

Investigation of Flotation Parameters for Copper Recovery from Enargite and Chalcopyrite Mixed Ore

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A flotation pre-treatment study for the separation of enargite (Cu_3AsS_4) from chalcopyrite (CuFeS_2) ores of different origins was investigated in this work. The copper ore bearing enargite mineral contained 5.87 mass% As and 16.50 mass% Cu while the chalcopyrite bearing ore contained 0.32 mass% As and 21.63 mass% Cu. The two ore samples were mixed at 7 : 3 (enargite : chalcopyrite) by weight ratio to prepare a mixed ore sample with As content at 3.16 and 18.25 mass% Cu for the flotation study. Effect of particle size, slurry pH, flotation time, collector type, collector addition or dosage and depressants were investigated to evaluate efficiency of enargite separation from chalcopyrite and recovery of both minerals as separate concentrates. For enargite single ore flotation, the 38–75 μm size fraction showed that over 98% of enargite was selectively recovered within 5 min at slurry pH of 4 and As content in the final tailings was reduced to 0.22 mass%. In mix ore (enargite + chalcopyrite) flotation, 97% of enargite was first removed at pH 4 followed by chalcopyrite flotation at pH 8, and over 95% recovery was achieved in 15 min flotation time. The As content in the final tailings was reduced to 0.1 mass%. [doi:10.2320/matertrans.M2011354]

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1. Introduction

In the mineral industry, many copper and iron sulfide ores such as covellite (CuS), chalcocite (Cu_2S), chalcopyrite (CuFeS_2) and pyrite (FeS_2), contain arsenic (As) and antimony (Sb) bearing minerals such as enargite (Cu_3AsS_4), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), tetrathedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) and arsenopyrite (FeAsS). These minerals reduce the economic value of copper (Cu) resources as penalties are imposed for their treatment in smelting process due to high As and Sb contents that cause serious toxicological and environmental problems.^{1–6)}

As demand for copper continues to grow globally, the need to develop processes and technologies to treat Cu resources from additional sources such as mine tailings, low grade deposits, industrial wastes and deposits with high impurity levels such as As and Sb will continue to increase. But for the resources containing such highly toxic impurities, development of technology incorporating systems to contain their release to environment must be highly considered.

Recently, controlled flotation as a separation process to selectively remove enargite (Cu_3AsS_4), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) and tetrathedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) from other Cu bearing minerals have been reported and such process could offer economic and environmental benefits.^{7–13)} The separation by flotation of such minerals offers many challenges as the flotation behavior of other Cu and Fe sulfides such as covellite (CuS), chalcocite (Cu_2S), chalcopyrite (CuFeS_2) and pyrite (FeS_2) are similar and require advanced studies as reported by many researchers.^{14–19)} These researchers have shown that proper control of reduction–oxidation (redox) potential and pH can be adopted to separate non As/Sb bearing minerals from As/Sb bearing minerals. The clean concentrates with <0.5 mass% As/Sb can be sent as feed to smelters and final tailings with <0.5 mass% As/Sb can be disposed to environment. The concentrate fraction containing

As/Sb bearing minerals can be treated separately for their removal and recover only copper. These studies on flotation for separation of enargite and other As/Sb bearing minerals from non As/Sb bearing minerals are related to naturally occurring ores.

In this study, flotation tests were performed to investigate behavior of enargite and chalcopyrite ore from different sources synthetically mixed. Flotation parameters including; pH, collector addition or dosage and type, flotation time and depressants were controlled to obtain an enargite concentrate with high As and chalcopyrite concentrate and final tailings with As content below 0.5 mass%.

2. Experimental

2.1 Samples

Two high grade copper ore samples hand picked from two different locations; (1) an enargite ore (Mt. Jinguang, Taiwan) and (2) a chalcopyrite ore (Mt. Miyatamata, Japan) were used in the current study. The enargite (Cu_3AsS_4) ore sample was first prepared by crushing/milling and sizing to obtain four size ranges: >150, 75–150, 38–75 and <32 μm . Chemical composition of main elements (Cu, As, Fe) varied in the different size fractions with both Cu and As higher above 16 mass% Cu and 5 mass% As at sizes finer than 75 μm (Table 1). Similarly chalcopyrite (CuFeS_2) was prepared to obtain 38–75 μm size fractions with Cu content above 21 mass% to be used with enargite of the same size range for mixed ore flotation separation studies and related chemical and phase contents are provided in Table 1.

The two ore samples of 38–75 μm size fraction were mixed at 7 : 3 (enargite : chalcopyrite mass/mass ratio) to obtain a mixed sample with As content around 3 mass% for use in mixed ore flotation study for evaluation of their separation. Phase analysis by XRD indicated enargite ore consisting mainly Cu_3AsS_4 (enargite), SiO_2 (quartz) and FeS_2 (pyrite) as main mineral phases and the chalcopyrite concentrate sample contained mainly CuFeS_2 and SiO_2 as indicated in Fig. 1.

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Table 1 Chemical composition of enargite and chalcopyrite ores used in this work.

Sample	Particle size (μm)	Chemical content (mass%)			Major mineral phase
		Cu	As	Fe	
Enargite ore	>150	5.36	1.99	9.79	Cu ₃ AsS ₄ , SiO ₂ , FeS ₂
	75–150	4.99	1.75	8.15	
	38–75	16.50	5.87	6.21	
	<38	16.36	5.50	2.53	
Chalcopyrite ore	38–75	21.63	0.32	23.45	CuFeS ₂ , SiO ₂
Mixed ore*	38–75	18.25	3.16	12.56	Cu ₃ AsS ₄ , CuFeS ₂ , FeS ₂ , SiO ₂

(Mixed ore* – enargite : chalcopyrite, 7 : 3 mass/mass ratio)

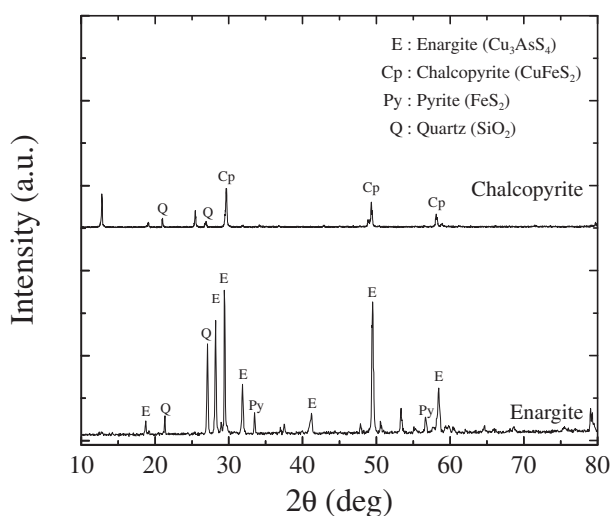


Fig. 1 XRD pattern of enargite and chalcopyrite ores used in this work.

2.2 Reagents

Potassium amyl xanthate (PAX, C₆H₁₁OS₂K) was used as collector and also kerosene to observe its effect on enargite flotation while Methyl isobutyl carbinol (MIBC, C₆H₁₃O) was the frothing agent used in this work. Sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were used as slurry pH regulators, and sodium hydrosulfide (NaHS) and sodium sulfite (Na₂SO₃) were used as depressants for chalcopyrite and pyrite respectively. All chemicals were of reagent grade supplied by Nacalai Tesque and Kanto Chemical Co., Japan.

2.3 Flotation

2.3.1 Procedure

Laboratory flotation experiments were performed using a mineral separation (MS) type laboratory flotation equipment with a cell volume of 250 mL capacity. The cell was divided into two sections; a mixing area where sample/slurry was introduced and the froth formation area separated by a wall with opening at the bottom for samples to pass and rise to top as froth for recovery.

25 g batch samples were first dispersed in 250 mL of water in a 300 mL beaker under constant stirring (600 rpm) to prepare slurry of 10% pulp density, and this was followed by

addition of pH regulators (H₂SO₄/NaOH) to adjust slurry pH to target pH ranging from 4 to 11 and conditioned for 10 min. When pH stabilized, PAX (collector) was introduced into the slurry at concentrations ranging from 0 to 1000 g/t and conditioned for a further 10 min before transferring the slurry into the flotation cell. The impeller speed of the cell was set at 1000 rpm and conditioned for 2 min before adding MIBC at 200 g/t into the slurry. After 30 s of froth formation, froth at the top of cell was scrapped into the trays as samples at different times from 1 to 15 min which were filtered and dried together with tails component for characterization and analyses.

2.3.2 Evaluation of the flotation process

The recovery and/or separation of enargite and chalcopyrite from the flotation study was evaluated by considering concentration (grade) of arsenic (As) balance f , c and t , respectively in the feed F , concentrate C , and tailings T (weights) using the following relationships;

$$R_M (\%) = \frac{C}{F} \times 100 \quad (\text{Mass yield}) \quad (1)$$

$$I = \frac{c}{f} \quad (\text{Enrichment factor}) \quad (2)$$

$$R_C (\%) = \frac{Cc}{Ff} \times 100 = R_M \times I \quad (\text{Valuables yield}) \quad (3)$$

where R_M is mass yield, R_C is valuables yield in the concentrates and I is the enrichment factor. F , C and T are weights of feed, concentrate and tailings respectively while f , c , t is their respective concentration of arsenic (As).^{20,21)}

2.4 Characterization and analyses

X-ray diffraction (XRD) measurements for phase analysis of all solid samples were performed by using Rigaku, RINT-2200/PC system with a CuK α irradiation source ($\lambda = 0.15405$ nm) at 40 kV and 50 mA. Samples were analyzed in a continuous scan mode between 10 and 80° 2 θ . Chemical analysis for all samples after dissolution was conducted using an Inductively Coupled Plasma (ICP–AES/OES) atomic/optical emission spectrometer, SPS-3000 (Seiko Instruments Inc.). Morphology of the samples was observed by Scanning electron microscope (SEM), SU-70 Hitachi High Technology.

3. Results and Discussion

3.1 Enargite-single ore flotation

3.1.1 Effect of particle size

Enargite ore samples of four different size fractions; >150, 75–150, 38–75 and <38 μm were used separately to study and investigate effect of particle size during flotation. 25 g of each size fraction was dispersed in 250 mL water to prepare slurries of 10% pulp density conditioned to pH 4 for all tests. PAX and MIBC additions were fixed at 50 and 200 g/t respectively and flotation performed for 5 min. Experimental results obtained for the different size fractions is shown in Fig. 2.

For sample size >150 μm, enargite recovery reached 53% and purity of the enargite concentrate was near 30%. Recovery increased significantly to 85% for the 75–150 μm fraction but purity remained near 30% and further decrease in

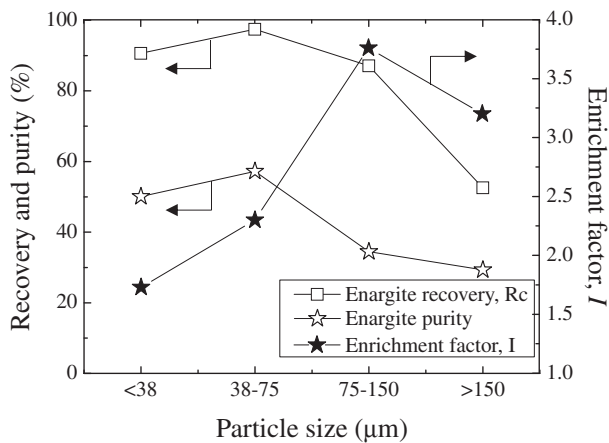


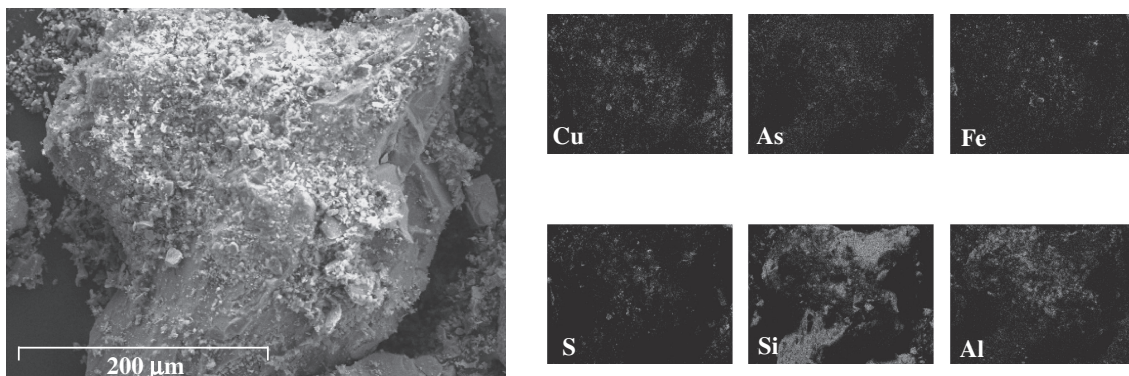
Fig. 2 Flotation behavior of enargite showing recovery, purity and enrichment factor as a function of particle size. (Test conditions: Slurry pH 4, 10% pulp density, 5 min flotation time, PAX and MIBC additions fixed at 50 and 200 g/t).

particle size to 38–75 μm , enargite recovery reached 97% with a purity of 58%. Flotation study on the fines (<38 μm) indicated a slight decrease in recovery of enargite to near 90% and purity decreased slightly to 50%. Since pure (100%) enargite contains 19% As and assuming all As is provided by enargite, the four different size fractions with varying contents of As according to Table 1 compute to give enargite contents at; 10% for >150 μm , 9% for 75–150 μm , 31% for

38–75 μm and 29% for <38 μm . Using eq. (2) for each size fraction the enrichment factors compute to give 3.2, 3.8, 1.9 and 1.7 for each size fraction respectively. Lower recovery in the coarse fraction indicates that enargite surfaces are not fully exposed and may be encapsulated in the gangue minerals requiring finer grind. On the other end, decrease in enargite recovery in the fine fraction could be attributed to by agglomeration and coating of fines onto enargite surface inhibiting it from exposure to collectors. Also decrease in purity can be due to reporting of fine gangue slimes into the concentrate fraction.

SEM images were taken for the flotation concentrates of the >150 and <38 μm sample fractions as shown in Fig. 3 and specific elemental mapping was also performed to discuss enargite distribution and recovery. For the >150 μm fraction, coarser particles above 200 μm were observed in the SEM photo [Fig. 3(a)]. Elemental mapping of the large particles indicated high levels of Si, Al, and Fe occurring together with Cu. This indicates that enargite was not fully liberated but locked with pyrite and quartz, supporting low enargite recovery data shown in Fig. 2 for the >150 μm fraction. Similarly a SEM image taken for the flotation concentrate of the <38 μm [Fig. 3(b)] fraction shows large number of particles in the sub-micron range. Elemental mapping of the fine particles also showed high levels of Si, Al, and Fe indicating fines as gangue and this could attribute to slight decrease in enargite recovery during flotation of the <38 μm fraction (Fig. 2).

(a) Flotation concentrate (>150 μm fraction)



(b) Flotation concentrate (<38 μm fraction)

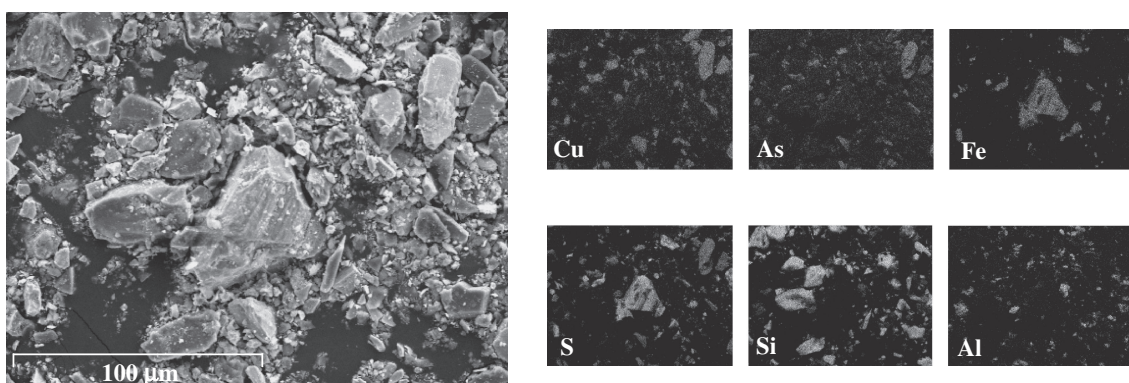


Fig. 3 SEM images of flotation concentrates obtained from enargite ore of two different size fractions (a) >150 μm and (b) <38 μm fraction.

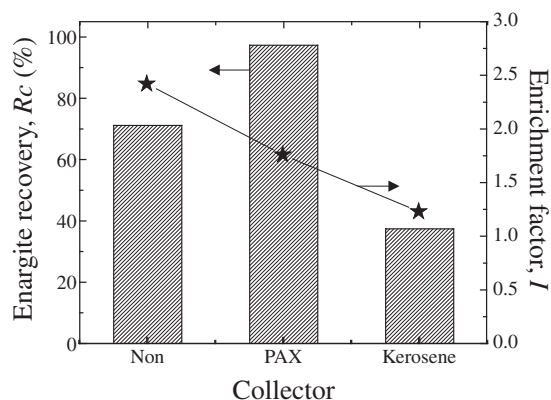


Fig. 4 Flotation response of enargite performed with different reagents at pH 4 and 10% pulp density for 5 min. (Collector and MIBC additions fixed at 50 and 200 g/t).

3.1.2 Effect of collector

Keeping pulp density, slurry pH and flotation time fixed at 10% solids, pH 4 and 5 min respectively, the flotation behavior of enargite ore (38–75 μm fractions) both with and without reagents addition was investigated. Firstly, flotation test was performed without addition of reagents for 5 min and according to Fig. 4; enargite recovery of around 70% with a purity of 75% was achieved, indicating that the enargite mineral was easily floatable at pH 4. The enrichment factor without reagent addition was 2.4 nearing 3.2 target when over 99% enargite is achieved and the high value was due to higher purity. Enargite recovery increased to 97% when flotation was performed with the addition of PAX (50 g/t) and MIBC (200 g/t), both these reagents are widely used in flotation of sulfide minerals including enargite. Analysis of the tailings fraction indicated that arsenic has been reduced to <0.5 mass%. The enrichment factor with reagent addition was 2.3 showing no significant increase despite high recovery was due to lower purity of 60% as other sulfide minerals and gangue as fine slimes report to concentrate. Effect of kerosene which is used in the flotation of fast floating or highly floatable minerals such as coal, molybdenite and galena^{22–24}) was investigated in this study as enargite was observed highly floatable. Addition of kerosene as collector at 50 g/t gave an enargite recovery of only 37% with purity below 30%, contrary to the 70% recovery during enargite flotation without reagents addition.

3.1.3 Effect of slurry pH

The flotation behavior of enargite and pyrite in the ore sample as a function of slurry pH was investigated from pH 4 to 11 and results obtained are shown in Fig. 5. PAX and MIBC additions were fixed at 50 and 200 g/t respectively and flotation time was kept constant at 5 min. Natural pH of the slurry and potential without addition of pH and redox potential regulators/modifiers was 4 and 450 mV (SHE) respectively. A 1 M NaOH solution was used to adjust pH accordingly between 4 and 11 to monitor flotation behavior of enargite and pyrite.

From Fig. 5 it can be seen that 98% of enargite and 60% of pyrite was recovered as flotation concentrate at pH 4, and chemical analysis of the tailings fraction showed that As content has been reduced from 5.87 mass% in the starting ore

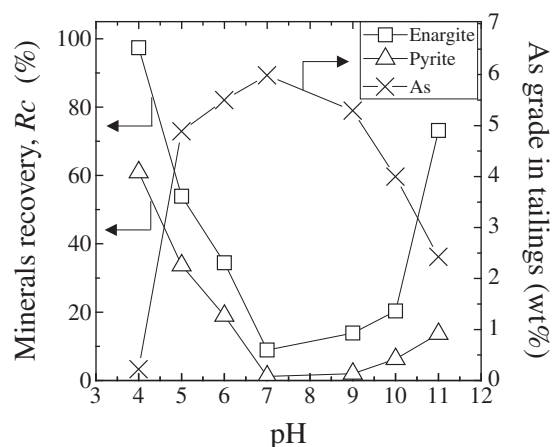


Fig. 5 Flotation behavior of enargite and pyrite as a function of slurry pH for 5 min with pulp density, PAX and MIBC additions fixed at 10%, 50 and 200 g/t.

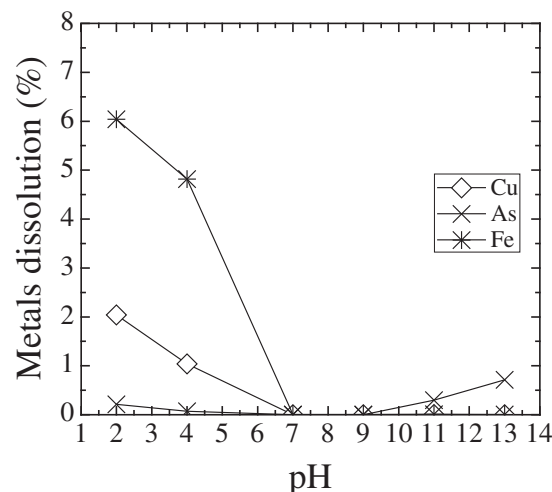


Fig. 6 Shows dissolution of metals into solution during flotation at different pH conditions. (Test conditions: 10% pulp density, 5 min flotation time, PAX and MIBC additions fixed at 50 and 200 g/t).

sample to 0.22 mass%. Consequently, As grade in the concentrate increased to 10.96 mass%, while Cu grade in the concentrate increased to 30.55 mass%. However, when the slurry pH was increased, recoveries of both enargite and pyrite decreased significantly and at pH 7 enargite recovery was only 10% and pyrite below 5% and remained consistently low up to pH 10. At pH 11 enargite recovery increased to 73% giving an increased copper grade of 37.01 mass%, and this was attributed to by decreased pyrite recovery of up to 20%. However, As content in the final tailings was higher at 2.40 mass% due to reduced recovery of enargite. The enrichment factor of As for flotation at pH 4 was 1.9, indicating the As content in the concentrate was 1.9 times the concentration of As in the feed. Similarly enrichment factors for flotation tests performed at pH values from pH 5 to 11 ranged between 2 and 2.5.

Chemical analysis of filtrates after flotation for each pH condition (pH 2 to 13) to monitor dissolution of Cu, As and Fe was also performed and results are presented in Fig. 6. At a more acidic condition of pH 2, 2.0% Cu, 6.0% Fe and less than 0.5% As dissolved into solution during flotation of

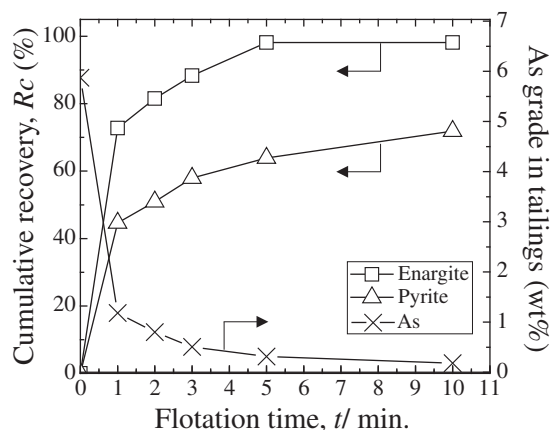


Fig. 7 Cumulative minerals recovery and change of As grade in tailing as a function of flotation time. (Test conditions: 10% pulp density, slurry pH 4, PAX and MIBC additions fixed at 50 and 200 g/t).

enargite. At pH 4 where high enargite recovery has been reported, Cu dissolution reduced to 1.0%, Fe to below 5% and As further decreased to less than 0.2%. No dissolution of Cu and Fe occurred from pH 5 to 14, however, As dissolution nearing 1.0% at pH 13 was observed. The effect of solution potential and slurry pH on enargite recovery and separation from other iron and copper sulfide minerals is widely discussed in literature.^{8,17} The highly hydrophobic behavior of enargite at pH 4 could be attributed to by the formation of elemental sulfur or arsenic sulfide and modification of surface condition by adsorption of dissolved components on enargite surface. Pyrite is naturally depressed at alkaline pH 11 and selective separation from enargite can be achieved, but the slight decrease in enargite recovery could be due to formation of hydrophilic oxidation products such as SO_4^{2-} and CuO as flotation was performed in open air.

For the enargite sample investigated in this study, all subsequent flotation tests were performed at slurry pH 4 as it successfully reduced As content in the tailings to below 0.5 mass% and increased copper to above 30 mass% in the concentrate.

3.1.4 Effect of flotation time

The effect of flotation time on enargite and pyrite recovery while keeping slurry pH constant at pH 4, PAX and MIBC additions at 50 and 200 g/t respectively was investigated from 0 to 10 min and the results are shown in Fig. 7. Recovery of enargite reached over 70% in the first 1 min and over 98% in 5 min while pyrite recovery reached 45% in the first 1 min and proceeded slowly and reached around 70% in 10 min. According to this result, a flotation time of 5 min was sufficient to obtain near complete recovery of enargite with As content in the tailings reduced to below 0.5 mass%. Prolonged flotation time to 10 min showed no significant change but slight increase in pyrite recovery; however Cu grade in the enargite concentrate was still high at over 31 mass%. Enrichment factor computed for As in the concentrates obtained at different times from 1 to 5 min ranged from 1.9 to 2.0 and 1.2 for concentrate obtained after 10 min flotation.

In other tests flotation time and slurry pH were fixed at 5 min and pH 4 while investigating PAX concentration and depressant additions.

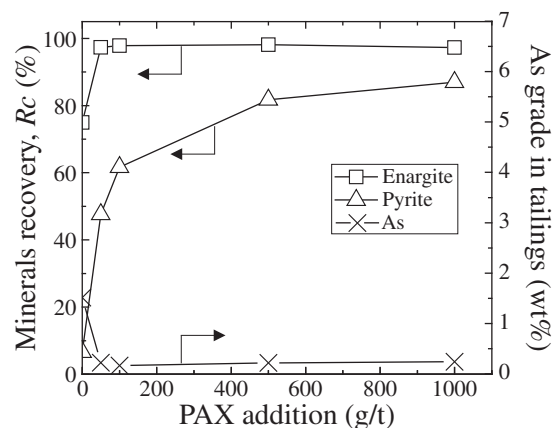


Fig. 8 Change of minerals recovery and As grade in tailing as a function of PAX addition. (Test conditions: 10% pulp density, slurry pH 4, 50 g/t MIBC addition).

3.1.5 Effect of PAX addition

The effect of PAX addition on the recovery of enargite and pyrite and change of As content in the tailings was investigated for PAX additions ranging from 0 to 1000 g/t and results obtained are shown in Fig. 8. MIBC addition was fixed at 200 g/t and pulp density, slurry pH and flotation time were all kept constant at 10%, pH 4 and 5 min respectively. For flotation test without PAX addition (0 g/t), up to 75% of enargite was recovered while pyrite recovery remained below 10%. When 50 g/t of PAX was introduced, enargite recovery reached over 98%, at the same time pyrite recovery also increased to 48%. Further increase in PAX concentration continued to increase pyrite recovery resulting in a decrease in Cu grade in final concentrate to 28 mass% for PAX additions exceeding 500 g/t.

According to this result, a PAX addition of less than 100 g/t (preferably 50 g/t) was sufficient to recover over 98% of enargite and purity nearing 70%, keep pyrite recovery below 50% and most importantly reduce As content in the final tailings to below 0.5 mass%. Enrichment factor computations showed concentrates obtained with 50 and 100 g/t PAX were constant at 1.9 indicating the concentrates contained near 2 times As concentration in the feed material. If over 99% of enargite is recovered and near 19% As closer to As content in enargite for pure sample is achieved, enrichment factor will be 3.2 (19/5.87).

3.1.6 Effect of depressants

The recovery of enargite and pyrite both with and without depressants during flotation is shown in Fig. 9. All other conditions were kept constant (PAX = 50 g/t, MIBC = 200 g/t, time = 5 min, pH = 4), and the depressants used were NaHS and Na_2SO_3 added at 1000 g/t. Firstly, flotation tests performed without depressants discussed in earlier sections showed that enargite recovery of above 98% and pyrite below 60% with As content in tails below 0.5 mass% were achieved. Addition of NaHS did not show any significant effect on the recovery of both enargite and pyrite, enargite decreased only slightly but remained same with the sample with no depressant. The addition of Na_2SO_3 showed significant change in pyrite flotation, reducing pyrite recovery to below 20% from over 60%, but it also reduced enargite by around 20% giving a Cu grade of 31.57 mass%.

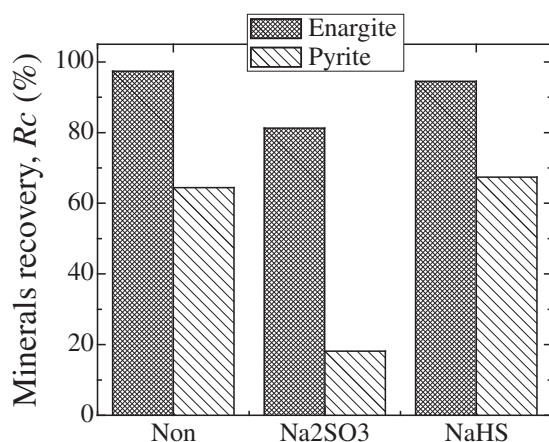


Fig. 9 Flotation behavior of enargite and pyrite both with and without NaHS and Na₂SO₃ depressants. (Test conditions: 10% pulp density, slurry pH 4, PAX and MIBC additions fixed at 50 and 200 g/t, NaHS and Na₂SO₃ additions at 1000 g/t).

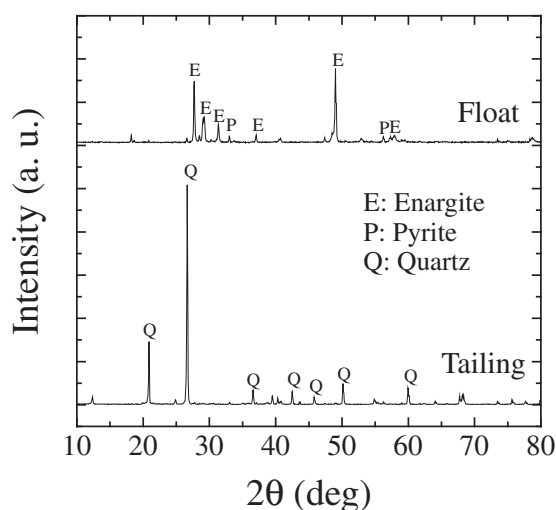


Fig. 10 XRD patterns of the froth and tailings fractions obtained from tests performed at optimum flotation conditions. (Test conditions: 10% pulp density, slurry pH 4, PAX and MIBC additions fixed at 50 and 200 g/t).

Subsequently, As grade in the tailing remained high at 2.0 mass%. The decrease in enargite flotation during pyrite depression could be due to the un-liberated enargite in pyrite responding to depressive effect of Na₂SO₃. The enrichment factor for concentrates obtained for all three conditions was constant around 1.8 to 2.0.

Figure 10 shows XRD patterns of the tailing and concentrates fractions obtained during flotation under optimum conditions. No enargite peaks were observed in the tailings fraction which correspond well with chemical analysis data which showed near complete removal of As.

3.2 Mixed ore flotation (enargite + chalcopyrite)

3.2.1 Effect of slurry pH

The flotation behavior of enargite, chalcopyrite and pyrite in a mixed ore sample at slurry pH values ranging from pH 4 to 11 was performed and results obtained are shown in Fig. 11. PAX and MIBC additions were fixed at 100 and

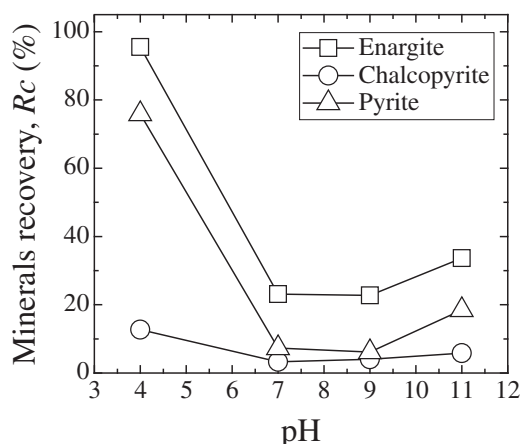


Fig. 11 Flotation behaviors of enargite, chalcopyrite and pyrite from mixed ore as a function of slurry pH. (Test conditions: 10% pulp density, 5 min flotation time, PAX and MIBC additions fixed at 100 and 200 g/t).

200 g/t respectively, pulp density at 10% solids and flotation runs were performed for 5 min. The result showed that at pH 4, 95% of enargite and 78% pyrite was recovered as flotation concentrate. Chemical analysis of the concentrate indicated Cu and As have been increased to 32.62 and 12.41 mass% respectively and As content in the tailings has been reduced to <0.5 mass% from 3.16 mass% in the starting sample. Recovery of both enargite and pyrite decreased to below 30% when slurry pH was raised and showed no significant improvement up to pH 11. In all slurry pH conditions, recovery of chalcopyrite remained consistent below 15%. The enrichment factors for As at pH ranging from 4 to 11 were 2, 2.2, 2.3 and 2.3 respectively. From these results, enargite and chalcopyrite could be separated at slurry pH 4 to obtain separate concentrates for further treatment.

3.2.2 Effect of flotation time

The effect of flotation time on recovery of enargite, chalcopyrite, and pyrite minerals at constant slurry pH 4, PAX and MIBC additions at 25 and 200 g/t respectively was investigated from 0 to 15 min and the results are shown in Fig. 12. Enargite recovery increased significantly to near 60% in 5 min, 80% in 10 min and 90% in 15 min flotation time. Pyrite recovery showed a similar trend reaching up to over 60% in 15 min while recovery of chalcopyrite was lower, remaining below 10% up to 10 min and only reaching 20% in 15 min. When PAX addition was increased to 75 g/t, enargite recovery reached 97% while chalcopyrite reached only 10% in 5 min. As flotation time was increased to 15 min, chalcopyrite recovery also increased and reached up to 60%. Since enargite is easily floatable at pH 4 within 5 min and at low PAX addition (25 g/t) as compared to chalcopyrite at higher PAX addition (75 g/t) and longer flotation time (>10 min), such situation can be used to separate the two minerals and recover enargite with high arsenic content and chalcopyrite with low arsenic content. Flotation kinetics and separation efficiency of the two minerals (enargite and chalcopyrite) as a function of time at varying pH and PAX additions is evaluated in section 3.2.4 to support discussions in this section. By that evaluation, it was seen that the enargite can be clearly separated from chalcopyrite.

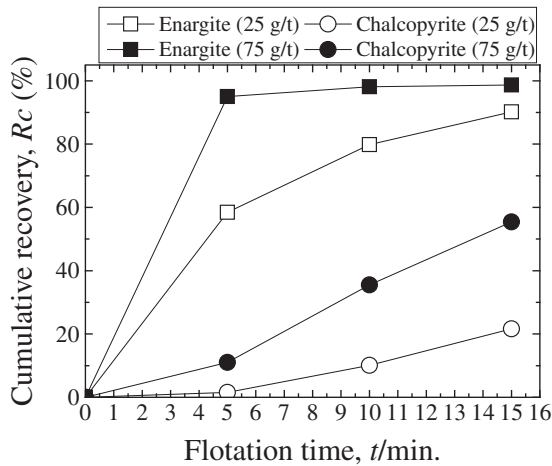


Fig. 12 Cumulative recovery of enargite, chalcopyrite and pyrite from mixed ore as a function of flotation time. (Test conditions: 10% pulp density, slurry pH 4, PAX and MIBC additions fixed at 50 and 200 g/t).

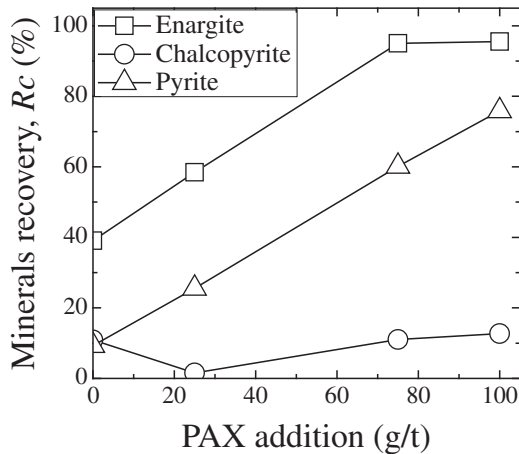


Fig. 13 Flotation recovery of enargite, chalcopyrite and pyrite from mixed ore as a function of PAX addition. (Test conditions: 10% pulp density, slurry pH 4, 5 min flotation time, 200 g/t MIBC addition).

3.2.3 Effect of PAX addition

The effect of PAX addition on the recovery or flotation behavior of enargite, chalcopyrite, and pyrite minerals investigated from 0 to 100 g/t and results obtained is shown in Fig. 13. All other conditions were kept constant (pulp density: 10%, pH: 4, MIBC: 200 g/t, time: 5 min). At 0 g/t PAX addition (collector-less flotation), 40% of enargite and less than 10% of chalcopyrite and pyrite were recovered as flotation concentrate. Enargite and pyrite recoveries increased with increased PAX addition and enargite reached over 95% for PAX additions above 75 g/t and pyrite recovery up to 60% at 75 g/t PAX addition. Chalcopyrite recovery remained consistently below 10% and due to high enargite recovery, As content in the tailings or fraction of sample containing high chalcopyrite was reduced to <0.5 mass%. Also at 75 g/t PAX addition when high enargite recovery was achieved, enrichment factor was 2.1.

3.2.4 Evaluation of flotation kinetics and separation efficiency

Many flotation systems and especially for copper ores, flotation is essentially a first-order process, giving a reasonably good fit to the experimental data. Equation (4)

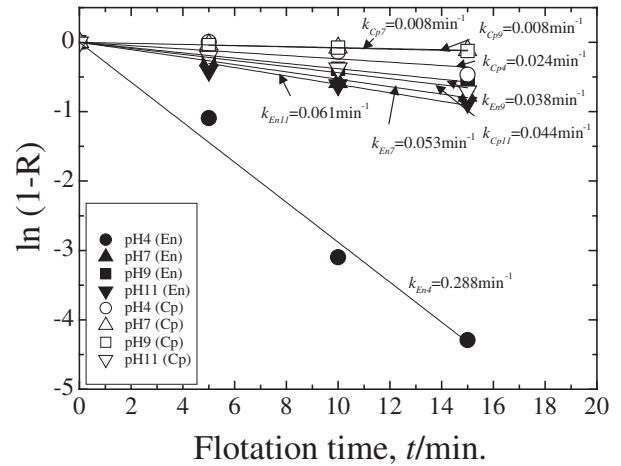


Fig. 14 Effect of pH on the flotation kinetic constant of mixed ore flotation. (Test conditions: 10% pulp density, PAX addition 100 g/t, 200 g/t MIBC addition).

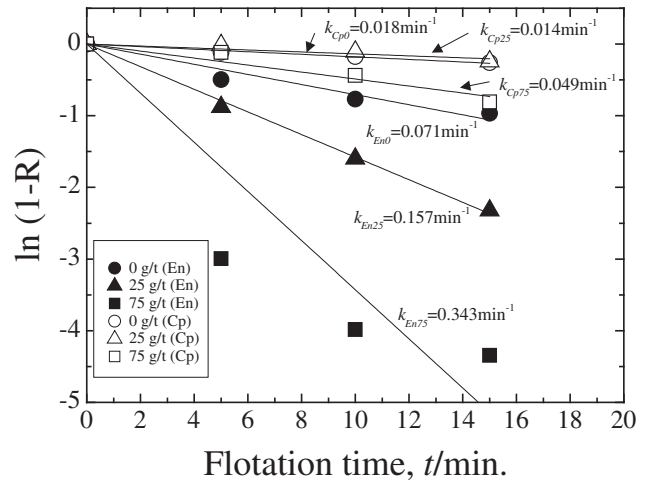


Fig. 15 Effect of PAX addition on the flotation kinetic constant of mixed ore flotation. (Test conditions: 10% pulp density, slurry pH 4, 200 g/t MIBC addition).

below shows the first-order rate equation where R is cumulative recovery after time t , k is the first order kinetic rate constant (time^{-1}) and t is the cumulative flotation time.

$$R = 1 - \exp(-kt) \quad (4)$$

The constant k depends on a large variety of variables which include factors related to ore characteristics, reagents and so on.²⁵⁾ Figure 14 shows kinetic constant values evaluated for both chalcopyrite and enargite at different slurry pH (used data from Fig. 11). All results produced a reasonably good fit of the first-order rate equation and kinetic constants (k) for both minerals are shown. At pH 4 enargite recovery was over 90% and kinetic constant was evaluated to be $k = 0.288$, highest compared to all other results. It is thought that surface of enargite was modified to more hydrophobic mineral by likely formation and coating of elemental sulfur and/or arsenic sulfide in the acidic condition of slurry. Evaluation of kinetic constants for effect of PAX is shown in Fig. 15. Kinetic constants increased linearly as PAX addition was increased, notably enargite flotation rate/speed was faster compared to chalcopyrite.

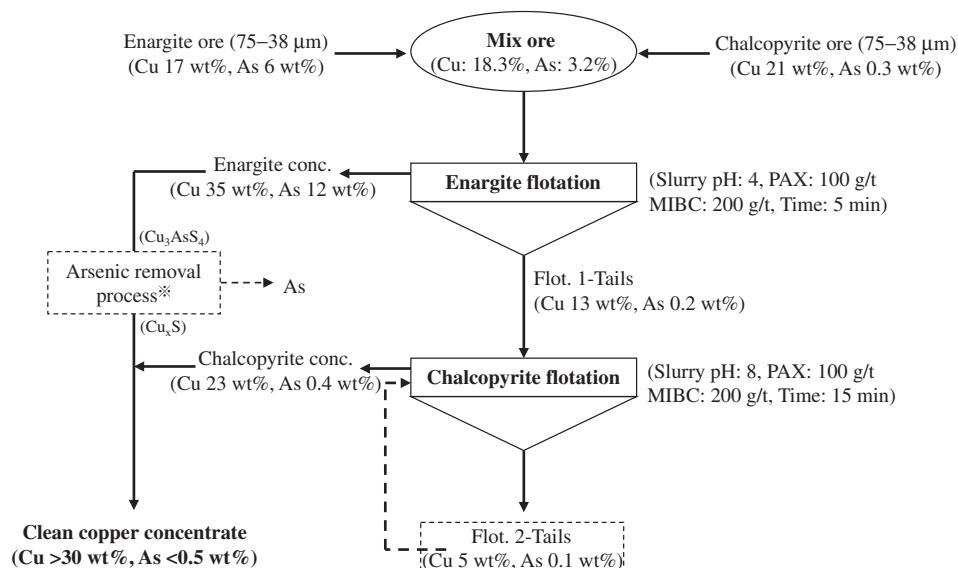


Fig. 16 Flow sheet showing process flow for enargite bearing copper (high arsenic content) and chalcopyrite for their separation and copper recovery. (*Arsenic removal process is detailed elsewhere^{24–26}).

4. Treatment Process of High As Bearing Minerals

From discussions on flotation recovery of enargite from a single ore and a mixed ore containing both enargite and chalcopyrite, a general flow sheet can be incorporated to discuss flow of process. A single enargite ore would require a single flotation process where enargite can be recovered and As content in the final tailings reduced to <0.5 mass%. However, a mixed ore with both enargite and chalcopyrite would require several stages to recover both minerals into separate concentrates, at the same time controlling As flow in the process for environmental control.

The overall process investigated in the current study to separate enargite from chalcopyrite and reduce As content in the tailings and chalcopyrite to <0.5 mass% is provided in Fig. 16. The tailings can be disposed to environment and chalcopyrite used as clean concentrate to smelter while enargite concentrate can be treated separately for its As removal before copper is recovered. The process generally has three stages; (1) crushing/grinding to obtain target size for subsequent processing, (2) first stage flotation for enargite removal or its separation from chalcopyrite, and (3) a second stage flotation stage for recovery of chalcopyrite from gangue minerals.

In the first stage the enargite and chalcopyrite samples were separately crushed and milled to obtain 38–75 μm size fraction followed by blending to obtain a mixture with about 3 mass% As for use in flotation work. The milled sample was treated in the second stage where flotation was performed at pH 4 for 5 min with PAX and MIBC additions at 100 and 200 g/t respectively to selectively remove over 95% of enargite. This becomes enargite concentrate with Cu grade above 30 mass% and As content also above 10 mass% to be treated separately. Research by the same group in recent studies have developed an alkaline leaching process for removal of As from enargite ore and/or concentrate and obtained clean copper resource with As content <0.5 mass% for feed to smelting operations.^{26–28} The tailings from

enargite flotation stage contains high chalcopyrite to be recovered in next stage of flotation but with very low As content <0.5 mass%.

For recovery of chalcopyrite in the tails after enargite flotation, time was increased to 15 min and slurry pH raised to around pH 8. Both PAX and MIBC additions were fixed at 100 and 200 g/t respectively. Copper grade in final chalcopyrite concentrate was improved to 23 mass%, while As grade decreased to 0.4 mass%. Overall target was to improve Cu grade/recovery as much as possible while reducing As content in the final tailings and concentrate to <0.5 mass% and Cu content in the final tailings to <1 mass%.

5. Conclusions

A single ore flotation study using high grade enargite ore and a mixed ore sample flotation study using enargite and chalcopyrite mixture were used in this work to recover enargite and chalcopyrite as separate copper concentrates. Results obtained can be summarized as follows;

- (1) In single ore flotation, up to 75% of enargite was recovered at pH 4 (natural) without PAX addition and improved further to 98% with 50 g/t PAX addition within 5 min. Most importantly As content in tailings was reduced to 0.22 mass% and Cu grade in the concentrate was improved to 30.55 mass% from 16.50 mass%.
- (2) In mixed ore flotation, up to 95% of enargite was selectively recovered at pH 4 and PAX addition of 100 g/t in 15 min. Cu grade was increased to 35 mass% and As content reached 12 mass%, while tailings fraction with chalcopyrite contained 13 mass% Cu and 0.2 mass% As.
- (3) Flotation to recover chalcopyrite for Cu was performed at pH 8, improving Cu grade to 23 mass% and low arsenic content of 0.4 mass%. The final tailing contained 5 mass% Cu and 0.1 mass% As.

According to these results, it was observed that enargite in the mixed ore can first be recovered at pH 4 followed by chalcopyrite recovery at pH 8. As content in both chalcopyrite concentrate and final tailings was reduced to below 0.5 mass%. The enargite concentrate can be treated separately for As removal.

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