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The effect of different clay minerals on the flotation kinetics of chalcopyrite

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Abstract

This study investigated the effects of clay minerals (montmorillonite, illite, and kaolinite) on chalcopyrite recovery and flotation kinetic parameters. Classical first-order flotation kinetic model was applied as a function of froth height and amount of clay minerals to fit overall flotation results on chalcopyrite recovery against flotation time. Clay minerals enhanced chalcopyrite recovery by mechanical entrainment and slime coating of valuable chalcopyrite particles. Flotation tests have shown that the deleterious impact of clay minerals on the chalcopyrite flotation is enhanced as follows: montmorillonite>kaolinite>illite. Montmorillonite significantly raised viscosity and also considerably diminished chalcopyrite grade. Recovery and selectivity were lower for montmorillonite than kaolinite and illite. The adjunct of illite was of little effect on chalcopyrite flotation kinetics. The obtained flotation rate constants indicate that clay minerals are carried to the concentrate together with the chalcopyrite. The flotation rate constants increased with increasing the amount of all clay minerals. Slime minerals easily entered to concentrate by mechanical entrainment, and the inhibition effect of clay particles on chalcopyrite became more obvious with increasing flotation time. However, the negative effect of clay minerals is reduced with high froth height.

Keywords

Flotation, kinetic models, classical first-order model, chalcopyrite, clay minerals.

Introduction

There is a growing need to enrich ores that are low-grade and hard to process. The most important reasons for this are the unprecedented resource demand and the high-speed decrease of good quality mineral resources (Galvin et al., 2012; Wang & Peng, 2013; Ni et al., 2018). The mines contain clay minerals which are gangue minerals, as well as valuable minerals. In some instances, clay minerals content can reach up to 80% (Forbes et al., 2014). The presence of clay zones is also common in complex sulfide polymetallic ores. One of the main problems encountered in the flotation of these ores is that they contain clay minerals. Since it is impossible to prevent or reduce clay formation, what needs to be done is to minimize the harmful effects on flotation (Aslan, 1996; Taner, 2019). The same dilemma is also encountered in the copper mine. Flotation is the most effective method for enriching copper ore, and chalcopyrite is a mineral used in copper production. However, fine chalcopyrite often contains large amounts of gangue minerals and clay minerals, and the invaluable minerals deteriorate the quality of chalcopyrite concentrate. It is important to develop appropriate approaches and identify the basic mechanisms to reduce their negative effects on flotation.

Flotation is powerfully influenced by several factors coupled with the floated mineral, such as grade, liberation, surface properties, etc., and a lot of operating factors (Cilek, 2004). Flotation is regarded as a time-rate recovery operation because the cumulative recovery is unquestionably proportional to the flotation time (Yuan et al., 1996; Sripriya et al., 2003). Hereby, flotation time-recovery graphics are generally utilized to define flotation kinetics, which can also be exactly specified utilizing mathematical models (Zhang et al., 2013; Ni et al., 2018). Flotation results can be analyzed with kinetic models. Batch flotation experiments promote the classical first-order rate equation under logical operating provisions in the literature (Xu, 1998; Agar et al., 1998; Oliveira et al., 2001; Cilek, 2004; Sokolovic et al., 2012; Stanojlovic & Sokolovic, 2014). The model is relatively preferable and is commonly used to optimize flotation (Bahrami et al., 2019).

The kinetics of chalcopyrite flotation have been studied in detail by some researchers as a measure of chalcopyrite recovery and as a function of time (Vizcarra et al., 2011; Stanojlovic & Sokolovic, 2014; Hassanzadeh & Karakas 2017; Asghari et al., 2018). Different kinetic models have been proposed in the literature. However, clay minerals' effect on the chalcopyrite flotation kinetics has been relatively little discussed (Wang et al., 2015; Farrokhpay et al., 2016).

The use of the flotation method is gaining importance in the enrichment of low-grade and high-clay-content ores. The content and type of clay in the ore change, and it is necessary to offer quick solutions to the problems that arise. Structural differences between clay minerals also show differences in their behaviour and effects during mineral processing. This study aims to broadly analyze the clay minerals effect (montmorillonite, illite, and kaolinite) on the flotation kinetics of chalcopyrite. The type of clay, amount of clay, and froth height were investigated as flotation parameters on chalcopyrite grade-recovery and kinetic parameters of the chalcopyrite flotation process. Classical first-order flotation kinetic model was utilized to analyze batch flotation results.

Materials and Methods

Materials

The samples containing 2.63% Cu and 38.38% Fe were obtained from various places of the Siirt Madenkoy ore deposits in the Southeastern Anatolia area of Turkey. The mineral compositions of the ore and clay minerals are specified utilizing an X-ray diffractometer (XRD), and the graphics are given in Fig. 1. The main mineral matters of clay minerals were montmorillonite peak for montmorillonite mineral, illite, and quartz for illite mineral, kaolinite, and halloysite for kaolinite mineral. The content of the ore sample was chalcopyrite and pyrite. The particle size distribution of the ground ore was determined by Malvern Mastersizer 2000 particle size analyzer that 80% of the particles are smaller than 79 µm, while 80% of montmorillonite, illite, and kaolinite samples are 60 µm, 34 µm, and 28 µm, respectively.

Flotation experiments were carried out using sodium silicate (Na_2SiO_3) as a dispersant, Aerophine 3418A as a collector, and methyl isobutyl carbinol (MIBC) as a frother. 3418A obtained from Cytec Industries involves ca. 50% w/w of sodium-diisobutyl dithiophosphinate, and the rest was water. The pulp pH was examined by adding lime and sulfuric acid. Tap water was utilized during the experiments.

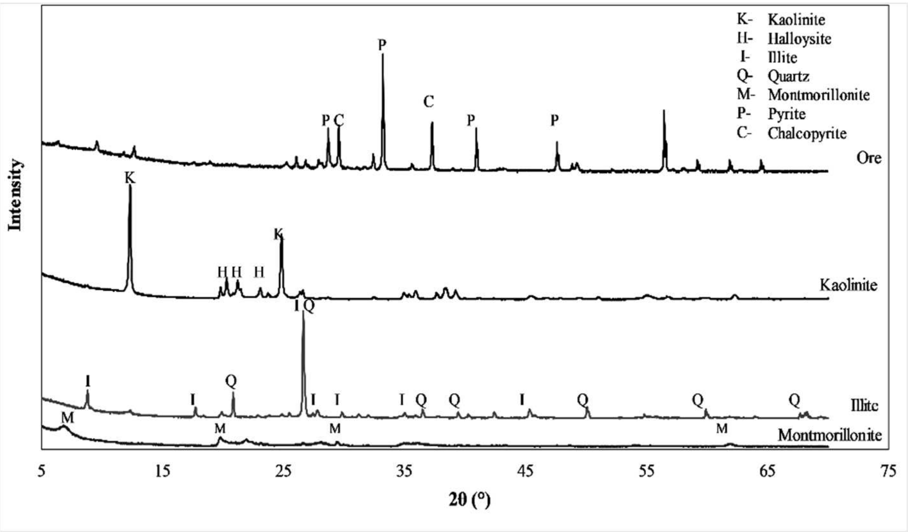

Fig. 1. X-ray diffraction patterns of ore, kaolinite, illite, and montmorillonite

Methods

Grinding of the ore was performed with a laboratory ball mill (400×125 mm), with a 15% ball charge and 10 min grinding time. All flotation experiments were carried out in a 2 L laboratory Denver flotation machine using a mixture of chalcopyrite and clay minerals at a pulp density of 10% solids, with a 200 g/t dosage of Na_2SiO_3, 50 g/t dosage of 3418A, and 100 g/t dosage of MIBC. The impeller speed was 1350 rpm, and the airflow rate was 10 L/min. For flotation kinetic tests, the pulp was first conditioned for 5 min in the cell, and then the pH was adjusted to about 11.5. The required amount of dispersant and collector was involved, and the pulp was conditioned for an additional 3 min for each reagent. Later, the last reagent, MIBC, was added and conditioned for 1 min. At the end of the frother addition, flotation was started by introducing air. The concentrate was collected at cumulative time intervals of 0.5, 1, 2, 3, 5, and 7 min of flotation. The samples were filtered, dried, weighed, and analyzed to calculate the grade and recovery of chalcopyrite. Chemical analysis was performed by AAS (Atomic Absorption Spectrometer) to calculate the metallurgical balance for Cu and Fe. In this way, chalcopyrite has been calculated.

The flotation of clay minerals-chalcopyrite mixture was performed to find out the chalcopyrite flotation behaviour in the existence of clay minerals. Classical first-order flotation kinetic model was utilized to define the flotation rate and ultimate chalcopyrite recovery (Eq. 1):

$$R = R_\infty (1 - e^{-kt}). \qquad (1)$$

Where R (%) is the recovery at the cumulative time t (min); R_∞ (%) is the ultimate chalcopyrite recovery at infinite flotation time; k is the flotation rate constant (min^{-1}) (Stanojlović & Sokolović, 2014). The following variables were selected as factors in the experiments: froth height (H_f), clay type, and amount of clay under optimized flotation conditions. The pulp density at 10% solids was calculated to determine the froth height. The amount of water added to the cell was determined according to the volumes at the moment when the H_f value was 1, 2, and 3 cm (the depth below the overflowing). These amounts were determined with the flotation machine running and the air closed (Taner, 2019).

Results

Effect of montmorillonite on chalcopyrite flotation kinetics

Fig. 2 demonstrates the time-recovery and time-grade graphics of chalcopyrite within various froth heights under different mass ratios of montmorillonite and ore mixture at pH 11.5. Chalcopyrite recovery increased with a rise in the amount of montmorillonite. On the contrary, the chalcopyrite grade decreased significantly.

The most appropriate flotation time for all experiments was decided as 3 min, and it was clear that chalcopyrite showed a rapid flotation. Under these conditions, a flotation time of 3 min occurred in 53-68% chalcopyrite recovery for all experiments. It should be noted that since the study aimed to explore further the role of different kinds of clay minerals in chalcopyrite flotation, we were not regarded of the proper flotation conditions.

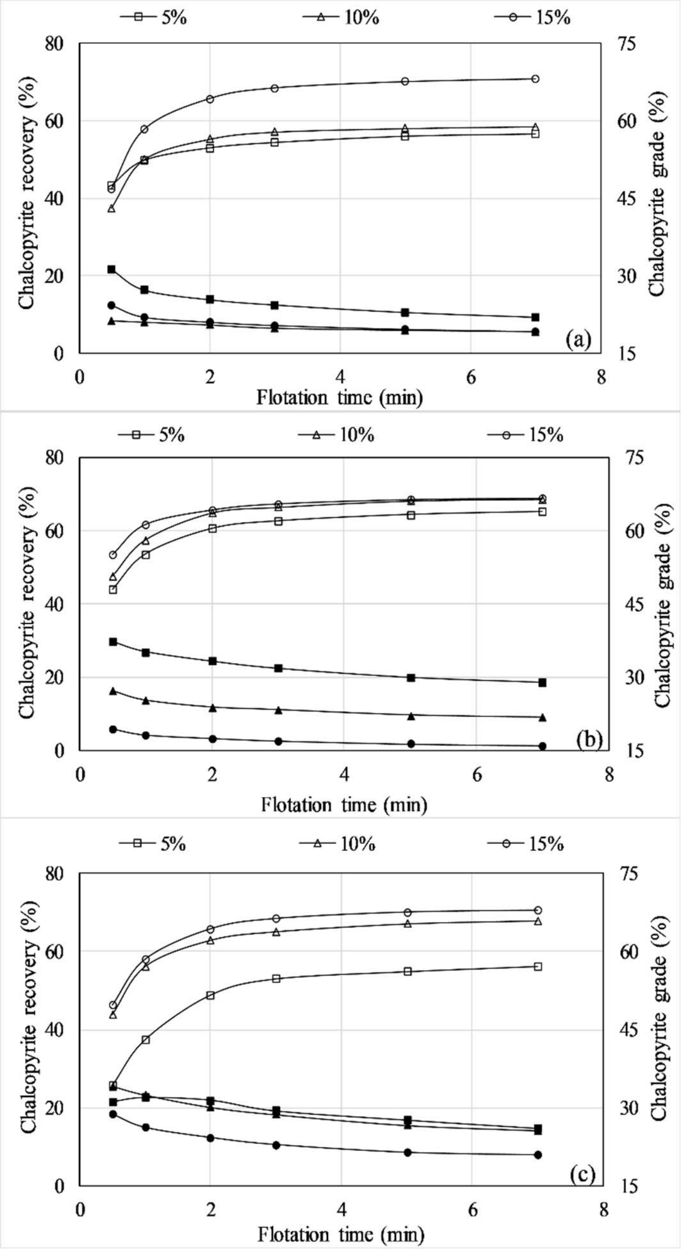

Fig. 2. Comparison of the chalcopyrite grade (with filling) and recovery (without filling) obtained in the rough flotation tests of the mixture of chalcopyrite ore and montmorillonite, (a) H_f 1 cm, (b) H_f 2 cm, and (c) H_f 3 cm

Higher chalcopyrite recovery and lower chalcopyrite grade are the results of the mixture of chalcopyrite ore and 15% montmorillonite. As seen in Fig. 2, while the amount of montmorillonite increased, chalcopyrite recovery expanded from 54.26% to 68.41% in the 1 cm froth height. In contrast, the chalcopyrite grade tended to decrease from 24.28% to 20.34%. Wang et al. (2015) have described that a rise in the bentonite quantity did not importantly influence the copper grade. This is contrary to the results of the present study, with a decrement in chalcopyrite grade of about 4% with the addition of montmorillonite.

The average correlation coefficient (R^2), the ultimate chalcopyrite recovery (R_∞), and the flotation rate constant (k) were calculated by the software, and the results were shown in Tab. 1. The ultimate chalcopyrite recovery increased with the growth of both froth height and amount of montmorillonite. The entrainment of gangue was more important in the concentrate when the montmorillonite concentration was high in the mixture. So, possible control of flotation time and a rise in the chalcopyrite flotation are significant for the grade and recovery of concentrate (Ai et al., 2017). While the flotation rate constant generally enhanced as the amount of montmorillonite increased, the ultimate chalcopyrite recovery also tended to grow. The flotation rate constant decreased only at high froth height. The highest flotation rate constant was achieved with a froth height of 2 cm, while the lowest chalcopyrite grade was obtained at this height.

Tab. 1. Flotation kinetic parameters under the influence of montmorillonite

Variables	H_f [cm]	1			2			3		
	Clay amount [%]	5%	10%	15%	5%	10%	15%	5%	10%	15%
Results	R^2 [%]	89.61	98.98	98.84	94.67	95.19	92.91	99.48	96.99	96.58
	R_∞ [%]	54.60	57.52	69.29	63.10	66.89	67.23	55.06	65.97	68.79
	k [min^{-1}]	2.95	2.06	1.82	2.19	2.30	3.02	1.17	2.05	2.06

Montmorillonite seems to have a superior affinity for chalcopyrite, resulting in a serious slime coating of montmorillonite particles on the chalcopyrite surface. The existence of hydrophilic montmorillonite particles on the chalcopyrite surface prevented air bubble-chalcopyrite attachment and eventually led to a notable decrease in the chalcopyrite grade. Similar results were also obtained by Xu et al. (2003). Experimental results have shown that montmorillonite has an effect on chalcopyrite recovery and concentrate grade with the addition of 10-15% montmorillonite. Montmorillonite forms a viscous structure in pulp due to its high swelling potential, even at low concentrations. This can affect the cell's hydrodynamics that guides the alteration of different flotation sub-process, comprising decreased air dispersion. Some of the latest studies have shown a powerful connection between flotation performance and rheology. In many cases, a rise in viscosity interrupts the flotation kinetics with high reagent consumption, low recovery, and poor selectivity (Patra et al., 2012; Wang et al., 2015; Zhang & Peng, 2015; Chen & Peng, 2018).

Effect of illite on chalcopyrite flotation kinetics

Chalcopyrite grade and recovery for illite minerals as a function of time and froth height are shown in Fig. 3. There were fluctuations in chalcopyrite recovery with different froth heights and increased illite content. The most appropriate flotation time for all experiments was determined as 3 min. Chalcopyrite recovery was enhanced in 3 min, then almost remained stable for entire froth heights. As the amount of illite increased, the chalcopyrite grade decreased significantly. In all experiments, a flotation time of 3 min resulted in 71-81% chalcopyrite recovery; these results gave the highest value compared to montmorillonite and kaolinite. The lowest chalcopyrite recovery and the lowest chalcopyrite grade were obtained with a froth height of 1 cm. As the froth height advanced, the negative effect of illite was reduced. According to the amount of chalcopyrite procured in the concentrate, the optimum froth height was 3 cm. Increasing the froth height decreased the mechanical entrainment and consequently increased chalcopyrite grade and recovery.

Flotation kinetics parameters under the influence of illite were given in Tab. 2. The flotation rate constant generally increased with a rise in the amount of illite. While the highest flotation rate constant was achieved with a froth height of 1 cm, the lowest chalcopyrite grade and recovery were obtained at this height. The addition of illite had little effect on chalcopyrite flotation kinetics. According to Farrokhpay et al. (2016), an agreement was given regarding the flotation and swelling of clays. Swelling is associated with clay hydration, yet not all clays swell when hydrated. Illite and kaolinite are not swelling, albeit with distinctive structures. Illite has a 2:1 structure, and kaolinite has a 1:1 structure, but they can be easefully dispersed and come to the concentrates.

Tab. 2. Flotation kinetic parameters under the influence of illite

Variables	H_f [cm]	1			2			3		
	Clay amount [%]	5%	10%	15%	5%	10%	15%	5%	10%	15%
Results	R^2 [%]	98.55	94.47	91.30	96.53	90.52	88.20	95.69	94.58	91.01
	R_∞ [%]	73.15	74.28	74.35	82.64	79.57	74.56	77.38	76.29	76.44
	k [min^{-1}]	1.79	2.16	2.56	1.83	2.25	2.24	1.42	1.70	1.88

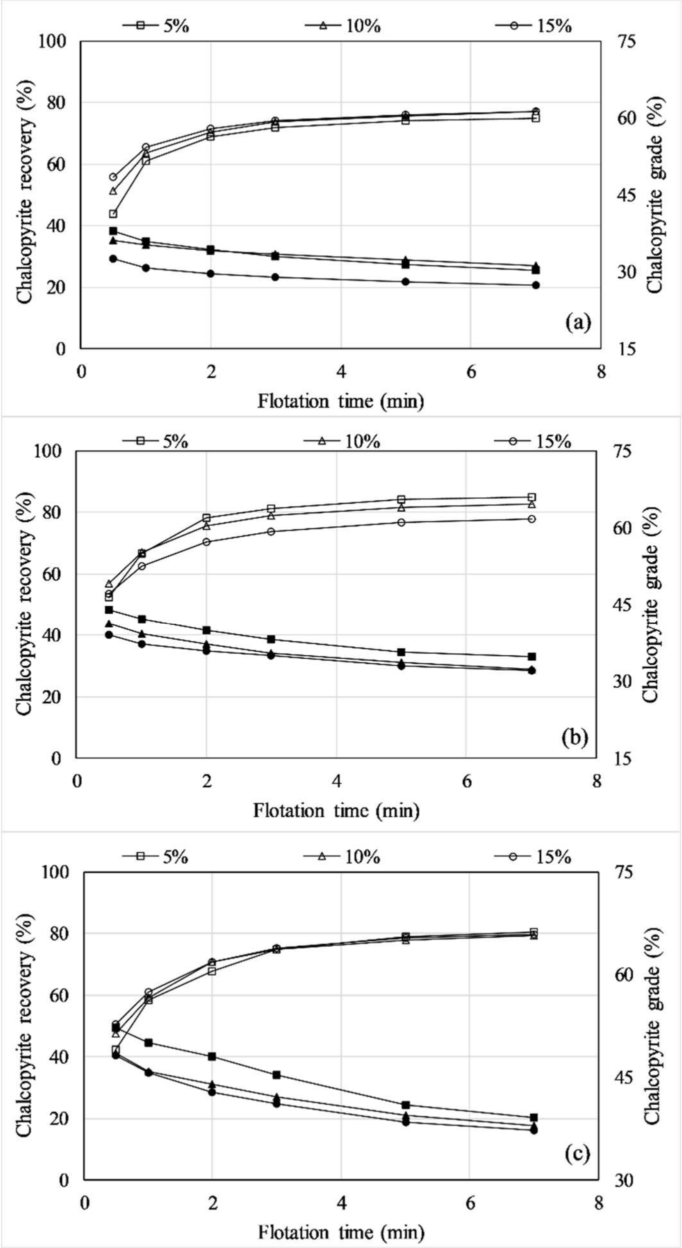

Fig. 3. Comparison of the chalcopyrite grade (with filling) and recovery (without filling) obtained in the rough flotation tests of the mixture of chalcopyrite ore and illite, (a) H_f 1 cm, (b) H_f 2 cm, and (c) H_f 3 cm

Effect of kaolinite on chalcopyrite flotation kinetics

The chalcopyrite grade and recovery as a function of the flotation time and froth height for kaolinite minerals are shown in Fig. 4. Chalcopyrite recovery increased with a growth in the amount of kaolinite. On the contrary, the chalcopyrite grade decreased. Under this condition, a flotation time of 3 min resulted in 63-70% chalcopyrite recovery. Both chalcopyrite grade and chalcopyrite recovery significantly increased as the froth height went up. The analysis of flotation kinetics shows that the froth height considerably reduces the flotation rate constant at which the slow-floating components of the pulp are entrained to the concentrate. While the highest flotation rate constant was achieved with a froth height of 1 cm, the lowest chalcopyrite grade and recovery were obtained at this height.

The flotation kinetics parameters obtained with the addition of kaolinite are given in Tab. 3. The flotation rate constant increased with enhancing the amount of kaolinite. The ultimate chalcopyrite recovery is enhanced with a froth height of 2 cm. As can be seen from the results in Tab. 1-3, the average correlation coefficients (R^2) are generally higher than 0.90, which indicates that this model fits experimental data. Wang et al. (2015) investigated the clay minerals' effect on copper flotation utilizing montmorillonite and kaolinite and found that montmorillonite and kaolinite caused different problems. Chalcopyrite recovery decreased as the amount of montmorillonite increased. High pulp viscosity resulted in a lower quantity of froth as it diminished the frequency of bubble-particle collisions and the mobility of bubble-particle aggregates. The kaolinite amount was a bit of impact on viscosity, but copper grade decreased. The increase in the amount of kaolinite also produced important entrainment qualified by small bubble size and high froth stability.

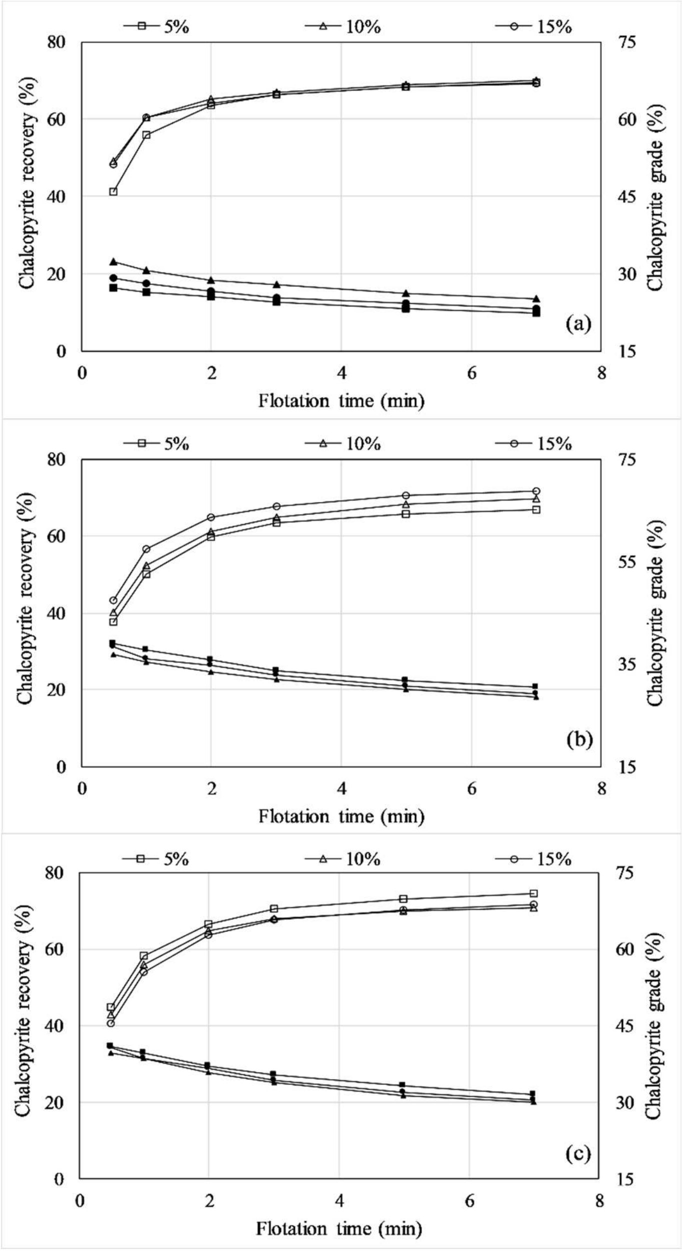

Fig. 4. Comparison of the chalcopyrite grade (with filling) and recovery (without filling) obtained in the rough flotation tests of the mixture of chalcopyrite ore and kaolinite, (a) H_f 1 cm, (b) H_f 2 cm, and (c) H_f 3 cm

Tab. 3. Flotation kinetic parameters under the influence of kaolinite

Variables	H_f [cm]	1			2			3		
	Clay amount [%]	5%	10%	15%	5%	10%	15%	5%	10%	15%
Results	R^2 [%]	98.07	95.19	95.59	97.43	95.49	96.50	95.99	97.40	97.03
	R_∞ [%]	67.42	67.80	67.08	64.81	66.81	69.30	71.67	68.83	69.16
	k [min^{-1}]	1.82	2.45	2.46	1.59	1.66	1.82	1.80	1.81	1.61

The evaluation of the effects of clays on chalcopyrite flotation kinetics

Although flotation recovery is the parameter used to understand the floatability or hydrophobicity of minerals, the flotation rate constant can also be used for this purpose. The flotation rate constant change was presented in Fig. 5 for three different clays as a function of froth height and amount of clay. The flotation rate constant generally decreased with increasing the froth height. The results showed that kaolinite and illite might similarly affect chalcopyrite flotation behaviour, while there was a fluctuation in montmorillonite. The flotation kinetics experiments reveal that the existence of clay minerals dramatically increases the rate constant at which the slow-floating components of the flotation pulp are entrained to the concentrate.

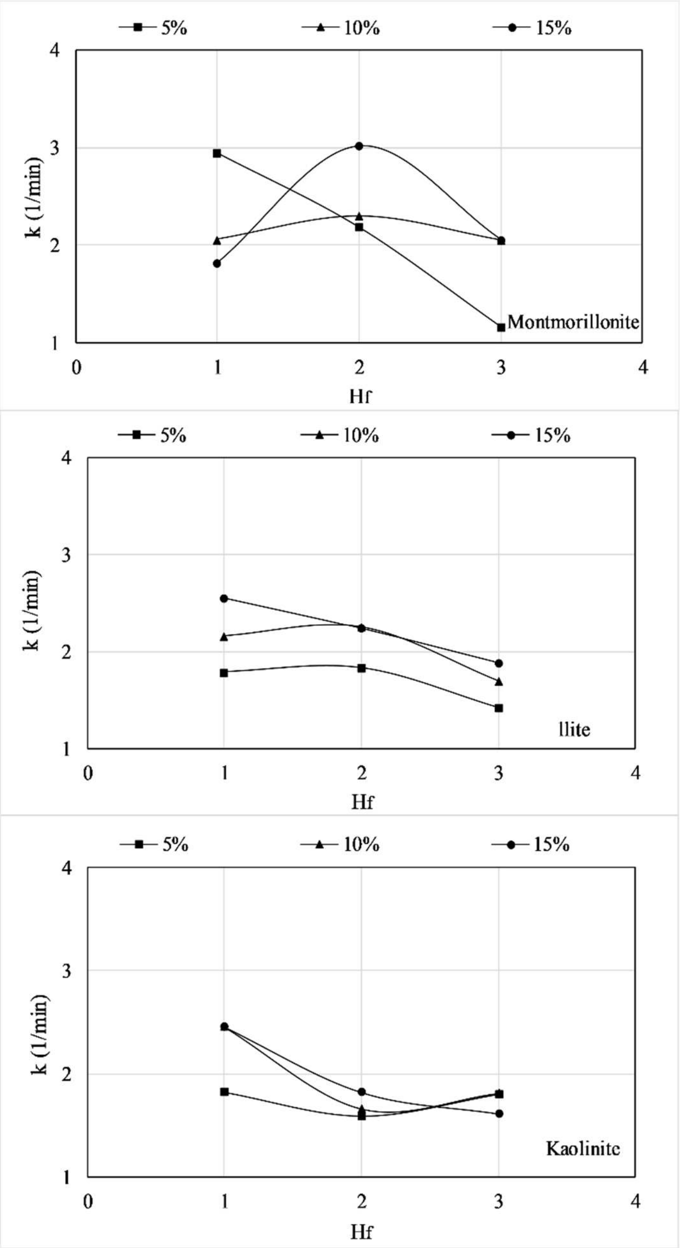

Fig. 5. Flotation rate constant change of different clay minerals depending on froth height and clay amount

The highest flotation rate constant was obtained with montmorillonite, indicating that the flotation of the chalcopyrite and montmorillonite mixture was very fast due to the excess amount of gangue and valuable minerals carried into the concentrate. While the flotation process got worse with montmorillonite addition, the flotation kinetics for the chalcopyrite-montmorillonite system is higher than other clay minerals. These results are not steady with the results procured by Xing et al. (2017) and Farrokhpay et al. (2016). Farrokhpay et al. (2016) have reported that the copper flotation rate constantly decreased because of a higher quantity of clay minerals. This is contrary to the present study's findings, with a rise in flotation rate constant with the increase of the amount of montmorillonite.

As illustrated in Fig. 5, the alteration trends of the flotation rate constant for different clay minerals were importantly varied. This indicates that the effects of clay particles on chalcopyrite flotation were distinctive (Hassanzadeh et al., 2019; Chen et al., 2020). A smaller flotation rate constant was sighted along with the flotation in clay minerals' existence with the increase in froth height. Consequently, the contrary impact of clay minerals on the chalcopyrite flotation is as follows: montmorillonite > kaolinite > illite.

The ultimate flotation recovery change was presented in Fig. 6 as a function of the froth height and the amount of clay for three different clays. The ultimate flotation recovery increased with a froth height of 2 cm for montmorillonite and illite, while it decreased at a froth height of 3 cm. There was not much change for kaolinite. The bubbles must be held for a sufficient time for the water between the froths to return to the pulp. Thus, the amount of water in the concentrate and mechanical entrainment can be reduced. This may only be possible by decreasing the froth flow rate or increasing the froth height. Conversely, as the froth height rose, the ultimate chalcopyrite recovery increased and the flotation rate constantly diminished.

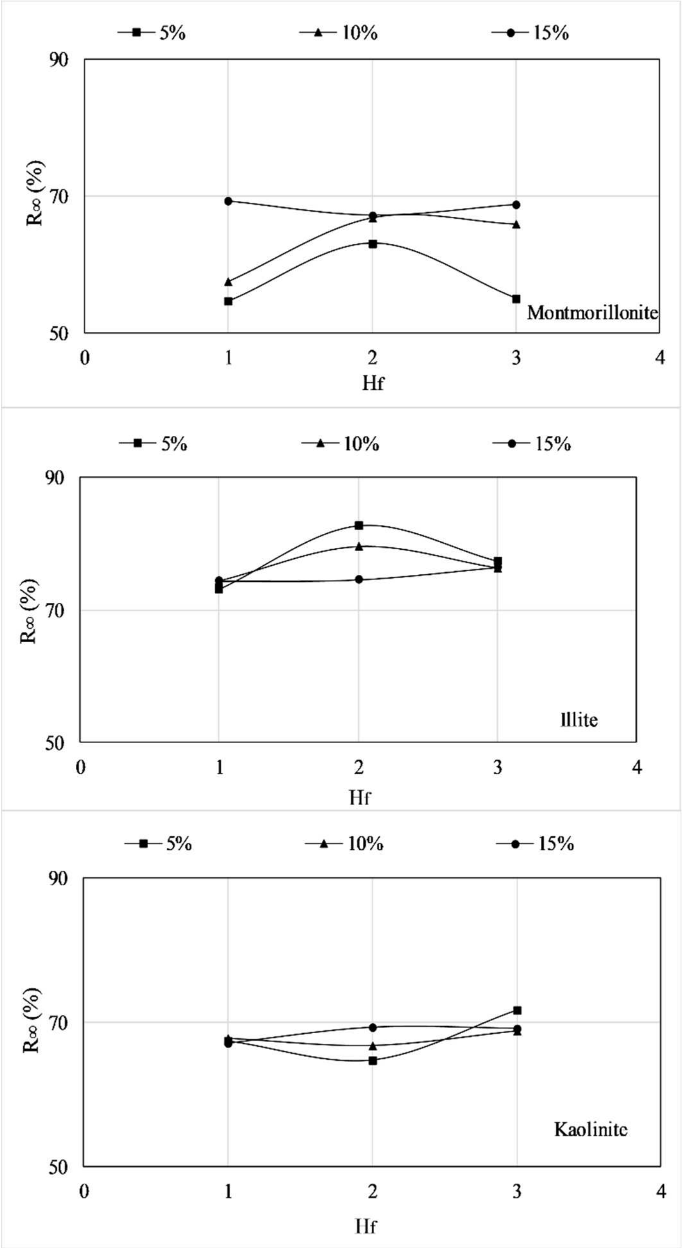

Fig. 6. Ultimate chalcopyrite recovery change of different clay minerals depending on froth height and clay amount

Particle size analyses using the Malvern Mastersizer 2000 device were performed on the concentrates obtained 0.5 and 7 min after the flotation kinetics experiments with a 2 cm froth height and 10% clay mixture. Particle size analyzes are given in Fig. 7; 80% of the particles and chalcopyrite grade are also indicated. While coarse particles easily entered the concentrate, the flotation of fine particles was late. It is understood that medium-sized particles float fast with high grade, and fine particles float slowly with low grade. Due to the poor collision and connection between fine particles and air bubbles, coarse particles float faster (Ai et al., 2017). As the flotation time enhanced, the amount of fine grain size in the concentrate increased significantly due to mechanical entrainment. While a finer grain size product was obtained with kaolinite mixture in 0.5 min, a finer grain size product was received with montmorillonite in the 7th min. Chalcopyrite grade significantly decreased for all clays between these two time periods. These results proved that the rise in the flotation time caused not only valuable minerals but also gangue minerals to be carried to the concentrate, thus reducing the concentrate grade. Non-selective entrainment of fine gangue particles led to a reduction in the chalcopyrite grade. The inhibition effect of clay minerals on the chalcopyrite flotation was clear as the flotation time was raised.

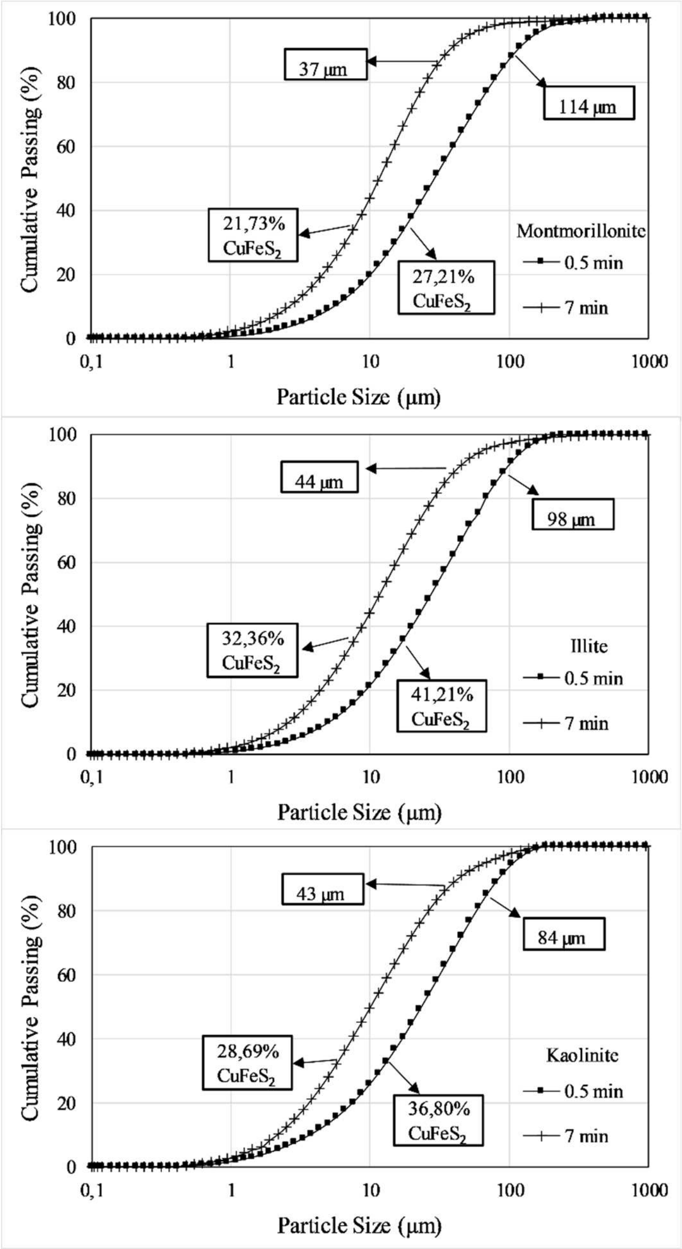

Fig. 7. Particle size distributions of concentrate at 0.5 and 7 min in flotation kinetics experiments

As seen in Fig. 8, generally, the flotation rate constant values of chalcopyrite within different clay minerals increased with the increment of the mass proportion of clay particles. The results proved that the rise in the clay minerals amount in the pulp enhanced the flotation rate of chalcopyrite. The presence of a higher amount of clay minerals in the pulp suggests a possible occurrence of slime coating. The obtained flotation rate constants propose that clay minerals trigger interactions among the chalcopyrite-bearing minerals and collectors. Also, as the second mechanism, mechanical entrainment between the bubbles raises the number of fine particles coming into the concentrate. Since there is no selectivity between hydrophobic and hydrophilic minerals in mechanical entrainment, fine particles are carried to the concentrate as the time is enhanced by mechanical entrainment.

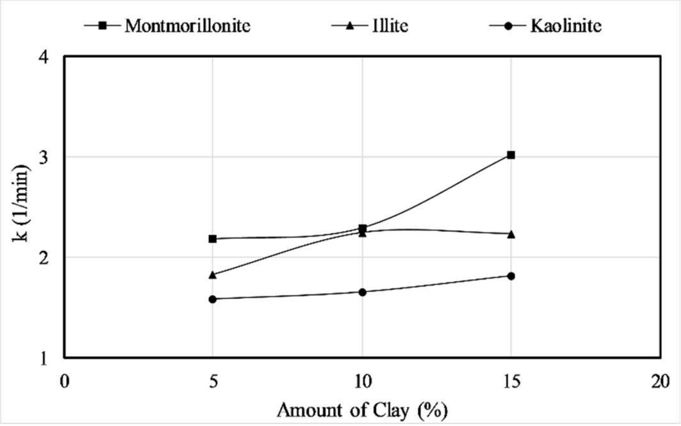

Fig. 8. Flotation rate constant values of chalcopyrite particles within a different amount of clays

Conclusions

In this study, the effect of various clay minerals (montmorillonite, illite, and kaolinite) on the flotation kinetics and recovery of chalcopyrite particles at different froth heights were investigated in detail. The results attained from this study led to the following conclusions:

(1) The most appropriate flotation time for all experiments was determined as 3 min, and it was noticeable that chalcopyrite showed rapid flotation kinetics. The average correlation coefficients (R^2) were higher than 0.90, which indicates that this model fits experimental data.

(2) The effect of clay minerals on the chalcopyrite recovery depended on the clay minerals' type and amount. Furthermore, the flotation recovery of chalcopyrite in all clay minerals increased with the rise of the clay minerals amount. Moreover, clay minerals' effect on the grade was more obvious by decreasing mechanical entrainment. These results proved that the rise in the flotation time caused not only valuable minerals but also gangue minerals to be carried to the concentrate, thus reducing the concentrate grade. The number of fine particles coming into the concentrate increased by mechanical entrainment between the bubbles, proved by particle size analysis. Since there is no selectivity between hydrophobic and hydrophilic minerals in mechanical entrainment, fine particles are carried to the concentrate as time increases.

(3) Another parameter affected by clay minerals in chalcopyrite flotation was the flotation rate constant. In flotation kinetics experiments, the flotation rate constant increased significantly with the addition of all clay minerals. But the flotation kinetics analysis indicates that the froth height significantly reduces the flotation rate constant at which the slow-floating components of the pulp are entrained into the concentrate. The highest flotation rate constant was achieved for all clay minerals when the lowest chalcopyrite grade and recovery were obtained. However, despite the higher flotation rate constant with montmorillonite, the worst results were obtained with montmorillonite from the point of chalcopyrite grade and recovery.

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