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Optimization of flotation of the Qaleh Zari mine oxidized copper ore sample by the sequential sulfidation approach using the response surface method technique

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Original scientific paper

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Abstract

One of the main challenges in the copper oxide processing industry is the application of flotation to reduce operating costs. Sulfidation-flotation is a commonly employed approach for floating oxide minerals using sulfidizers in order to sulfide the mineral's surface. In this research work, an oxidized sample from the Qaleh Zari copper mine was used which was a high grade with 5.4% of copper (malachite and azurite). The prepared sample was subjected to mineralogical studies, and the obtained results indicated that the sample was oxidized. Malachite and azurite were the predominant minerals of copper oxide, and the predominant waste minerals were quartz and iron oxides (hematite and magnetite). The addition of sodium sulfide and flotation in four consecutive steps was a successful approach to meet the proper recovery and grade. Sodium sulfide, amyl potassium xanthate, sodium sulfide preparation time, and pH were selected as operating parameters using a central composite design (CCD). Also, by measuring the zeta potential, the electric charge of malachite was determined in different conditions after adding chemicals. Finally, under optimal conditions, the consumptions of sodium sulfide and amyl potassium xanthate, sodium sulfide preparation time, and pH value were 6790 g/t, 736 g/t, 10 minutes, and 9, respectively. By applying the mentioned conditions, a concentrate with a grade of 22.13%Cu and 90.51% recovery was achieved.

Keywords:
Oxidized copper; flotation; sulfidation; response surface technique; optimization

1. Introduction

Sulfide and oxide minerals are the primary sources of copper in nature. Oxidized minerals are difficult to recover in mineral processing compared to sulfide minerals. With continuous industrial developments, the demand for copper resources has increased. Therefore, adequate enrichment of oxide mineral ore can help in the reduction of this demand. Among mineral processing methods, flotation would be one of the most common to enrich copper oxide minerals (**Lee et al., 2009; Mohammadkhani et al., 2020**). The two main methods for flotation of copper oxide minerals are: i) direct flotation, and ii) flotation with employing sulfidation (**Liu et al., 2020; Xingrog et al., 2021**). The traditional method of copper oxide flotation involves sulfidation of the mineral surface prior to the addition of a copper sulfide collector (**Bulatovic, 2016**). During sulfidation flotation, the mineral surface and the sulfidizing agent undergo chemical adsorption through chemical changes (**Xingrog et al., 2021**). When the sulfidizing agent is at very low levels, the ions in the pulp inevitably consume it which leads to an incomplete sulfidation of the oxide copper ore. Therefore a reduction in the overall recovery occurs, and conversely, when too much sulfide is added, it would trap oxide minerals, and accordingly a reduction in the recovery takes place. Considering the mentioned states, sulfidation is a key factor in the recovery process of copper oxide minerals (**Wang et al., 2021**).

As an alternative to the sulfidation method, several different oxidryl collectors have been employed for the direct flotation of copper oxide minerals, such as fatty acids, amins, phosphonic acids, phosphinic acids, and hydroxamic acids. They often have poor selectivity in the case of waste minerals, while all of them have been effective in recovering copper oxide minerals. The effective and selective way to recover copper oxide minerals is to choose hydroxamic acids as collectors (**Zhou and Chander, 1993**). However, the direct flotation method and hydroxamic collectors are rarely used on an industrial scale, as flotation using a sulfidizing agent is widely selected as a relatively effective approach to recover oxide minerals (**Asadi et al., 2019**).

Different materials have been applied for sulfidation, and there are commonalities between them. The sulfida-

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tion reaction is a heterogeneous process with two secondary reactions in which a primary sulfide layer is first formed on the surface. The formed layer contacts the sulfide ions with CuO, resulting in the formation of copper sulfide. This layer is critical in flotation using xanthate collectors. Secondary sulfidation reactions include forming a secondary sulfide copper layer and the formation of oxysulfide species. A secondary sulfide layer is formed with the diffusion of copper ions through the cracks in the primary sulfide layer (**Lee et al., 1998**). Sodium sulfide (Na_2S) is often used in the sulfidation method. Sodium hydrosulfide (NaSH) and ammonium sulfide ($(NH_4)_2S$) are among the sulfidizers employed on an industrial scale (**Bulatovic, 2010**). In a study conducted by Tebgo et al. on a copper sample from the Region mine in Central Africa, it was found that the application of acid leaching increases acid consumption due to the presence of carbonate and silicate tailings. For this reason, a pre-concentrating process was performed, and flotation consisting of several stages of adding a sulfurizing agent was chosen for the pre-concentrating process. The feed copper grade was 4% which increased to 18% after flotation (**Phetla and Muzend, 2010**) synthesized the novel 3-hydroxybutyrate-carboxymethylcellulose xanthate (HCMCX) collector to increase the flotation efficiency of copper oxide ore from Dangchuan, Yunnan, and China copper mines. This collector achieved 20.19% copper grade and 89.39% of recovery with which copper recovery increased by 5.69% compared to amyl xanthate (AX) (**Chen et al., 2017**). The effect of ammonium sulfate ($(NH_4)_2SO_4$) on the flotation of sulfidated malachite was studied in which sodium butyl xanthate (NaBX) was collector. By adding this salt to the solution before adding the sulfurizing agent ($Na_2S.9H_2O$), the HS ions' activation increased, and the adverse effects of the remaining HS- ions were eliminated or reduced. Ammonium ions increased the recovery in the case of oxidized copper flotation (**Wu et al., 2017; Shen, 2019**).

Nowadays, it is commonly accepted that xanthate adsorption on sulfide minerals occurs through corrosion of the hybrid potential mechanism. According to hybrid potential theory, an anodic reaction can occur only if a cathodic reaction with a limited velocity can be performed at that potential (**Mendiraatta, 2000**). For flotation systems, the cathodic reaction is usually performed by reducing oxygen. The corresponding anodic reaction involves the interaction of xanthate on sulfide mineral in three ways: i) chemical adsorption of the xanthate (X-) ion, ii) the reaction of xanthate with the sulfide mineral (MS), to form metal xanthate (MXn), and iii) the oxidation of xanthate to Di xanthogen (X2) at the sulfide mineral's surface (**Zhang, 2013; Mendiraatta, 2000**). Mileszami has studied the mechanism of xanthate adsorption on the copper plate. For the lowest substrate coatings, the adsorbed xanthate molecules are randomly oriented. Then, as the adsorption layer grows, the degree of random orientation of the molecules increases and varies for different xanthates. Their observations showed that the heterogeneous structure of amyl xanthate in the adsorption layer consisted of areas with monolayer or multilayer coatings (**Mielczarski and Leppinen, 1987**).

Wan Jun Yin et al. proposed the innovative use of NaBX+DDA as a mix collector for copper oxide flotation. Flotation results yielded that the synergistic effect of NaBX+DDA on malachite flotation was better than using merely NaBX at optimal ratios (2:1), and a pH range of 7-11, and maximum recovery was achieved at a pH of 10 (**Yin et al., 2019**). John Liu introduced new tetrazine-tion compounds include 6-hexyl-1, 2, 4, 5-tetrazine-3-tion (HTT), 6-propyl-1, 2, 4, 5-tetrazine-3-tion (PrTT) and synthesized 6-phenyl-1, 2, 4, 5-tetrazinan-3-tion (PhTT) as an effective collector for oxidized copper minerals. Micro-flotation studies indicated that HTT leads to higher malachite recovery in the selective flotation of malachite versus calcite than octyl hydroxyamic acid (OHA). The three tetrazinane-tion surfactants significantly improved the hydrophobicity of malachite levels as follows: HTT> PhTT> PrTT. They are well-matched with the value of hydrophobicity index (LogP), as well as their flotation response to malachite. In-situ AFM images clearly showed that malachite surfaces were coated with HTT. Zeta potential measurements also confirmed the chemical adsorption of HTT on malachite (**Liu et al., 2019**). Fengshu Li et al. synthesized a new collector of decyl-salicylic hydroxamic acid (DSHA), and used it for malachite flotation. The flotation experiments described that DSHA has a remarkable ability to collect malachite and satisfactory selectivity against quartz. It should be noted that DSHA is an effective collector for copper oxide ore. In addition, the mixture of DSHA and isobutyl sodium xanthate (SIBX) collectors had a better selective performance on CuO than DSHA, SIBX, or only hydroxamic salicylic acid (SHA) (**Li et al., 2020**). Han Wang et al. investigated the effect of Pb (II) on the flotation of sulfidized malachite with sodium sulfide. Micro flotation results presented that the floatability of sulfidized malachite increased after the addition of lead (II), and it also boosted the recovery to its maximum value (89.8%) (**Wang et al., 2021**).

Although flotation is usually a selective separation process in mineral processing (**Gao et al., 2016; Li and Gao, 2017; Gao et al., 2018**), but it is inefficient for fine particles (**Matis et al., 1993**). According to the physical properties of copper oxide ore, slime production (size fraction of 8-38 μm) is inevitable in the crushing and milling stages. Therefore, assessing the effects of copper oxide ore on flotation performance would be interesting and is a key factor. This study investigates the concentrating behaviour of oxidized copper samples prepared from the Qale Zari mine, using the flotation method. Thus, after providing the required sample, mineralogy and flotation studies were carried out. In this paper, sequential sulfidation and flotation were applied in order to counteract the negative impact of slimes. Also, the effect of pH, sodium sulfide consumption, collector consumption, and sodium sulfide preparation time were investigated. The process parameters were optimized using Design Expert 13 software based on the RSM method's central composite design (CCD) approach. In addition, using XRD, XRF analysis, mineralogical studies, and zeta potential measurement are presented to compare the properties of oxidized copper minerals under optimal conditions.

2. Materials and methods

2.1. Materials

The studied sample was copper oxide ore from the Qaleh Zari copper mine located in the southwest of Birjand city in South Khorasan province, Iran.

The composition of oxidized copper minerals was analyzed using X-ray diffraction (XRD). **Figure 1** shows the graph of XRD analysis peaks. Copper was present in the form of malachite ($Cu_2(CO_3)(OH_2)$) and azurite ($(CuCO_3Cu(OH)_2)$) in the ore sample. The ore also consisted of other minerals, including quartz (SiO_2), alkyl feldspar ($KAISi_3O_8$), hematite (Fe_2O_3), and magnetite (Fe_3O_4). X-ray fluorescence (XRF) was employed to analyze the elements which its results showed that the sample contains 5.84% copper. Silica, aluminum, and iron were the most important impurities. The composition of the ore is given in **Table 1**.

Table 1: The studied ore sample composition

Composition or element	%	Composition or element	%
MnO	>	SiO_2	80.79
Na_2O	0.07	Al_2O_3	2.40
P_2O_5	>	BaO	>
SO_3	0.52	CaO	0.16
TiO_2	0.05	Fe_2O_3	5.94
LOI	3.67	K_2O	0.28
Cu	5.84	MgO	0.14

Mineralogical studies indicated that in -106+75 µm fraction, malachite was presented in both crystalline and involved forms. The content was 5-10% in volume, and its liberation degree was around 85-90%. Malachite was involved with non-metallic tailings, iron oxides-hydroxides, and Chalcocite-Covellite. Chalcocite-Covellite was also present in the sample with a total amount of 0.8-0.4% in volume. In this fraction, accessible parts of pyrite were found at a maximum value of 0.5% in volume. **Figure 2** presents malachite's crystalline and involved form (with iron oxides and other tailings).

2.2. Flotation tests

Flotation experiments were carried out, using a Denver laboratory cell with a volume of 2.5 liters at an adjusted rotor speed of 1200 rpm. Conditions and chemicals were as follows: 33% pulp density, 40 g/t polypropylene glycol (A_{65}) as a frother and preparation time of 1 minute, 1000 g/t sodium silicate as a dispersant with 4 minutes of preparation time, sodium sulfide (Na_2S) as sulfidizer, amyl potassium xanthate (PAX) as collectors with 3 minutes of preparation time, and lime ($Ca(OH)_2$) which was used to adjust the pH. The concentrate and tailings were collected, dried, and weighed at the end of each test. Representative samples from the concentrate and tailings were then analyzed, using atomic absorption spectroscopy (AAS).

2.3. Zeta potential

The required suspension was prepared to determine the zeta potential, using malachite finer than 5 µm in 100 ml of deionized water. Then pH adjuster, sulfidizer, and collector were added to the pulp, and they were mixed

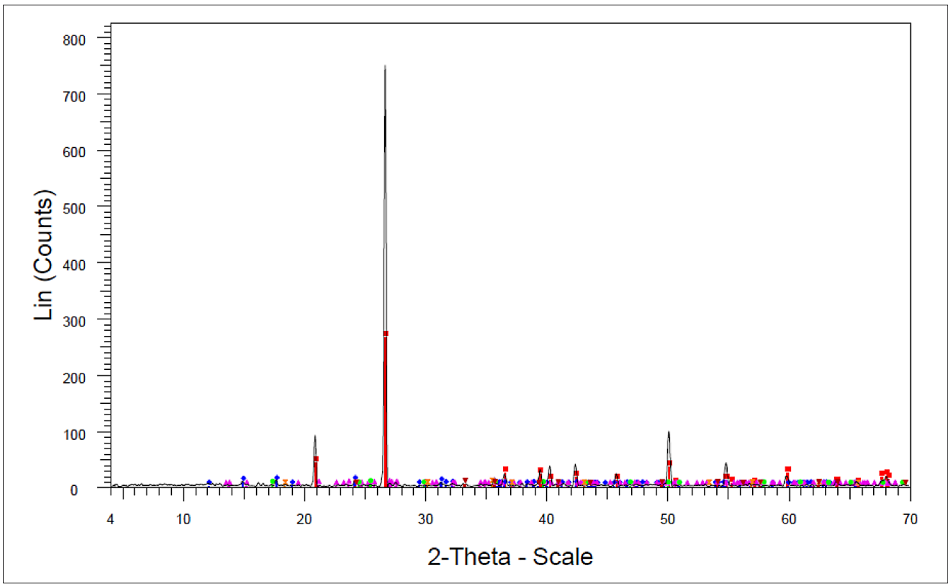

Figure 1: XRD pattern of the studied sample

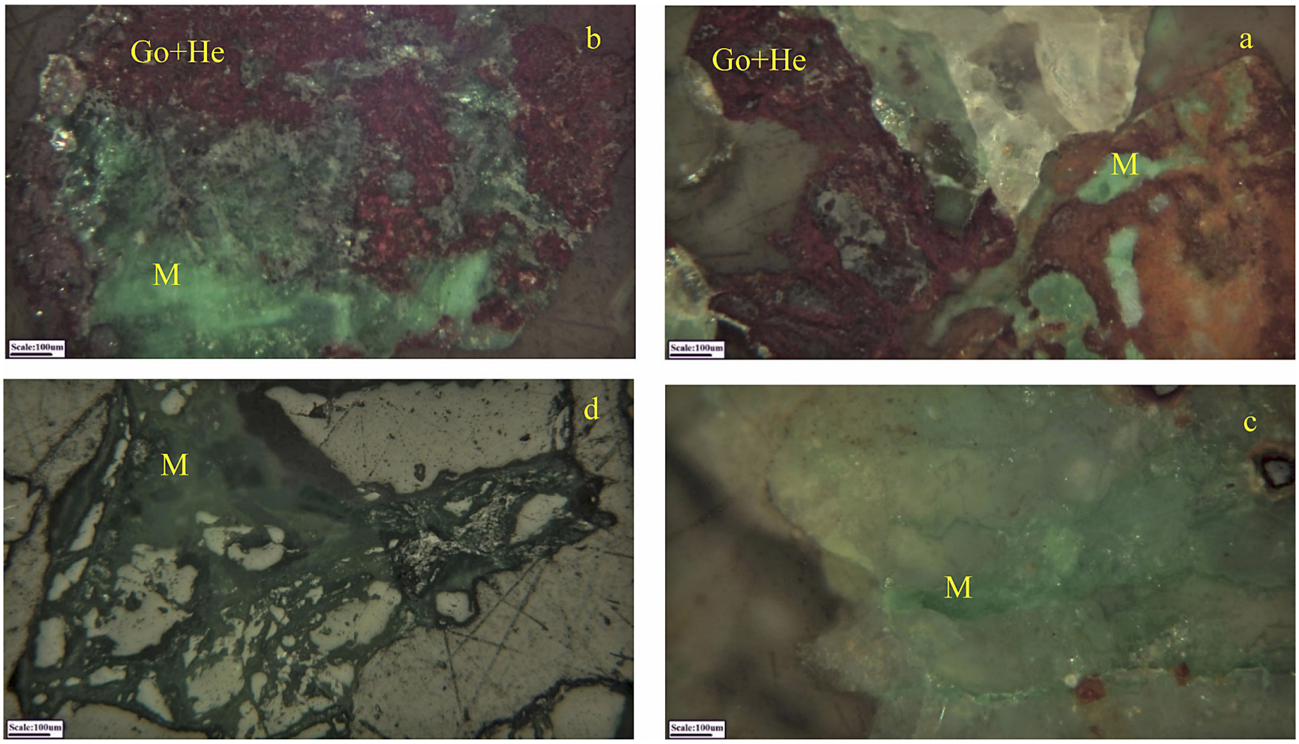

Figure 2: Malachite involved with goethite and hematite ((a) and (b)), malachite in crystalline form (c), and involved with other tailings (d)

Table 2: Results and applied conditions of initial tests

Test no.	Sodium silicate (g/t)	Sodium sulfide (g/t)	Sodium sulfide preparation (min)	Potassium Amyl Xanthate (g/t)	pH	Grade (%)	Recovery (%)
1	1500	2000	10	200	9.3	29.43	32.17
2	500	500	5	150	8.8	22.10	17.33
3	1000	1500	8	150	9	29.74	30.53
4	800	1000	8	100	8	21.5	17.45
5	800	1500	8	50	8.2	22.01	20.47
6	1500	1500	10	200	10	26.38	31.92
7	1500	5000	10	200	9.8	25.09	18.33

using a magnetic stirrer for 10 minutes. Finally, 10 minutes were allocated for particle settlement in order to measure the zeta potential of malachite.

3. Results and discussion

3.1. Operational factors

Initial tests were performed to determine the operational parameters and their appropriate levels for designing experiments. These tests are presented in **Table 2**, along with the adequate parameters. The results of the initial tests showed that the recovery of oxide minerals was not desirable. According to previous research, the presence of slime is one of the most important reasons and difficulties to achieve such a low recovery (**Phetla and Muzenda, 2010; Asadi et al., 2019**).

3.2. Sodium sulfide

The effect of multi-stage sequential addition of $Na_2S.9H_2O$ on flotation performance was investigated through the following conditions: preparation time for sodium silicate and potassium amyl xanthate was set to 4 and 3 minutes, and their dosages were 1000 and 150 g/t, respectively. The preparation time of sodium sulfide was 5 minutes for each step, and 40 g/t of frother (A_{65}) with 1 minute of preparation time was used. In all tests, froth collecting time and pH were 5 minutes and 9, respectively. Other relevant operating conditions are listed in **Table 3**. The results indicated that adding sulfidizing agents in multiple stages did not cause any significant changes in either grade or recovery. The size distribution of the feed and the floated concentrate described that in the feed about 55% of the particles were -38 µm in size.

These fine particles (slimes) were calculated to be about 75% in concentrate. Therefore, it can be concluded that the most used $Na_2S.9H_2O$ was adsorbed on fine particles due to their high contact surface.

3.3. Potassium amyl xanthate (PAX)

Several experiments were implemented to study on the effect of adding a collector in multiple stages. In these experiments, the preparation time for sodium silicate was 4 minutes with 1000 g/t. The preparation time for potassium amyl xanthate and sodium sulfide was 3 and 5 minutes. 1500 g/t sodium sulfide was added to the pulp for each step. The frother (A_{65}) went through 1 minute of preparation time, and the amount of 40 g/t, 33% pulp density, froth collecting time of 5 minutes, and pH was adjusted to 9. The results are documented in **Table 4**. It can be concluded that the sequential addition of the collector did not cause a noticeable impact on increasing the grade and recovery, and it was identical for the sequential addition of the sulfidizing agent.

Table 3: The results of stepwise addition of sodium sulfide

Test no.	Steps	Sodium sulfide in each step (g/t)	Grade	Recovery
1	2 steps	750	29.84	31.48
2	3 steps	500	26.54	25.6
3	4 steps	400	31.08	25.95

Table 4: The results of stepwise addition of collector

Test no.	Steps	Sodium sulfide in each step (g/t)	Grade (%)	Recovery (%)
1	2 steps	75	28.29	26.69
2	3 steps	50	31.07	28.71
3	4 steps	40	27.07	26.44

3.4. Froth collecting or sulfidation stages

To evaluate this method, flotation tests were carried out in the presence of sodium silicate at 1000 g/t with a preparation time of 4 minutes. The mentioned chemical was only added in the first stage. In all stages, the activator and collector preparation times were 8 and 3 minutes, respectively. The preparation time for the frother (A_{65}) was 1 minute with 10 g/t in each stage. Pulp density, froth collecting time and pH were 33%, 5 minutes, and 9. This procedure in the second stage increased the grade and recovery values. However, in the third stage (compared to the second one), there was a decrease, but in comparison to the first stage, a jump of recovery was realizable. The obtained results are given in **Table 5**.

To maximize copper recovery, flotation tests were performed with the assistance of the mentioned method in four stages. The obtained results confirm the efficiency and necessity of this procedure. Operating conditions for subsequent tests are provided as follows:

- 1000 g/t of sodium silicate was added in stage 1 with a preparation time of 4 minutes.
- Collector preparation time was 3 minutes, and 40 g/t frother was prepared in 1 minute for the process.
- At each stage, a quarter amounts of the collector and activator (sodium sulfide) were added to the system.

3.5. Recovery model

Four critical factors (amount of sodium sulfide, preparation time, amount of xanthate collector, and pH) were selected to model and optimize the parameters affecting oxide copper flotation, and their changes were accordingly identified. The response surface method was used to design the experiments in the user interface of Design Expert 13 software. Based on the results obtained from the software, the best model for recovery was the sec-

Table 5: Results related to the extension of the froth collecting steps

Test no.	1	2	3	4	5
First step activator amount (g/t)	500	750	1000	1000	1500
First step collector amount (g/t)	50	75	50	100	150
Grade of the first froth zone	26.02	25.37	22.91	25.09	24.87
Recovery of the first froth zone	15.21	17.89	17.34	18.62	22.59
Second step activator amount (g/t)	500	380	1000	1000	1500
Second step collector amount (g/t)	50	38	50	100	150
Grade of the second froth zone	29.34	30.63	27.8	26.50	26.38
Recovery of the second froth zone	22.78	16.16	24.81	29.44	33.17
Third step activator amount (g/t)	500	380	1000	1000	1500
Third step collector amount (g/t)	50	38	50	100	150
Grade of the third froth zone	24.6	22.36	17.17	24.17	20.04
Recovery of the third froth zone	22.07	15.55	23.59	27.58	28.45
Total recovery	60.03	49.60	65.74	75.64	84.21

Table 6: The ANOVA values of the presented model

Source	**Sum of squares**	**df**	**Mean squares**	**F-value**	**P-value**	
Model	2780.58	14	198.61	43.18	>0.0001	**significant**
A	52.93	1	52.93	11.51	0.0040	
B	553.54	1	553.54	120.35	>0.0001	
C	944.01	1	944.01	205.24	>0.0001	
D	130.29	1	130.29	28.33	>0.0001	
AB	0.2916	1	0.2916	0.0634	0.8046	
AC	9.06	1	9.06	1.97	0.1808	
AD	0.2116	1	0.2116	0.0460	0.8331	
BC	16.73	1	16.73	3.64	0.0758	
BD	2.07	1	2.07	0.4508	0.5122	
CD	1.88	1	1.88	0.4081	0.5327	
A^2	305.56	1	305.56	66.43	>0.0001	
B^2	605.63	1	605.63	131.67	>0.0001	
C^2	432.89	1	432.89	94.12	>0.0001	
D^2	10.89	1	10.89	2.37	0.1446	
Residual	68.99	15	4.60			
Lack of Fit	57.51	10	5.75	2.51	0.1613	**not significant**
Pure Error	11.48	5	2.30			
Cor Total	2849.57	29				

Table 7: Evaluation of the statistical data

Std. Dev.	2.14	**R^2**	0.97
Mean	75.71	**Adjusted R^2**	0.95
C.V%	2.83	**Predicted R^2**	0.87
		Adeq Precision	21.36

ond-order equation. Analysis of variance showed the significance of the model and the most influential factors in terms of their effect on the flotation process. It is a series of mathematical calculations used to determine whether the differences in the mean of groups are significant or not. The variance analysis yielded the F value of the model equal to 43.18, and the P-value of the model was <0.0001 (see **Table 6**). Thus, the model is significant, and the lack of model fitting is non-significant.

According to **Table 7**, the correlation coefficient is 0.97, indicating desirable and logical compatibility between the predicted and actual values. Also, the value of Predicted R^2 is adequate to Adjusted R^2, and their difference is less than 0.2; Adequate Precision indicates the signal-to-confusion ratio and will be ideal when the value is greater than 4. Finally, the mathematical model presented to the software for calculating the recovery rate of copper in terms of coded factors is as follows (**Equation 1**):

$$\begin{aligned} \textit{Cu Recovery} = {} & +85.82 + 1.48 \times A + 4.80 \times B + 6.27 \\ & \times C + 2.33 \times D - 0.1350 \times AB \\ & - 0.7525 \times AC - 0.1150 \times AD - 1.02 \\ & \times BC - 0.3600 \times BD - 0.3425 \\ & \times CD - 3.34 \times A2 - 4.70 \times B2 - 3.97 \\ & \times C2 - 0.6302 \times D2 \end{aligned} \qquad \text{(Eq. 1)}$$

3.6. Model validation

The standard distribution diagram of the residuals is one of the important criteria to check the correctness of the fitted regression equation, in predicting different response values for varying levels of factors. The typical distribution diagram of the residues should be centered along a straight line and about zero value which is presented in **Figure 3.**

3.7. Parameters affecting recovery

3.7.1. pH

The effect of pH on recovery is shown in **Figure 4**, which increases with pH increase. At a pH of 9, it reaches its maximum value and then begins to decrease. The reason was the instability of xanthate as a collector and the formation of the hydroxy-copper species.

3.7.2. Sodium sulfide

As shown in **Figure 5**, an increase in the amount of sodium sulfide increased recovery, but it should be noted that the sulfide ions must not surpass the optimum amount in the medium; otherwise, the depression of the copper ores takes place. Copper oxide flotations are very sensitive to the amount of sodium sulfide. At low sulfide concentrations, the S^{2-} ion is precipitated in the form of CuS using Cu^{2+} in the solution. After completely removing Cu^{2+} from the solution, S^{2-} ion adsorbs on the malachite surface and forms copper sulfide, making the flotation process easier to operate. However, increasing the sulfide ions in the medium is absorbed on the mineral surface instead of xanthate, causing mineral depression (**Park et al., 2016**).

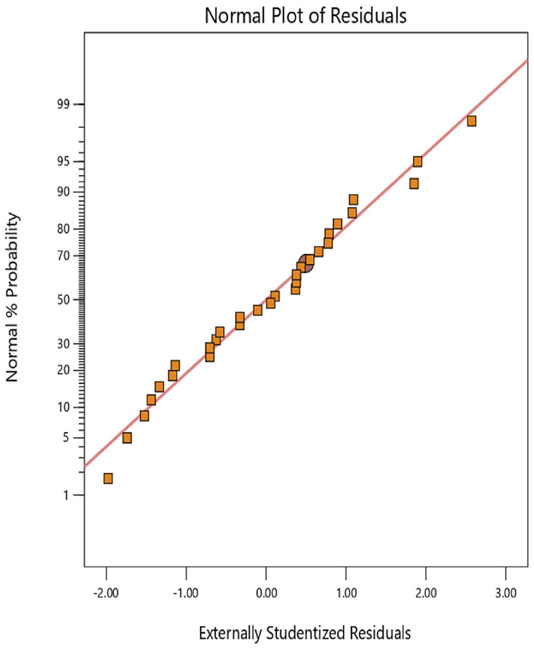

Figure 3: The normal distribution diagram of the residuals

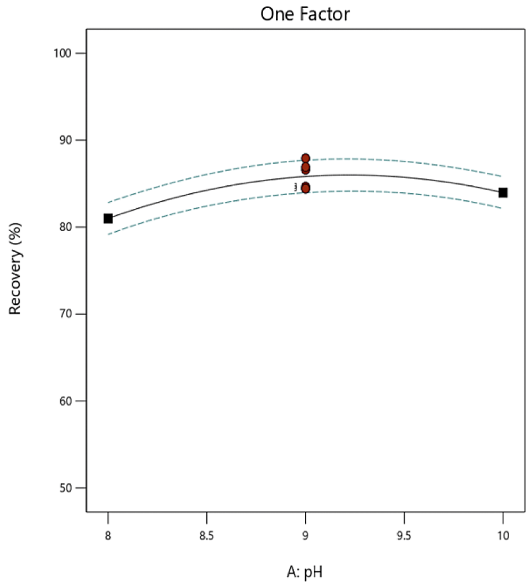

Figure 4: The effect of pH on recovery

3.7.3. Potassium amyl xanthate

The effect of amyl potassium xanthate on recovery is shown in **Figure 6**. In the flotation process, the number of floating particles usually increases as long as the collector volume increases. Recovery usually increases with an increase in collector consumption until it reaches to the critical concentration of micelles (CMC).

3.7.4. Preparation time of sodium sulfide

The effect of sodium sulfide preparation time on the recovery of copper oxide is shown in **Figure 7**, which indicates that the recovery is increased as long as the preparation time of sodium sulfide ions increases. They would act more effectively on oxide-minerals by allocating more time to sulfide ion preparation.

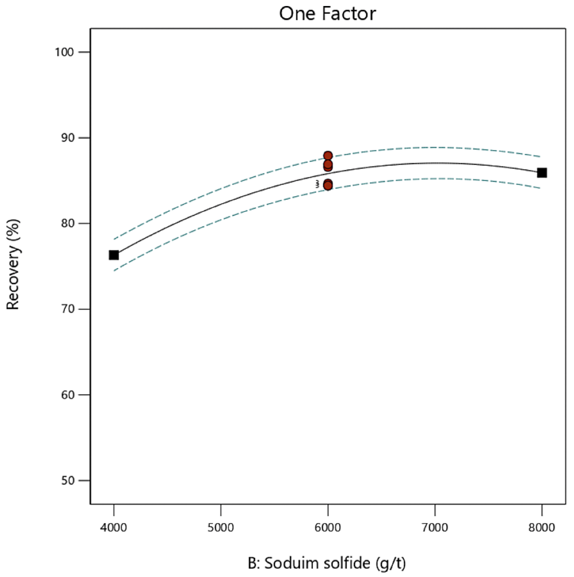

Figure 5: The effect of sodium sulfide on recovery

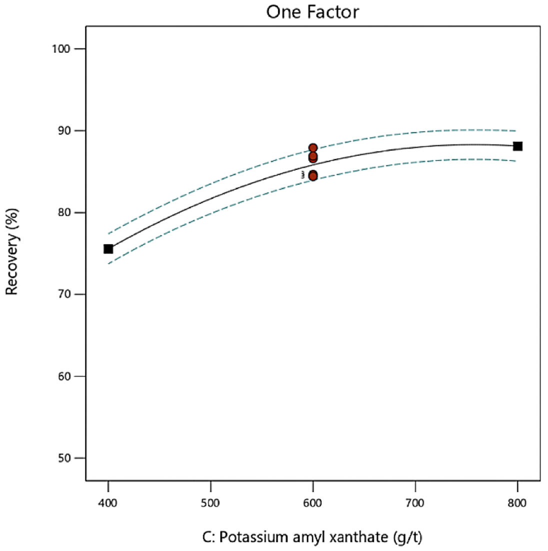

Figure 6: The effect of potassium amyl xanthate on recovery

3.8. Optimization

Optimization is one of the most critical targets of designing experiments to find the optimal conditions, which was conducted in two different cases. The optimization in the first case was done to achieve maximum recovery. The next case was performed to reduce the destructive effects on the environment while minimizing the collector consumption and maximizing the recovery.

Table 8 presents the results of both optimization modes. According to the recovery reduction of about 10%, it is not reasonable to consider the minimum amount of the collector for optimization. To ensure the accuracy of the data, experiments were performed under the optimal conditions for both cases. Each experiment was repeated twice, and the results were acceptable compared to the results predicted by the software. The obtained results are given in **Table 9.**

3.9. Zeta potential

Figure 8 shows the effect of Na_2S and Z6 on the zeta potential of malachite as a function of pH. The results indicated that the ZPC (zero point of charge) of malachite was about pH=8.6, and with the addition of Na_2S, the surface charge curve of malachite moves in the negative direction. However, the HS^- and $S2^-$ ions released by Na_2S are hydrolyzed to metal ions or hydroxyl metal complexes. They adhere to the malachite surface, resulting in an increase in negative charges at the mineral surface (**Park et al., 2016**). When xanthate was added, the negatively charged surface of malachite gains tended to reach even more negative charges. The lowest zeta potential was associated with these phenomena would be an indication of the chemical adsorption of xanthate on the malachite surface.

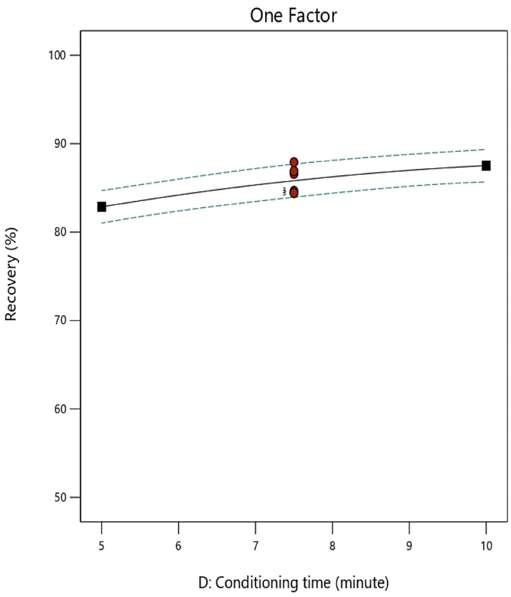

Figure 7: The effect of sodium sulfide preparation time on recovery

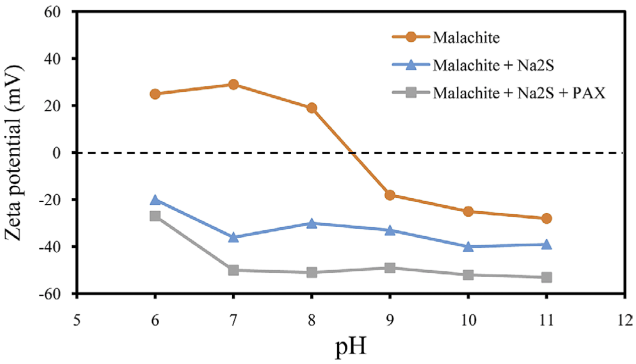

Figure 8: Zeta potential of malachite in the presence and absence of Pax, Na_2S

4. Conclusion

In this research work, a copper oxide ore sample from the Qaleh Zari mine was studied by the flotation method using the response surface statistical technique, and the following results were achieved:

Mineralogy studies and chemical analysis on the initial sample revealed that malachite and azurite were the predominant minerals of copper oxide, and tailings were presented in the ore as quartz, and alkyl feldspar, hematite, and magnetite.

According to the mineralogical results of the samples, 85-90% of copper ores in the size of -106+75 µm reach the liberation degree. Based on the experimental results, pH, sodium sulfide as sulfidizer, amyl potassium xanthate as a collector, and sodium sulfide preparation time were considered the most influential parameters that were controlled and limited to slight changes.

Table 8: Related results to the optimized conditions

No.	**Response**	**Goal**	**pH**	**Sodium sulfide concentration**	**Preparation time**	**Potassium amyl xanthate concentration**	**Recovery**
1	Recovery	Maximum	9.12	6790.31	10	736.85	90.51
2	Recovery Collector concentration	Maximum Minimum	9.3	7144.24	10	411.78	80.27

Table 9: Related results to the validation of the optimized conditions

Test no.	**pH**	**Sodium sulfide concentration(g/t)**	**Potassium amyl xanthate concentration**	**Preparation time of sodium sulfide**	**Recovery**
1	9.12	6790.31	736.85	10	88.4
2	9.12	6790.31	736.85	10	91.03
3	9.3	7144.24	411.78	10	81.57
4	9.3	7155.24	411.78	10	80.92

The presence of fine particles had an adverse effect on the flotation. In order to overcome the negative impact of these fine fractions, it was necessary to reduce the production of these particles in the crushing stage or eliminate them through the process. In order to reduce or eliminate this problem, in this study, sequential sulfidation and froth collecting methods were employed.

Stepwise addition of chemicals did not make any noticeable changes in recovery.

Four stages of sulfidation-flotation were selected as the appropriate method for flotation. According to the results, the addition of chemicals after the initial froth collecting increased the grade and recovery in the second stage.

The results indicated that recovery also increased with a simultaneous increase in sodium sulfide and collector concentrations. However, an excessive increase in sodium sulfide concentration caused the depression of copper ores. Also, with a further increase in the collector concentrations, the trend of recovery slope decreased. This was the case at all pH levels except pH 9 where the absorption of chemicals was acceptable.

To evaluate the correctness of the fitted regression equation, the normal distribution diagram of the residuals was used to predict different response values for different levels of factors. It was observed that they are located along a straight line, and therefore the proposed regression model predicts the response variable pretty well.

Optimal values of pH parameters, sodium sulfide, potassium amyl xanthate concentration, and sodium sulfide preparation time were obtained as 9.12, 6790.31 g/t, 736.85 g/t, and 10 minutes, respectively. Under these optimized conditions, the concentrate was produced with a copper grade of 22.13% and 90.51% of recovery.

According to the results with the target of optimizing for maximum recovery with minimum collector consumption, the recovery rate was reduced by about 10%. This optimization was chosen to reduce the harmful effects of xanthate on the environment.

Measurement of zeta potential showed the ZPC (zero point of charge) of malachite was about pH=8.6, and with the addition of Na_2S, the surface charge curve of malachite moved in a negative direction. When xanthate was added, the negatively charged surface of malachite gained even more negative charges. The lowest zeta potential was associated with these phenomena, indicating the chemical adsorption of xanthate on the malachite surface.

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SAŽETAK

Optimizacija flotacije uzoraka oksidirane rude bakra rudnika Qaleh Zari sekvencijalnim pristupom sulfidacije korištenjem metodologije odzivne površine

U industriji oplemenjivanja odnosno prerade oksida bakra jedan od najvećih izazova jest smanjivanje operativnih troškova primjenom flotacije. Uobičajeno se u flotaciji oksidnih minerala površina minerala aktivira postupkom sulfidizacije. U ovome radu provedeno je istraživanje flotacije na uzorku oksidirane rude iz rudnika bakra Qalej Zari koja sadržava 5,4 % bakra (malahit i azurit). Pripremljeni uzorak podvrgnut je mineraloškim istraživanjima, a dobiveni rezultati pokazali su da je uzorak oksidiran. Od bakrovih oksida prevladavali su minerali malahit i azurit, a od jalovinskih minerala kvarc i željezni oksidi (hematit i magnetit). Aktivacija dodavanjem natrijeva sulfida te flotacija u četiri uzastopna koraka pokazali su se kao uspješan pristup za postizanje odgovarajućega iskorištenja i kvalitete. Za dizajn eksperimenta odabran je centralni kompozitni dizajn (CCD) s radnim parametrima: potrošnja aktivatora (natrijev sulfid), potrošnja kolektora (amilov kalijev ksantat), vrijeme aktivacije i pH. Također, mjerenjem zeta-potencijala određen je električni naboj malahita u različitim uvjetima nakon dodavanja kemikalija. Zaključno, u optimalnim uvjetima parametri su bili: potrošnja natrijeva sulfida 6790 g/t, amilova kalijeva ksantata 736 g/t, vrijeme aktivacije 10 minuta i pH vrijednost 9. Primjenom navedenih uvjeta dobiven je koncentrat sadržaja 22,13 % Cu i iskorištenja korisne komponente u koncentratu od 90,51 %.

Ključne riječi:
oksidirani bakar, flotacija, sulfidacija, metodologija odzivne površine, optimizacija

Author’s contribution

Hassan Maleki (1) (MSc Student of Mineral Processing) performed tests, analyses, provided reports and wrote the article. **Mohammad Noaparast (2)** (Full Professor of Mineral Processing) proposed the idea and guided the research. **Sajjad Chehreghani (3)** (Assistant Professor of Minerals Processing) proposed the idea and guided the research. **Mir Saleh Mirmohammadi (4)** (Assistant Professor of Minerals Processing) performed Mineralogical studies. **Ali Rezai (5)** (MSc of Mining Engineering) proposed ideas and provided the samples.