OPTIMIZATION OF FLOTATION PARAMETERS FOR BENEFICATION OF A MOLYBDENUM ORE

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Abstract: The importance of molybdenum deposits has been increased in Turkey as well as the molybdenum industry in the world. In this context, the aim of this study was to evaluate the flotation behavior of low-grade porphyry copper-molybdenum ore obtained from the Kirklareli region of Turkey. The ore sample used in this study contained 0.18% Mo and 0.15% Cu. In this study, the effect of several parameters such as particle size, pH, types and amounts of collector, depressant, and frother on the flotation were investigated. Based on the results obtained from this study, gas oil as collector, pine oil as frother, and sodium sulphide as depressant at pH 12 were found to be optimum parameters for the flotation of molybdenite ore. Meanwhile, the kinetics of batch flotation behavior of the molybdenum ore was obtained by applying the first order and second order kinetics models. The results indicated that the flotation rate constant responds to second-order kinetics model with correlation coefficient of 0.99. At the end of the multi stage flotation test performed under the optimum flotation parameters, Mo recovery and content for final concentrate were found as 72.3% and 52.15%, respectively.

Keywords: molybdenum ore, depressant, collector, frother, flotation kinetics

Introduction

Molybdenum is a strategic metal used in steel industry for facilitating thermal operations and increasing mechanical properties. Additionally, it can supersede precious elements such as nickel, wolfram or rare elements in some applications. While 80% of molybdenum is used in production of alloy steels, stainless steels, and cast irons, 20% of the usage area consists of chemical applications. Furthermore, the saleable molybdenum concentrate needs a purity grade of 50% Mo as long as with maximum copper content of 0.5%.

Porphyry copper deposits, which are the world's main copper and molybdenum source, have a share of 50% of the world molybdenum production (Bulatovic, 2007). The most common source of molybdenum is molybdenite (MoS_2), which is generally

found in low-grade ores and associated with copper sulfides. In order to produce molybdenite concentration, firstly, a bulk copper-molybdenum concentrate is obtained by floating Cu-Mo together. Secondly, molybdenite is enriched selectively by depressing copper and iron sulfides (Wills, 1997). In addition, it should be noted that conditioning time, pulp density, and reagent additions are the most important parameters in the separation of copper-molybdenum (Bulatovic, 2007).

The floatability of molybdenum in porphyry copper ores depends on some factors such as the effect of mineralogy, slime coatings, grinding and mineral liberation, and flotation reagents (Shirley and Sutulov, 1985; Hernlund, 1961).

Mostly kerosene, diesel oil, transformer oil, and solar oil are used as collectors in molybdenum flotation operations due to its natural flotation behavior (Kelebek, 1988; Cumming et al., 2000; Tingshu et al., 2011). Smit and Bhasin (1985) observed that if a two-component blend of a higher molecular weight of petroleum hydrocarbon and lower molecular weight diluent oil were used, the better results could be obtained rather than using single component of higher molecular weight oil. The efficiency of hydrocarbon oil depends on its carbon chain length. As the carbon chain length increases, locked in gangue or coarse molybdenite particles can be enriched easier. On the other hand, too long carbon chain length leads to adverse the effect on dispersibility of hydrocarbon oil (Crozier, 1979; Smit and Bhasin, 1985; Song et al., 1999; Xia and Peng, 2007; Wang et al., 2008).

The studies related the interaction of molybdenite with thiol collectors have shown that xanthates are weak collectors. The efficiency of xanthate on molybdenite flotation depends on particle size. Fine particles of molybdenite (6.8 μm) cannot be floated despite increasing amount of xanthate. However, coarse particles (51.7 μm) respond to an increase in xanthate dose as the hydrophobicity of molybdenum enhances because of increasing faces/edges ratio (Castro and Mayta, 1994; Castro et al., 2016).

It is widely known that sodium hydro-sulfide (NaHS), Noke's reagent (thiophosphorus or thioarsenic compounds), and cyanides are used to depress chalcopyrite selectively in the copper-molybdenum separation. Ansari and Pawlik (2007a) examined the effect of lignosulfonates, which are strongly anionic polyelectrolytes and by-product of wood processing to extract cellulose. As all kind of lignosulfonates has similar effects on molybdenite surface, any type of lignosulfonates can depress molybdenum at any pH. However, the lignosulfonates can cause depression of chalcopyrite at high pH values in flotation (Ansari and Pawlik, 2007b).

According to Bulatovic (2007), while the low viscosity of oils leads to lower recoveries, the high viscosity oils ensure higher recoveries in molybdenum flotation. However, in order to increase molybdenum recovery, the use of aromatic alcohols such as pine oil and alkoxy paraffin instead of straight alcohol or glycol provides raise in recovery. Besides, the use of propylene oxide and aliphatic alcohols together as frother has a positive effect in recovery of coarse mineral particles. On the other hand, branched alcohols with propylene oxides have better effect in selectively recovering for fine particles (Klimpel, 1988; Xia and Peng, 2007).

It was reported by Chander and Fuerstenau (1972) that the pH range was determined as 5.5–6.5 in molybdenum flotation, while molybdenite might be depressed at high pH due to calcium ions. Besides, the ferrous and ferric species at higher pH values caused depression of molybdenite too (Castro and Bobadilla, 1995).

In this study, the determination of the flotation behavior of a molybdenum ore was investigated testing different particle sizes, pH values, types and amounts of collector, and frother. With the optimized flotation parameters, copper depression was examined. Finally, different kinetics models were applied.

Experimental

Materials

The molybdenum ore used in this study was obtained from the Demirkoy district of Kirklareli, Turkey. The chemical analysis of the sample is presented in Table 1. Additionally, the mineralogical analyses of the sample were performed on four different polished section samples. The cross-sectional images of the ore sample are also illustrated in Figs. 1a-d. The mineralogical investigations revealed that the ore sample contained molybdenite, chalcopyrite, pyrite, covelline as valuable minerals and powellite, malachite, azurite, hematite, limonite as oxide minerals while epidote, calcite, feldspar, plagioclase, quartz, sericite, and muscovite were the gangue minerals. The liberation size of the molybdenum sample was obtained in a range of 10 µm and 800 µm. It was observed that chalcopyrite particles partially transformed to covelline, malachite, and azurite depending on the ambient conditions.

Table 1. Chemical analysis of ore sample

Element	Mo	Cu	Fe	S	Ti	SiO_2	Ca	Al	Mg	K
Content (%)	0.18	0.15	4.40	1.60	0.89	51.40	3.76	0.83	0.77	0.37

The reagents used for the flotation experiments were sodium silicate (Merck) as silicate depressant, pine oil and methyl isobutyl carbinol (MIBC, Merck) as frothers, sodium sulfide (Merck), Nokes reagent (Merck), lignosulfonate (Sigma-Aldrich), and sodium metabisulfite (Merck) as copper depressants. Gas oil (commercial product) and Aero 3302 (Cytec) were used as collectors. Gas oil was added into pulp in the form of pure oil without mixing water. Lime and sulphuric acid were used to adjust pH.

Methods

The ore sample was first crushed using a jaw, a cone, and a roll crusher. After three-crushing stages, the particle size of the sample was reduced down to 2 mm, and the representative samples were taken homogenously with cone and quartering method for

the flotation experiments. Finally, the sample was ground in a stainless steel ball mill at a pulp density of 60% by weight for the flotation experiments.
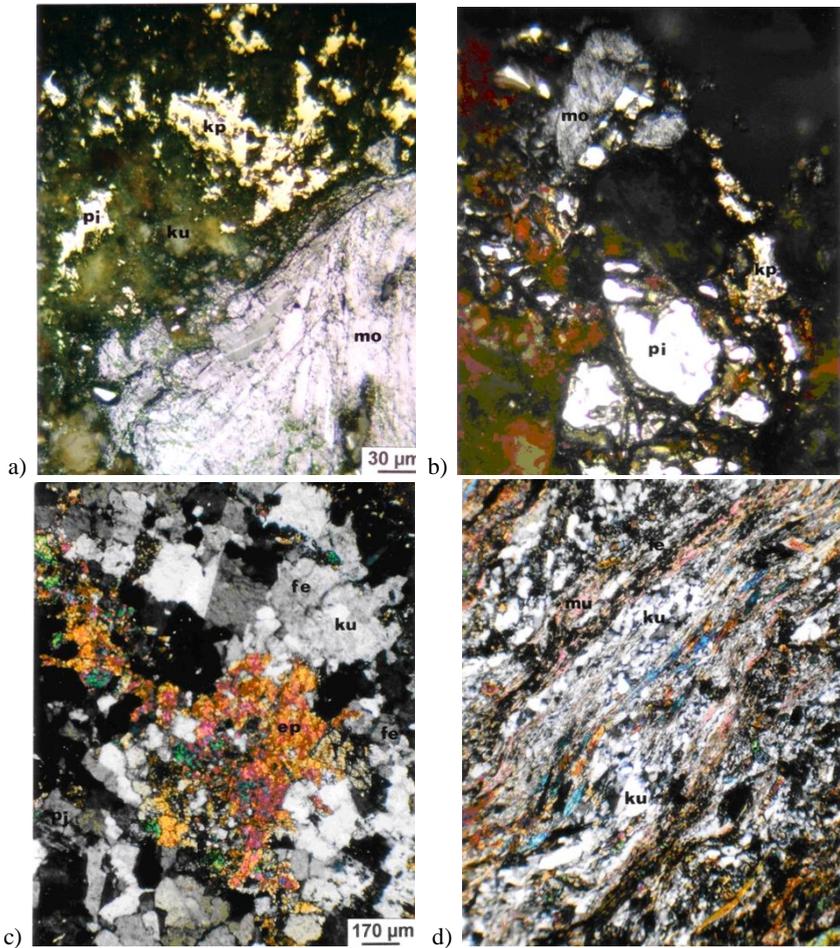
Fig. 1. (a) Molybdenum (mo) particles along with chalcopyrite (kp) and pyrite (pi) in case of scattering (b) Molybdenum (mo), chalcopyrite (kp), and pyrite (pi) and particles in case of crumbled (c) Partly sericitization feldspar (fe) with quartz (ku), plagioclase (pj), and epidote (ep) (d) Quartz (ku), feldspar (fe), plagioclase (pj), and muscovite (mu) after metamorphism.

The bench-scale flotation tests were conducted using a laboratory scale Denver flotation machine. At the first stage, the effect of particle size, pH, types and amounts of collector, depressant, and frother were investigated. The ore sample of 1 kg was used for each flotation test. The flotation tests comprised of four-stage rougher at impeller speed of 1500 rpm in a 2.5 dm^3 cell and one-stage cleaning at impeller speed of 1100 rpm in a 1 dm^3 cell. While the depressants were conditioned for 10 min, the collectors were conditioned for 3 min in each stage. The conditioned pulp was floated

for a total of 12 min in the rougher stage and 3 min in the cleaning stage. Furthermore, 1 kg/Mg (10%, w/w) sodium silicate was used as the slime depressant for the gangue minerals. The flowsheet is illustrated in Fig. 2.
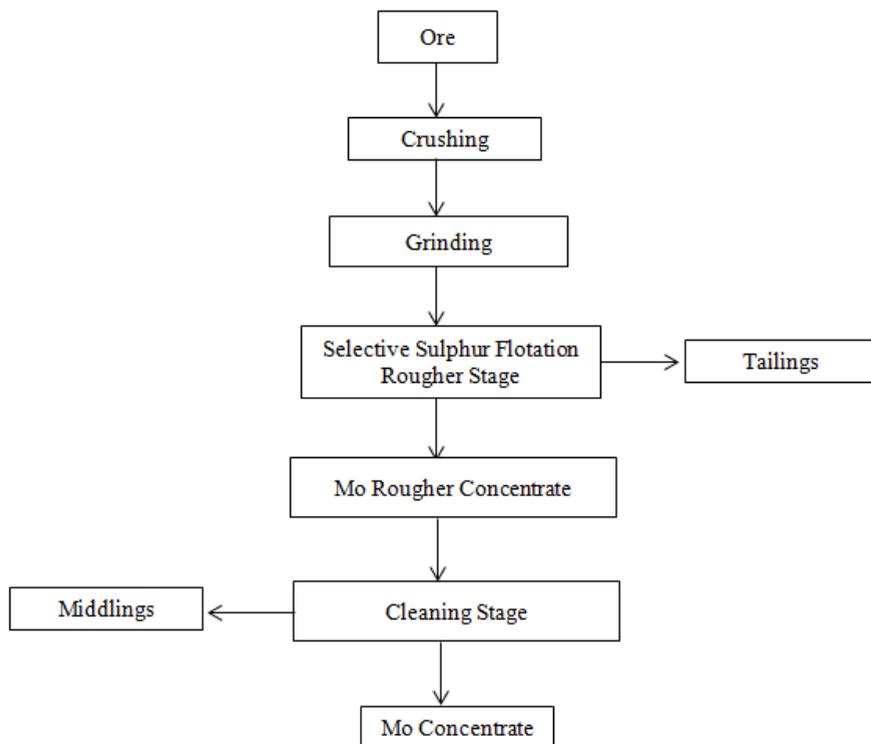
Fig. 2. Flowsheet applied for flotation tests

At the second stage, the flotation kinetic was examined as depending on the flotation time. After the optimum conditions were determined, finally flotation experiment was carried out using 16 kg ore sample. The flotation test was conducted in a 10 dm^3 flotation machine at an impeller speed of 2200 rpm for each test of 4 kg. Rougher molybdenum concentrates obtained from each test of 4 kg were combined and fed to ten-stage cleaning circuit. Molybdenum and copper contents of the samples were analyzed by AAS (Varian) after dissolving in *aqua regia*.

Results and discussion

Effect of particle size

Initially, the sample was ground at different grinding times such as 20, 30, and 40 min in order to find the optimum particle size for the flotation experiments. The wet sieving analyses were performed for the products round at different grinding times,

and the results are shown in Fig. 3. The flotation tests were performed to obtain the optimum particle size. In the tests, 10 kg/Mg Na_2S as copper depressant, 440 g/Mg gas oil as collector, and 56 g/Mg pine oil as frother were used at pH 12. The influence of the particle size on the flotation is seen in Fig. 4.

It can be seen from Fig. 4 that while the recovery of molybdenum increased gradually, the molybdenum content decreased as the particle size got finer. The reason for this can attributed to mechanical carrier effect, which caused entrainment of the fine particles to the frother layer with air bubble or water. According to Engelbrecht and Woodburn (1975), all the fine particles move to surface with this mechanism because the selectivity between hydrophobic and hydrophilic minerals cannot be occurred in mechanical carry. It can be concluded based on this information that the molybdenum concentrates with higher recovery-lower content were obtained as the grinding time increased because valuable and gangue minerals at finer particle sizes moved together to froth surface. Based on the high molybdenum recovery, the optimum particle size was determined as 58 µm at 40 min grinding time with the molybdenum grade of 2.65% and recovery rate of 79.2%.
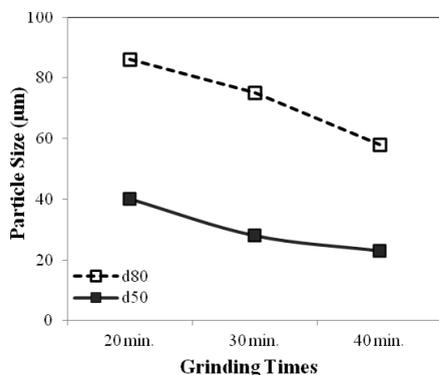
Fig. 3. d_{50} and d_{80} sizes of the sample ground as a function of grinding time
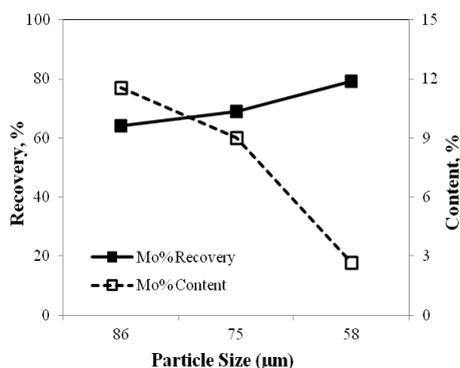
Fig. 4. Effect of particle size on molybdenum flotation (1 kg/Mg Na_2SiO_3, 10 kg/Mg Na_2S, 440 g/Mg gas oil, 56 g/Mg pine oil, pH 12)

Effect of pH

The effect of pH at different values as 6, 9, and 12 was investigated without adding copper depressant in order to determine the flotation behavior of molybdenum and copper based on the flotation conditions mentioned above. The result for these tests is seen in Fig. 5 which shows that the lowest copper content of 2.34% and the highest molybdenum recovery of 78.2% in molybdenum concentrate were obtained at pH 6.
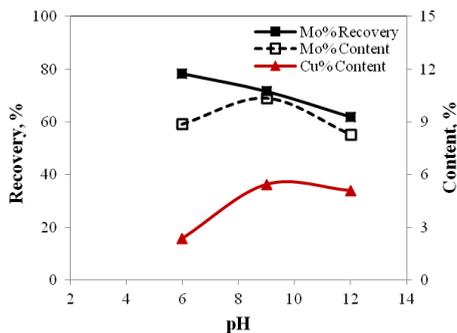
Fig. 5. Effect of pH on molybdenum flotation in absence
of copper depressants (1 kg/Mg Na$_2$SiO$_3$, 10 kg/Mg Na$_2$S,
440 g/Mg gas oil, 56 g/Mg pine oil, 58 μm particle size)

Since the copper content was high in molybdenum concentrate, Na$_2$S of 10 kg/Mg as copper depressant was added at pH 6. According to the results presented in Table 2, the addition of Na$_2$S caused detrimental effect on the molybdenum flotation because of the increasing copper content and decreasing molybdenum recovery. While Na$_2$S showed activator effect on copper, it also had depression effect on molybdenum at pH 6. Therefore, the next test was carried out at pH 12, where the low copper content obtained, and in order to see whether Na$_2$S addition could have any effect on the copper depression. The test results showed that the optimum pH value for the depressing copper with Na$_2$S of 10 kg/Mg addition was 12 where the recovery of molybdenum and the copper content in the molybdenum concentrate were 79.2% and 0.31%, respectively.

The dissociation of Na$_2$S in water occurs as follows:

$$Na_2S + 2H_2O \rightarrow 2NaOH + H_2S \tag{1}$$

$$H_2S \rightarrow H^+ + HS^- \tag{2}$$

There are not sulfide ions present below pH 5, and H$_2$S is the dominant species between pH 5 and 6. While the half the H$_2$S is ionized to HS$^-$ at pH 7, over 90% of sulphide ions are in HS$^-$ form between pH 8 and 11. Particularly, the moles of HS$^-$ and S^{2-} are equal at pH 12 (Crozier, 1992). The reason for depression of copper sulphide minerals in the presence of Na$_2$S at pH 12 can be explained as HS$^-$ and S^{2-} ions may be formed on the mineral surfaces or the sulfhydrate ion could destroy the collector coating on the floated copper sulphide mineral. However, it is known that in the aqueous solution containing Na$_2$S, only H$_2$S is present at pH 6. Since HS$^-$ and S^{2-} ions are not present, copper sulfide minerals are not depressed. Besides, oxide copper minerals such as malachite and azurite in this ore were treated with Na$_2$S, and the layer of sulfide might form on the mineral surface. Therefore, copper content might be increased at pH 6 compared to pH 12.

Table 2. Effect of Na$_2$S on the depression of copper at pH 6–12
(1 kg/Mg Na$_2$SiO$_3$, 440 g/Mg gas oil, 56 g/Mg pine oil, 58 µm particle size)

pH	Amount of Na$_2$S (kg/Mg)	Products	Weight (%)	Mo (%)		Cu (%)	
				Content	Recovery	Content	Recovery
6	–	Concentrate	1.8	8.88	78.2	2.34	28.8
		Middlings	7.6	0.23	8.5	0.30	15.6
		Tailings	90.6	0.03	13.3	0.09	55.6
		Total	100.0	0.20	100.0	0.15	100.0
	10	Concentrate	1.0	7.35	38.0	7.27	51.8
		Middlings	4.4	0.58	13.2	0.25	7.8
		Tailings	94.6	0.10	48.8	0.06	40.4
		Total	100.0	0.19	100.0	0.14	100.0
12	–	Concentrate	1.3	8.30	62.0	5.08	43.6
		Middlings	4.2	0.45	10.9	0.23	6.4
		Tailings	94.5	0.05	27.1	0.08	50.0
		Total	100.0	0.17	100.0	0.15	100.0
	10	Concentrate	5.3	2.65	79.2	0.31	11.4
		Middlings	14.3	0.09	7.2	0.16	16.0
		Tailings	80.4	0.03	13.6	0.13	72.6
		Total	100.0	0.18	100.0	0.14	100.0

Table 3. Effect of type of collectors on molybdenum flotation
(1 kg/Mg Na$_2$SiO$_3$, 10 kg/Mg Na$_2$S, 56 g/Mg pine oil, 58 µm particle size, pH 12)

Type of Collector	Products	Weight (%)	Mo (%)		Cu (%)	
			Content	Recovery	Content	Recovery
Gas Oil	Concentrate	5.3	2.65	79.2	0.31	11.4
	Middlings	14.3	0.09	7.2	0.16	16.0
	Tailings	80.4	0.03	13.6	0.13	72.6
	Total	100.0	0.18	100.0	0.14	100.0
Aero 3302	Concentrate	1.3	8.47	64.8	0.42	3.7
	Middlings	10.8	0.39	24.8	0.26	19.0
	Tailings	87.9	0.02	10.4	0.13	77.3
	Total	100.0	0.17	100.0	0.15	100.0

Effect of collector

In these tests, gas oil of 440 g/Mg and Aero 3302 (collector) of 150 g/Mg was studied in order to determine the differences between these collectors. The flotation tests were accomplished according to the aforementioned conditions. As seen in Table 3, the highest molybdenum recovery of 79.2% was obtained with gas oil. It is known that

hydrocarbon oils as collector are usually used in molybdenum flotation. In recent years, the use of kerosene has become widespread due to its strong collecting ability and good selectivity. However, in these tests with gas oil (pure) which is less combustible than kerosene and has more carbon atoms and the oily collector Aero 3302 which is xanthate ester were preferred. When these collectors were compared in terms of molybdenum grade, it could be said that Aero 3302 was more selective than gas oil. However, since high molybdenum recovery was preferred instead of selectivity in concentrate, gas oil was selected as the optimum collector.

Effect of frother

In order to examine the effect of the frothers, the tests were performed with 56 g/Mg pine oil and 40 g/Mg methylisobutyl carbinol (MIBC, 1% w/w) under the optimum conditions obtained previously. The results in Table 4 show that 79.2% Mo recovery, 2.65% Mo, and 0.31% Cu content were obtained with pine oil. It can be concluded that pine oil was more effective than MIBC in the molybdenum flotation, since the higher molybdenum recovery and the lower copper content were provided with pine oil. It is worth pointing out that pine oil plays an important role for both collector and frother in the molybdenum flotation.

Table 4. Effect of type of frothers on molybdenum flotation
(1 kg/Mg Na_2SiO_3, 10 kg/Mg Na_2S, 440 g/Mg gas oil, 58 μm particle size, pH 12)

Type of frother	Products	Weight (%)	Mo (%)		Cu (%)	
			Content	Recovery	Content	Recovery
Pine oil	Concentrate	5.3	2.65	79.2	0.31	11.4
	Middlings	14.3	0.09	7.2	0.16	16.0
	Tailings	80.4	0.03	13.6	0.13	72.6
	Total	100.0	0.18	100.0	0.14	100.0
MIBC	Concentrate	1.9	6.03	56.3	0.68	8.5
	Middlings	5.6	0.27	7.4	0.33	12.2
	Tailings	92.5	0.08	36.3	0.13	79.3
	Total	100.0	0.20	100.0	0.15	100.0

Effect of copper depressants

The copper content in the molybdenum concentrates, which should be lower than 0.5% Cu, is the most important criteria for terms of sale. As molybdenum is generally found with porphyr copper ores, copper content is generally a problem in molybdenum flotation. For that purpose, the tests were performed using copper depressants at different dosages and types such as sodium sulfide (5, 10, 15, and 20 kg/Mg), Nokes reagent (1, 2, 4, and 6 kg/Mg), lignosulfonate (0.2, 0.5, 1, and 2 kg/Mg), and sodium metabisulfite (1, 2, 4, and 8 kg/Mg) based on the optimum conditions.

The obtained results at different amounts of sodium sulfide are shown in Fig. 6. It can be seen from Fig. 6 that the copper content in the molybdenum concentrate showed a decreasing trend as the sodium sulfide dosage increased. However, the increasing the sodium sulfide dosage also caused a minor decrease in the molybdenum recovery with higher amounts than 10 kg/Mg. Therefore, the optimum sodium sulfide dosage with a content of 0.31% Cu and a recovery of 79.2% Mo was determined as 10 kg/Mg.

Figure 7 shows the effect of Nokes reagent (Na_3PO_3S) on the copper depression. With the increasing the amount of Nokes reagent, the copper content in the molybdenum concentrate decreased from 5.08% to 0.82%. By adding 4 kg/Mg Nokes reagent, the copper content was obtained as 0.71% which remained of the sale terms. Besides, Nokes reagent caused a negative effect on the molybdenum recovery as it dropped to 57.4%.
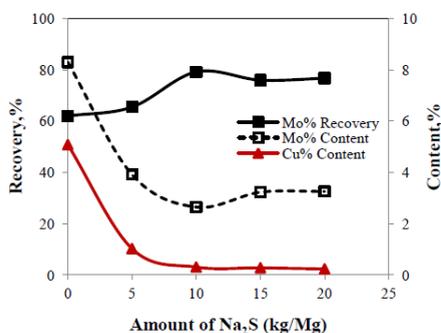
Fig. 6. Effect of Na_2S on copper and molybdenum flotation (1 kg/Mg Na_2SiO_3, 440 g/Mg gas oil, 56 g/Mg pine oil, 58 μm particle size, pH 12)
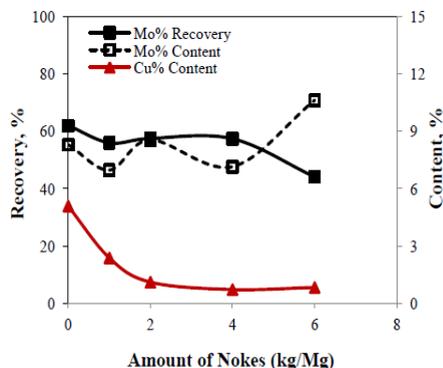
Fig. 7. Effect of Nokes on copper and molybdenum flotation (1 kg/Mg Na_2SiO_3, 440 g/Mg gas oil, 56 g/Mg pine oil, 58 μm particle size, pH 12)

The Nokes reagent used as copper depressant in the separation of molybdenite-copper are thiophosphorus or thioarsenic compounds (Bulatovic, 2007). The phosphate Nokes is produced by reacting P_2S_5 with NaOH:

$$P_2S_5 + 10NaOH \rightarrow Na_3PO_2S_2 + Na_3PO_3S + 2Na_2S + 5H_2O \qquad (3)$$

Crozier (1992) determined that in Nokes reagent there is a trace amount of residual HS^- concentration and the phosphorous compounds which are probably important depressants for copper. It can be concluded that Nokes reagent has depression characteristic for not only copper and but also molybdenum under these flotation conditions.

As can be seen from Fig. 8, when the lignosulfonate was added, the molybdenum recovery sharply decreased. As the amount of lignosulfonate was increased, its adverse effect increased on the molybdenum flotation.

Ansari and Pawlik (2007b) reported that the depression of chalcopyrite using lignosulfonate at a relatively low dosage could be achieved at high pH adjusted with lime. Calcium-hydroxy species formed in alkaline solutions, adsorbed on the chalcopyrite surface and reversed the negative surface charge. Since the adsorption of chalcopyrite with collector did not occur due to surface charge, chalcopyrite was depressed. Besides, they observed that the molybdenite could easily be depressed by any type of lignosulfonates regardless of pH.

The related results with sodium metabisulfite ($Na_2S_2O_5$) are seen in Fig. 9. According to the results, the copper content was ranged from 3.57% to 6.59%. The molybdenum recovery decreased to 46.7% with the addition of sodium metabisulfite of 1 kg/Mg, while it was 62% without adding any copper depression reagent. Although the amount of sodium metabisulfite was increased from 1 kg/Mg to 8 kg/Mg, the effective results could not be achieved in terms of neither copper content nor molybdenum recovery. It was obvious that sodium metabisulfite showed a depression effect on the molybdenum flotation as Nokes reagent and lignosulfonate.
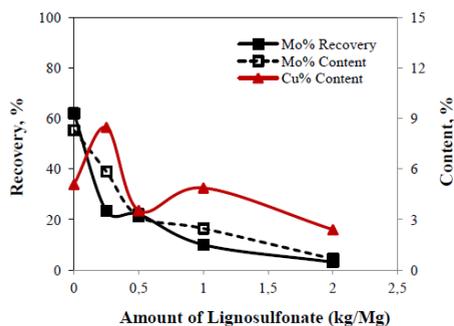
Fig. 8. Effect of lignosulfonate on copper and molybdenum flotation (1 kg/Mg Na_2SiO_3, 440 g/Mg gas oil, 56 g/Mg pine oil, 58 μm particle size, pH 12)
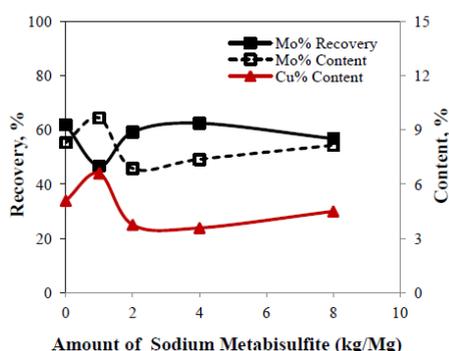
Fig. 9. Effect of sodium metabisulfite on copper and molybdenum flotation (1 kg/Mg Na_2SiO_3, 440 g/Mg gas oil, 56 g/Mg pine oil, 58 μm particle size, pH 12)

Effect of flotation time

The effect of flotation time on the molybdenum recovery with adding Na_2S of 10 kg/Mg, gas oil of 440 g/Mg, and 56 g/Mg pine oil was investigated from 0 to 15 min of the flotation time. The results are shown in Fig. 10. The molybdenum recovery reached over 82.2% in 10 min, while it reached over 50.0% in the first 1 min. According to the results, a flotation time of 10 min was sufficient to obtain the acceptable molybdenum recovery. Prolonged flotation time to 15 min showed no

significant change but slight increase in the molybdenum recovery. It was suggested that the metal loss of approximately 15% was result of non-liberated grain and presence of molybdenum oxide mineral as powellite ($CaMoO_4$).

Flotation kinetics models, which are the most widely used in the literature, are formulated in terms of the rate of flotation, and can be quantified in terms of the physical, chemical and hydrodynamic parameters for flotation system (Ofori et al., 2014). Rate of flotation can be expressed the amount of flotation particles with regard to flotation time (Bulatovic, 2007). The rate constant depends on ore characteristics such as mineralogy, grain size, and surface chemistry. Additionally, it is related to operating variables, such as amount of reagent and degree of aeration (Kelebek and Nanthakumar, 2007).
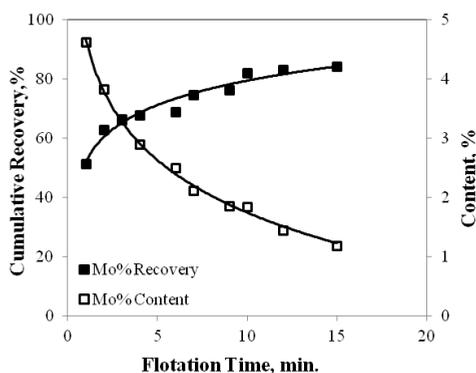
Fig. 10. Flotation recovery of molybdenum as a function of flotation time
(1 kg/Mg Na_2SiO_3, 10 kg/Mg Na_2S, 440 g/Mg gas oil,
56 g/Mg pine oil, 58 μm particle size, pH 12)

The flotation kinetics is examined applying the first order and second order models. The first-order process gives a reasonably good fit to the experimental data for many flotation systems. The equations used in determining flotation kinetic are described with chemical kinetic equations. The equations for first kinetic model can be written as:

$$\frac{dC}{dt} = -k_1 C \tag{4}$$

$$C = C_o e^{-k_1 t} \tag{5}$$

$$\ln\left(\frac{C_o}{C}\right) = k_1 t \tag{6}$$

where C_o is the concentration of valuable material in the cell at initial time, C is the concentration of valuable material remaining in the flotation cell at time t, t is flotation

time, and k_1 is the flotation rate constant. To obtain 100% recovery in flotation is not possible, therefore the concentration of valuable material remaining unfloated in the cell at infinite time is called C_∞. In consideration of C_∞, Eq. (6) is rearranged as follows;

$$\ln\left(\frac{C_o - C_\infty}{C - C_\infty}\right) = k_1 t \tag{7}$$

$$\frac{C_o - C}{C_o - C_\infty} = 1 - e^{-k_1 t} \tag{8}$$

Flotation kinetic can be also expressed in terms of recovery. Eqs. (9), (10), and (11) can be written as:

$$R = \left(\frac{C_o - C}{C_o}\right) \tag{9}$$

$$R_\infty = \left(\frac{C_o - C_\infty}{C_o}\right) \tag{10}$$

$$\frac{R}{R_\infty} = \left(\frac{C_o - C}{C_o - C_\infty}\right) \tag{11}$$

where R is cumulative recovery at time t, R_∞ is the maximum recovery after prolonged flotation time (Arbiter and Harris,1962; Pecina et al., 2009). When Eq. (8) is substituted into Eq. (11), and Eq. (12) is obtained as first order kinetic equation.

$$R = R_\infty(1 - e^{-k_1 t}) \tag{12}$$

The kinetic parameters used in the first order kinetic model were given in Table 5. The first order kinetic model shown in Fig. 11 was plotted in terms of Eq. (12). R_∞ was obtained from Fig. 9 as 84.6%. The kinetic constant (k_1) was found as 0.36 min^{-1} with 0.89 determination coefficient (r^2). To increase the value of correlation coefficient obtained with the first order kinetics model, the second order kinetics model was applied by fitting the experimental data to the flotation model Eq.(13) as follows (Arbiter and Harris, 1962),

$$\frac{t}{R} = \frac{t}{R_\infty} + \frac{1}{R_\infty^2 k_2} \tag{13}$$

In this equation, k_2 is the second order rate constant. R and R_∞ fitted in Eq. (13) are the values previously used in the first order kinetics model. The obtained kinetic parameters were given in Table 6. As seen in Fig. 12, the obtained values were plotted in a straight line, and confirmed to the second order flotation kinetics in good correlation.

Table 5. Parameters for the first order flotation kinetics

t	R	$\ln((R_\infty - R)/R_\infty)$
0	0	0
1	51.5	−0.938
2	62.9	−1.361
3	66.2	−1.525
4	68.0	−1.628
6	69.1	−1.697
7	74.7	−2.145
9	76.5	−2.346
10	82.2	−3.562
12	83.4	−4.256
15	84.5	−6.740

Table 6. Parameters for the second order flotation kinetics

T (min)	C (g/dm^3)	$R= (C_o-C)/C_o$ (g/dm^3)	t/R
0	0.683	–	–
1	0.331	0.515	1.940
2	0.253	0.630	3.175
3	0.231	0.662	4.528
4	0.218	0.681	5.875
6	0.211	0.691	8.677
7	0.173	0.747	9.369
9	0.160	0.765	11.760
10	0.121	0.822	12.158
12	0.113	0.834	14.381
15	0.105	0.846	17.737

The second order rate constant (k_2) was found from the intercept value as 0.989 min^{-1} with 0.99 correlation coefficient (r^2). In terms of these data, it is possible to say that the second kinetics model is more applicable than the first order kinetics model. Nguyen and Schulze (2004) reported that flotation kinetics was in general between the first and second order. As the first order kinetics model fitted for the flotation of single minerals, or in dilute pulps, the second order kinetics model fitted for low grade ores or more concentrated pulps.
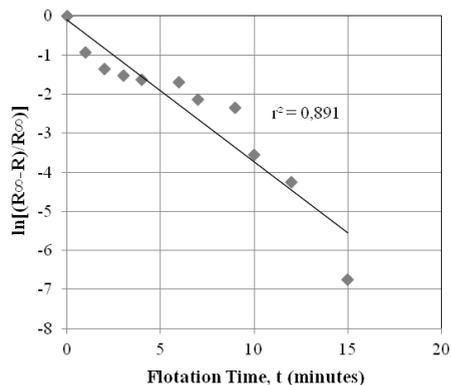
Fig. 11. Experimental data plotted according the first order flotation kinetics
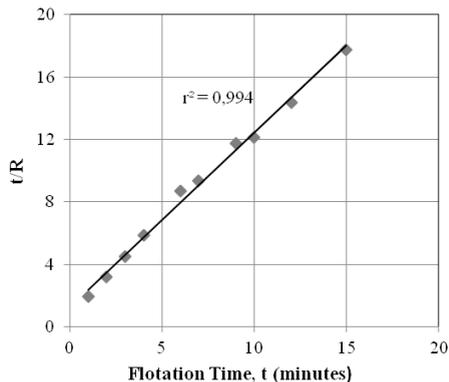
Fig. 12. Experimental data plotted according the second order flotation kinetics

The flotation test was carried out at pH 12 using optimum flotation parameters such as sodium silicate of 1 kg/Mg, sodium sulfide of 10 kg/Mg, pine oil of 56 g/Mg, and gas oil of 440 g/Mg. As can be seen from Table 7, after ten-stage cleaning, the molybdenum concentrate content reached to 52.15% with the molybdenum recovery of 72.3% and the copper content of 0.45% with the addition of 5 kg/Mg Na_2S in the cleaning stages.

Table 7. Result of multi stage flotation test in optimum conditions
(1 kg/Mg Na_2SiO_3, 10 kg/Mg Na_2S, 440 g/Mg gas oil, 58 µm particle size, pH 12)

Products	Weight (%)	Mo (%)		Cu (%)	
		Content	Recovery	Content	Recovery
Concentrate	0.23	52.15	72.3	0.45	0.8
Middlings	11.37	0.17	11.7	0.16	13.6
Tailings	88.40	0.03	16.0	0.13	85.7
Total	100.0	0.17	100.0	0.13	100.0

Conclusions

The ore sample contained 0.18% Mo and 0.15% Cu obtained from the Kirklareli region of Turkey used in this study. In the flotation tests, the influence of flotation parameters such as particle size, pH, collectors, frothers, and copper depressants on the molybdenum flotation was examined.

The results related to particle size were demonstrated that molybdenum concentrate with higher recovery – lower content was obtained with 58 µm due to increases of valuable and gangue minerals at finer particle size.

Regarding to the pH tests, the results indicated that Na_2S had an activator effect on copper, and depression effect on the molybdenum flotation at pH 6. On the other hand,

it can be said that the depression of copper sulphide minerals were achieved since HS^- and S^{2-} ions formed with the dissociation of Na_2S in water at pH 12 destroyed the collector coating on the floated copper sulphide mineral.

The optimum flotation reagents were determined for gas oil as the collector, pine oil as the frother, sodium sulphide as the depressant at pH 12. When the collectors were compared in terms of molybdenum grade, it was concluded that Aero 3302 (collector) was more selective than gas oil. As can be noted that pine oil showed collector and frother characteristic, and it was a better frother than MIBC for the molybdenum flotation. The results also showed that it was possible to obtain a molybdenite concentrate containing Mo content of 2.65% with the recovery of 79.2%, and Cu content of 0.31%. The flotation parameters were examined applying the first order and second order kinetics models. When the flotation kinetics of the molybdenum as a function of time was evaluated with the kinetics models, it was seen that second order model represents the data with determination coefficient (r^2) of 0.99.

Finally, the flotation test contained ten stages cleaning circuit was performed with optimum flotation parameters. In the obtained final concentrate, the molybdenum content which was sufficient Mo content for international commerce was found as 52.15% with 0.45% Cu content.

Overall, it can be said that there is limited study on the flotation behavior of molybdenum ores in the world. Therefore this study will surely contribute to the limited number of investigations that have been carried out so far. Furthermore, this current study has proved that a saleable molybdenum concentrate could be obtained with acceptable recoveries from a low grade porphyry copper-molybdenum ore.

Acknowledgements

References

ANSARI A. and PAWLIK M., 2007a, *Floatability of chalcopyrite and molybdenite in the presence of lignosulfonates. Part I. Adsorption Studies*, Minerals Engineering, 20, 600-608.

ANSARI A. and PAWLIK M., 2007b, *Floatability of chalcopyrite and molybdenite in the presence of lignosulfonates. Part II. Hallimond tube flotation*, Minerals Engineering, 20, 609-616.

ARBITER N. and HARRIS C.C., 1962, *Flotation Kinetics in Froth Flotation*, 50th Anniversary Volume, In: Fuestenau, D.W. (Ed.), AIME, 215-246.

BULATOVIC S.M., 2007, *Handbook of Flotation Reagents: Chemistry, Theory and Practice: Flotation of Sulfide Ores*, Elsevier B.V., Amsterdam: 1, 235-293.

CASTRO, S.H., MAYTA, E., 1994. *A kinetics approach to the effect of particle size on the flotation of molybdenite.* In: Castro, S., Alvarez, J. (Eds.), Flotation. A. Sutulov Memorial Volume, 331–344.

CASTRO S.H. and BOBADILLA C., 1995, *The depressant effect of some inorganic ions on the flotation of molybdenite*. In: Laskowski, J.S., Poling, G.W. (Eds.), Processing of Hydrophobic Mineral and Fine Coal: Proceedings of the First UBC-McGill Bi-Annual International Symposium on Fundamentals of Mineral Processing, Metallurgical Society of CIM, Montreal, 95-103.

CASTRO S., LOPEZ-VALDIVIESO A. and LASKOWSKI J.S., 2016, *Review of the flotation of molybdenite. Part 1: Surface properties and floatability*, International Journal of Mineral Processing, 148, 48-58.

CHANDER S. and FUERSTENAU D.W., 1972, *On the natural floatability of molybdenite*, Transactions of AIME, 252, 62-68.

CROZIER R.D., 1979, *Flotation reagent practice in primary and by-product molybdenite recovery*, Mineralogical Magazine, 140, 174-178.

CROZIER R.D., 1992, *Theory, Reagents and Ore Testing*, Pergamon Press, England.

CUMMING I.W., HOLDICH R.G., SMITH I.D., S, 2000, *The rejection of oil by microfiltration of a stabilised kerosene/water emulsion*, Journal of Membrane Science, 169, 147-155.

ENGELBRECHT J.A. and WOODBURN E.T., 1975, *The Effect of Froth Height, Aeration Rate and Gas Precipitation on Flotation*, Journal of South African Institute Mining and Metallurgy, 76, 125-132.

HERNLUND R.W., 1961, *Extraction of molybdenite from copper flotation products*, Quart. Colorado School, 56 (3), 177-195.

KELEBEK S., 1988, *Critical surface tension of wetting and of floatability of molybdenite and sulphur*, Journal of Colloid and Interface Science, 124, 504-514.

KELEBEK S. and NANTHAKUMAR B., 2007, *Characterization of stockpile oxidation of pentlandite and pyrrhotite through kinetic analysis of their flotation*, International Journal of Mineral Processing, 84, 69-80.

KLIMPEL R.R., 1988, *Consideration for improving the performance of froth floating system*, Minerals Engineering, 40, 1093-1100.

NGUYEN A.V. and SCHULZE H.J., 2004, *Colloid Science of Flotation*, Chapter 30, in Surfactant Series, 118, Marcel Dekker, Inc, New York.

OFORI P., O'BRIEN G., HAPUGODA P., FIRTH B., 2014, *Distributed flotation kinetics models – A new implementation approach for coal flotation*, Minerals Engineering, 66-68, 77-83.

PECINA E. T., RODRIGUEZ M., CASTILLO P., DIAZ V., ORRANTIA E., 2009, *Effect of Leptospirillum ferrooxidans on the flotation kinetics of sulphide ores*, Minerals Engineering, 22, 462-468.

SHIRLEY J.F. and SUTULOV A., 1985, *By-product molybdenite*, In: Weiss, N.L. (Ed.), SME Mineral Processing Handbook. AIME, New York.

SMIT F.J. and BHASIN A.K., 1985, *Relationship of petroleum hydrocarbon characteristics and molybdenite flotation*, International Journal Mineral Processing, 15, 19-49.

SONG S., LOPEZ-VALDIVIESO A., DING Y., 1999, *Effects of nonpolar oil on hydrophobic flocculation of hematite and rhodochrosite fines*, Powder Technology, 101, 73.

TINGSHU H., WAN H., SONG N., GUO L., 2011, *The influence of composition of nonpolar oil on flotation of molybdenite*, Minerals Engineering, 24, 1513-1516.

WANG H., GU G.H., FU J.G., HAO Y., 2008, *Study of the interfacial interactions in the molybdenite flotation system*, Journal of China University of Mining and Technology, 18, 82-87.

WILLS B.A., 1997, *Mineral Processing Technology*, sixth ed. Butterworth-Heinemann, Oxford.

XIA Y.K. and PENG F.F., 2007, *Selection of frothers from residual organic reagents for copper–molybdenite sulfide flotation*, International Journal Mineral Processing. 83, 68-75.