flash smelter, ultimately yielding copper matte with around 64% Cu. This matte is transformed into high-purity blister copper, further refined to 99.5% Cu anodes. The off-gas system controls and manages the emissions from the smelter and converter sections; sulfur-containing gasses are used to produce sulfuric acid. The copper anodes undergo electrorefining inside a tank house operated under controlled conditions. The tank house belonging to the cathode production line, is dedicated to copper electrorefining bringing high-grade (99.99% Cu) cathodes.

Iron silicate slags, produced by flash smelting and converting are sent after being cooled and blended to the processing plant, where they undergone size reduction and flotation. Chemical reagents involving collectors (xanthogenate) and frother are added at the various stages to facilitate flotation. The flotation plant with an annual capacity of approximately 900000 tons produces final copper concentrate, grading about 20–27% Cu. Further on, the copper concentrate is recycled back into the furnace as a blend with raw (mineral) copper concentrates. The overall process enables production of high-purity copper products through sequence of metallurgical process units and operations, as shown in the flowsheet (Figure 1).

## **EXPERIMENTAL**

### **Sampling**

Approximately 150 kilograms of copper slags were sourced for the current study at Pirdop plant site. The material was sampled from the cyclone overflow stream after the Autogenous Mill. The sampling campaign lasted 4 days, during which samples were collected ten times per day in buckets, with each bucket collected 20 minutes after the previous one. After overnight drying at 105 °C, around 4 kg of dry sample was left in each bucket out of the initial mass of 12–12.5 kg. Mixing and quartering of the collected slags took place at Aurubis R&D laboratory on site, resulting in 14 bags with lots of 10.5 kg each, plus a sample lot of 5 kg. The 14 bags were then shipped to the University of Liege, while the 5 kg sample remained at Pirdop for comparative cross-check assays with the results obtained in Liege.

### **Batch Flotation Tests**

#### **Grinding**

The grinding tests were done with a sample of 1.4 kg which was obtained by sub-sampling of the feed using riffle splitters. The grinding/milling under lab conditions aimed to generate granulometry and  $P_{80}$  of the ground slag similar to the one coming out from the autogenous mill stage at the plant. For this purpose, 1.4 kg of copper slag and 1400 mL of tap water were added to a laboratory ball mill ‘Magotteaux,’ leading to a prepared slurry of 30% w/w solids. The grinding media consisted of approximately 20 kg forged steel balls of 34 mm diameter. The ball mill calibration tests indicated that grinding duration of 16 minutes was required to achieve the granulometric target of  $D_{80}$  38  $\mu$ m.

#### **Flotation**

Flotation was performed using a bottom-driven laboratory Magotteaux Floatcell® fitted with a 5-L cell. Air injection is

realized from the bottom thanks to the valves located below the rotor. Agitation was kept constant at 900 rpm for all the tests. Air flow rate was fixed at 15 L/min. Values for pH and Eh were constantly monitored. The flotation sequence followed the steps described in Table 1.

The reagents used have been the same as the ones employed at Aurubis flotation plant, namely Potassium Isobutyl Xanthate (PIBX) as collector and Dowfroth 200 E as frother. For the collector, 1% fresh solution was prepared on a daily basis by diluting 2 g PIBX in 200 mL deionized

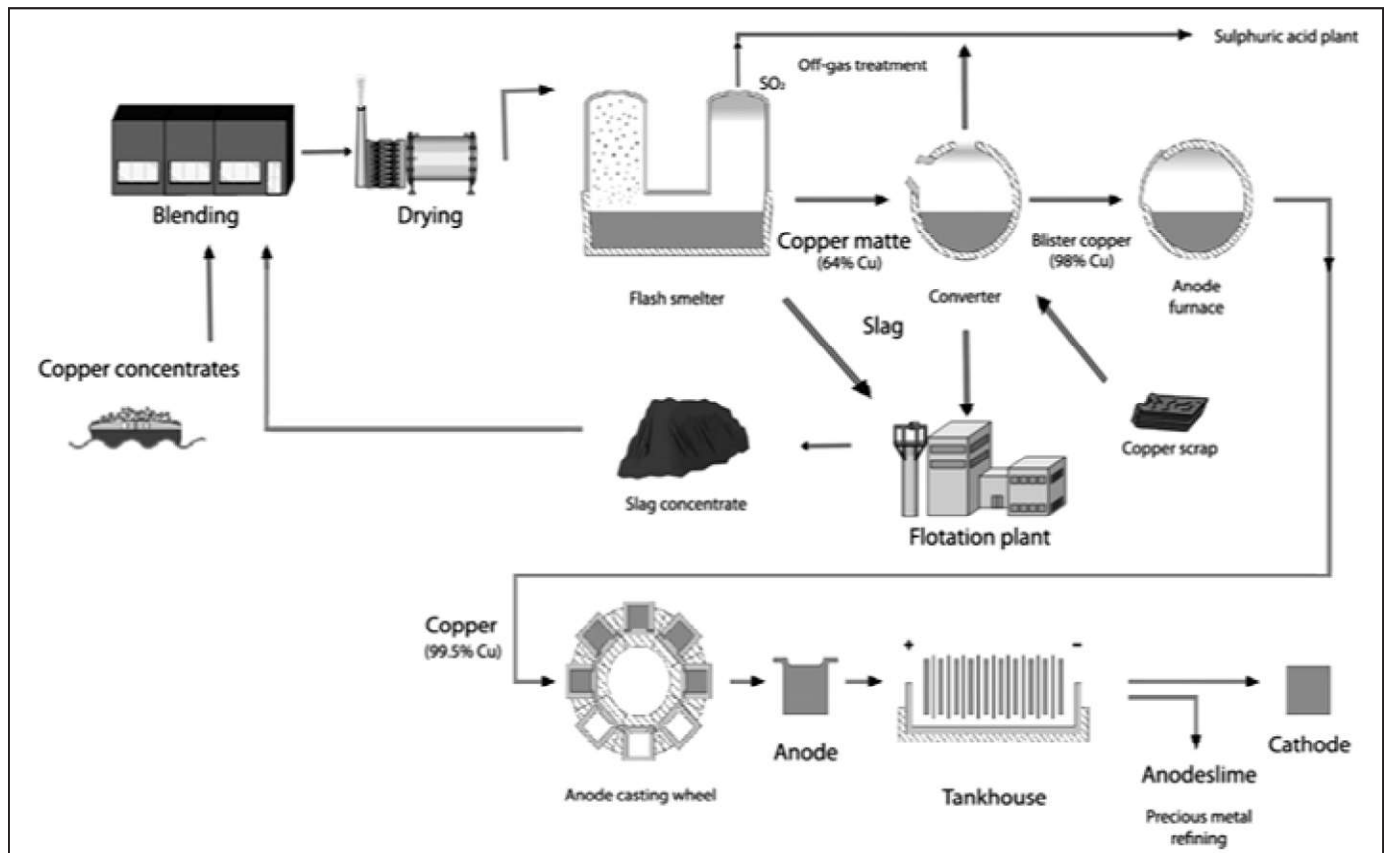


Figure 1. Production process of copper refining in Pirdop’s processing facilities

Table 1. Reagents suite and flotation procedure designed in accordance with Aurubis processing plant flowsheet. Cond. = conditioning, Conc. = concentrate

Step	Reagents		Duration, min		
	PIBX, mL	Dowfroth (drops)	Grinding	Conditioning	Flotation
<b>Grinding</b>			16		
	*pulp heating/cooling without reagents			20	
<b>Cond. rougher</b>	29			2	
		14		1	
<b>Conc. 1</b>					1
<b>Conc. 2</b>					2
<b>Conc. 3</b>					3
<b>Cond scavenger</b>	7			2	
		3		1	
<b>Conc. scav.</b>					5
<b>Total</b>	36	17	16	*26	11

\*In case no heating or cooling performed on the pulp, overall conditioning time was equal to a total of 5 min (1+2+3) before flotation begin.

water. The suggested collector dosage was 260 g/t corresponding to 16.4 mL for 1.4 kg of ore. Out of this quantity, 80% (29.12 mL) was added at the rougher and the rest (7.12 mL) at the scavenger flotation stage. Frother dosage of ca. 30 g/t was followed and accordingly 14 drops were added at the rougher and 3 at the scavenger stage, with each drop weighting 4.4 mg.

Conditioning of the pulp prior to addition of the reagents was carried out as follows. Hot water of about 60 °C was added into the flotation cell together with the ground pulp from the mill. Warm air was blown from outside to maintain pulp temperature at the desired levels. For the tests at low temperatures, ice sockets stored in advance inside a freezer were placed into the cell, as illustrated in Figure 2. Before addition of the reagents, the white ice socket (on the left) was removed, and cold water with temperature of 4–6 °C was used to compensate the volume, as well as wash water to skim the froth fraction.

To reach statistical representativeness, the tests were repeated for each temperature (15, 20, 25, 30 and 35 °C), with the rest parameters being kept constant. Therefore the reported data present a mean from the duplicated tests. From each flotation test, five products were recovered in

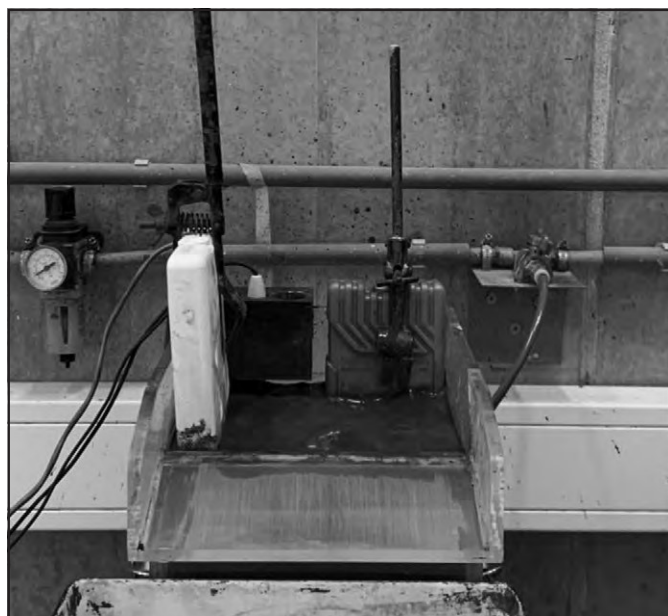


Figure 2. Flotation cell setup for the tests with cooled pulp

total: four concentrate fraction and bulk tailings, and their chemistry was accordingly assayed.

### Characterization

**Chemical composition.** ICP-AES was used for copper and iron analysis, following an indispensable acid digestion of the slags with aqua regia. XRF assay (BRUKER S8 TIGER) was done for complete characterization of the slags. The matrix with the higher confidence level was that of Fe<sub>3</sub>O<sub>4</sub>. Another purpose of using XRF spectrometry was to benchmark XRF and ICP-AES protocols. Sulfur content was determined by Leco analyzer. Table 2 represents main composition of the slags as determined by the above-described methods.

**Mineralogy.** Mineralogical quantification (X-ray diffraction) has been done using a Bruker D8-ECO diffractometer, with CuK<sub>α</sub> radiation ( $\lambda=1,9373 \text{ \AA}$ ). The respective sample was pulverized before being scanned between 5 and 75 °2 $\theta$  at a speed of 0.02 °2 $\theta$  per second. The identification of all minerals from the XRD patterns was done with a Panalytical Xpert suite and WebPDF4 + ICDD relational database. Figure 3 depicts the XRD data for the untreated feed slag. It could be seen, that apart from fayalite and magnetite being largely present, pyroxene is detected, specifically identified as “diopside.” The refined mesh parameters obtained from the analysis, namely; a = 9.79 Å, b = 8.94 Å, c = 5.29 Å, and  $\beta = 105.77^\circ$ , suggest values larger than those observed for pure diopside, yet smaller than those for hedenbergite. Consequently, the composition is likely to be closer to augite. It is important to note, that the detected “diopside” is, in fact, a different pyroxene variant with a higher iron content, and that these mixed-phase compositions (as detected by the automated mineralogy) align well with augite.

A SEM-based automated mineralogy inspection was accomplished using a Zeiss Sigma300 system controlled by a Mineralogic Mining software. The SEM-EDS system was equipped with two Bruker xFlash 6|30 X-ray detectors. System magnification was set to 6000 $\times$  and voltage tension to 20kV.

Sub-sampling of product streams for thin sections preparation was performed with a rotary splitter to ensure statistically reliable samples. The polished sections preparation for the SEM analysis was based on four-step procedure:

Table 2. Mean chemical composition of the feed slags

Content, %	Fe	Cu	S	Ca	Al	Zn	K	Pb
ICP-AES	42.4	2.47						
XRF	42.9	2.41		2.17	2.05	1.09	0.74	0.34
Leco			0.86					



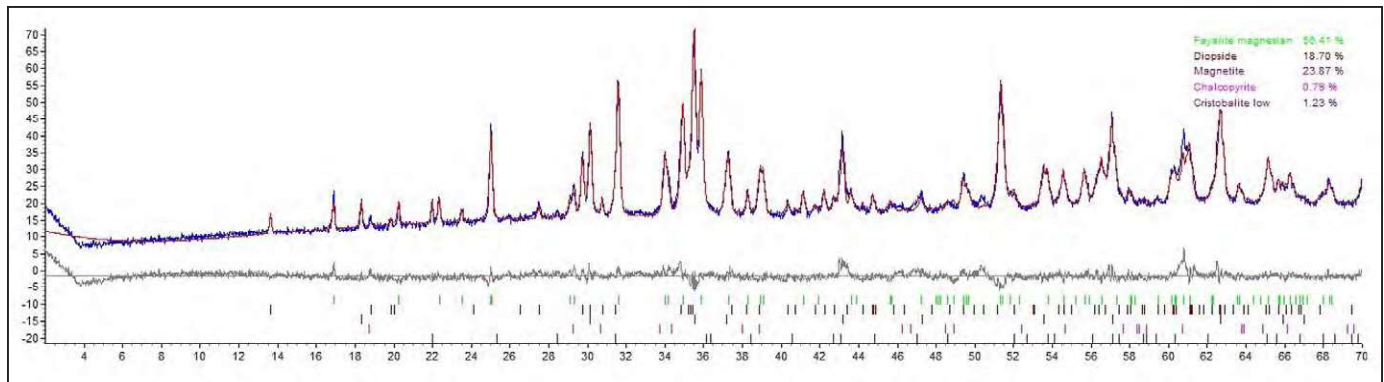


Figure 3. XRD pattern of the input slag

resin preparation, mixing with sample, curing and polishing. The resin media used is a mix of epoxy resin and carbon black.

The copper department results obtained by the Automated Mineralogy System revealed that copper is available as two principal phases: native/metallic (composition Cu 100%), and “mixed sulfides” with the following average composition, (wt. %): Cu 62.3, S 21.5, Fe 15.9, and Zn 0.28. The modal mineralogy of the input slag as given by the SEM-EDS indicated fayalite as principal mineral phase (gangue)—44.25%, while mixed sulfides were present at 2% and native copper accounted to 0.87%.

### *Eh, pH, dissolved oxygen (DO) and temperature monitoring*

A TPS device-90-FLMV Field Lab analyzer equipped with probes for oxidation reduction potential (ORP or Eh), pH, Dissolved Oxygen (DO) and temperature was used for monitoring pulp physicochemical properties. The ORP probe measurements were referred against Ag/AgCl electrode. Calibration was done for the pH and DO probes, and drift correction for the ORP probe every 2–3 days. When reporting redox potential readings, it is common practice to refer them to the standard hydrogen electrode (SHE), also known as the normal hydrogen electrode (NHE). To accomplish this, a  $E_{ref}$  value from Table 3 was chosen, which corresponds to temperature of the solution. By substituting the  $E_{ref}$  value in the equation and solving for Eh, the redox potential is determined.

$$Eh = E + E_{ref} \quad (1)$$

where,  $Eh$ : oxidation-reduction potential of the sample relative to the SHE,  $E$ : potential developed by the ORP electrode,  $E_{ref}$ : potential developed by the reference electrode portion relative to SHE.

Table 3. Relation between temperature (°C) and Eh (mV)

Temperature (°C)	Redox Potential, mV ( $E_{ref}$ )
70	172.1
65	176.4
60	180.3
55	184.4
50	188.4
45	192.3
40	196.1
35	199.8
30	203.4
25	207.0
20	210.5
15	214.0
10	217.4
5	220.9
0	224.2

## RESULTS & DISCUSSION

In total, 23 flotation experiments were conducted, with all parameters, except temperature, maintained constant. The registered values of Eh, pH and DO show a strong correlation with temperature variations. It is generally expected that since oxygen solubility in water increases as temperature drops, the lower temperature ranges will bring increased dissolved oxygen (DO) in the pulp compared to higher temperatures. When interpreting the temperature effects on Eh, pH, and DO in flotation, the results were grouped into two temperature clusters, namely 15 and 20 °C and 30 and 35 °C. Figure 4 provides the mean values for redox potential, DO and pH recorded within these two temperature ranges.

With increase in temperature, redox potential is increasing, while DO is decreasing. pH values do not witness marginal fluctuations with temperature variation. DO shows a clear temperature dependent trend, with the solubility of

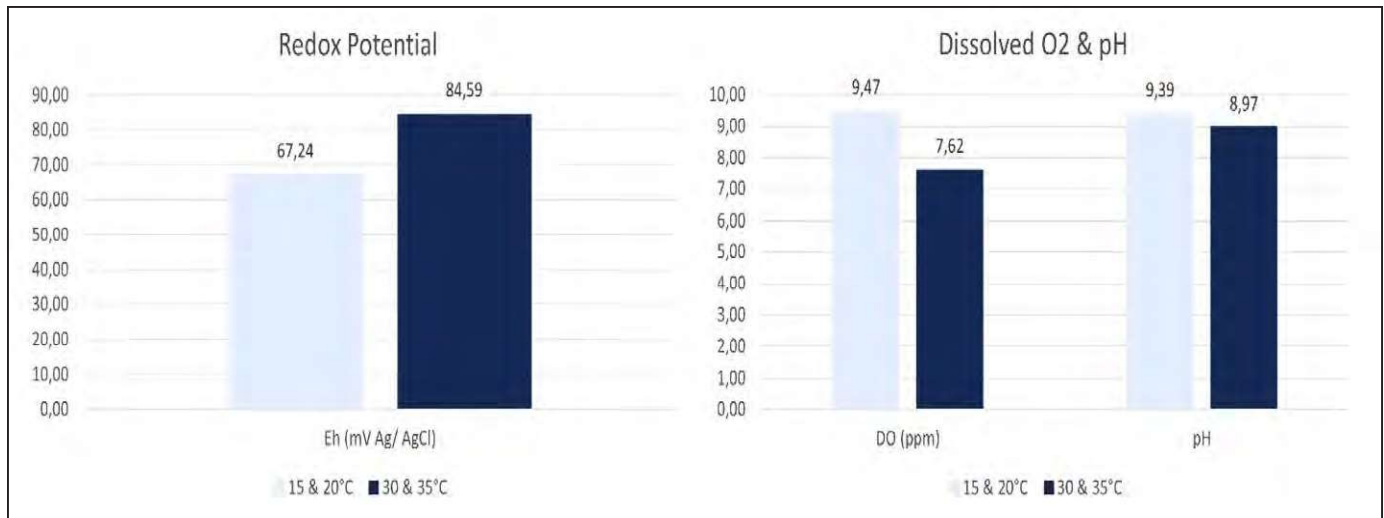


Figure 4. Mean values of Eh, DO and pH recorded at the two temperature ranges (15-20 °C and 30-35 °C)

oxygen decreasing with temperature increase. This is logical since given that oxygen solubility is described by Henry's law and Van't Hoff-type equations, Henry's constant increases with temperature increase. Higher temperatures should theoretically lead to DO deficiency inside the flotation pulp, and hence negatively impact mineral floatability. Such effect has, however, not been observed in the current study. Another important process-related parameter is viscosity, which influences entrainment phenomena of gangue minerals leading ultimately to lower selectivity in flotation (Pashkevich, Li, and Waters, 2022). Images taken during the scavenger stage clearly indicate a visual difference in froth appearance at 15 °C and at 35 °C, supporting the assumption of more rapid reagent "consumption" at higher temperatures—Figure 5. Finer-sized bubbles definitely predominate the froth fraction at higher temperatures.

When comparing the results obtained from the tests realized at the two extreme temperature ranges, the following observations could be made:

- At the scavenger stage performed at 35 °C, the froth was less shiny having finer air bubbles, compared to the froth generated at lower temperatures.
- A more consisted froth structure was observed in all tests after the first 6 minutes of flotation (scavenger stage).

## AUTOMATED MINERALOGY OBSERVATIONS

Figure 6 depicts the liberation degree for the native Cu in the slags before the ball milling stage and after it. The immediate impression is that the liberation degree of the native copper does not change significantly following ball

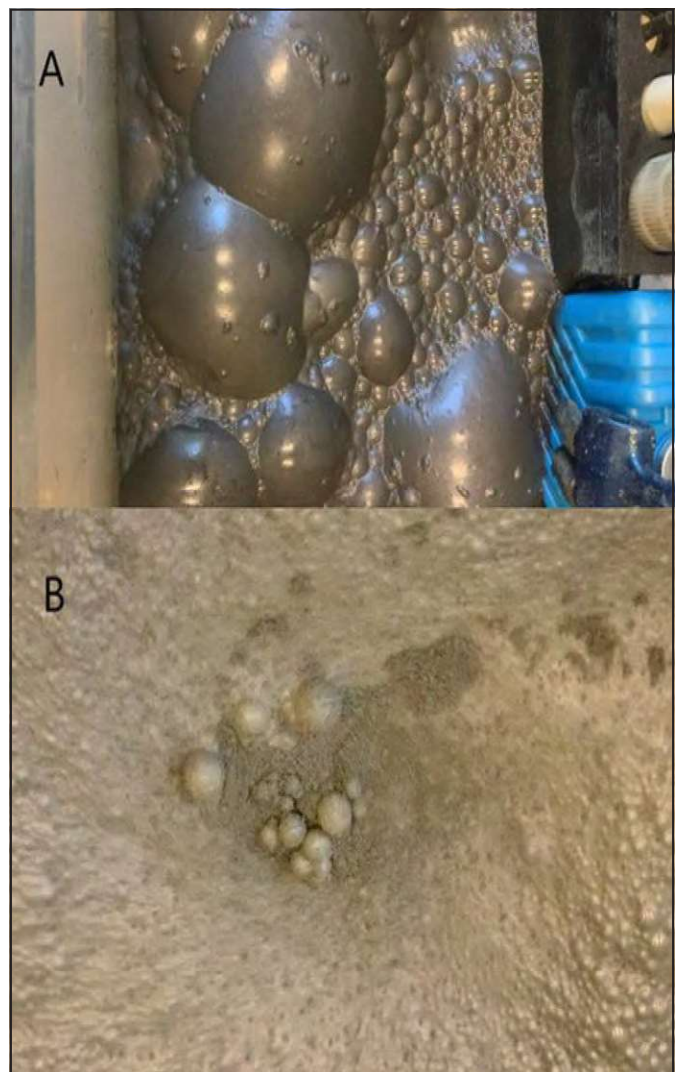
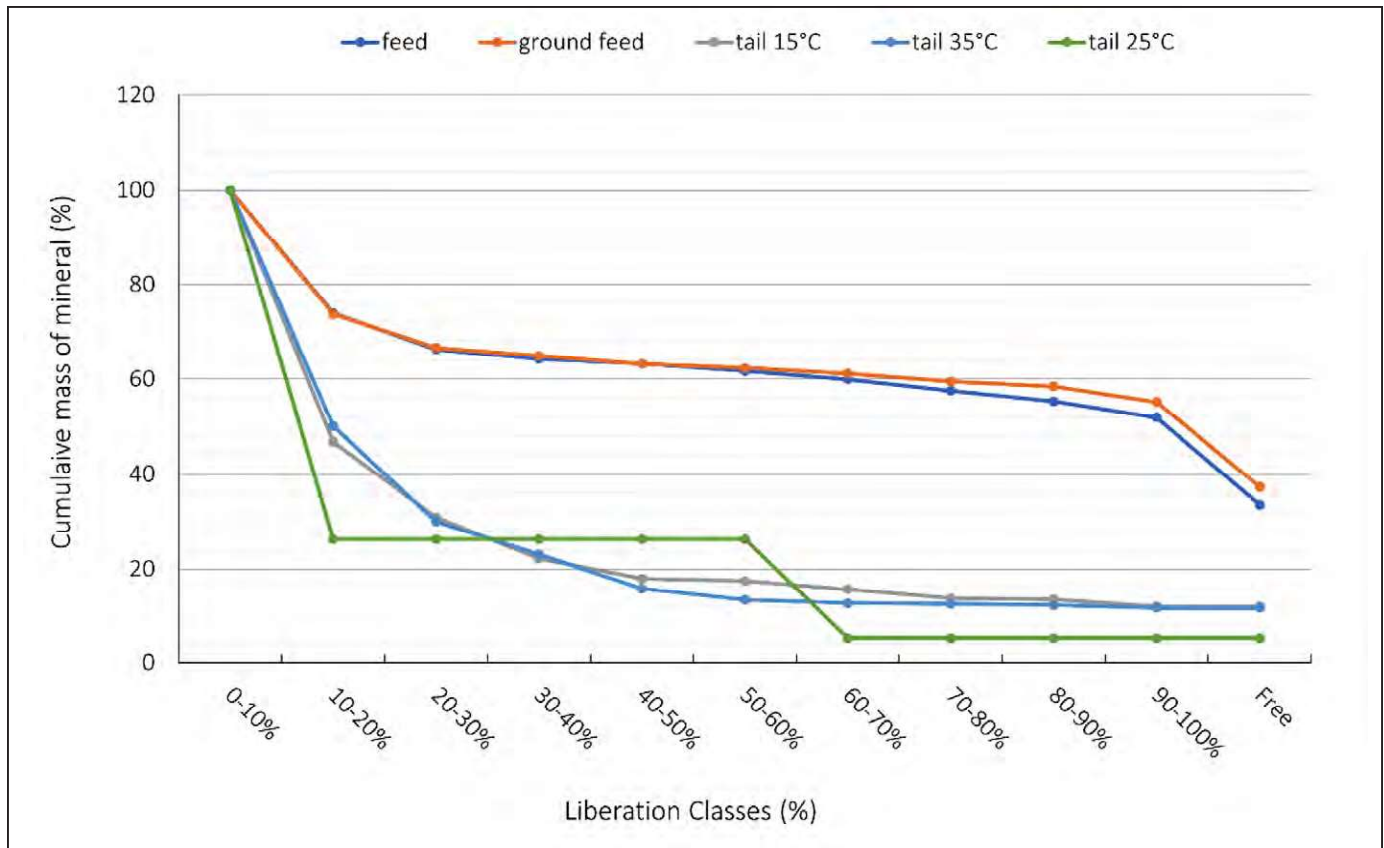


Figure 5. Froth view during scavenger stage flotation at: (A) 15°C and (B) 35°C



**Figure 6. Liberation curves for native copper in the feed slag before milling, ground slag after ball milling and tailings for the three temperature conditions (15°C, 25°C and 35°C)**

mill grinding. At the same Figure, the liberation curves derived for the tailings at 15 °C and 35 °C are nearly overlapping, in contrast to the observed trend for the tailings obtained at 25 °C.

It should be noted that the mean size of the native copper particles in the feed slag is around 10.5 µm, while this drops to approx. 4–5 µm in the tailings, whatever the flotation temperature. At the same time, fayalite’s grain sizes remain virtually unchanged both in feed and in tailings—around 12 µm. This might suggest that fine-grained copper bearing particles (< 5 µm) are difficult to float and hence are lost in tailings, and that these losses are inevitable whatever the pulp temperature is. This reaffirms the assumption that the lab-scale grinding step merely is refreshing slag/mineral surfaces, rather than reducing slag particles size and therefore contributed to surfaces reactivation (e.g., refreshed surfaces).

The primary objective of the work was to examine pulp temperature effect on the overall copper recovery. To reach this aim, the recovery of copper presented both as native and as mixed sulfides was calculated based on copper

deposition in the tailings and in the feed (SEM-based automated mineralogy data).

The results depicted in Figure 7, indicate that the raise in temperature provoked recovery increase for both native copper and mixed sulfides fractions. For native copper, a recovery difference of 1.6% is observed when temperature was modified from 15 to 35 °C, while the respective value for the mixed sulfides recovery was close to 5% (4.73%). The recovery figures are calculated based on the absolute percentages of mineral/element grades assayed in the tailings. Like evoked earlier, these two phases, constitute the principle Cu-bearing fractions.

Figure 9 summarizes the cumulative Cu recovery and grades achieved at each of the investigated temperature range. At first glance, the tests performed at the two extreme temperature ranges offer the best metallurgical results, while those at 20 °C were the worst performing ones. The results however should be considered with caution in light of the different flotation behavior of the two principal copper bearing phases – native Cu and mixed sulfides.

The results shown in Figure 9 clearly reveal the positive impact from temperature increase on copper metallurgy,

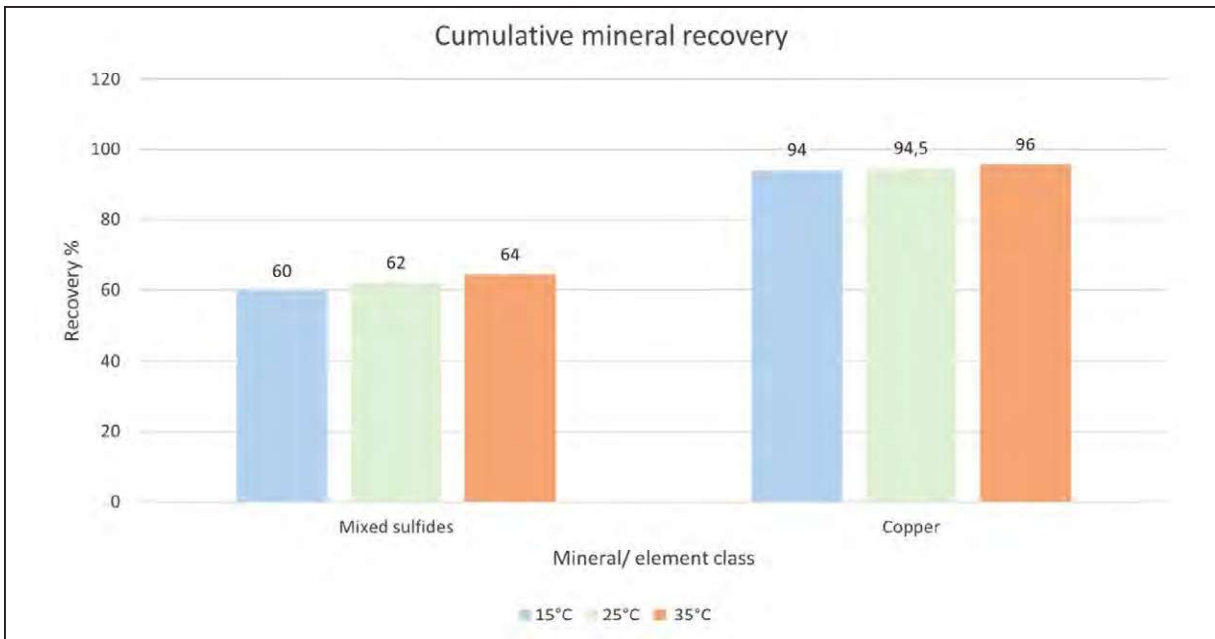


Figure 7. Recovery of mixed sulfides and native copper at three different temperatures (based on chemical assay)

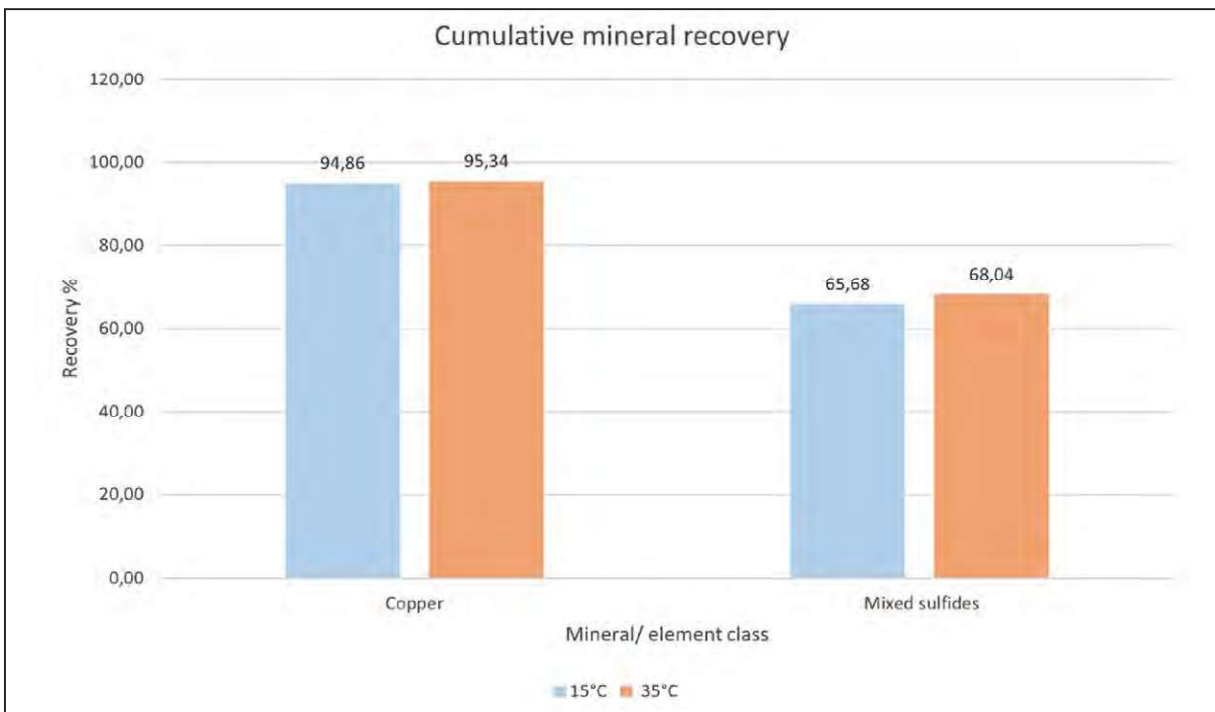


Figure 8. Cumulative recovery of native copper and mixed sulfides at 15 and 35 °C (based on SEM-EDS area % multiplied by weighted concentrate sample)

since both copper grade and recovery do increase. Obviously, Cu grade in the concentrate at the rougher stage (Figure 9— left, 6 mins of flotation) was more than 2% higher than that registered at 15 °C. However, by minute 11 (flotation end), the gap in Cu grade registered for the two temperature

extremities dropped by 0.35% (12.1% against 11.75%). In addition, copper recovery in the concentrate demonstrates a increasing pattern with temperature raise. However, it is noteworthy that the recovery discrepancy between the rougher and scavenger stages remains relatively constant,



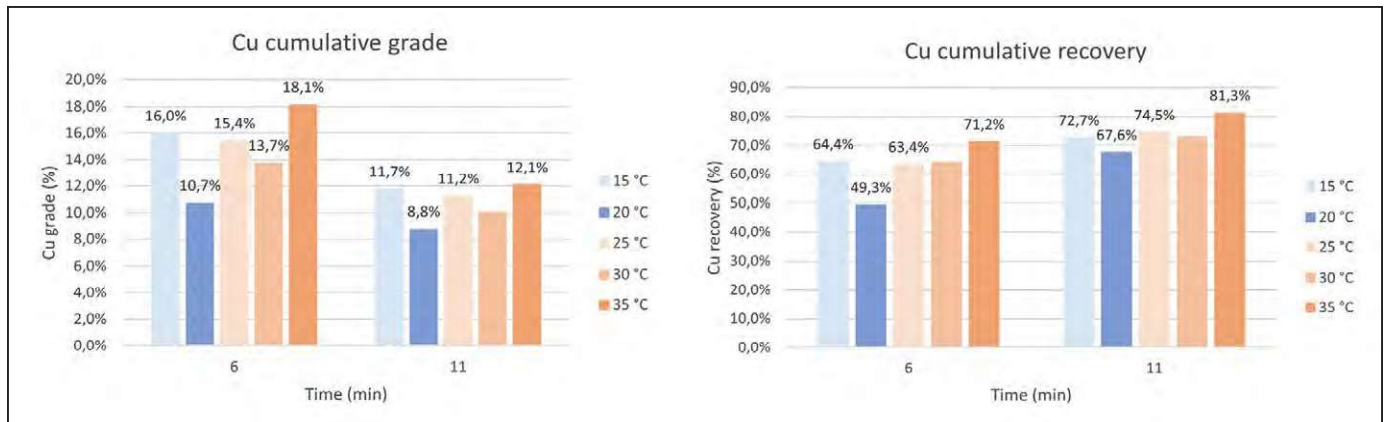


Figure 9. Cu grade (left) and cumulative recovery (right) at rougher and scavenger stages as function of temperature

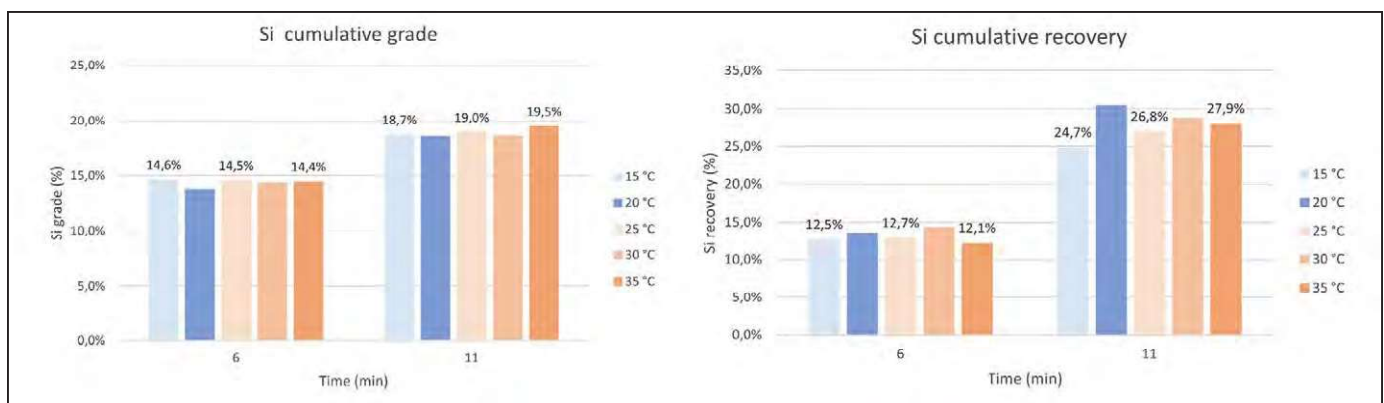


Figure 10. Cumulative Si grades and recoveries at rougher and scavenger stages as function of temperature

with approximately 7% higher recovery observed at 35 °C, compared to the one seen at 15 °C. Based on the latter observations, it could be reconfirmed that higher temperatures do favor slag flotation kinetics.

The recoveries and grades of silicon, (proxy of fayalite) demonstrate a well-defined increasing trend with temperature increase – Figure 10. This trend corroborates the higher mass pull during high temperature flotation, which together with the higher recoveries of Cu, is possibly leading to an elevated Si-content inside the concentrate. However, this can be an indication of more fayalite being recovered into the concentrate, knowing that fayalite is not the compound of economic value. It should be noted however that to maintain smelter process efficiency the recycled to the furnace concentrate should carry fayalite to a certain extent.

## CONCLUSIONS

Higher temperatures seemed to have a positive impact on pulp viscosity and possible collector adsorption on the copper-bearing sulfides present in the slag, while has limited or no influence when native copper phases are concerned.

The recovery of mixed sulfides was 2 to 4% higher at 35 °C in comparison to that achieved at 20 °C. As a result, cumulative copper recovery (rougher and scavenger) increased markedly when slag flotation was carried out at 35 °C in comparison to 20 °C option. Cu grade of approximately 3% higher has been registered for the tests performed at 35 °C, compared to the one at 20 °C, implying positive effect from temperature on froth carrying capacity. This trend also means that oxygen content in the pulp plays a subordinate role in the floatability of copper bearing phases in the investigated slag material.

Increased temperature possibly stimulate release of Cu cations into the pulp which could facilitate collector adsorption on mineral surface. On a more fundamental side, it could be studied whether chemisorption or physical sorption of the collector is the predominant mechanism for the two Cu-bearing phases identified in the slags.

Based on the liberation curves derived from the SEM-EDS it could be assumed that the (re)-grinding stimulates merely surface reactivation of slag particles rather than real fragmentation and size reduction.

During tests execution it has been challenging to maintain constant pulp volume in the cell due to the presence of cooling blocks necessary to sustain lower temperatures. This methodological issue might have provoked slight fluctuations in the obtained results. However, the observed trends in Cu-grade and recovery with temperatures variation remain valid and hence do shed light on the role of temperature on slag floatability. These observations highlight the need to carefully consider temperature effects when optimizing flotation. The recovery of Cu-bearing phases in the slag could be enhanced on that basis while minimizing the entrainment of undesirable gangue minerals.

The selection of collectors should be carefully evaluated, taking into account their solubility and dispersibility properties at the different temperature ranges. For the copper associated with the sulfides which demonstrates poor metallurgical performance under 'cold' conditions, choosing different collector with enhanced performance at low temperature could be proposed. Current study observations suggest faster dispersion and rapid intrinsic adsorption of the reagents at higher temperatures.

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