Increased liberation and flotation performance of bulk copper flotation concentrate following its regrinding in a stirred media mill

A. Stefanov[a], K. Grossman[b], V. Stoilov[c], A. Angelov[c], U. Peuker[d], and S. Gaydardzhiev[e]*

[a]*Aurubis Bulgaria AD, 2070 Pirdop, Bulgaria*
[b]*UVR-FIA Freiberg Chemnitzer Str. 40, 09599 Freiberg, Germany*
[c]*Asarel-Medet AD, 4500 Panagyurishte, Bulgaria*
[d]*MVTAT, TUBAF, Agricolastraße 1, 09599 Freiberg, Germany*
[e]*GeMMe - Minerals Engineering and Recycling, University of Liege, B52, 4000 Liège, Belgium*
**Corresponding author: s.gaydardzhiev@uliege.be*

ABSTRACT

Flotation concentrate originating from the Asarel-Medet porphyry copper mining and processing complex in Bulgaria has been subjected to regrinding using a Ro-Star mill and the effects from which on the downstream metallurgical behavior are discussed. Particularly the effect on the liberation degree was studied through an optical microscopy and MLA-SEM automated mineralogy.

On the other side, copper selective flotation of the reground bulk concentrate was realized to evaluate the anticipated metallurgical improvement. Process parameters such as involvement of prior hydrocycloning and variation of collector dosage have been evaluated.

Within a 2-minute residence time inside the Ro-Star mill, an improved liberation degree of the copper bearing minerals has been observed. As a consequence, enhanced copper recovery and selectivity against pyrite was noted. It has been found, that in order to guarantee efficient flotation of the resulting ultrafine particles a modified flotation regime (i.e. changing collector suite and dosages) should be followed.

Keywords: RoStar Mill, liberation, flotation recovery, ultrafine particles

1. Introduction

The constantly decreasing content of valuable minerals in the ore bodies requires more energy and cost effective grinding resulting in improved liberation. Grinding down to fine and ultrafine range using conventional tumbling mills requires high energy and is associated with intensive lining wear and therefore significant maintenance costs. New type of fine and ultrafine grinding technology based on stirred media has been gaining popularity bringing energy efficient comminution. The grinding units belonging to this niche are divided according to rotor design, and can be horizontal and vertical.

The rotor-stator geometry could vary depending on manufacturer and customer requirements and can be adapted to the grinding tools being used: pins, discs, segmented discs, spirals or perforated discs rotating at high speeds.

ISA mill (Glencore Technologies) is a horizontal stirrer mill having a rotor that rotates at high speed (tip speed >20 m/s) in order to achieve annular flow in the grinding chamber. The rotor encompasses circular discs and a “screening” device in proximity to the discharge aperture of the mill. It does not possess a stator and the mill is relatively long because of the high length diameter ratio (Technologies, 1991; Larson *et al.*, 2011). The VPX- Mill (FLSmidth) is a vertical mill having rotor geometry similar to that of ISA mill. The rotor consists of a circular disc without stator and it operates as an ideal agitator (FLSmidth AIS, 2011; Allen, 2013). The HIG high intensity grinding mill (Outotec) is characterized by a small diameter of the chamber, consisting of stator discs attached to the chamber and rotor discs with round holes. The tip speed of the HIG is around 20 m/s causing a strong centrifugal force bringing a narrow particle size distribution (Astholm, 2015). Metso Minerals is marketing Stirrer Media Detritor (SMD) and Vertimill system, both being a vertical mills operating at low tips speeds - < 3 m/s (Metso, 2002; Allen and Ntsele, 2012). In the SMD mixing is generated by grinding pins (Allen and Ntsele, 2012), whereas the Vertimill has a spiral rotor and no stator.

Maelgwyn Mineral Services has developed a new type stirred mill system - the Ro-Star® vertical high intensity ultra-fine wet mill. It consists of a chamber with internal segmented discs welded to it and an agitator shaft with similar arrangement. The cavities between the agitator and the stator are filled up with grinding beads. Feed slurry is pumped from the bottom to the top and leaves the mill by means of an overflow. One of the assets of the RoStar mill is the stable shape of the grinding bed caused by the relatively low rotational speed, hydrostatic pressure and gravity motion. This brings lower energy consumption and reduced wear.

It has been reported that stirred mill technology can be used in two main process streams in the PGM industry (Rule 2010). Firstly, as a mainstream inert grinding (MIG) targeting grinding levels with p80 of 45 μm aiming at improved recovery and secondly, an ultrafine grinding (UFG) producing products at p80 under 20 μm aiming at improved concentrate grade. Stirrer media mill technology has shown that it is possible to grind finer in economical and energy effective manner. Moreover, ultrafine grinding technologies have the ability to reduce oxidation-reduction effects provoked by steel media, which hinders mineral flotation. It is known that fine particles do not float efficiently due to low probability of interception and collision efficiency. A decrease of bubble size clearly indicates that increase the bubble-particle collision, bubble-particle attachment efficiency and number of generated bubbles (Ralston *et al.*, 1999; Miettinen *et al.*, 2010).

Based on the above, the aim of the present work is to evaluate the performance of the Ro-Star mill when regrinding a porphyry copper concentrate and follow the flotation behavior of liberated minerals.

2. Experimental

2.1. Sample origin

The bulk sulphide collective concentrate was obtained from the flotation plant at Asarel-Medet mining and processing complex in Bulgaria. Representative samples of 1100 g for the grinding test have been prepared following a standard sample division procedure. P80 of the sample after bulk flotation was 150 µm.

2.2. Characterization

The chemical composition of the concentrate showed a copper and iron content of 4.11% and 28.18 % respectively. Detailed mineralogical characterization of the ore was available in advance. Chalcopyrite, covellite, bornite and chalcocite have been found as main copper bearing minerals, while pyrite was the main iron bearing mineral. Complementary automated mineralogy analysis (ZEISS Sigma 300 SEM) showed that the ore feed contains about 59 wt. % pyrite and 11 wt. % chalcopyrite.

2.3. Equipment and methodology

A 18-L RoStar prototype mill available at the chair for Mineral Processing, TUBAF, Freiberg, Germany was used for concentrate regrinding. Since re-grinding and flotation tests have been realized at two different laboratories, it has been necessary to replicate the particle size distribution obtained by the RoStar prototype using a conventional tumble mill available at the laboratory where flotation tests were performed. To this end, a fully instrumented Magotteaux® mill was used. Steel balls (Ø30 mm) were used as grinding media. Particle size analysis was carried out using laser diffraction unit (Malvern Mastersizer 2000). To follow the particle size reduction effects grinding duration was set as 7, 15, 30 and 45 minutes. In each trial, 1100 g sample of bulk concentrate was mixed with 1 L of tap water and introduced to the mill. Lime solution was added constantly to maintain pH of 11.

2.3.1. Classification

Classification of the mill discharge was realized via laboratory scale hydrocyclone having a cut-off size of 20 µm. Following hydrocycloning, the underflow was immediately introduced to flotation, while the overflow was left to settle overnight.

2.4. Flotation

A bottom driven Magotteaux® flotation machine was used. Fig. 1 illustrates the experimental flowsheet being used. Concentrate was collected at 1, 3, 6 and 10 min enabling to obtain 4 selective cleaner concentrates, one scavenger product and tailings. Sufficient conditioning time was used at the correct pH at cleaning and scavenger stages. Sodium Isobutyl Xanthate (SIBX) was used as collector (1 % solution) with dosage at 40, 60 and 80 g/t. As frother, MIBC ($C_6H_{14}O$) was used at 30 g/t. Lime solution was added during conditioning stage to maintain the desired pH of 12.

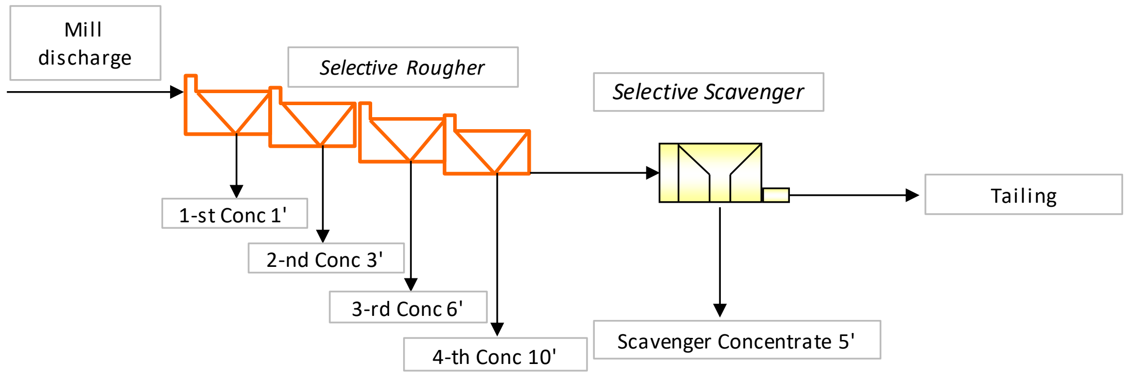

Fig. 1. Flotation flowsheet

In case of classification, the underflow was floated following the procedure explained above, while the overflow was floated inside a 1.5 L cell and increased dosage of collector 80 g/t.

2.5. Element to mineral conversion

Chemical assays for Fe and Cu by were realized by ICP-AES. A simplified model was created further to realize element to mineral conversion. This latter was derived from mineralogical and liberation analysis. Considering the percentage of every copper mineral in the feed a weighted average content was calculated.

$$Wt_{average} = \sum_{i=1}^{w} (\%\, Cu/Fe\ in\ each\ mineral\ \times \%\, mineral\ in\ the\ group) \quad (3)$$

where, $Wt_{average}$ is the weighted average content for certain mineral group.

This equation was used also for iron bearing minerals. It has been assumed that the entire copper content is linked to copper bearing minerals only, while iron goes to iron bearing mineral group. A simple element to mineral conversion was performed by following equations by grouping copper and iron minerals into two major groups explained below:

$$\%\ \mathrm{CuBM} = \frac{\%\ \mathrm{Cu\ grade\ from\ Assay}}{\mathrm{Wt}_{\mathrm{average\ content\ of\ Cu\ in\ copper\ mineral\ group}}} \quad (4)$$

where: CuBM means copper bearing minerals, which includes the most abundant copper minerals in the feed sample. These are chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS) and bornite (Cu_5FeS_4). $Wt_{average}$ is the average content of copper in CuBM (copper mineral group)

Then, the excess amount of iron (%, Fe) consumed by copper bearing minerals was determined, depending on the % of Fe associated with pyrite – eq. 5. Finally, the amount of gangue was obtained – eq. 6

$$\begin{aligned}\%\ \mathrm{Fe\ in\ FeBM} = \%\ \mathrm{Fe\ grade\ from\ Assay} - (\%\ \mathrm{Cp} \times \%\ \mathrm{Fe\ in\ Cp}) \\ - (\%\ \mathrm{Br} \times \%\ \mathrm{Fe\ in\ Br})\end{aligned} \quad (5)$$

$$\%\ \mathrm{Gangue} = 100\ \% - \%\ \mathrm{CuBM} - \%\ \mathrm{FeBM} \quad (6)$$

where: FeBM combines main iron bearing minerals in the feed sample which are pyrite (FeS_2), pyrrhotite ($Fe_{(1-x)}S$) and sphalerite ($(ZnFe)S$).

3. Results and discussion

3.1. Particle size distribution from RoStar and Magotteaux grinding tests

Initial comminution trials at different grinding durations using Magotteaux ® tumbling mill, have suggested that it is possible to replicate the particle size distribution profiles derived from the RoStar fine mill. Table 1 summarizes the obtained results from these comparative tests.

Table 1.

Granulometric characteristics of RoStar and Magotteaux milled products at different times

Grinding time, min	D10	D20	D50	D80	D90
Feed	8.43	24.55	80.12	150.71	223.18
30'	2.72	6.00	22.83	55.56	79.60
45'	2.28	4.34	14.01	33.40	50.62
RoStar-1'	3.27	-	25.00	69.4	95.61
RoStar-3'	1.93	-	11.88	37.9	40.28

A perusal of the results shown in Table 1 suggests that 30-minute grinding with Magotteaux mill enables to achieve a D80 of 55.5 µm while 45-minute duration brings D80 of 33.4 µm. RoStar grinding at 1 and 3 minutes brings comparable granulometry with D80 of 69.4 µm and 37.9 µm respectively. Grinding at 30 minutes with Magotteaux achieves a slightly finer distribution for the coarse fraction range, while below 25µm, the PSD curve matches exactly the particle size distribution obtained by RoStar. Grinding at 45 minutes provides somehow coarser material than RoStar at 3 minutes. The difference between the D80 achieved under Magotteaux and RoStar milling is only 4.5 µm.

3.2. Mineralogical observation

Optical microscopy observation – Figure 2, illustrate that the Cu bearing minerals in the feed are mainly interlocked with the gangue. Most of the chalcopyrite grains are associated with pyrite and gangue. On the other hand, chalcopyrite tends to be associated with chalcocite, covellite and bornite. Pyrite is locked with gangue but it is not mineral of economic interest and is rejected during further processing. There is occurrence of covellite, cuprite, chalcopyrite, enargite and pyrite inside the fine fractions.

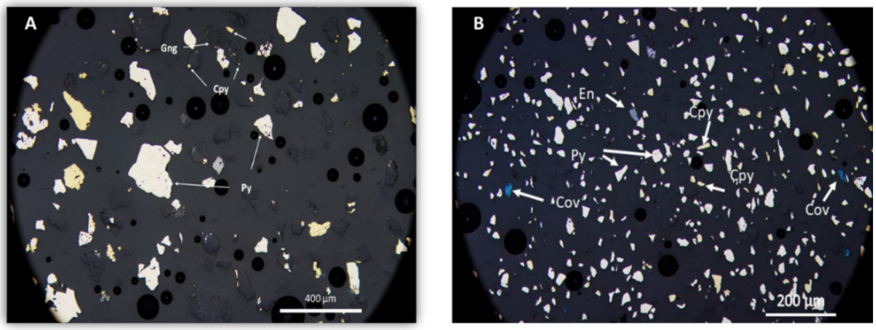

Fig. 2. Image view of bulk concentrate (feed). A – size class +63 µm; B - size class -20 µm.

Figure 3 gives optical microscopy images after regrinding with RoStar mill at 1 and 3 minutes. It could be noted that liberation increases with grinding time. Locked chalcopyrite grains in the material ground for 1 min. are mainly associated with gangue and pyrite. In contrast, after 3 minute grinding, chalcopyrite grains occur as locked with pyrite, where the amount of chalcopyrite grains locked with gangue is reduced. It is clear from the images that grain size is decreasing concomitantly to grinding time increase (1 to 3 minutes), provoking an improved liberation.

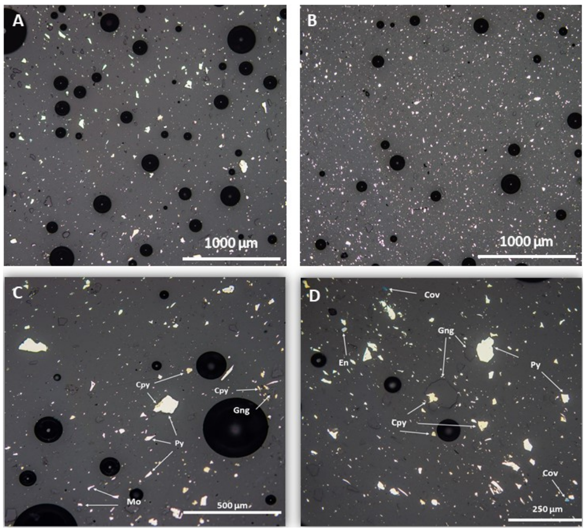

Fig. 3. Micrograph of concentrate after 1 (A) and 3 (B) minutes regrinding. Locked chalcopyrite in pyrite grain and molybdenite (C). Chalcopyrite grains interlocked with gangue (D).

The modal mineralogy of the three size classes from the bulk concentrate in Figure 4 that pyrite, show that mixed silicate minerals (gangue) together with chalcopyrite are the most abundant minerals. Chalcopyrite together with covellite, bornite, chalcocite constitutes main copper bearing minerals. 25.7 % wt. of the chalcopyrite grains are found in -63 µm and < -20 µm size fraction accompanied by other sulphide minerals. In contrast pyrite is mostly met inside the +20-63 µm size fraction reaching nearly 79 % wt., while gangue is presented at 42.7 % wt. in the coarsest size fraction.

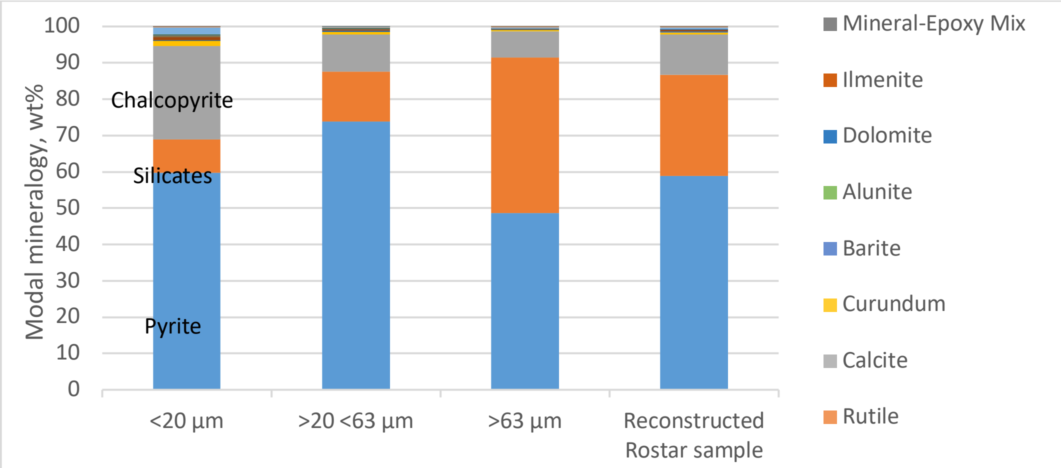

Fig. 4. Bulk concentrate modal mineralogy

The modal mineralogy of ground products using RoStar at 1 and 3 min (Figure 5) shows that the main identified copper minerals are chalcopyrite, covellite, chalcocite, tennantite and enargite, although the latter four present 0.70 %wt only.

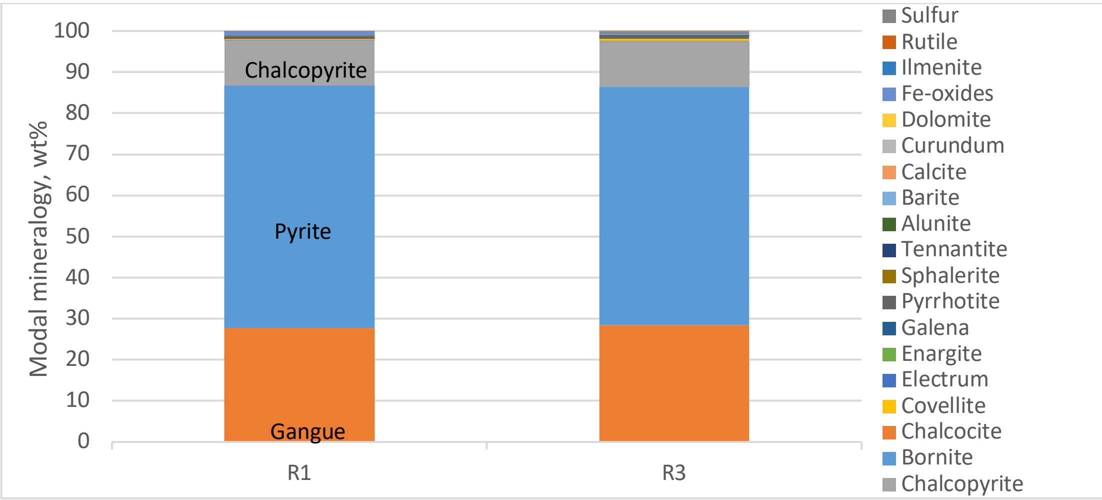

Fig. 5. Modal mineralogy of RoStar output after 1 min (R1) and 3 min (R3) grinding

It is evident that increased grinding time do not change copper bearing minerals in terms of mineralogical appearance, especially for chalcopyrite the results are almost identical. Pyrite presence is higher after 1 min then after 3min., but the gangue presence follows reverse trend, being higher after 3 minutes. Table 2 presents the availability of chalcopyrite, pyrite and gangue minerals following regrinding with RoStar at 1 and 3 minutes.

Table 2.

Mineral composition after regrinding with RoStar mill

Product	Mineral average wt%		
	Chalcopyrite	Pyrite	Gangue
RoStar 1	10.93	59.06	27.69
RoStar 3	10.94	58.01	28.5

The degree of chalcopyrite liberation following RoStar re-grinding at 1 and 3 minutes is shown in Figure 6. At 3 min. nearly 43 % of the chalcopyrite is 100 % liberated, while curves overlap for the liberation levels 0-10 to 50-60.

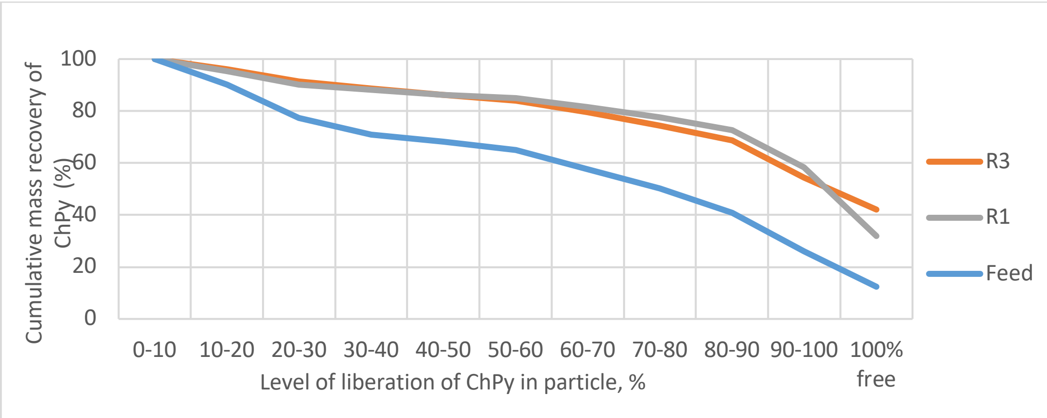

Fig. 6. Chalcopyrite mass recovery to different liberation classes as function of grinding time

Common mineral phases are associated between translucent gangue, pyrite and chalcopyrite. The chalcopyrite is mainly interlocked with the gangue and pyrite to a different extent. But increased grinding time lowers its associations with the gangue but enhances its association with the pyrite.

3.5. Flotation

3.5.1. Flotation without prior hydrocycloning at 40 and 60 g/t xanthate dosage

The grade/recovery curves of the concentrate reground at 7, 15, 30 and 45 minutes at a SIBC dosage of 40 g/t is shown in Figure 7 left. It seems that regrinding between 7 and 15 min is leading a similar trend of the curves. Re-grinding at 7 and 15 min. have brought nearly identical results, with maximum recovery in the range of 77 % and grade of 48 and 39 % for 7 and 15 min regrinding, respectively. After 30 min regrinding, recovery reaches 80.3 % but grade remains 49.8 %. Re-grinding at 45 min. do improve grade significantly (up to 83 %), but on the expense of modest recovery – 72 %.

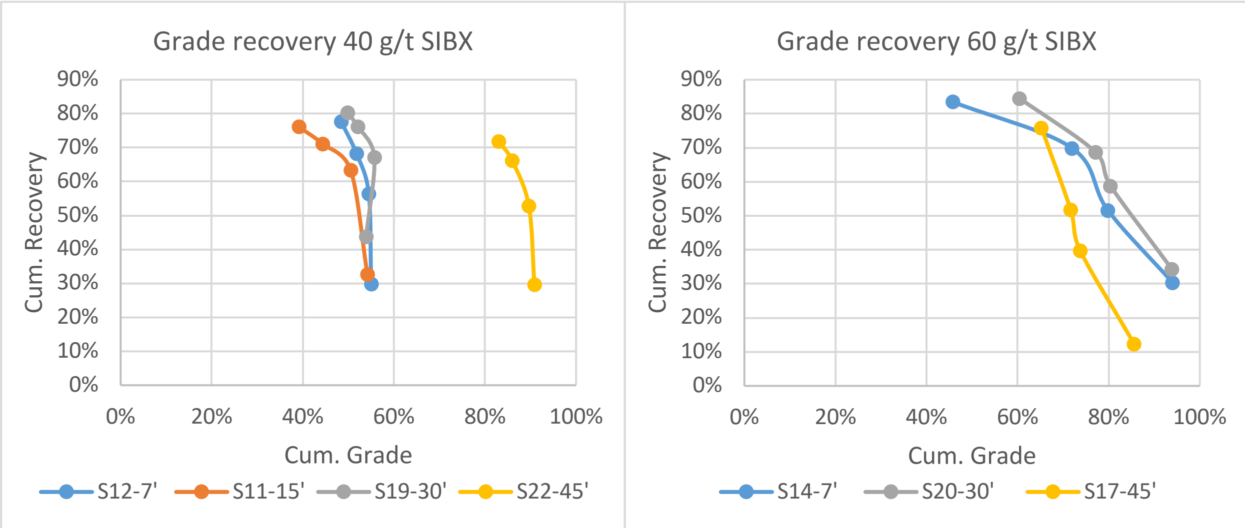

Fig. 7. Grade recovery curves for Cu bearing minerals at 40 and 60 g/t and various grinding times

When collector dosage was increased to 60 g/t, the re-grinding at 30 minutes brought the best results both in grade (60.4 %) and recovery (84.5 %). On the other hand, increase in regrinding time to 45 minutes does not brought better flotation performance compared to regrinding at 7 and 30 min. Perhaps the increased milling time generates finer size classes, which demand longer retention time inside the flotation cell, regardless the increased collector.

3.5.2. Flotation following prior classification

3.5.2.1. Flotation of underflow fraction

Flotation of the underflow after classification is reported in Table 3. High grade (82.7 % and 84 %) is achieved in the first minute fraction for grinding both at 30 and 45 minutes. However, 30 min of milling obtains higher final recovery of 75.1 % compared to 71.0 % and 45 minutes. The 45 min. grinding brings concentrate with higher grade than 30 min of grinding. Part of the valuable minerals are reporting into tailings, which calls the need of increased amount of xanthate or retention time. The tailings grade at 30 min and 45 min are respectively 2.8 % and 3.2 %. If the prolonged grinding time has brought improved CuBM liberation degree, it would be logical that 45 min tailing shows lower recovery losses.

Table 3.

Cumulative grade and recovery of underflow product at 60 g/t collector and grinding of 30 and 45 minutes

Product	Time, min	30 min				45 min			
		Cum. Grade		Cum.Recovery		Cum. Grade		Cum.Recovery	
		CuBM	FeBM	CuBM	FeBM	CuBM	FeBM	CuBM	FeBM
Conc 1	1	82.7%	17.5%	38.9%	1.9%	84.0%	12.0%	32.4%	0.9%
Conc 2	3	77.8%	19.8%	57.9%	2.9%	81.9%	14.2%	54.0%	1.8%
Conc 3	6	74.4%	22.7%	66.0%	3.6%	79.1%	16.2%	62.9%	2.5%
Conc 4	10	65.7%	29.8%	75.1%	5.6%	75.5%	20.5%	71.0%	3.8%
Sc. Conc	5	28.2%	57.5%	4.8%	1.4%	45.2%	47.6%	7.0%	1.4%
Tails		2.8%	96.7%	20.1%	93.8%	3.2%	54.4%	21.9%	94.8%
Calc Feed		9.7%		100.0%	100.0%	9.8%		100.0%	100.0%

3.5.2.2. Flotation of overflow fraction

The results derived from the flotation of overflow product are presented in Table 4.

Table 4.

Overflow product flotation at 60 and 80 g/t collector after 30 and 45 minutes grinding

Product	Time, min	60 g/t				80 g/t			
		Cum. Grade		Cum. Recovery		Cum. Grade		Cum. Recovery	
		30 min	45 min	30 min	45 min	30 min	45 min	30 min	45 min
Conc 1	1	22.6%	14.8%	8.8%	3.2%	21.2%	20.0%	8.3%	7.3%
Conc 2	3	27.4%	17.6%	23.4%	11.4%	23.3%	24.0%	22.0%	21.1%
Conc 3	6	30.6%	19.8%	35.0%	17.9%	26.1%	27.0%	33.1%	33.1%
Conc 4	10	31.2%	28.7%	42.1%	43.5%	29.6%	33.3%	45.0%	54.0%
Sc. Conc	5	19.3%	24.7%	7.4%	14.9%	19.5%	16.3%	8.0%	7.4%
Tails		9.2%	9.1%	50.5%	41.7%	9.8%	7.7%	46.9%	38.6%
Calc Feed		12.5%	12.0%	100.0%	100.0%	13.2%	12.4%	100.0%	100.0%

The results suggest that maximum grade of mineral of interest is achieved for concentrate 4, regardless grinding duration. This implies that fine particles remaining in the overflow need more time to report to the concentrate. At 60 g/t, maximum grade of 31.2 % is obtained at 30 min and 28.7 % at 45 min regrinding. On the other hand, increasing dosage to 80 g/t improves the grade at 45 min to 33.3 %, whereas 30 min obtain only 30 %, suggesting an improved liberation of minerals of interest.

4. Conclusions

The RoStar Mill® and Magotteaux Mill® cannot be compared by any other means, but by particle size distribution outputs. RoStar mill brought an improved liberation of the tested chalcopyrite concentrate evidenced via optical microscopy and automated mineralogy. Achieving improved liberation degree of the valuable minerals will inevitably reflect in improved flotation, regardless of the increased generation of ultrafine particles. Our flotation results do confirm observations made by Pease *et al.*, (2006) indicating that under certain physicochemical conditions ultrafine particles do float efficiently. An increased collector dosage at 60 g/t generally gave higher recoveries and grades than that at 40 g/t. RoStar milled products at 1 and 3 minutes have shown improved liberation of copper bearing minerals. Nevertheless, after concentrate regrinding there are still finely disseminated copper minerals inclusions in pyrite, while the extent of copper minerals associations with the gangue is strongly reduced. Regrinding with RoStar Mill® enhances liberation ratio, recovery and grade.

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