Kinetic modelling and optimization of flotation process of electrum

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Abstract: The investigation of flotation as an alternative method to cyanide leaching of gold ores is significant in terms of economic and environmental aspects. In this study, a gold ore sample containing 4.79 ppm Au and 7.72 ppm Ag was used. Gold and silver were observed to be present as liberated electrum or associated with or within quartz, galena, and sphalerite. Initially, five-stage rougher flotation tests were conducted, and then three-stage scavenger circuits and four-stage cleaning flotation circuits were performed in order to obtain high-content gold concentrate and decrease losses of Au and Ag in tailings. As a result of tests, the flotation concentrate assayed as 437 ppm Au and 511 ppm Ag was obtained with recoveries of 76.3% and 58.5%, respectively. This study reveals that the concentrates ready for direct smelting without any additional process can be obtained with flotation. In order to determine kinetic characteristic of electrum in the sample, the tests were conducted using first-order model, first-order model with rectangular distribution of rate constants, second-order model and second-order model with rectangular distribution of rate constant. The second-order model was considered as most reasonable for fitting the recoveries of gold as a function of flotation time during the flotation process.

Keywords: electrum, flotation, separation efficiency, kinetic models

1. Introduction

Electrum is a naturally occurring alloy containing 60–80% gold and 20–40% silver, often with low amounts of copper, platinum, or other metals (Allan and Woodcock 2001). Recovery of electrum from gold ores and base-metal ores is performed using conventional methods, which can be applied alone or by the combination of gravity, flotation, and cyanidation.

It is known that cyanide leaching has been the most widely used method to recover gold. However, increasing environmental and health concerns related to use of cyanide have concluded with the legislation of stringent rules or prohibitions (Kuzugüdenli and Kantar 1999). Therefore, the necessity of developing environmentally friendly methods such as flotation has arisen for gold recovery.

Flotation is an advanced technology that has been used for the recovery of gold. Even though there is more knowledge related to characteristics of flotation of base-metal–bearing ores, reported research on flotation of gold-bearing ores is limited. According to fundamental studies of gold flotation, native gold can float without the addition of any collector (Hoover, 1916; Rickard, 1917; Taggart, 1945; Wang and Poling, 1983; Aksoy and Yarar, 1989), but the mechanism has not yet been fully explained. Electrum is an unusual mineral, as it does not have a definite composition. The properties such as density, softness, and malleability may variably affect flotation behaviour. Furthermore, the crushing and grinding process can affect the surface properties of gold and gold alloys, leading to surface coating and impregnation of foreign material on the gold surface (Marsden and House 2006; Bulatovic 2010; Yalcın and Kelebek 2011). It should be noted that identification of the mineralogical characterization of gold-bearing ores is a significant process because it provides information related to the distribution of gold particles associated with gangue minerals in each fraction (Agorhom et al. 2013). The determination of flotation conditions such as particle size, pH, type, and amount of chemicals are also critical to obtain

high-content concentrate and recovery. The particle size is a significant effect on gold flotation that should be between 200–10 μm for applicable flotation because of the high density of gold. Finer particles have low collision efficiencies and typically low recovery.

Collector–gold interactions and the nature of adsorption of collector ions or molecules onto the gold surface have been determined using high-purity gold and gold–silver alloys on most of the reported fundamental work (Dunne, 2016). Besides, some of the work has been considered to decide whether pure gold has a natural hydrophobicity. Gold surfaces are naturally hydrophilic, however, if a monolayer of carbonaceous contaminants is adsorbed from the air or solution, those may be sufficient to produce a hydrophobic surface. Gold hydrophobicity is enhanced by the addition of flotation collectors such as xanthates, dithiophosphates, and mercaptobenzothiolates for its recovery. Naturally occurring or free gold is optimally recovered in a flotation circuit at natural or near-natural pulp pH values and with the addition of small amounts of the collector (Chryssoulis et al., 2009; Dunne, 2016; Bustamante-Rúa et al., 2018). Very few gold flotation plants use single collectors, in general adding the blended collector, which is a mixture of a number of collectors, is prefer to obtain better results on flotation recoveries (O'Connor et al., 1990).

Mathematical flotation models are generally applied to evaluate different operating conditions such as recovery rate, concentrate grade, equilibrium recovery in flotation tests. In kinetic studies conducted with batch or continuous tests, time-recovery and grade-recovery are calculated by measuring incremental mass flows of concentrate and tailings (Ningbo et al. 2018; Vinnett et al. 2019).

There are a limited number of studies about flotation of gold and silver–bearing ore other than native gold in the literature when compared to gold cyanidation. This work presents the results of a study related to flotation behavior of electrum that is a gold–silver alloy, applying conventional flotation. In flotation tests, parameters such as the amount of collector, the addition of diesel oil, and different particle sizes were investigated. With the optimized flotation parameters, cleaner and scavenger flotation tests were performed and separation efficiencies (SE) were determined. Besides, this work aimed to study the kinetics of electrum based on cumulative recovery and time. First-order, first-order with rectangular distribution of rate constants, second-order, second-order with rectangular distribution of rate constants equations were compared to identify the most appropriate model with three different statistical criteria such as sum of squared error (SSE), coefficient of determination (R^2) and root mean square error (RMSE) using semi-batch flotation data of gold.

2. Kinetic theory

The efficiency froth flotation is based on factors such as grade, degree of liberation, properties of interfaces, and operating variable (Cilek 2004). The batch flotation tests are evaluated according to recovery obtained at a specified time. Particles of the same minerals float at different rates because of different particle characteristics and cell condition (Polat and Chander, 2000; Albijanic et al. 2015; Gupta and Yan 2016). The mathematical models that are an essential requirement to undertake plant-scale tests based on batch laboratory evaluation can be applied to describe flotation-time–recovery profiles (Mazumdar, 1994; Zhang et al., 2013).

Flotation kinetics can be studied by analogy between chemical kinetics and flotation mechanism due to effects such as the collision between either hydrophilic or hydrophobic particles, and air bubbles in the pulp volume. Firstly, Zuniga proposed the flotation model and published the first paper in Chile (Garcia-Zuniga 1935; Bu et al. 2016). In later years, many researchers performed studies related to the flotation kinetics process of minerals (Bu et al. 2017; Hassanzadeh and Karakas, 2016; Bahrami et al. 2019).

The flotation rate, which is equal to the rate of change of concentration of floatable material in the cell, is defined as Eq. (1):

$$\frac{dC}{dt} = -k(C - C_\infty)^n \tag{1}$$

in which C is the concentration of valuable material in the cell at time t, C_∞ is the concentration of valuable material remaining unfloated in the cell after infinite flotation time, the value of n denotes the reaction order and k is the flotation rate constant. Particle size, liberation, surface properties, operating conditions, and the design of flotation cells are significant criteria in determining the flotation rate

constant (k) which is a term of the speed of the process (Chau et al., 2009). As the flotation kinetic rate constant increases, the flotation time in flotation cell decreases. Due to the shorter flotation time, the particles rapidly leave from flotation cell; this creates the potential for using the lower volume capacity cell (Jiang et al. 2019). In addition, the selecting the best model is based on the order of flotation kinetics (n) that characterizes of the process (Bu et al., 2017).

The first-order flotation kinetics that dates back to Garcia-Zuniga (1935) gives a reasonably good fit to the experimental data. The first-order model is based on the change in concentration of valuable minerals within a certain time. The first-order kinetic equation can be written as Eq. (2):

$$R = R_\infty(1 - e^{-k_1 t}) \tag{2}$$

In Eq. (2), R is the recovery at time t, R_∞ ($t \rightarrow \infty$) is the maximum possible recovery, which is less than %100, and k_1 is the first-order model flotation rate constant.

The many modified first order equations were proposed to use for providing more knowledge related to flotation rate for a wide range of conditions. Rectangular distribution model, which is one of the modified first-order kinetic models, commonly known as the Klimpel model. This model can be given by the following Eq. (3) (Huber-Panu et al., 1976; Klimpel, 1984):

$$R = R_\infty[1 - \frac{1}{k_{1r}t}(1 - e^{-k_1 r t})] \tag{3}$$

where, k_{1r} is rectangular rate of coefficient; R is recovery after long flotation time t.

Based on the classical first-order kinetic model and its modification, the second-order kinetic model was proposed by Arbiter and Harris (1962). If the degree of n in Eq. (1) is 2, then after integrating, the equation for the second order becomes as Eq. (4):

$$R = \frac{R_\infty^2 k_2 t}{1 + R_\infty k_2 t} \tag{4}$$

in which R_∞ is the maximum possible recovery with prolonged time, R is cumulative recovery, k_2 is the second order flotation rate constant, t is time.

Regarding the second-order kinetic model, some researchers pointed out that mathematical relationship between the R(t) formula or on the estimated parameters and goodness-of-fit values are found to be identical to that of the first-order reaction with exponential (fully mixed reactors) (Dowling et al., 1985; Ek, 1992; Zhang et al., 2013).

The first-order reaction with exponential model which was defined by Imaizumi and Inoue (1963), is an expression analogous to the equation describing the time concentration. This model provides an added flexible over the classical first order model and enables it to the experimental data very well with the assumption of the exponential distribution of floatability. The algebraical equivalence of the R(t) expressions from the first-order model with exponential was shown in Eq. (5). (Bu et al., 2016; Vinnett and Waters 2020). Vinnett and Waters (2020) indicated that the same recovery can be obtained from second-order reaction with a single rate constant and first-order reaction with exponential. Besides, they reported that first-order reaction with exponential involves a fraction of floatable material with slow rate constants approaching to k = 0:

$$R = \frac{R_\infty k_{exp} t}{(1 + k_{exp}t)} \tag{5}$$

Rectangular distribution function into the second-order flotation kinetics was applied by Klimpel (1980). This model can be given as in Eq. (6):

$$R = R_\infty \{1 - \frac{1}{k_{2r}t}[\ln(1 + k_{2r}t)]\} \tag{6}$$

where k_{2r} is the rate constant of the second-order with rectangular distribution model (Dowling et al., 1985; Saleh, 2010).

The statistical analysis with fitting model firstly was applied by Dowling et al. (1985) to determine the applicable model. Mazumdar (1994) used the criteria such as the model fit and stability that are based on the model's predictive for model discrimination. Ahmed (2004), performed several statistical analyses on eight flotation models by applying the flotation tests at different conditions of collector dosages, frother dosages, and agitation speeds.

According to Polat and Chander (2000), the three parameter first-order model fitted well to flotation kinetics that incorporated distribution of flotation rate constants. Hernainz and Calero (2001) found that

the removal of solids from the pulp phase is defined by a first-order rate equation. Mori et al. (1983) reported that though the process follows zero-order kinetics at initial stages, it follows second order at the end. Yalcin and Kelebek (2011) noted that the best fitting can be obtained with second-order flotation kinetics for pyritic gold ore. Bu et al. (2017) found that the first-order kinetic model (with rectangular distribution of floatabilities) gives the best fit to flotation rate data of average particle sizes of 375 and 37μm in performed the study about coal fine. Mao et al. (2020) investigated the effects of conventional flotation and simultaneous ultrasonic flotation in the pulp/froth zones on the separation selectivity and kinetics of high-ash lignite flotation. They showed that the second-order model with rectangular distribution of floatability is the most reasonable model to describe the processes.

3.   Materials and methods

3.1. Material

The gold ore used in this study was obtained from the Çanakkale region of Turkey. The chemical and mineralogical compositions of the sample were determined at ALS (Australian Laboratory Services) Laboratory using fire assay (Au and Ag) and microscopy methods. The other elements containing the sample were analysed with ICP-MS (Inductively Coupled Plasma–Mass Spectrometry). According to the result of the chemical analysis presented in Table 1, the sample contains 4.79 ppm Au and 7.72 ppm Ag.

Table 1. Chemical analysis of ore sample

Element	Content, ppm	Element	Content, %
Au	4.79	Al	0.52
Ag	7.72	Ca	0.08
As	327.0	Fe	1.79
Cu	74.3	Mg	0.07
Pb	40.0	Si	42.6
Zn	106.0	S	0.14

The mineralogical analysis was performed on polished section samples employing the QEMSCAN method (Quantitative Evaluation of Minerals by Scanning Electron Microscopy). The QEMSCAN images of the ore sample are illustrated in Fig.1a–c.

According to mineralogical analysis, the ore sample was dominated by quartz, feldspar, and pyrite, and the remaining was kaolinite and muscovite. The detected electrum (20–80% Au and 20–80% Ag) grains were practically liberated. However, some degree of association with some galena, sphalerite, and quartz was noticeable. In Fig. 1a–c, the grain size of the electrum was determined to be in a range of 25 to 40 μm. Quartz was well liberated, and other mineral phases were moderately intergrown with major silicates, particularly quartz and feldspar. Pyrite accounted for practically all of the sulfur (98.2%). The remaining sulfur existed as sulfates. Half of the assayed iron originated from pyrite. The remaining iron mainly is derived from Fe-Ti oxides and steel contamination.

3.2. Methods

The ore sample was initially crushed to the size below 2 mm using a jaw, a cone, and a roll crusher, respectively. The representative sample was homogenously mixed employing the cone-and-quartering method. Afterward, it was divided into 1 kg samples using a sample splitter, for the flotation tests. The sample was ground in a stainless-steel ball mill at a pulp density of 60% by weight for the flotation tests. The bench-scale flotation tests were conducted in the Denver flotation machine at 1500 rpm in a 2.5 L cell for five-stage rougher flotation. The tap water was used in grinding, flotation, and preparing reagents. Each flotation tests were performed with fresh water. The silicate depressant was added at the first stage and conditioned for 10 min. The pulp was then conditioned with collectors for 3 min, followed
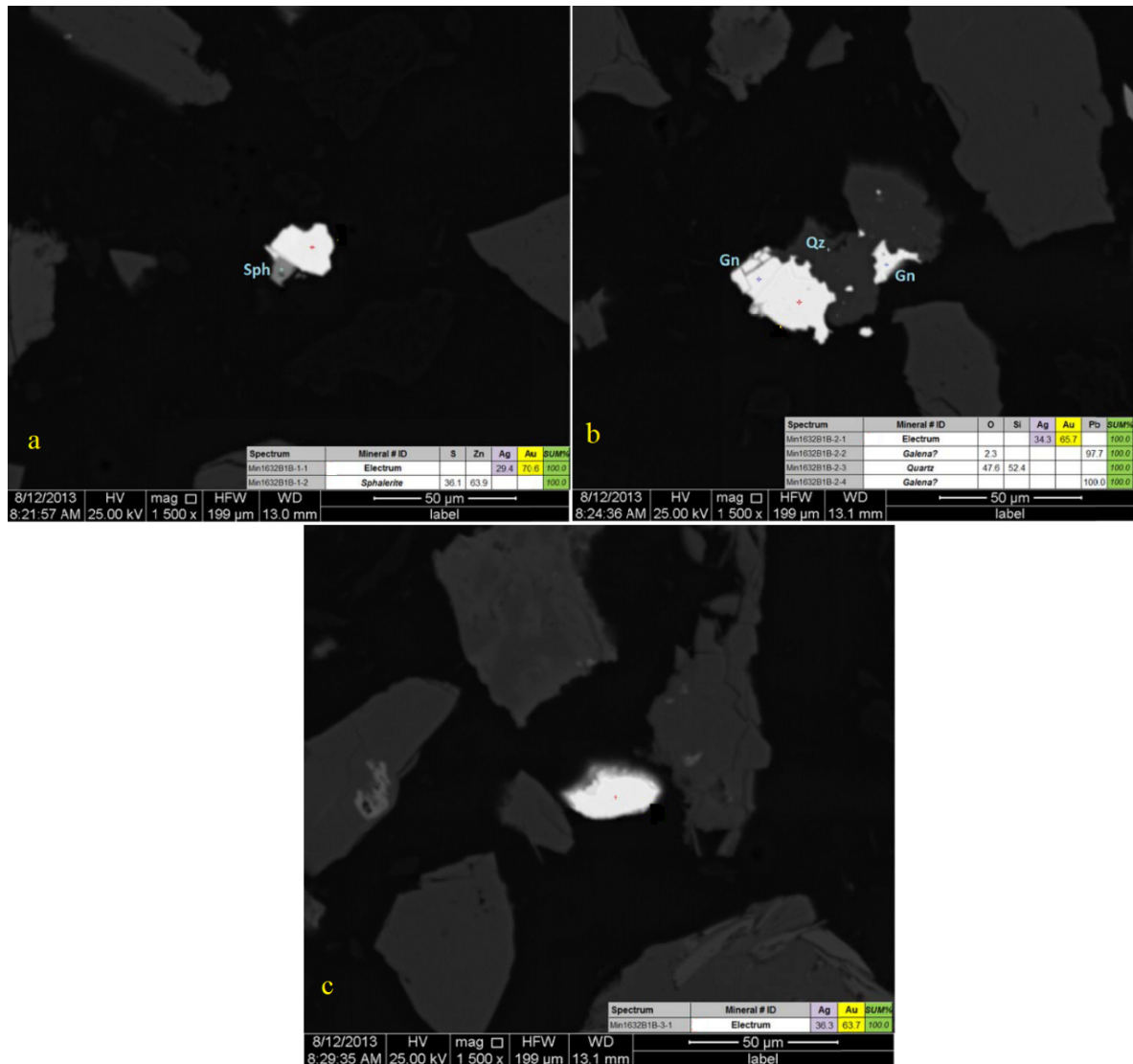
Fig. 1a–c. QEMSCAN images of the ore sample. (a) Electrum associated with sphalerite. (b) Electrum associated with galena and quartz. (c) Liberated electrum

by frother for 1 min. The total flotation time is 15 minutes, 3 minutes at each stage. The reagents used for the flotation tests were sodium silicate (Merck; 7.5 - 8.5% Na₂O; 25.5 - 28.5% SiO₂) as silicate depressant, Aerophine 3418A (Solvay, sodium diisobutyldi-thiophosphinate of 50-52% and %50-48 water (w/w)) and Aerofloat 208 (Solvay, 25% diethyldithiophosphate, 25% disec-butyldithiophosphate and 50% water (w/w)) as collectors, and MIBC (methyl isobutyl carbinol, Merck, purity of 98%) as frother. The diesel used was conventional diesel fuel oil obtained from a Turkish gas station. The depressant was prepared at a concentration of 10% (w/w). The collectors and frother were prepared at a concentration of 1% (w/w). Slurry pH was adjusted to 4.5–5.0 with sulphuric acid (Merck, purity of 95-97%). All the concentrate and tailings were collected, dried, weighed, and analysed. The tests were performed in duplicate and the average results were used.

4.   Results and discussion

4.1.   Flotation tests

4.1.1. Effect of collector type and amount

Phosphorous-based collectors such as Aerofloat 208, Aerophine 3418A are usually used as secondary collectors in gold flotation (Cytec 2010). However, there are some reports of dithiophosphate used as the primary collector that resulted in good separations. Aerofloat 208, an alkyl dithiophosphate, has

been suggested to be particularly useful for floating native gold, but the evidence needs to be proven (Allan and Woodcock, 2001). Aerophine 3418A, which is dialkyl dithiophosphinate type collector, has found application in flotation of silver, silver sulphides and other sulphides mineral such as chalcopyrite, galena and sphalerite. Thus, Aerophine 3418 is effective not only in the recovery of silver or silver sulfide minerals but also in the recovery of silver associated to other sulfide minerals. The dosage required for Aerophine 3418A on many ores may be considerably lower than that needed for a xanthate collector (Dunne, 2005; Cytec 2010).

The flotation behavior of electrum with Aerophine 3418A and Aerofloat 208 of 150+150, 250+250 and, 350+350 g/t addition is presented in Fig. 2. The tests were accomplished by adding Na_2SiO_3 of 1000 g/t, MIBC of 60 g/t at 100 μm particle size. It is seen from the results that the usage of collectors of more than 350+350 g/t considerably increases the recovery of Au and Ag. However, considering collector cost, the optimum amount of collector was determined as 350+350 g/t at which Au of 85.6% and Ag of 82.2% recoveries were obtained with contents of 19.35 ppm Au and 28.0 ppm Ag. The high gold recovery in the rougher flotation may be correlated with the existence of silver on the surface of the electrum. Nagaraj et al. (1989; 1992), have reported that if the gold is alloyed with even a small amount of silver or copper, adsorption is significantly enhanced. Basilio et al. (1992) studied FTIR spectroelectro-chemical techniques to investigate the interaction of diisobutyldithiophosphinate (DIBDTPI) and other modified thiol collectors on silver, gold and silver/gold alloys found that Ag-DIBDTPI was formed on silver and $(DIBDTPI)_2$ on gold. Contact angle measurements showed that a hydrophobic surface was formed at the potentials where these species formed. Similarly, Chryssoulis and Dimov (2004) indicated that the presence of silver on a gold particle surface enhances its collector adsorption kinetics.
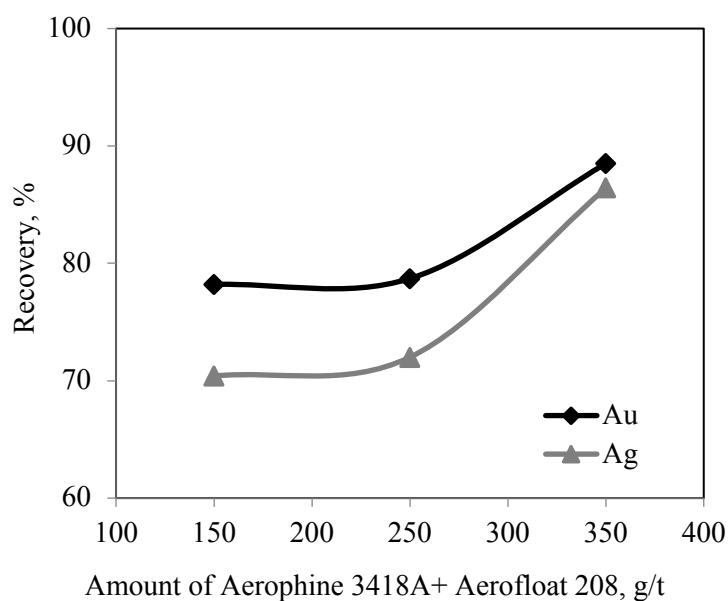

Fig. 2. Effect of collectors on gold and silver flotation

4.1.2. Effect of diesel oil

It is known that diesel and vegetable oils can be used to agglomerate gold particles, due to the natural hydrophobicity of gold, in order to increase flotation recovery (Calvez et al. 1998; Sen 2005). Agglomerates are produced by the collision of oil-coated particles with each other because of the interfacial tension of the oil and the capillary attraction of the oil bridges between particles in the presence of an adequate amount of oil and sufficient mechanical agitation (Mehrotra et al. 1983). Therefore, the effect of the addition of diesel oil on decreasing the amount of the collector was investigated. In order to determine the effect of diesel oil, Aerophine 3418A and Aerofloat 208 were used at 250+250 g/t dosages instead of 350+350 g/t. The flotation tests were accomplished according to the aforementioned conditions. After the addition of 500 g/t diesel oil only in the first stage, the pulp was conditioned for 20 min. Au content of 1.16 ppm and Ag content of 2.10 ppm in tailings was obtained for 250+250 g/t Aerophine 3418A and Aerofloat 208 in flotation tests related to the effect of the amount

of the collector. As seen in Table 2, the addition of diesel oil provides a slight improvement in terms of Au and Ag recovery. The results imply that gold and silver losses in the tailings were a result of unliberated electrum association or locked with quartz. Thereby, diesel oil could not attach to the unexposed surface of electrum, preventing an adequate amount of agglomerate formation.

Table 2. The effect of diesel oil

Diesel Oil, g/t	Product	Weight, %	Content, ppm		Recovery, %	
			Au	Ag	Au	Ag
	Concentrate	13.6	28.77	36.11	80.2	73.0
500	Tailings	86.4	1.12	2.1	19.8	27.0
	Total	100.0	4.88	6.72	100.0	100.0
	Concentrate	10.8	35.19	44.40	78.7	72.0
-----	Tailings	89.2	1.16	2.10	21.3	28.0
	Total	100.0	4.76	6.60	100.0	100.0

4.1.3. Effect of particle size

The flotation tests were conducted at different particle sizes such as 100, 74, 53, and 38 µm (P_{80}, 80% passing size) in order to optimize the recovery of gold and silver. In those tests, 350+350 g/t of Aerophine 3418A and Aerofloat 208 was used at the flotation conditions described in Section 4.1.1.

Fig. 3 shows that the recovery of Au and Ag increased as particle size decreased, particularly below -38 µm. This is because the surface of the electrum associated and locked with quartz was exposed by grinding. Although, the best result for Au and Ag recovery was achieved at -38 µm particle size, the tests were carried out below 74 µm particle size because of the cost of grinding. A bulk concentrate assaying at 13.38 ppm Au and 22 ppm Ag with 91.0% and 89.3% recoveries were achieved at that particle size, respectively. Besides, the tailings were obtained with a content of 0.78 ppm Au and 1.50 ppm Ag.
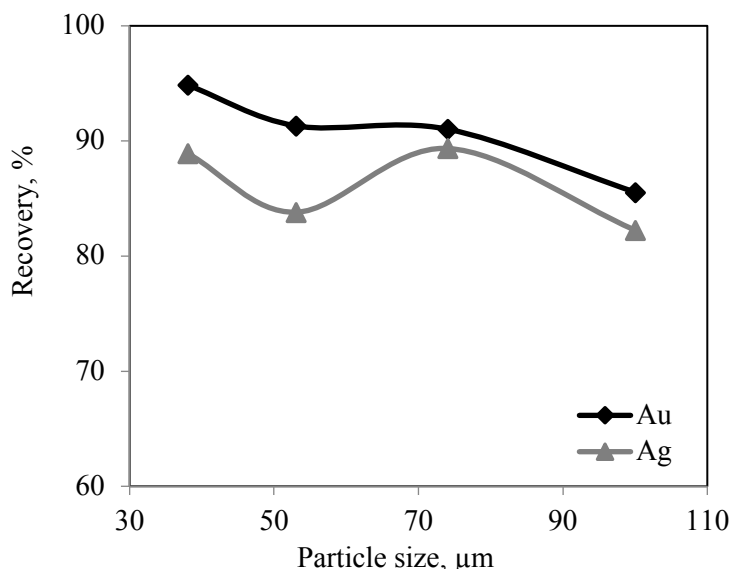

Fig. 3. Effect of particle size on gold and silver flotation

4.1.4 Effect of cleaner and scavenger stages

It is known that sufficiently high gold-content flotation concentrates can be directly smelted, although flotation is often used as a pre-enrichment process in gold recovery. Therefore, a flotation test containing a four-stage cleaner circuit was carried out to obtain a concentrate assaying high Au and Ag values. The three-stage scavenger flotation test was performed following the rougher tailings were ground below 38 µm to reduce the loss of Au and Ag in the tailings. The cleaner flotation tests were conducted at 1200

rpm in a 1.7 L cell. Total flotation time for four-stage was 35 min (15, 8, 7, 5 min) in the cleaner stage. In the scavenger stages, the total flotation time was 9 min as 3 min for each of the stages. In the rougher stage, 250+250 g/t Aerophine 3418A + Aerofloat 208 was used, 100+100 g/t Aerophine 3418 A + Aerofloat 208 was added in the scavenger stage, and 290+290 g/t Aerophine 3418A + Aerofloat 208 was added in the cleaner stage. The flotation flowsheet and conditions are shown schematically in Fig. 4.

According to the test results in Table 3, the concentrate having 437 ppm Au with a recovery of 76.3% and 511 ppm Ag with a recovery of 58.5% was obtained. After regrinding and scavenger flotation, Au and Ag content in tailings reduced to 0.4 ppm and 1.2 ppm, respectively.
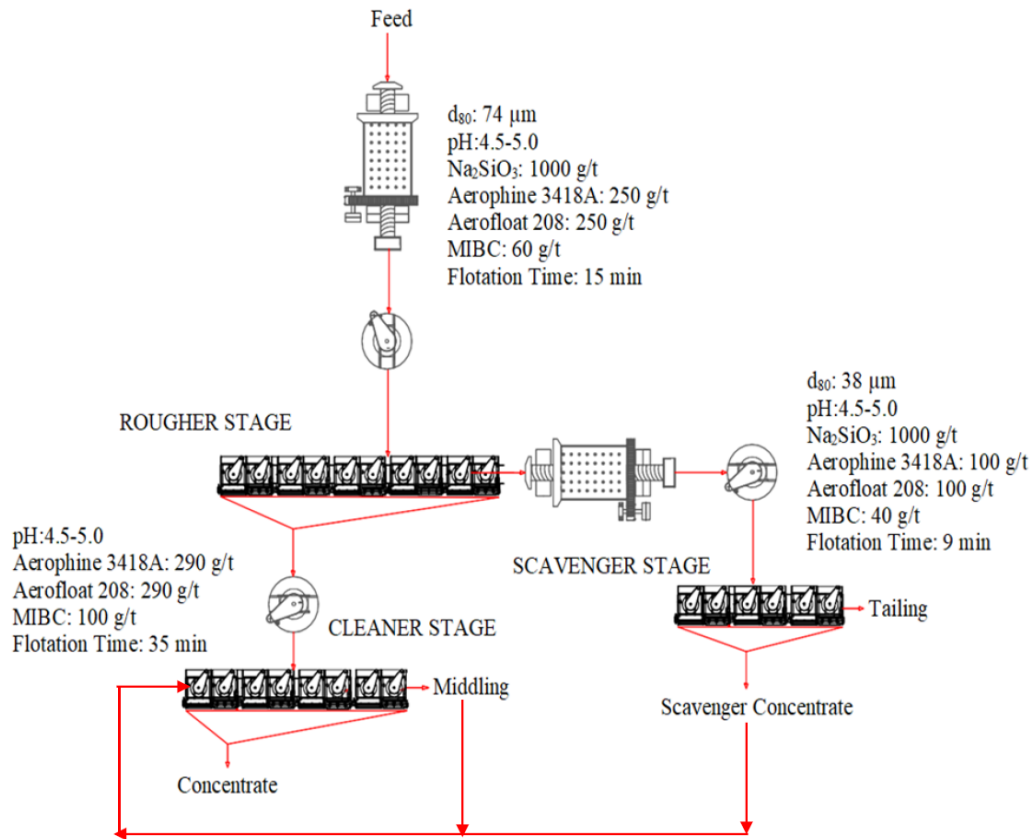

Fig. 4. The flotation flowsheet and conditions

Table 3. The results of effect of cleaner and scavenger stages

Product	Content, ppm		Recovery, %	
	Au	Ag	Au	Ag
Concentrate	437.0	511.0	76.3	58.5
Scavenger concentrate	1.8	4.1	9.3	13.5
Middling	2.6	7.5	9.2	17.8
Tailings	0.4	1.2	5.2	10.2
Total	4.6	7.0	100.0	100.0

According to the test results, the concentrate ready to be directly smelted was obtained with four cleaner stages. However, Au and Ag losses in the tailings have not been sufficiently prevented despite regrinding. The electrum particles in sizes finer than 10 μm were difficult to recover, and this to a lesser extent may be attributed to insufficient liberation (Agorhom 2013). The particle size is known to play a critical role in the probability of particles colliding with bubbles, attachment of particles to bubbles after collision. Therefore, the particles finer than 10 μm with low collision efficiency can have a considerable impact on grades and recoveries (Whelan and Brown, 1956; Spedden and Hannan, 1984; Shahbazi et al., 2010; Leister et al., 2017). Besides, it should be noted that the flotation properties of the native gold and

its alloys depend strongly on the deformation and final shape of the particles after grinding. Due to their high ductility, gold particles can form platelets that present a higher exposed surface area to a collector and air bubbles (Allan and Woodcock 2001). However, if the gold particles have sharp edges with grinding, they tend to detach from the air bubbles, resulting in gold losses (Bulatovic 1997). Furthermore, gold surfaces coated with gangue components at finer particle sizes may cause a decrease in flotation performance.

4.1.5. Determination of separation efficiency

In determining separation efficiency (SE), it is important to know how long rougher flotation is performed and when the rougher stage should be stopped, as the optimum content of the cleaner concentrate is dependent on the content of the rougher concentrate. Besides, the amount of the non-valuable minerals carried to the rougher concentrate is also significant. The optimum rougher flotation time is determined where separation efficiency is maximum. If the optimum rougher flotation time is exceeded, the non-valuable minerals start to entrain more than the valuable minerals and the quality of the rougher concentrate is adversely affected. Therefore, the rougher concentrate will require more cleaner stages and it will increase the cost of operation (Agar 1987; Wills 1997, Çilek 2006). The separation efficiency (SE) equation is given in Eq. (7) (Schulz 1970) where R_m is recovery of valuable mineral and R_g is recovery of gangue:

$$SE = R_m - R_g \qquad (7)$$

In order to determine the optimum rougher flotation time, the rougher concentrate samples were collected at 1, 2, 4, 6, 9, 12 and 15 min time intervals at flotation conditions described previously. Because quartz is the most abundant gangue mineral in the sample, the entrained fractions were analysed for quartz and gold. The test results are shown in Table 3, and the flotation data obtained from Table 4 are plotted in Fig. 5.

Table 4. The cumulative results of the performed tests to determine rougher flotation time

Flotation Time, min	Weight, %	Content, ppm		Recovery, %		Separation Efficiency, % (SE)
		Au	Si	Au (R_m)	Si (R_g)	
1	2.5	86.30	39.60	47.1	2.3	44.8
2	5.8	50.13	42.5	62.4	5.5	56.9
4	11.6	29.65	41.9	74.0	11.0	62.9
6	17.3	21.25	42.3	78.9	16.4	62.5
9	23.5	16.30	41.8	82.1	22.2	59.8
12	28.6	13.64	44.1	83.9	27.4	56.4
15	33.7	11.80	43.6	85.3	32.4	52.9
Tailings	66.3	1.03	44.9	14.7	67.6	
Total	100.0	4.65	44.1	100.0	100.0	–

As clearly shown in Table 4, the maximum separation efficiency was found as 62.9%, but it decreased after this value as the gangue minerals began to entrain faster than the valuable mineral. The optimum rougher flotation time was determined as 4 min at maximum separation efficiency, and at the end of this duration the rougher concentrate containing 29.65 ppm Au with a recovery of 74% was obtained. As seen in Fig. 5, after 4 min of rougher flotation time, the scavenger flotation should be performed.

4.1.6. Kinetic modelling

The test for determination of flotation kinetics was carried out with the optimum conditions obtained from previous tests (the addition of 1000 g/t Na_2SiO_3, 350 g/t +350 g/t Aerophine 3418 A and Aerofloat 208 and 60 g/t MIBC at pH 4.5-5.0 with 1 kg sample in a 2.5 L flotation cell). Total flotation time was fixed as 15 min; the seven concentrates were floated at 1, 2, 4, 6, 9, 12, 15 min. As a function of time, cumulative recoveries and contents of gold calculated from the test are given in Fig. 6.
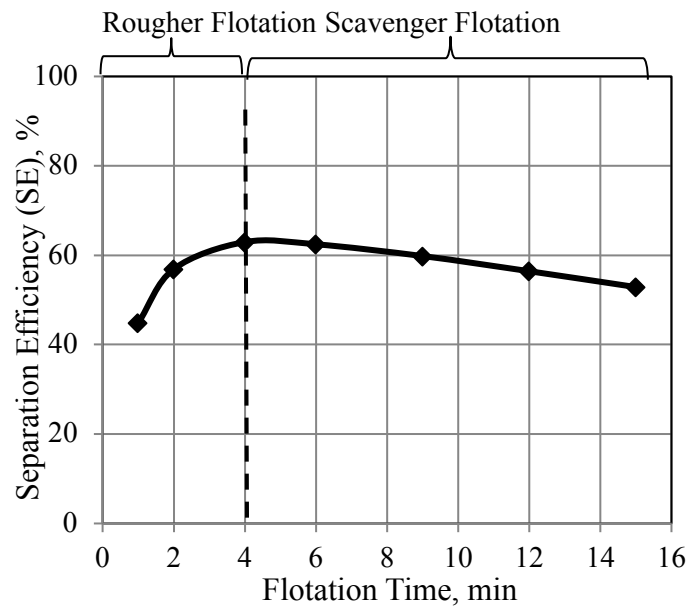
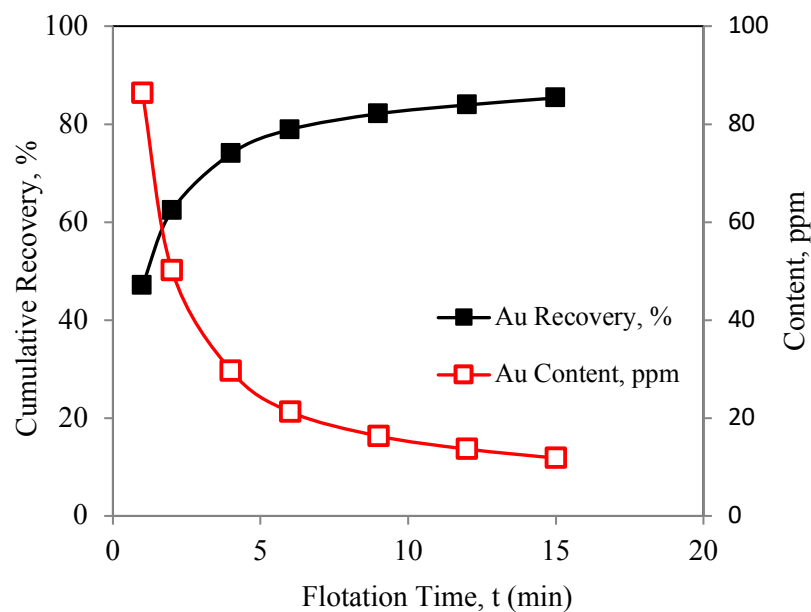Fig. 5. The change in separation efficiency with respect to time

Fig. 6. Flotation recovery and content of gold as a function of time

The flotation rate constant (k), the maximum concentrate recovery ($R\infty$), the sum of squared error (SSE), the coefficient of determination (R^2), and the root-mean square error (RMSE) were obtained for four kinetic models by using the Microsoft Excel all-over spreadsheet program SOLVER function based on non-linear regression (Brown, 2001). Fig. 7 illustrates the fitting of the kinetic models for the recovery-time data. The values of the kinetic ad fitting parameters for each kinetic model are presented in Table 5.

Although generally, mineral flotation is considered as a first-order model, according to the results, first-order model showed the poorest fit and $R\infty$ value was found smaller than the maximum recovery. Similarly, Bu et al. (2017) investigated the order of kinetic models in coal fines flotation on six kinetic models with different orders and obtained the lower ultimate recovery than combustible recovery with first-order model. Compared to the models, second order kinetic model was selected as the best-fitted model to the experimental data with regard to the lowest SSE and RMSE values and highest values of
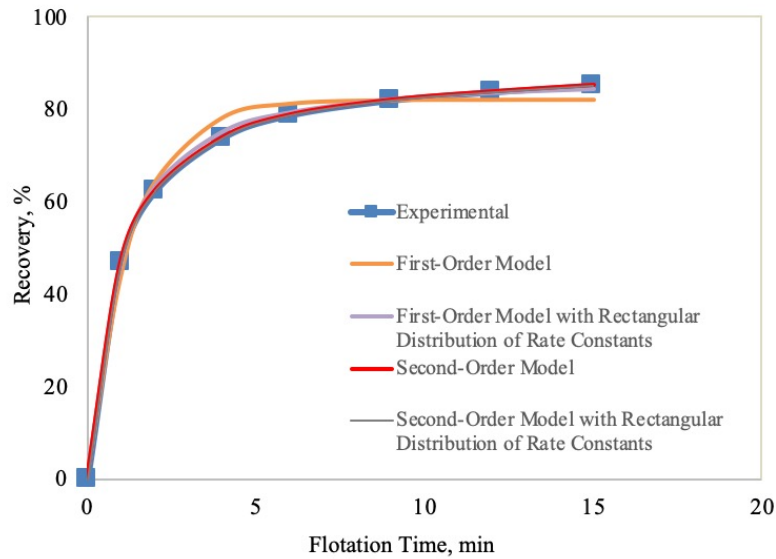
Fig. 7. Comparison of the four kinetic models fitted to the test data

Table 5.   Non-linear regression results for four models that fit to the flotation data

Models	Kinetic Parameters		Fitting Parameters		
	$R\infty$	k	SSE	R^2	RMSE
First-Order Model	81.98	0.759	51.68	0.9559	2.717
First-Order with Rectangular Distribution of rate Constants	87.73	1.725	4.35	0.9962	0.789
Second-Order Model	90.56	0.012	0.3	0.9997	0.207
Second-Order with Rectangular Distribution of Rate Constants	95.09	2.609	4.74	0.9959	0.823

R^2. In some studies, it was emphasized that if the flotation process is carried out with low content ores or high-density pulp, this process is expressed in the second order kinetic model (Mehrotra and Kapur 1974; Nguyen and Schulze 2004). Besides, Yalcın and Kelebek (2011) noted that second-order flotation kinetics is more applicable than the first-order model at the recovery of both native gold and pyrite from pyritic gold ore.

Considering the first order rectangular distribution of rate constants and second order model with rectangular distribution of rate constants, it was seen that better results could not be attained in comparison with the second order model. However, in recent years, there are studies that have achieved good results with either of these two models. Ni et al. (2016) reported that the first-order model with rectangular distribution of floatability gave the most reasonable the results for both the rougher and cleaner flotation processes of bituminous coal. Zhu et al. (2020) researched the influence of four common sulfate salts on the flotation kinetics of MoS_2 using three flotation kinetic models. They found that first-order model with rectangular distribution is the best model for fitting MoS_2 flotation in sulfate solution. Fitting performance of kinetic models used in the conventional flotation and carrier flotation of −74 μm coal fines was investigated by Bu et al. (2020). They pointed out that all kinetic models tested gave good levels of goodness of fit, but the second-order model with rectangular distribution provided the best fitting performance for the experimental data of conventional flotation and carrier flotation. In addition,

Yang et al. (2021) studied the effect of cations such as Na^+, Mg^{2+} and Al^{3+} found in recycled water or seawater on chalcopyrite and pyrite flotation and indicated that second-order with rectangular distribution model had the highest accuracy for fitting the flotation tests' kinetic process. However, contrary to the above-mentioned studies, it was observed that the second-order model was the most accurate model in gold flotation in this study.

5. Conclusions

In the past hundred years, hydrometallurgical processes that particularly include cyanidation have been applied to recover gold. Several research studies related to gold recovery were reported; however, there has been very limited knowledge about gold flotation behavior. The aim of the present study is to examine flotation behavior of electrum minerals contained in gold ore. The flotation tests showed that Aerofloat 208 and Aerophine 3418A collectors could be used as primary collectors, and the adsorption ability of these collectors increased due to the presence of silver. Diesel oil could not adequately promote flotation because of probably insufficient particle liberation. Regarding particle size tests, the results indicated that Au and Ag recoveries increased with decreasing particle size. That finding suggests that gold is associated with or within quartz. While the concentrate containing 511 ppm Au with the recovery of 76.3% and tailings assaying 0.4 ppm Au were obtained when applying cleaner and scavenger flotation stages. Flotation is a more environmentally friendly method compared to cyanide leaching that has severe legislation in practice due to its hazardous impact on the environment and human health. This current study has proved that a gold concentrate ready to be directly smelted could be obtained from a gold ore containing electrum employing flotation. In the literature, it is clear that there are very few studies reported related to second order kinetic model compared the other models particularly first-order model. It was concluded that second order kinetic model gives the best fit to data due to providing the lowest SSE and RMSE and the greatest value of R^2 than other models in this study. In addition, although it has been stated by many authors that first-order models, first-order model with rectangular distribution of rate constants, and second-order model with rectangular distribution of rate constants are compatible with flotation of minerals, it has been determined that the second-order kinetic model is more suitable for gold flotation.

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