Improvement of copper sulfide flotation using a new collector in an optimized addition scheme

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Abstract: Selection of appropriate types of collectors as the main basis of flotation can have a significant impact on the process efficiency. In this regard, 2, 5-Dimercapto-1, 3, 4-thiadiazole (DMDT) was introduced as a new collector. And, its performance was compared with the prevalent collector C7240 (a mixture of 10–20 wt% sodium alkyl dithiophosphate and 20–30 wt% sodium mercaptobenzothiozole) and Sodium Isobutyl Xanthate (SIBX) on the flotation of copper sulfide ores. The effect of the reagent dosage (collector and frother) and pH level were studied using a design of experiment (DOE). Results showed effect of factors was significant in the case of copper recovery and grade of product. Consequently, the optimum range of the DMDT was 8 g/t at pH=11.8 in which the maximum grade and recovery were obtained. Also, the application of chemical agents also had a significant effect on flotation performance, so that the result of sequential addition of the collector indicated significantly improved recovery and grade. The use of a combination of collectors resulting in both physisorbed and chemisorbed surface products can also affect the froth structure and influence the final grade achieved. Accordingly, the best route of collector addition was DMDT at first, then C7240, and finally SIBX. Through this offer, the maximum recovery and grade of product were achieved 86.2% and 14.1% respectively. So, DMDT as a mixture of two others has a positive effect on the copper flotation efficiency.

Keywords: flotation, copper sulfide, reagents addition scheme, DMDT

1. Introduction

1.1. Copper sulfide flotation

Flotation is one of the most important method to separate valuable minerals based on the difference in physiochemistry of surface of particles (Nguyen and Schultze, 2004; Furstenau et al., 2007) Among influential factors on the flotation performance, rate of particle attachment to the bubbles is critical (Xing et al., 2017a; Xing et al., 2017b; Li et al., 2020; Gautam and Jameson, 2019). From this prospective, the difference between the hydrophobicity of surfaces is not usually considerable. Therefore, various agents such as frothers, collectors and modifiers are used to improve the selectivity of the flotation (McFadzean et al, 2013; Liu et al., 2017; Muganda et al., 2011; Chipfunhu et al., 2012). The significant raw materials for copper production are of copper sulfide and oxide minerals. With the rapid and continuous exploitation of copper sulfide ores, copper oxide or mixed oxide-sulfide copper ores have become indispensable in compensation of copper shortage (Han et al., 2021; Zhang, 2021a; Zhang, 2021b). The different collectors and their interactions on the recovery and grade has been studied. Bradshaw (1998) and Lotter and Bradshaw (2010) have investigated the effect of the mixed collector on the sulfide flotation (Bradshaw, 1998; Lotter and Bradshaw, 2010). The results show that mixed collector have a positive effect on the rate of surface absorption of collector. Another important point is the importance of degree of mixing and the percent of any type of collector in the final mixed agent. Wakamatsu et al. (1980) indicate the simultaneous adsorption of ethyl xanthate and dibutyl dithiophosphate at low concentration as well as their competitive absorption at high concentrations (pH=6-7) (Wakamatsu et al., 1980). Surface adsorption studies indicate that there is an interaction between ethyl xanthate and

dibutyl dithiophosphate when both agents mixed in 50:50 ratio. Woods (1984) has investigated the effect of mixture of xanthate and dithiocarbamate to explain the rate of chemical adsorption. It has been shown that they are distributed more uniformly than the physical adsorption on the surface (Woods, 1984). McFadzean et al. (2012) reported an increase in flotation rate of pure minerals using a mixture of diethyl dithiophosphate and isobutyl xanthate as collector (McFadzean et al. 2012). Results shows that the sequential addition of collector has a significant effect on the rate of flotation. Bagci et al. (2007) and Critchley and Riaz (1991) have shown that dithiophosphate before sodium isobutyl acetate can improve surface adsorption of collector significantly (Bagci et al., 2007; Critchley and Riaz, 1991; Dehar et al. 2019). Dehar et al. (2019) investigated the effect of sodium isobutyl xanthate, N-butoxycarbonyl-O-N-ethyl thionocarbamate and butyl dithiophosphate as well as their mixtures on the selective flotation of copper sulfide. Results show the significant effect of the mixture agent on the flotation recovery.

1.2. 2, 5-Dimercapto-1, 3, 4-thiadiazole structure

Mercaptans are one of the simplest alcohol-derived thiol collectors (R-OH), in which sulfur is replaced by oxygen and produces R-SH. 2, 5-Dimercapto-1, 3, 4-thiadiazole (DMT) is mercaptan collector as strong proton donor (pKa1=-1.36, pKa2=7.5) (Shouji et al., 1997), and it can react with copper. Huang et al. (2001) investigated the interaction mechanism of DMT on the copper surface using Surface-enhanced Raman spectroscopy (SERS), infrared spectroscopy (IR), and X-ray photoelectron spectroscopy (XPS) (Huang et al., 2001). Results show that DMT can attach to particle surface through two mercapto exocyclic groups. In other words, when DMT collide to copper surface, mercapto group (R-SH) desorbs from DMT to the surface. Due to increasing H^+ on the surface, copper oxidation may occur to convert Cu^0 to Cu^+. Fig. 1 shows the structure of DMT and its polymerization process on the surface.
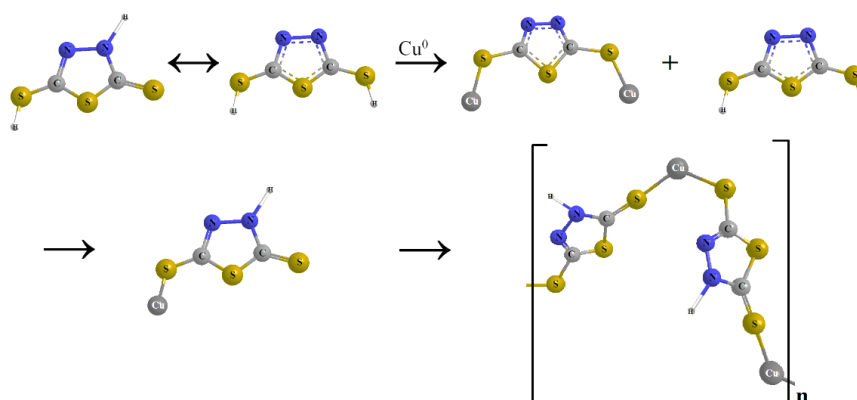

Fig. 1. Mechanism of DMTD interaction with copper ore surface

The use of mixtures of collectors has long been recognized in plant practice and has been shown to enhance flotation performance. These benefits have been reported for a wide range of collector mixtures (anionic, cationic and non-ionic) and include lower dosage requirements, improved selectivity and rates and extents of recovery and an increase in the recovery of coarse particles. In many cases an optimum ratio of constituent collectors was shown to exist. Dithiophosphates are a class of thiol collectors that are so widely used in mixtures that they are known as promoters.

In the present study, the main purpose was to investigate the efficiency of 2, 5-Dimercapto-1, 3, 4-thiadiazole (DMDT) as a new collector, as well as the effect of its mixture with the common collectors. Also, sequential addition of various collectors may significantly impact on the copper flotation from sulfide ores.

2.   Materials and Methods

2.1. Sample analysis

In this study, the copper sulfide ore used in all the tests was obtained from Sarcheshmeh Copper Complex, Rafsanjan, Iran. Modal analysis of the sample shown in Table 1.

Table 1. XRF analysis of copper sulfide ore

Elements	Cu	CuO	Fe	SiO$_2$	Al$_2$O$_3$	S	MgO	K$_2$O	Na$_2$O	LOI
Mass (%)	0.71	0.03	6.04	51.74	13.43	4.49	2.87	2.59	1.43	16.67

Presence of silicates indicates the negative effect on the copper recovery and grade from the surface chemistry point of view because it may impact the particle surface characterization due to their minor dissolution (Nuri et al., 2019; Kang et al., 2018; Taguta et al., 2019; Mohammadi-Jam et al., 2014; Irannajad et al., 2019).

2.2. Copper flotation test

Flotation tests were performed in two schemes: 1- flotation tests with individual collectors 2- flotation tests with the mixture of agents. At the first route, maximum concentration of collectors used to perform all experiments but the second series performed in two level for collectors concentration. It should be noted that the specific route of collector addition has been selected to obtain the best route in copper flotation. Full factorial design has been selected to perform experiments including dosages of flotation agents (collector and frother) and pH as factors in three levels (36 runs) (Table 2). It should be noted that the amount of collector for each test was obtained with the mixture of three collectors with specific contribution empirically as shown in Table 2. In other words, due to decreasing the number of experiments as well as considering the effect of each collector on the overall recovery and grade, mixture of three collectors indicated as one factor. This route used in case of frother as another factor. DX7 software used for experimental design and data analysis. According to previous empirical results, level of factors has been selected to perform all flotation tests as well as ANOVA method used to determine the effect of factors on the flotation responses. Model for calculation of recovery and grade according to effective factors presented based on software output. In other words, mathematical model to predict recovery and grade of concentrate obtained based on effective factors and ANOVA output by software. of All flotation experiments were conducted in a 4.3L Denver flotation cell with solid percent 28%- and -74-micron particles. After addition of the preconditioned ore into the water, the resultant slurry was agitated for 4 min. Lime was used for pH adjustment to 10-11.8, and then the flotation agents added to the slurry with 3 min and 1 min conditioning time for collector and frother, respectively. The impeller speed was 1400 r/min. The aeration rate was 6 l/min. All the concentrate products and tailings were filtered and dried in an oven at 60 °C, then weighed for suitable analysis.

Table 2. Experimental scheme for flotation test

Factor		Low level	Medium level	High level
Collector (g/t)	SIBX	7		19
	C7240	12		24
	DMTD	6		12
	Sum	25	40	55
Frother (g/t)	MIBC	12.5		22.5
	NAS	12.5		22.5
	Sum	25	35	45
pH		10.0	10.6 11.6	11.8

3. Results and discussion

3.1. Flotation characteristics

Fig. 2 shows the result of flotation tests with different collectors. Accordingly, the maximum grade and recovery achieved by using DMTD and SIBX collector respectively. It seems that mixture of them could

improve the separation efficiency of copper flotation. In this Fig., DMDT had a better efficiency than the rest due to achievement of higher grade of copper.
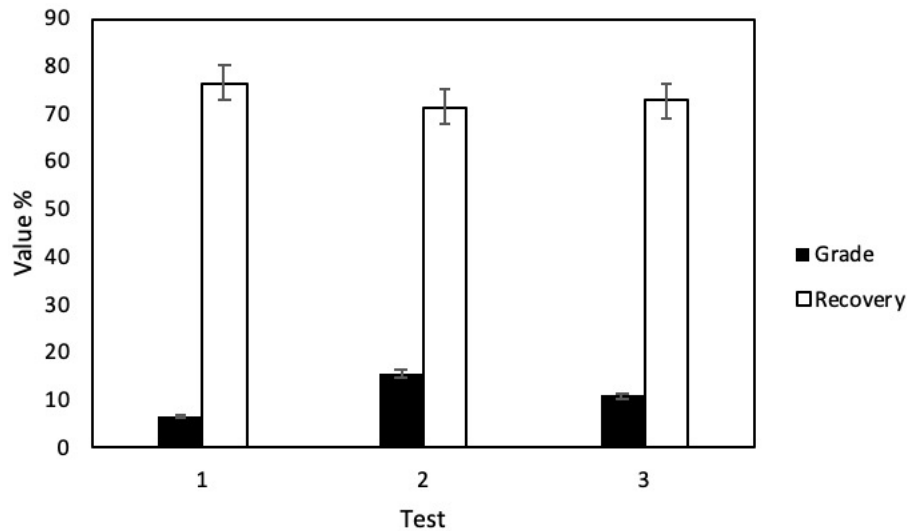

Fig. 2. Effect of common collectors on the grade-recovery profile (1: SIBX 2: DMTD 3: C7240)

3.2. Flotation optimization

Fig. 3(a), shows the effect of collector dosage and type on the copper recovery and grade at pH 10 -11.8. In the presence of the collector, copper recovery and grade increased with increasing pH. Increasing collector dosage from 25 to 35 g/t improved maximum copper recovery at pH=11.8. On the other hand, according to Fig. 3(b), the maximum grade was obtained using 25-40 g/t of the collector at pH=11.8. From Fig. 3(a) it can be seen that the area that give best values for the product recovery is towards high collector and pH. Taking the region or contour with a collector dosage range of 25–55 g/t and pH range of 10–11.2 as the optimum region. From Fig. 3(b) it can be seen that the area that give best values for the product grade is towards low collector and high value of pH. Taking the region or contour with a collector dosage range of 25–37 g/t and pH range of 11.2–11.8 as the optimum region.
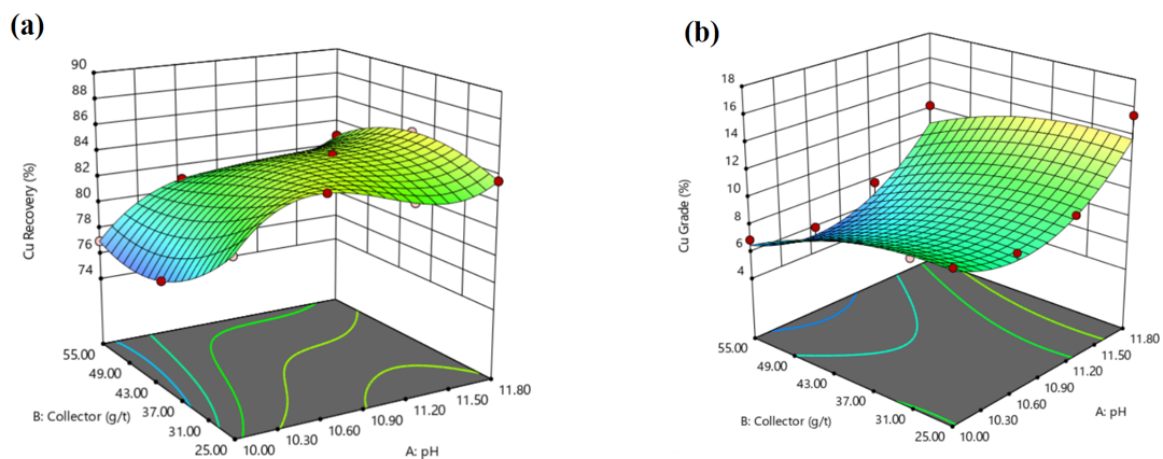

Fig. 3. Simultaneous effect of collector dosage (g/t) and pH on (a) Cu recovery (%) and (b) Cu grade (%)

According to Fig. 4(a), the maximum copper recovery was obtained by using 25 g/t of frother at pH=11.8, and 45 g/t at pH=10.0. Therefore, it can be concluded that increasing pH (up to 11.8) may be reduce the frother consumption. Fig. 4(b) shows the maximum grade obtained by increasing frother dosage to 45 (g/t) at pH 11.8. From Fig. 4(a) it can be seen that the area that give best values for the product recovery is towards high frother and lower values of pH. Taking the region or contour with a frother dosage range of 40–45 g/t and pH range of 10.6–11.2 as the optimum region. From Fig. 4(b) it

can be seen that the area that give best values for the product grade is towards high frother and high value of pH. Taking the region or contour with a frother dosage range of 35–45 g/t and pH range of 11.2–11.8 as the optimum region.
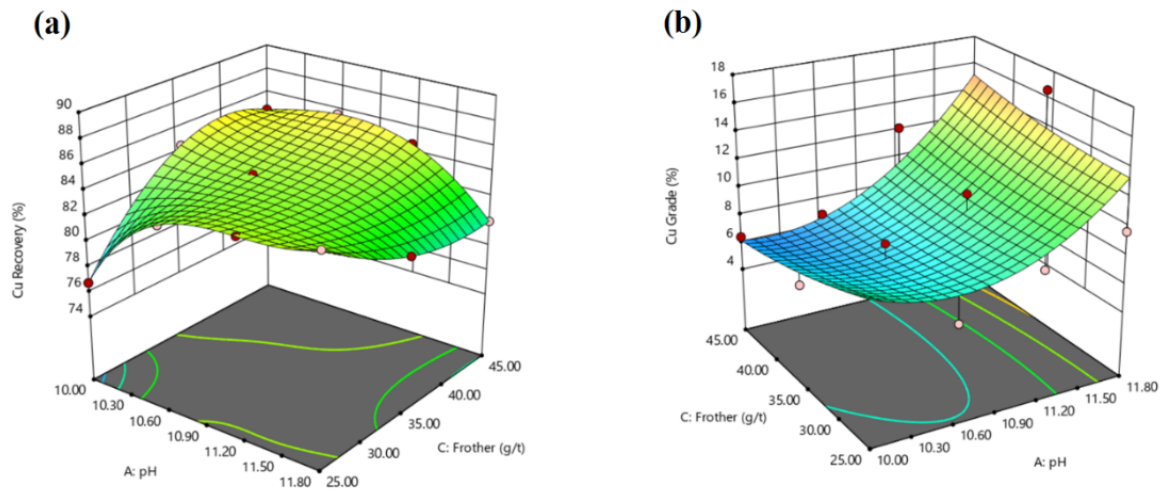

Fig. 4. Simultaneous effect of frother dosage (g/t) and pH on (a) Cu recovery (%) and (b) Cu grade (%)

Fig. 5(a) shows the effect of collector and frother dosages on the copper recovery. Results showed frother plays an important role in flotation system to improve the collector performance. The maximum copper recovery was obtained at 25 - 40 g/t of collector, which could be due to the fact that the desired particles are becoming more hydrophobic, but it fell with increasing collector dosage up to 40 (g/t). Fig. 5(b) indicates the minimum concentration of frother and collectors to obtain the maximum level of grade of copper concentrate. From Fig. 5(a) it can be seen that the area that give best values for the product recovery is towards high frother and high collector. Taking the region or contour with a collector dosage range of 25–43 g/t and frother ange of 25-35 as the optimum region. From Fig. 5(b) it can be seen that the area that give best values for the product grade is towards low frother and low collector. Taking the region or contour with a frother dosage range of 25–35 g/t and collector range of 25-37 g/t as the optimum region.

The optimum level of the factors, collector, frother and pH, was shown in Table 3. Optimum levels obtained according to value of the separation efficiency of any experiments. In other words, optimum level caused the maximum separation efficiency factor.
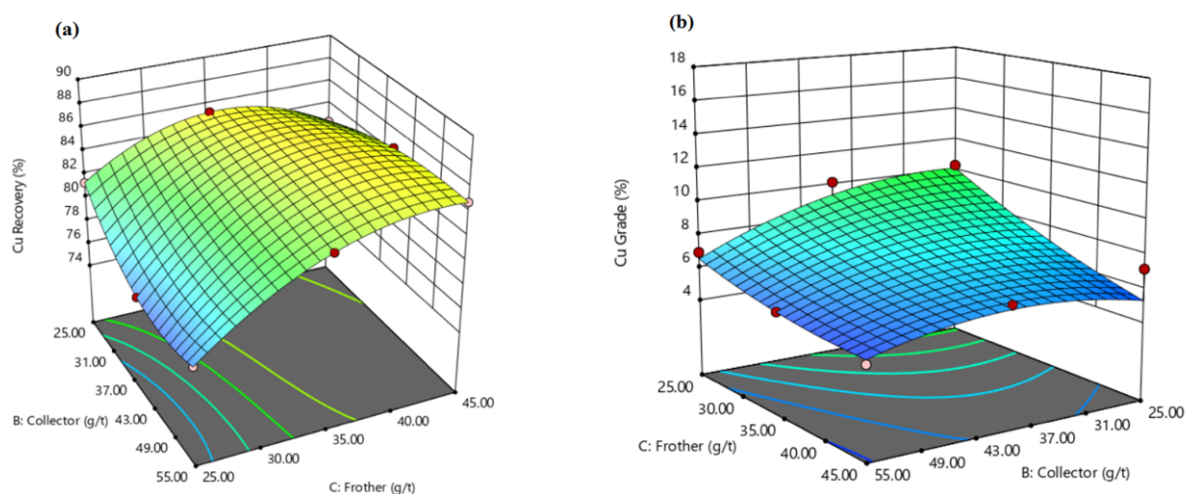

Fig. 5. Simultaneous effect of frother dosage (g/t) and collector dosage (g/t) on (a) Cu recovery (%) and (b) Cu grade (%)

Table 3. The optimal level of variables in floatation process

Variable		Optimal level
Collector (g/t)	SIBX	11
	C7240	16
	DMTD	8
Sum		35
Frother (g/t)	MIBC	12.5
	NAS	12.5
Sum		25
pH		11.8
Cu recovery (%)		85.1
Cu grade (%)		13.7

$$y_r = -330.39 + 66.61\ X_1 + 0.14\ X_2 + 2.92\ X_3 - 0.03\ X_1 X_2 - 0.20\ X_1 X_3 + 0.005\ X_2 X_3 - 2.68\ X_1^2 - 0.001\ X_2^2 - 0.01\ X_3^2 \tag{1}$$

where y_r is the copper recovery; X_1, X_2 and X_3 are pH, collector and frother dosages respectively. According to Table 4, all the three factors had significant effect on the copper recovery and the order of influence was: collector > frother > pH. It should be noted that the interaction between the effect of three factors were significant except between pH and frother dosage. In sum, Table 4 indicated the predicted model was significant (P-value of 0.0222<0.05) to predict of recovery data based on values of factors.

Table 4. Variance analysis for copper recovery data

Source	Sum of squares	df	Mean square	F-value	P-value
Model	258.25	34	7.60	1276.28	0.0222
X_1-pH	0.0703	1	0.0703	11.81	0.0183
X_2-Collector	5.12	1	5.12	859.90	0.0217
X_3-Frother	1.67	1	1.67	280.27	0.0380
$X_1 X_2$	8.42	1	8.42	1414.28	0.0169
$X_1 X_3$	0.5631	1	0.5631	94.62	0.0652
$X_2 X_3$	1.15	1	1.15	193.01	0.0457
X_1^2	0.6320	1	0.6320	106.20	0.0616
X_2^2	8.16	1	8.16	1371.23	0.0172
X_3^2	1.44	1	1.44	241.80	0.0409

3.4. Prediction of grade

As mentioned before, effect of three factors (pH, Collector and frother) was investigated by using analysis of variance (ANOVA) (Table 5). Based on the results, the grade may be predicted as follow:

$$y_g = 7.71 + 3.24\ X_1 - 0.81\ X_2 - 0.35\ X_3 + 0.19\ X_1 X_2 + 1.26\ X_1 X_3 + 0.81\ X_2 X_3 + 2.91\ X_1^2 - 1.06\ X_2^2 + 0.39\ X_3^2 \tag{2}$$

where y_g is the copper grade; X_1, X_2 and X_3 are coded values for pH, collector and frother dosages, respectively. According to Table 5, all three factors had significant effect on the copper grade of the concentrate. It should be noted that the interaction between the effect of three factors were significant except between pH and collector dosage. In sum, Table 4 indicated the predicted model was significant (P-value of 0.0001<0.05) to predict of grade data based on values of factors.

3.5. Sequential addition of collectors

Six series of experiment were performed to investigate the effect of sequential addition of any collectors as well as their mixture on the grade-recovery profiles. The optimum levels were achieved in early experiments used for these series (Table 3). In sequential tests, conditioning time adjusted for 3 minutes for each agent. Results of these test indicate in Table 6.

Table 5. Variance analysis for copper grade data

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	331.86	9	36.87	14.59	< 0.0001
X_1-pH	210.43	1	210.43	83.25	< 0.0001
X_2-Collector	15.83	1	15.83	6.26	0.0190
X_3-Frother	2.93	1	2.93	1.16	0.0291
$X_1 X_2$	0.4650	1	0.4650	0.1840	0.6715
$X_1 X_3$	21.28	1	21.28	8.42	0.0075
$X_2 X_3$	10.50	1	10.50	4.15	0.0518
X_1^2	60.32	1	60.32	23.87	< 0.0001
X_2^2	8.91	1	8.91	3.53	0.0717
X_3^2	1.20	1	1.20	0.4742	0.4971

Table 6. Effect of sequential addition of collectors on the grade-recovery values

Collector mixtures			Cu recovery (%)	Cu grade (%)
First	Second	Third		
C7240	SIBX	DMDT	75.7	9.8
C7240	DMDT	SIBX	81.7	12.4
SIBX	C7240	DMDT	74.4	9.9
DMDT	C7240	SIBX	86.2	14.1
DMDT	SIBX	C7240	85.9	13.8
SIBX	DMDT	C7240	81.2	11.6

shown in Table 6, the maximum grade and recovery were achieved in sequential addition related to specific condition in Table 6. When using mixtures of collectors it has often been observed that there is a greater extent of adsorption on the mineral surface. This could either enhance the overall hydrophobicity of the mineral surface or result in an adsorbed surface layer of collector molecules more suitable for frother-collector interactions. The length of hydrocarbon chain of agents has significant effect on the grade-recovery profile. DMDT with a shorter hydrocarbon chain, improved the grade of concentrate. This was the main step of increasing the copper grade. On the other hand, addition of next two agents (SIBX and C7240) with longer chain (4 and 7 carbon), improved copper recovery rather than the copper grade. Thus, the optimum sequential addition to maximize grade and recovery was as follows: first DMDT, second C7240 and finally SIBX.

4. Conclusions

Effect of a new type of collector (DMDT) and its mixture with the common types (SIBX and C7240) on the flotation performance of copper sulfide were investigated. Results of flotation tests indicated the positive interaction of DMDT on the copper grade (about 16%) with any type of collectors. On the other hand, there was a small difference between the recovery of this reagent compared with the other. Results of statistical analysis of the effect of three factors (collector, frother and pH) showed all of them had a significant effect on the recovery and grade of copper concentrate as well as it was found

interaction between pH and frother dosage was not considerable in recovery model as well as interaction between pH and collector dosage in grade model.it should be noted that prediction model for grade and recovery obtained in the specific range of collector, frother and pH based on empirical data therefore there will be limitations for results of another same route. It is also achieved the significant effect of combination of three types of collectors and addition scheme on the metallurgical performance. Then, the best route for using these reagents were as follows: first DMDT, then C7240 and finally SIBX. With this scheme, optimal separation results were 86.2% recovery and 14.1% grade, as well as the better selectivity in copper flotation.

Acknowledgment

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