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A successful operational initiative in copper oxide flotation: Sequential sulphidisation-flotation technique

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Abstract: One of the main challenges in the copper oxide processing industry is implementation of a flotation method to reduce operating costs. Sulphidising flotation is the most common used technique in which a sulphidisation agent is used to sulphidise the surface of the oxide minerals. In this research, the mentioned technique was used sequentially for the concentration of silicate-carbonate ore containing 3.1% Cu (malachite). The presence of 39% Cu in -38 µm size fraction (fine particles) of feed led to poor grades and recoveries in the initial tests. The addition of sodium sulfide and subsequent flotation at three sequential stages was identified as a successful operational initiative to solve this problem in the following tests. The dosages of 1500, 1567 and 100 g/Mg of sodium silicate, sodium sulfide and potassium amyl xanthate, respectively, the conditioning time of 5 min for sulphidisation and pH=9.72 were chosen as optimum operational conditions using central composite design (CCD) method of experiments design. The rougher concentrate with 9.28% grade and 81.15% recovery was obtained under these conditions. The grade of obtained concentrate was reached to 24% in the cleaner step. The total recovery of both steps was over 74%.

Keywords: copper oxide, sulphidisation, flotation

1. Introduction

Until a few decades ago, most of the world's copper were produced from sulfide reserves. Oxide reserves were considered with decreasing sulfide reserves, developing technological methods and increasing global demand for copper. In most cases, this type of Cu reserves are processed by hydrometallurgical methods. High acid consumption, long processing cycle and high extractant cost are among the main shortcomings of these methods for treatment of low-grade copper oxide ores (Li et al., 2015). For these reasons, the concentration of copper oxide ores by low cost methods such as flotation method is taken into consideration. A large number of studies in this area indicate the importance of the subject.

In general, the conventional flotation methods of copper sulfide ores do not apply to oxide ores. Flotation with fatty acids or surface sulphidisation of copper oxide minerals and their subsequent flotation using sulfhydryl collectors are two main methods for the Cu recovery from oxide ores. The first method is more suitable for the ores containing silicate gangue because the carbonate gangue has a high tendency to float with fatty acids. The second method is more applicable for the ores containing carbonate gangue (Lee et al., 2009; Bulatovic, 2010).

Nowadays, sulphidising flotation method is the most commonly used method in the researches for the concentration of copper oxide ores containing carbonate gangue, which has also been utilized for

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industrial applications. In these studies, agents such as sodium hydrosulfide (NaHS), ammonium sulfide ($(NH_4)_2S$) and sodium sulfide (Na_2S) were used as sulphidiser (Bulatovic, 2010).

In this regard, Castro et al. (1974 a, b) evaluated the chemical factors in the sulphidisation of copper oxide. In the following, they studied role of the adsorption and oxidation of Na_2S in the flotation of chrysocolla and malachite. Synergistic combination of NaHS and $(NH_4)_2S$ was evaluated for sulphidising flotation of oxide copper–cobalt ores of Katanga, Democratic Republic of Congo by Kongolo et al. (2003). Saleh et al. (2008) used the reverse flotation technique by oleic acid for beneficiation of Egyptian Abu-Swayel 6% Cu ore containing chalcopyrite, malachite, calcanthite and brochiantite. In the mentioned research, about 90% Cu recovery with 10% Cu grade was obtained. With a 1/1 combination of sulphidisers, about 80% Cu and Co have been recovered with a concentration ratio of 3.5. Cao et al. (2009) studied the joint techniques of flotation and leaching for Cu recovery from Mexican copper ore (1.19%) containing mainly copper oxide (ramsbeckite and malachite) and some copper sulfide (chalcopyrite) minerals. In their research, flotation with butyl xanthate as collector and Na_2S as sulphidiser merely led to a concentrate containing 19.01% Cu at a recovery of 35.02%. Lee et al. (2009) investigated the flotation of a blend of 70% sulphide ore (bornite and chalcopyrite) and 30% oxide ore (malachite and minor azurite) from Sherwood Copper's Minto Mine in Yukon, Canada. These researchers showed that hydroxamate collector in conjunction with traditional sulphide collectors (xanthate) can successfully simultaneously recover copper sulphides and oxides by flotation from blended ore minerals. A multistage sulphidising flotation procedure by NaHS at high temperature and extended residence time was developed by Phetla and Muzenda (2010) for producing an 18% Cu concentrate from an oxide copper ore (4%) at a region in Central Africa. The Cu recoveries achieved from their research were less than 50%. Lutandula and Maloba (2013) studied the recovery of copper and cobalt through reprocessing of tailings from flotation of oxidized ores in the Katanga province of the Democratic Republic of Congo. The highest recovery of the metals of interest (45% Cu and 83% Co) was achieved at consumption of 0.6 kg/t potassium amyl xanthate (KAX) and 6 kg/t NaHS. Choi et al. (2016) investigated the influence of a salt solution on the flotation behaviour of synthetic malachite using a sodium oleate as a collector. They proved that increasing the monovalent salt concentration helps to increase the flotation efficiency. However, the use of divalent salts, in particular those that strongly form hydration layers, should be used with care, as they would significantly decrease the floatability. The floatability of a Kansanshi mixed copper ore in the north western province of Zambia with sodium isobutyl xanthate (SIBX) was investigated by Corin et al. (2017). The main focus of the mentioned research was on the use of two different methods of sulphidisation, viz. slug sulphidisation with NaHS and controlled potential sulphidisation (CPS) using variable NaHS:SIBX ratios. In both case, the average Cu recovery was about 30%. Chen et al. (2017) synthesized a novel collector 3-hydroxy butyrate-carboxy methyl cellulose xanthate (HCMCX) to enhance the flotation efficiency of fine copper oxide ore from Dongchuan Copper Mine, Yunnan, China. This collector achieved an excellent mean concentration containing 20.19% Cu with 88.39% Cu recovery, and the Cu recovery increased by 5.69% compared to that of amyl xanthate (AX). The effect of ammonium sulfate ($(NH_4)_2SO_4$) on the sulphidising flotation of malachite in the presence of sodium butyl xanthate (NaBX) as the collector was investigated by Wu et al. (2017). They showed that addition of this salt to the slurry solution prior to the addition of the sulfidising agent ($Na_2S.9H_2O$) can not only enhance the activation of HS^- ions but also eliminate or reduce the adverse effects of residual HS^- ions. In their research, ammonium ions improved the flotation recovery up to 27%.

Although flotation is a commonly applied selective separation process in mineral processing (Gao et al, 2016; Li and Gao, 2017; Gao et al, 2018), it becomes inefficient for beneficiating fines (Matis et al, 1993). The physical properties of copper oxide ores are such that the high production of fines (-38 μm size fraction) is inevitable during the crushing and milling stages. The evaluation of the effects of fine copper oxide ore on the results of flotation performance is a key issue that has not been taken into consideration. Among the mentioned studies, Chen et al. (2017) are just focused on this issue through the synthesis of a novel collector (HCMCX). This paper aimed to find an operational procedure to reduce the negative effects of fines on the flotation performance of copper oxide ore. The sequential sulphidisation-flotation (SSF) technique is proposed to achieve this aim and its effective factors is optimized.

2. Material and methods

2.1. Ore sample

The ore sample used in this study was taken from the Chahmora mine in Semnan province, Iran. The d_{80} of the sample was 10 cm with a specific gravity of 2.69 g/cm^3. The ore composition is given in Table 1. Philips PW 2404 X-ray Fluorescence (XRF) was used for the bulk elemental analysis. The analysis shows that the ore sample contains 3.1% Cu, and silica, calcium, aluminium and magnesium are the most important impurities.

The characterization of the mineral composition was performed using a D8-Advance X-ray diffraction (XRD) from Bruker axs. Copper is present in the ore as malachite ($Cu_2CO_3(OH)_2$). The other constituent minerals of the ore include vermiculite ($Mg_3SiO_{10}(OH)_2$), albite ($Na(AlSi_3O_8)$), calcite ($CaCO_3$), quartz (SiO_2), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4.2H_2O$) and pyrite (FeS_2). Therefore, the ore is of silicate-carbonate type.

Fig. 1 shows the ore microscopic images in the thin sections. Study of the distribution of minerals in Fig. 1 revealed that the copper sulfide minerals such as chalcocite (Cu_2S), covelite (CuS), cubanite ($CuFe_2S_3$), and borenite (Cu_5FeS_4) exist in the ore, too. However, the total Cu content of these minerals is less than 5%. Iron oxides can be also seen in some sections of Fig. 1.

Table 1. Chemical composition of the ore sample (in %)

CaO	MgO	TiO_2	SiO_2	SO_3	Na_2O
18.43	4.47	0.40	37.04	0.63	2.12
P_2O_5	K_2O	Al_2O_3	Fe_2O_3	Cu	Sr
0.26	1.1	11.25	3.75	3.1	0.06
Zn	Zr	Pb	Cl	L.O.I	-
0.05	0.02	0.04	0.18	17.08	-

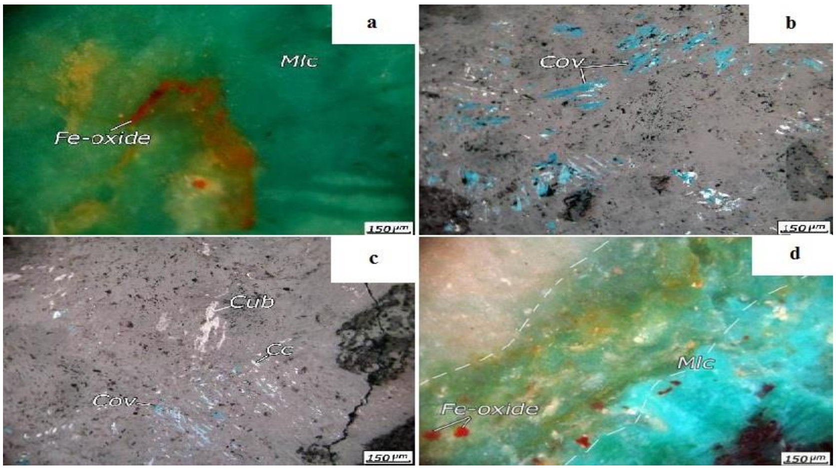

Fig. 1. Distribution of copper minerals in the ore: (a) Malachite bulk (Mlc) along with iron oxide, (b) Covelite, (c) Covelite together with chalcocite (Cc) and sometimes cubanite (Cub) as dispersed particles, (d) Mineralization boundary of malachite vein within the host rock

Microscopic investigations of sections revealed that the primary ore has included microcrystalline silica and clay minerals due to the silicidation phenomenon. Then, the carbonate solutions have formed the calcite/dolomite minerals as vein in the siliceous texture. Afterwards, the copper mineralization has occurred and malachite/azurite veins formed along with sulfide copper minerals in the margin of carbonate veins.

Study of polished microscopic sections showed that 72% and 80% of malachite was liberated in the size fractions of -106+53 μm and -53+38 μm, respectively. This means that about 20 % of malachite was locked by gangue minerals and did not even liberated by milling to about 53 μm.

2.2. Reagents

Reagent grade chemicals of potassium amyl xanthate (PAX) (KEMCORE), 98% $Na_2S.9H_2O$ (Sigma-Aldrich), sodium silicate (Na_2SiO_3) (Sigma-Aldrich) and methyl isobutyl carbinol (MIBC) (KYOWA HAKKO KOGYO) were used as the collector, sulphidiser, dispersant and frother, respectively, for all tests. The pH of the pulp was adjusted with 1 M aqueous solutions of sulfuric acid and sodium hydroxide (MERCK).

2.3. Flotation

Flotation tests were performed using a laboratory scale Denver flotation machine (mechanical agitation) with a 1.6 L cell volume under a 1000 r/min impeller speed. The sample was agitated for 5 min to ensure complete wetting of particles. After the addition of Ni_2SiO_3, PAX and MIBC, the pulp was continuously stirred for 3, 4 and 1 min, respectively. The rougher flotation was carried out using 30 g/t MIBC at 30% pulp density for 5 min. The constant operational conditions in the cleaner stage were the frother dosage of 20 g/t, pulp density of 15% and pH=10. In both stages, the concentrate and tailings were collected, dried, and weighed. The representative subsamples of the feed and products were analysed by atomic absorption spectrometry (AAS) (Varian model).

3. Results and discussion

3.1. Evaluation of operational factors

Primary tests were conducted to identify the operational factors affecting the flotation of copper oxide ores. The operational conditions and the results of some tests are presented in Table 2.

Table 2. Evaluation of operational factors (conditions and results)

Run	Na_2SiO_3 (g/t)	$Na_2S.9H_2O$ (g/t)	Cond. time of $Na_2S.9H_2O$ (min)	PAX (g/t)	pH	Grade (%)	Recovery (%)
1	500	500	8	40	9.2	6.6	21
2	500	500	15	40	9.0	7.2	27
3	500	1000	8	40	9.1	8.4	24
4	500	1500	8	40	9.1	8.5	22.7
5	500	1500	9	80	9.5	7.3	26
6	700	500	8	40	8.8	7.7	24

According to Table 2, the change in levels of operational factors had little effect on the flotation performance and the Cu recoveries were low in all the tests. The presence of fine particles in the flotation feed were the most important reason for the obtained results based on the previous investigation by Phetala and Muzenda (Phetla and Muzenda, 2010).

3.2. Evaluation of the fine content effects

Crushing and grinding stages were chosen based on the liberation degree of malachite. The d_{80} of the sample reached 2200 and 100 μm after the crushing and grinding steps, respectively. The grinding by a ball mill was performed for 30 min. Fines content of product was 35.54%. Replacement of the ball mill with a rod type mill was evaluated due to the high sensitivity of flotation process to the presence of fine particles. The product of rod mill reached d_{80}=1400 μm after 1 h. This low rate of grinding did not allow for the replacement of ball mill with rod mill.

Fig. 2 shows the grade distribution of Cu in various size fractions after the crushing and grinding steps. According to this figure, the copper was mainly present in coarse size fractions after the crushing step, however, over 39% of Cu content of the grinding product was transferred to the size fraction of -38 μm.

Some tests were conducted to investigate the effect of fines on the malachite flotation performance. The operational conditions and results of tests are presented in Table 3. All of the tests were conducted by using 40 g/t of PAX and 800 g/t of $Na_2S.9H_2O$ (time of 8 min) at pH=9.

In the absence of Na_2SiO_3, the removal of fine particles (-38 µm) led to the increase of the Cu recovery and grade, and with the removal of +106 µm size fraction, the results of the flotation performance were further enhanced. However, the removal of size fractions of feed, especially high-grade fines, from the flotation process does not seem to be logical. The dispersion of the fine particles through the addition of Na_2SiO_3 did not also have a significant effect on the grade and recovery results, as well as, this positive effect was reduced by removing the size fraction of +106 µm. It seems that the low recovery of Cu in the presence of fines is due to the loss of sulphidiser. The increase of surface area of particles by their conversion to fines enhance the $Na_2S.9H_2O$ consumption.

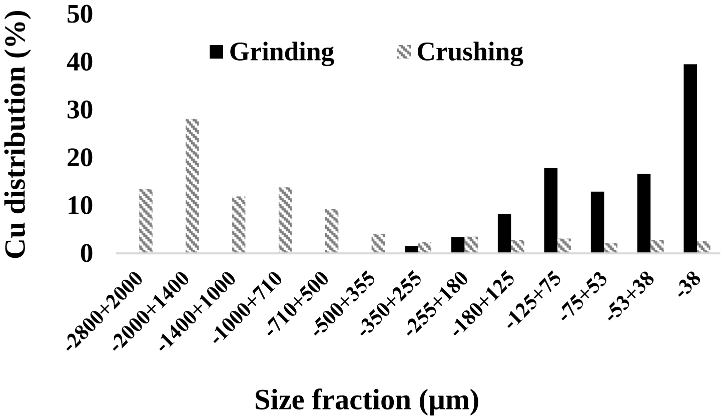

Fig. 2. Grade distribution of Cu in various size fractions after crushing and grinding steps

Table 3. Evaluation of fine effects (conditions and results)

Run	Na_2SiO_3 (g/t)	Sample	Grade (%)	Recovery (%)
1	0	Feed	8.3	17.12
2	0	Feed without -38 µm size fraction	16.33	31.62
3	0	Feed without +106 & -38 µm size fractions	39.8	39.27
4	500	Feed	12.13	26.0
5	500	Feed without +106 µm size fraction	8.48	23.7

3.3. Effect of the multistage addition of $Na_2S.9H_2O$

Phetla and Muzenda (2010) reported the low recovery of Cu in the flotation of fine malachite. In their research, the total Cu recovery from an oxide copper ore (containing 4% Cu) remained less than 37% despite the changes in reagent conditions as well as the de-sliming. They suggested the multistage sulphidisation procedure at high temperature and extended residence time to improve the performance of flotation. The Cu recovery reached 50% using this technique.

The effect of multistage $Na_2S.9H_2O$ addition on the flotation performance was studied in the presence of 500 g/ton of Na_2SiO_3 and 40 g/ton of PAX at pH=9. The conditioning time of $Na_2S.9H_2O$ was 5 min at each stage. Other operational conditions and the related results are shown in Table 4. Results demonstrate that the Cu recovery and grade were not significantly increased by the multistage addition of Na2S.9H2O. Size distribution of the flotation concentrate in the test 6 showed that 71.77% of the concentrate is in the size fraction of -38 µm. This means that the most $Na_2S.9H_2O$ used in the flotation test has been adsorbed on the fine particles due to the larger surface area. Fuerstenau et al. (1985) have also confirmed this phenomenon.

3.4. Evaluation of the SSF technique

The SSF technique was suggested to solve the problem of fine particles in the copper oxide flotation. The distinction of this technique with the technique proposed by Phetla and Muzenda (2010) is that the ore is floated after each stage of sulphidisation. This procedure selected to maximize the removal of fine particles from the cell at the first stage of flotation. Therefore, the residual particles in the presence of added $Na_2S.9H_2O$ in the next stages will have adequate opportunity for the sulphidisation and subsequent flotation.

Table 5 shows the operational conditions and results from tests performed to evaluate the new technique. The tests in the first stage were conducted in the presence of 500 g/ton of Na_2SiO_3 and 40 g/ton of PAX at pH=9. According to this table, the Cu recovery and grade were enhanced in the second stage compared to the first stage. This technique has significantly improved the flotation performance in the second stage even in the low dosage of $Na_2S.9H_2O$. Moreover, the results of the second stage indicated that the conditioning time of $Na_2S.9H_2O$ is more effective factor than its dosage on the flotation performance. A view of the cell concentrate in the second stage of flotation is shown in Fig. 3.

Evaluation of the concentrates of the run 5 showed that 80.42 and 46.48 wt% of the concentrates in the first and second stages of flotation consist of fine particles (finer that 38 micron), respectively. The increase in size of particles and the decrease of fines in the concentrate of the second stage indicate the improvement of $Na_2S.9H_2O$ consumption by performing the two-stage sulphidisation-flotation technique.

Table 4. Evaluation of multistage sodium sulfide addition (conditions and results)

Run	$Na_2S.9H_2O$ at each stage (g/t)	Stages (No.)	Grade (%)	Recovery (%)
1	500	1	6.6	21
2	250	2	8.6	21
3	500	2	10.7	32
4	700	2	9	35.3
5	250	3	6.2	19.6
6	500	3	9.8	40

Table 5. Evaluation of the SSF technique (conditions and results)

Run	$Na_2S.9H_2O$ in stage 1 (g/t)	Cond. time in stage 1 (min)	Grade in stage 1 (%)	Recovery in stage 1 (%)	$Na_2S.9H_2O$ in stage 2 (g/t)	Cond. time in stage 2 (min)	Grade in stage 2 (%)	Recovery in stage 2 (%)	Total grade (%)	Total recovery (%)
1	250	6	5.9	15.2	250	1	13	33.4	9.45	48.6
2	500	6	7.7	21.2	500	1	14.2	36.4	10.83	57.6
3	700	6	8.2	23.3	700	1	14	48.3	11.38	71.6
4	800	6	7.3	24.6	800	1.3	9.2	21.6	8.08	46.2
5	700	6	7.8	25.3	500	1.3	16	44	11.56	69.3
6	700	6	7.5	24	250	1.3	15.1	46.2	11.21	70.2
7	700	6	7	26	100	1.1	12.8	38.7	9.60	64.7

Fig. 3. A view of malachite concentrate in the second stage of sulphidisation-flotation

Maximizing the Cu recovery is important in the rougher step. Based on the values of the total recoveries in the Table 5, the primary tests were conducted by using the new SSF technique in three stages. Reasonable results obtained from the tests confirmed the necessity of conducting the sulphidisation-flotation technique in three stages. Therefore, the following operational conditions were selected for the subsequent tests:

- Addition of 50 wt% of $Na_2S.9H_2O$ in the first stage, 25 wt% of $Na_2S.9H_2O$ in the second stage with the conditioning time of 1.5 min and 25 wt% of $Na_2S.9H_2O$ in the third stage with the conditioning time of 2 min (the conditioning time of the first step obtains from the difference of the total conditioning time and the conditioning time of second and third stages).
- Flotation of the first, second and third stages at 2.5, 3 and 2 min, respectively.

3.5. Evaluation of the supplementary tests

Based on the previous studies and the results of primary tests, pH, dosages of Ni_2SiO_3, $Na_2S.9H_2O$ and PAX, and conditioning time of $Na_2S.9H_2O$ were chosen as the key and independent factors in the supplementary tests with the levels presented in Table 6.

Table 6. Experimental factors and their levels to optimize the flotation process

Actual factors	Unit	Coded factors	Limit & Level		
			-1	0	+1
pH	-	A	8	9	10
Na_2SiO_3	g/t	B	500	1000	1500
$Na_2S.9H_2O$	g/t	C	600	1200	1800
PAX	g/t	D	40	70	100
Cond. time of $Na_2S.9H_2O$	min	E	5	7.5	10

The response surface methodology (RSM) based on central composite design (CCD) with a rotatable deign ($\alpha = 1.82$) was used to optimize the selected factors. The variance analysis (ANOVA) of tests was performed using the Design-Expert software package (version 7.0.0) from Stat-Ease, Inc., USA. Optimized conditions were estimated using the software's numerical and graphical optimization tools.

3.5.1. Modelling of the Cu recovery and grade

Based on the Design-Expert results, the best models for the Cu recovery and grade included quadratic and 2-factor interaction terms. The ANOVA results indicate the significance of the recovery and grade models with F-values of 155.7 and 37.4, respectively. The terms of models are also significant (p-values<0.05). In contrast, the lack of fit for the models are not significant. The significance of this indicator means that either repeated tests have been incorrect or the model is not well fitted to the experimental data (Whitcomb and Anderson, 2004; Myers et al., 2009).

The high correlation coefficients of the models indicate the good agreement between the experimental and predicted data. The adjusted R^2 and predicted R^2 for the models are also close to each other with maximum difference of less than 0.2, which is statistically important for validity of the models. The second-order response functions for the Cu recovery and grade can be expressed in terms of coded factors as follows:

1. Cu recovery (%)= $+76.44 + 4.56A + 3.05B + 7.13C + 5.39D + 1.90E + 3.34AD + 1.67BC - 5.42A^2 - 3.47B^2 - 8.25C^2 - 4.17D^2$
2. Cu grade (%) = $+9.26 - 0.33A - 0.34B - 0.52C - 0.40D - 0.11E - 0.24AD - 0.21BE - 0.12\ CE - 0.22DE + 0.39A^2 + 0.29B^2 + 0.44C^2 + 0.36D^2$

Empirical models for Cu recovery and Cu grade were presented based on the coded factors (-1, 0, 1 levels for each factor). When the models are presented based on the coded factors (not based on the actual factors), the importance of different factors can be compared on the basis of their coefficients in the fitted models. Based on the coefficients of factors in the proposed models, coefficient of the $Na_2S.9H_2O$ (C factor) is 7.13 and 0.52 in the Cu recovery and Cu grade fitted models, respectively. Therefore, $Na_2S.9H_2O$ is the most effective factor on the Cu recovery and grade. In contrast, the conditioning time of $Na_2S.9H_2O$ has no effect on the Cu grade in the concentrate and its effect on the recovery is negligible.

3.5.2. Evaluation of the effective factors

In this section, the effect of each effective factor on the Cu recovery and grade was evaluated in the central level of other factors.

3.5.2.1. pH

The changes of the Cu recovery and grade with pH is shown in Fig. 4. According to this figure, the recovery was increased up to pH=10 and after that it was decreased. This trend has been reverse for Cu grade. The Eh-pH diagram of the copper-xanthate compounds (Wiess, 1985) was evaluated to find the reason of this behaviour. The copper flotation takes place in the area on the Eh-pH diagram where the hydrophobic species of CuEX(s) is formed. In contrast, the depression of Cu occurs in the stability area of $Cu(OH)_2(s)$ and $(EX)_2(aq)$ compounds. This fact shows that the decrease of the Cu recovery in pH>10 is due to the formation of $Cu(OH)_2(s)$ instead of CuEX(s).

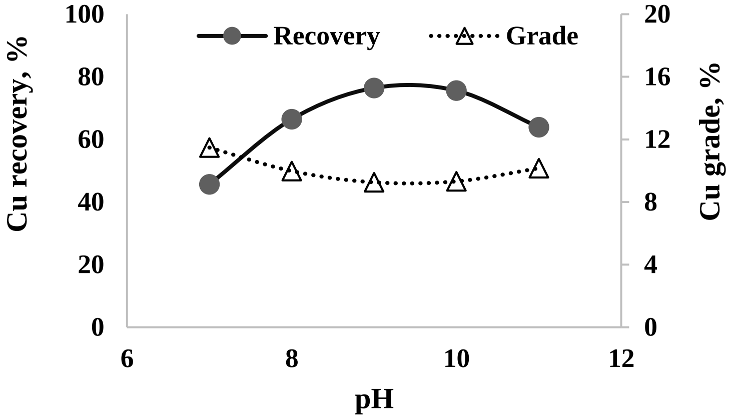

Fig. 4. Effect of pH on the Cu recovery and grade. Curves indicate regression models

Based on the Cu recovery and grade models, this factor interacts with the PAX dosage, as shown in Fig. 5. According to Fig. 5a, the positive effect of pH increase (up to <10) on the Cu recovery is obviously enhanced in the higher dosage of collector. Fig. 5b confirms the subsequent decrease of Cu grade under these conditions.

3.5.2.2. Sodium silicate

Fig. 6 shows the effect of Na_2SiO_3 on the Cu recovery and grade. The incremental recovery trend by adding Na_2SiO_3 up to 1500 g/t proves the positive effect of chemical agents with dispersion property in improving the flotation of fine minerals. Moreover, higher dosages of Na_2SiO_3 helps to improve the flotation performance by the depression of silicate minerals (Jorjani et al., 2011). Of course, in any flotation operation, the dosage of Na_2SiO_3 used would be such that it will not exceed the solubility limit of silica in the slurry. The silica will be in the polymeric or colloidal form with negative surface charge above its solubility limit. With the addition of dense Na_2SiO_3 solution into slurry, the insoluble limit will go down and the depolymerisation of colloidal silica will start. Then, these will combine with silicate minerals by hydrogen bond and depress them selectively. Consequently an increase in grade and a decrease in recovery are expected (Naik and Sita Rama Reddy, 2006). The changes of Cu grade and recovery at dosages higher than 1500 g/t of Na_2SiO_3, Fig. 6, confirms this subject.

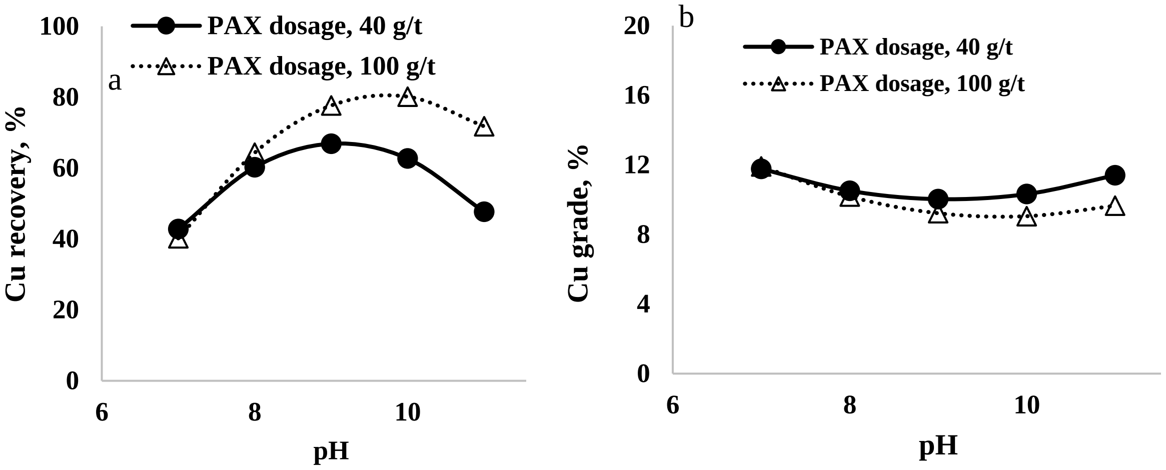

Fig. 5. Interaction effect of pH and PAX dosage: (a) effect on the Cu recovery, (b) effect on the Cu grade. Curves indicate regression models

The terms of the Cu recovery and grade models display that Na_2SiO_3 has a common effect with the dosage and conditioning time of $Na_2S.9H_2O$. Fig. 7 shows the interactions between these factors. According to Fig. 7a, the Cu recovery was enhanced with the increase of $Na_2S.9H_2O$ in the same dosages of Na_2SiO_3. This is obvious because the depression of silicate minerals and the dispersion of fine particles from the malachite surfaces result in the better sulphidisation of surfaces at the higher dosages of Na_2SiO_3, which leads to the increase in Cu recovery. Fig. 7b reveals that the interaction of Na_2SiO_3 and conditioning time of $Na_2S.9H_2O$ on the Cu grade is not appreciable. However, the increase of Na_2SiO_3 dosage and the better dispersion of fine particles from the malachite surfaces leads to the decrease of the conditioning time required for $Na_2S.9H_2O$.

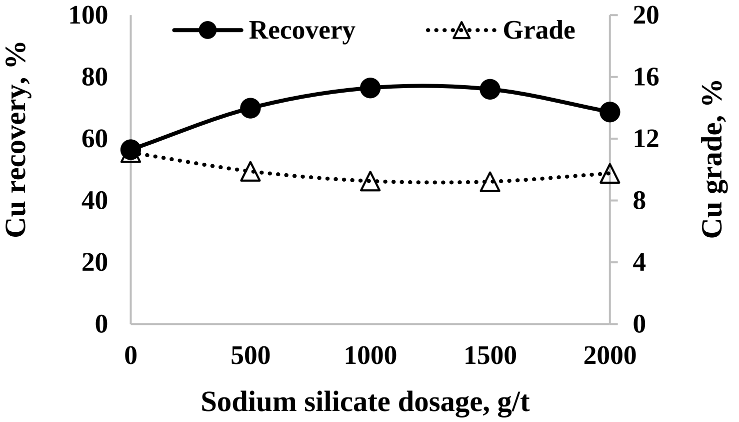

Fig. 6. Effect of sodium silicate dosage on the Cu recovery and grade. Curves indicate regression models

3.5.2.3. Sodium sulfide

Flotation of the copper oxide minerals is very sensitive to the consumption dosage of $Na_2S.9H_2O$. In the low concentrations of the sulfide ions, the soluble Cu^{2+} ions in the pulp precipitate as CuS. By removing Cu^{2+} ions, the additional S^{2-} ions is adsorbed on the malachite mineral surface. In this way, the copper sulfides are formed on the surfaces and their flotation is conducted readily. In the high concentrations of the sulfide ions, these ions are preferably adsorbed on the surfaces rather than xanthate and consequently, the depression of malachite occurs (Fuerstenau et al., 1985). The changes of the Cu recovery and grade with the change of $Na_2S.9H_2O$ dosage in Fig. 8a confirms this subject.

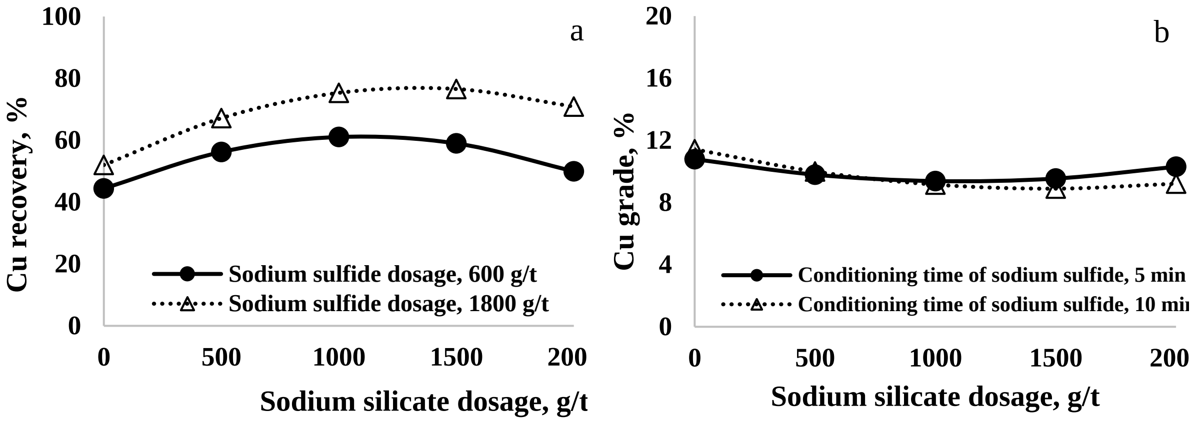

Fig. 7. Interaction effect of factors on the Cu grade: (a) Sodium silicate & sodium sulfide dosages, (b) Sodium silicate dosage & conditioning time of sodium sulfide. Curves indicate regression models

3.5.2.4. *PAX*

The effect of collector dosage on the Cu recovery and grade is shown in Fig. 8b. In the flotation systems, the amount of concentrate content particles is usually increased with the increase of collector dosage up to critical micelle concentration (CMC). It has been shown that if the amount of collector exceeds the CMC, the collector is removed from the surface of target mineral in the form of clusters (Fuerstenau et al., 1985). Therefore, the recovery of target mineral is decreased. To the authors' knowledge no value has been reported for PAX CMC. According to Mirgorod and Dolenko (2015), PAX has a critical micelle concentration and can form micelles. In fact, by increasing the collector dosage, Cu recovery is increased and Cu grade is decreased. This issue is confirmed in Fig. 8b.

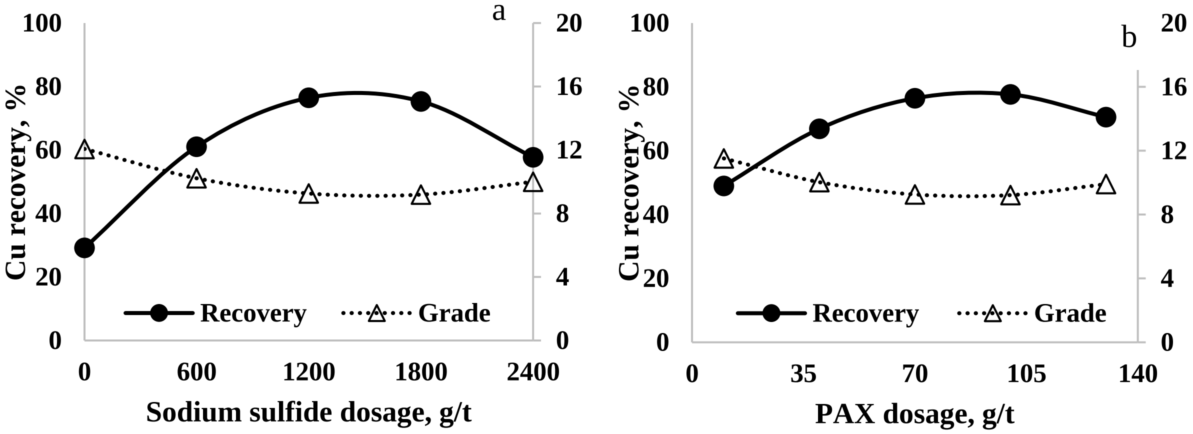

Fig. 8. a) Effect of sodium sulfide dosage on the Cu recovery and grade, and b) effect of PAX dosage on the Cu recovery and grade. Curves indicate regression models

3.5.2.5. *The conditioning time of sodium sulfide*

Results of the supplementary tests proved that the conditioning time of $Na_2S.9H_2O$ also affects the performance of the SSF technique. Fig. 9 shows the positive effect of this factor on the Cu recovery, however, the changes of Cu grade are not noticeable with the increase of this factor.

According to the ANOVA results, the interaction of this factor with the factors of $Na_2S.9H_2O$ and PAX dosages significantly affects the Cu grade. The decrease of Cu grade with increasing the conditioning time in the higher dosages of $Na_2S.9H_2O$, Fig 10a, is probably due to the sulphidisation-flotation of gangue minerals and/or the preferred adsorption of sulfide ions on the surfaces rather than xanthate, subsequently, the re-depression of malachite. The intangible changes of Cu grade with increasing the conditioning time in the low dosages of $Na_2S.9H_2O$ confirms these results. According to

Fig. 10b, the same interaction was observed between this factor and the PAX dosage. As shown in Fig. 9, the Cu recovery in the central level of $Na_2S.9H_2O$ dosage (1200 g/t) was enhanced with the increase of the conditioning time of $Na_2S.9H_2O$. Therefore, the simultaneous increase of collector dosage was obviously enhanced the recovery of minerals and was subsequently reduced the Cu grade (Fig. 9).

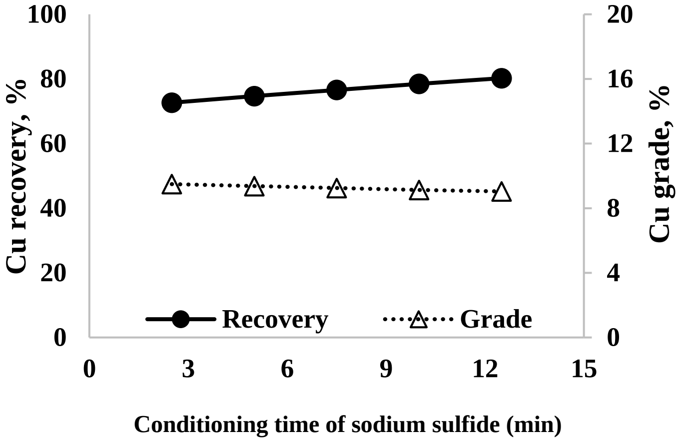

Fig. 9. Effect of conditioning time of sodium sulfide on the Cu grade and recovery. Curves indicate regression models

3.5.3. *Optimization*

The optimization process of flotation aimed to find the operational conditions that would maximize the Cu recovery and grade. This process was performed using the Design-Expert software in two states. In the first state, the factors were optimized throughout their range used in this research. In the second state, the minimization of reagents consumption was considered to have a more economical process. Regarding the price of reagents and their optimum consumption in the first state, the more importance was considered to minimizing the dosage of $Na_2S.9H_2O$ relative to the dosages of Na_2SiO_3 and PAX in the second state. In addition, since the optimization process was conducted on the results of rougher step, the maximum and minimum importance was chosen for Cu grade and recovery, respectively. The optimum operational conditions and the validation results are presented in Table 7. The results show a good agreement between the model prediction and the experimental data.

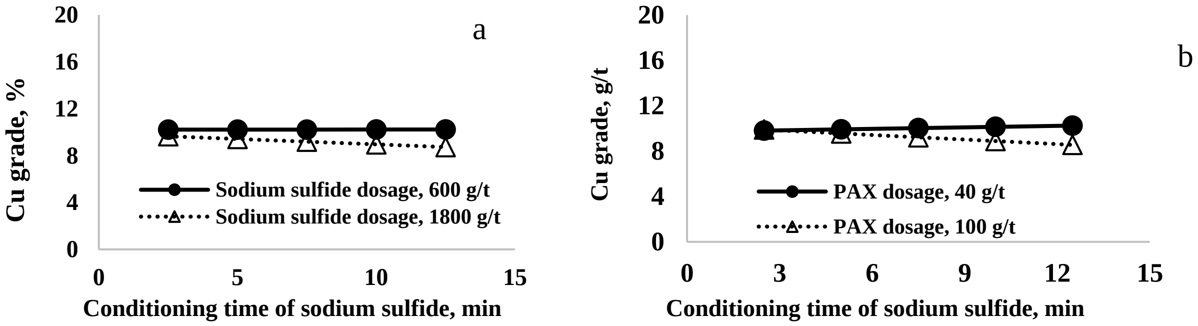

Fig. 10. Interaction effect of factors on the Cu grade: (a) conditioning time of sodium sulfide & sodium sulfide dosages, (b) conditioning time of sodium sulfide & PAX dosages. Curves indicate regression models

Table 7. Results of supplementary tests under optimum operational conditions

State	pH	Na_2SiO_3 (g/t)	$Na_2S.9H_2O$ (g/t)	PAX (g/t)	Con. time (min)	Predicted		Experimental	
						Recovery (%)	Grade (%)	Recovery (%)	Grade (%)
1	9.72	1500	1567	100	5	80.52	9.44	81.15	9.28
2	9.30	556	866	59	10	65.00	10.62	66.41	10.09

3.6. Evaluation of the cleaner step

The tests of the cleaner step were conducted for the Cu concentrated product of the rougher step. The operational conditions and related results are presented in Table 8. According to this table, the flotation performance is not desirable in the absence of additives. In addition, the consumption of the collector and sulphidising agent in this step have been increased due to the improvement of Cu grade and the subsequent enhance of malachite surfaces. The results indicate that the application of the new technique significantly improved the flotation performance in the cleaner step, too. An illustration of the concentrate of this step is shown in Fig. 11. The best test in this step led to the production of a concentrate containing 24% Cu with the recovery of 91.8%.

Table 8. Cleaner tests (conditions & results)

Run	Operational conditions	Recovery (%)	Grade (%)
1	Flotation for 1.5 min	23	10
2	100 g/t of $Na_2S.9H_2O$ with the conditioning time of 4 min, 10 g/t of PAX with the conditioning time of 2 min and flotation for 1.5 min	39	14.2
3	400 g/t of $Na_2S.9H_2O$ with the conditioning time of 4 min, 40 g/t of PAX with the conditioning time of 2 min and flotation for 1.5 min	48	13.65
4	200 g/t of $Na_2S.9H_2O$ with the conditioning time of 2 min in two stages, 40 g/t of PAX with the conditioning time of 2 min and flotation for 1.5 min	63.28	17.32
5	200 g/t of $Na_2S.9H_2O$ with the conditioning time of 2 min in four stages, 80 g/t of PAX with the conditioning time of 2 min and flotation for 1.5 min	91.8	24

Fig. 11. Cleaner concentrate

4. Conclusions

The fine particles have an adverse effect on the sulphidising flotation of copper oxide minerals. Primary solutions to reduce these effects on the flotation performance are the decrease of fine production in the crushing and grinding operations and/or the remove of this size fraction from the concentration process.

In this research, despite the executive considerations in the crushing and grinding operations, the presence of 39% Cu in the size fraction of -38 µm prevented the remove of this particles from the flotation process. The new SSF technique was identified as a successful operational initiative to solve the processing problems of the fine particles. In this technique, most of the fine particles were removed from the cell in the first step of flotation and consequently, the residual particles found enough opportunity for the contact with $Na_2S.9H_2O$ in the subsequent flotation steps. One potential concern with the proposed SSF technique is time dependant surface area/Na_2S concentration relation which could be investigated for a mixture of malachite and various gangue minerals.

Based on the results obtained from the primary tests, three stage sulphidisation-flotation was chosen as the suitable experimental procedure in the supplementary tests. The response surface methodology

(RSM) based on central composite design (CCD) was used to optimize the factors of pH, Na_2SiO_3 dosage, Na2S.9H2O dosage, PAX dosage and conditioning time of $Na_2S.9H_2O$. Based on the optimum operational conditions (pH=9.72, 1500 g/t of Na_2SiO_3, 1567 g/t of $Na_2S.9H_2O$, 100 g/t of PAX and conditioning time of 5 min for sulphidisation), the rougher concentrate was achieved with the Cu recovery and grade of 81.51% and 9.28%, respectively. The best result in the cleaner step (Cu recovery of 91.8% and Cu grade of 24%) was obtained by using 200 g/t of $Na_2S.9H_2O$ with the conditioning time of 2 min in four stages, 80 g/t of PAX with the conditioning time of 2 min and flotation for 1.5 min. The total Cu recovery and grade of the rougher and cleaner steps achieved to 74.5% and 24%, respectively.

Dissolution of the high-grade concentrate produced in the agitation leaching process can lead to the dense pregnant leach solution (PLS). The presence of dense PLSs in the subsequent concentration processes (solvent extraction-electrowinning) will accelerate the copper production process.

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