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Flotation separation of enargite from complex copper concentrates by selective surface oxidation

Tengfei Li, Yansheng Zhang, Bo zhang, Fen Jiao, Wenqing Qin

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China;

Corresponding author: zhangyansheng405@126.com (Yansheng Zhang)

Abstract: In previous study, the promising results of separating enargite from non-arsenic copper sulfides were obtained using selective surface oxidation in pure mineral systems. However, this technology was not well understood in real ores or concentrates. In this study, the flotation separation of enargite from complex copper concentrates by selective surface oxidation was investigated. The effects of regrinding, pulp pH, NaClO concentration, conditioning time and flotation time on separation of enargite from NECu minerals were studied. The mineralogical characteristics of the flotation feed and products were showed as an instructive tool to understand the separation results. According to the results of EDTA extraction, the possible mechanism for separation of enargite from NECu minerals is that enargite is more resistant to oxidized compared to NECu minerals. The following order for the oxidation of NECu minerals and enargite is obtained: chalcopyrite (chalcocite, digenite)> enargite (covellite).

1. Introduction

In copper deposits, enargite (Cu_3AsS_4), one of the most undesirable arsenic-bearing minerals, is widely associated with non-arsenic copper sulfide minerals such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S) and covellite (CuS) (Long et al., 2014; Plackowski et al., 2012; Plackowski et al., 2013). The difference of flotation behaviour between enargite and non-arsenic copper sulfides is slight when xanthate collectors are used, which results from the non-selective adsorption of xanthate to these minerals and forming cuprous xanthates on mineral surfaces (Pineda et al., 2015). Therefore, enargite often reports to the final copper concentrates in conventional copper flotation circuits, which causes not only the detrimental impact on environment and human health during the copper smelting, but also decreases the properties of copper products such as electrical conductivity and ductility (Tayebi-Khorami et al., 2017). There are many sources of environmental contamination in the world (Bigdeli and Dehaghi, 2018; Rezaee et al., 2017; Meshkat et al., 2018; Barzegar and Fallahiyekta, 2018), among which arsenic pollution from mining and metallurgy of nonferrous metals is one of the most serious problems. High financial penalties are imposed by smelters to treat copper concentrates containing high than 0.2% As and the rejection limit for smelting is 0.5% As (Tayebi-Khorami et al., 2017). Thus, the removal of arsenic from copper concentrates becomes ever important at an earlier stage such as froth flotation due to the stricter environmental rules related to the arsenic pollution.

Various strategies have been reported in previous studies for selective flotation of enargite from copper sulfide minerals, in particular chalcopyrite, including selective flotation reagents (Abeidu and Almahdy, 1980; Tajadod and Yen, 1997), selective surface oxidation (Fornasiero et al., 2001; Huch, 1994) and pulp potential control (Long et al., 2014; Tayebi-Khorami et al., 2017; Bruckard et al., 2007; Smith and Bruckard, 2007; Senior et al., 2006; Bruckard et al. 2010; Guo and Yen, 2005). Among them, controlled pulp potential flotation has been extensively researched. However, the amount of the literature reporting the two other strategies is scarce.

Mineral surface oxidation, a common and important phenomenon during flotation, plays a critical role in sulfide minerals flotation. Slight surface oxidation can promote the adsorption of collectors and the formation of element sulfur, which can increase the floatability of minerals (Rumball and Richmond, 1996). Extensive surface oxidation can decrease the floatability of minerals by the formation of a physical barrier of oxidation products (mainly metal oxide and hydroxide), which prevents the adsorption of collectors to the mineral surface (Senior and Trahar, 1991; Smart, 1991). Selective surface oxidation is based on the differences in the type and amount of oxidation products on mineral surface between sulfide minerals after reacting with oxidizing reagents. Huch (1994) found that chalcocite was preferentially oxidized and depressed after oxidation treatments using hydrogen peroxide which enargite can be floated. Fornasiero et al. (2001) found that it is feasible to separate enargite and tennantite from non-arsenic copper sulfide minerals after selective surface oxidation at pH 5.0, or after oxidation and selective dissolution of the surface oxidation products with EDTA at pH 11.0. For a change, the non-arsenic minerals have a stronger floatability than enargite and tennantite at above two conditions. Fullston et al. (1999) reported the oxidation rate of copper sulfide minerals follows the order: chalcocite > tennantite > enargite > covellite > chalcopyrite. This result indicates that enargite and tennantite can be separated from the non-arsenic copper sulfide minerals in the absence of chalcocite. Kappes et al. (2007) reported a copper rougher concentrate was reground to liberate tennantite and chalcopyrite, resulting in an effective separation of tennantite from chalcopyrite. Long et al. (2014) investigated the effect of regrinding on rejecting tennantite from copper concentrates at Rosebery. The results showed the liberation degree of tennantite was increased slightly, which resulted in a significant selectivity of copper against arsenic. However, there is disagreement about the oxidation order between enargite and non-arsenic copper sulfide minerals. These contradictory results may be resulted from impurities associated with these arsenic and copper minerals that modify the electrochemical properties of minerals (Long et al. 2014). Furthermore, galvanic interaction between these sulfide minerals which plays a significant role in redox reactions on minerals surfaces was neglected in their reports. Previous studies mostly focused on the single mineral system with respect to selective oxidation, the separation of arsenic minerals from non-arsenic copper sulfides in real ores or concentrates by selective surface oxidation is not well understood at present.

EDTA (ethylenediaminetetraacetic acid) extraction technique has been used to evaluate the extent of oxidation of minerals in sulfide minerals flotation. EDTA as a complexing reagent can dissolve metal oxidation products from the surfaces of minerals such as oxides/hydroxides, sulfates, and carbonates, but not the metal sulphides (Tayebi-Khorami et al. 2018; Greet and Smart, 2002). Rumball and Richmond (1996) used EDTA extraction to demonstrate that Hellyer ore is fresh with little or no oxidation products before grinding, undergoing mild oxidation during grinding and extensive oxidation in flotation circuit. Greet and Smart (2002) examined the effect of the addition of EDTA on galena oxidation products. They found that all oxygen containing oxidation products are rapidly dissolved in EDTA solution, but not polysulfide or sulfur. They also observed that EDTA does not extract lead from unreacted galena. Shannon and Trahar (1986) employed EDTA to remove the oxidation species from chalcopyrite surface, increasing the floatability of chalcopyrite.

The aim of this study is to evaluate the effect of selective surface oxidation on separation of enargite from a complex copper concentrate. The mineralogical characteristics of arsenic-bearing copper concentrates were investigated as an instructive tool for flowsheet design to remove arsenic-bearing minerals. EDTA extraction experiments were conducted to determine the location and extent of minerals oxidation within the processing circuits and the possible mechanisms for selective flotation of enargite from the complex copper concentrates.

2.   Materials and methods

2.1. Materials

The complex copper concentrate samples used in this study were obtained from a copper flotation plant in China. The copper ores were comminuted by coarse crushing, SAG milling and ball milling and transferred to the flotation stage. The detailed copper flotation conditions were shown in Fig. 1. The average grade of the copper concentrate is 21.5% Cu and 1.1% As. The samples were dried,

homogenised and split into 500 g of sub-samples using laboratory splitter for regrinding and flotation experiments. The representative sample was chosen to investigate the mineralogical characteristics using MLA (mineral liberation analyser). The particle size distribution of the complex copper concentrate was shown in Fig. 2 (45% passing 38 µm). Sodium hypochlorite solutions of analytical grade was used as oxidizing reagent. Lime and dilute sulfuric acid were used for pH adjustment. There is no need for the addition of other flotation reagents due to the high reagent residue in the concentrate.
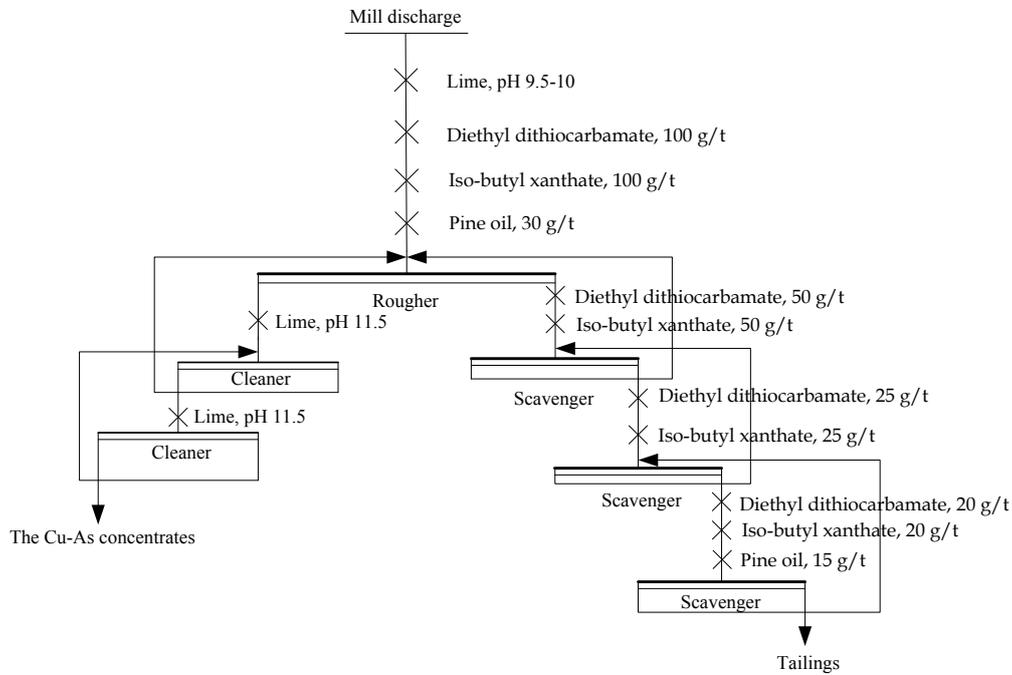
Fig. 1. The flotation flowsheet of the copper flotation plant
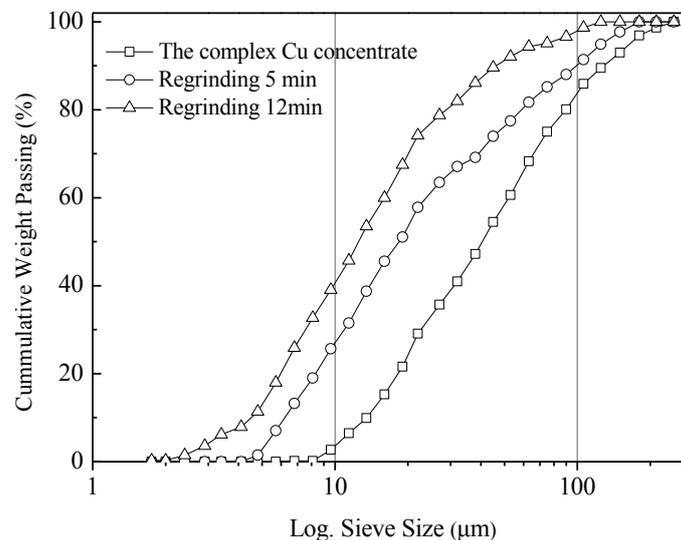
Fig. 2. Particle size distributions of the complex copper concentrate and regrinding products

2.2. Regrinding and flotation experiments

For each test, 500 g of the concentrate sample was reground in a laboratory ball mill using stainless steel balls at a pulp density of 67% solids. A series of regrinding tests were performed to determine the time required to produce the desired size distribution. The particle size of 70% and 80% passing 38

μm can be obtained after regrinding 5 min and 12 min respectively. Before the regrinding tests, the ball mill was cleaned by grinding pure quartz.

After regrinding, the resulting pulp was transferred to 1.5 L XFD flotation cell and changed the pulp density to 33% solids by addition of the tap water. Accurate amounts of lime werw added into the flotation cell followed by a one minute of conditioning to adjust the pH values of pulp. The NaClO solution was added and made up to the concentration of NaClO in the pulp varying from 0 to 1.5% (v/v). Following the addition of NaClO, the sufficient conditioning time was required to reach the satisfied oxidation results before starting scraping froth. The concentrate and tail samples were dried, weighed and assayed for arsenic and copper by chemical analysis. The grade of arsenic and copper in the feed were calculated from that of in the concentrates and tails by elements mass balance.

2.3. EDTA extraction tests

A series of EDTA tests were performed to determine the location and extent of oxidation of the samples. The flowchart of EDTA extraction experiments is shown in Fig. 3.

5% (w/w) EDTA solutions were prepared by dissolving ethylenediaminetetraacetic acid di-sodium salt with the deionized water. According to the flowchart, three sets of EDTA extraction tests were performed. For the first, 5 g of the feed sample was added to 300 mL of prepared EDTA solutions. Sodium hydroxide was used to adjust the pH of EDTA solutions to 7.5. Nitrogen was purged into the solution to remove the dissolved oxygen prior to the extraction. The pulp was mixed continuously and leached for 10 min. For the other two, 10 mL of the pulp was taken from the regrinding stage and the conditioning stage respectively. The extraction procedure was the same as above.

The filtrate and residue were assayed for arsenic, iron and copper to calculate Em value (the mass of metal extracted per unit mass of dry solid), with unit of mg/g, which indicates the oxidation extent of the mineral in a pulp sample (Kant et al. 1994).
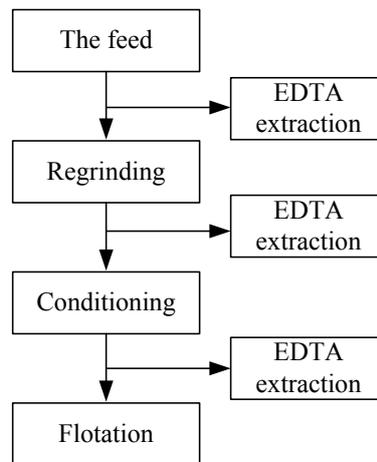
Fig. 3. The flowchart of EDTA extraction tests

2.4. Mineralogical and chemical analysis

The representative samples of the complex copper concentrate (feed) and flotation products were analysed by MLA (MLA650, FEI, USA) to investigate the mineralogical characteristics, such as particle size distribution, mineral weight distribution and mineral liberation and association. Prior to the MLA studies the sample powder was fixed and polished. The detailed procedure was described by Gräbner and Lester (2016). The XBSE mode was used to collect the backscatter image, followed by background removal and particle de-agglomeration. Once individual particles have been identified, the next step of the liberation analysis is phase segmentation to identify all distinct mineral phases (or grains) and defines their boundaries accurately (Fandrich et al. 2007). X-ray analysis was used for mineral identification, including point X-ray, area X-ray and X-ray mapping. Afterwards, the raw data files generated from MLA measurements were analysed using MLA-Dataview 3.

The Cu-As concentrate (feed) and flotation products were assayed for Cu and As using inductively coupled plasma–mass spectroscopy(ICP-MS, IRIS Intrepid II XSP). Arsenic assays were used to determine the amount of enargite and then calculate the content of NECu (copper not accounted for in enargite). Cu, Fe and As were assayed in EDTA extraction tests using ICP-MS.

3.   Results and discussion

3.1.   Mineralogy analysis

The mineral constituents of the copper concentrate are shown in Fig. 4. Four kinds of non-arsenic copper minerals (chalcopyrite, covellite, chalcocite and digenite), named NECu (non-enargite copper minerals), were included in the concentrate, with enargite as the only one arsenic-bearing mineral. It is believed that a complete separation of enargite from these NECu minerals is extremely difficult by selective oxidation, since not all NECu minerals are more oxidized than enargite as the Introduction discussed. The mineral weight distributions are given in Fig. 5. It can be seen that chalcopyrite is the most common NECu mineral followed by chalcocite and covellite, while the least is digenite. The major sulfide gangue is pyrite whose content is 39 wt.% in the concentrate, with minor amounts of galena. Non-sulfide gangue minerals with 15 wt.% were mainly comprised of quartz, kaolinite, muscovite and fluorite. Fe oxides content of the concentrate is 1.3 wt.%.
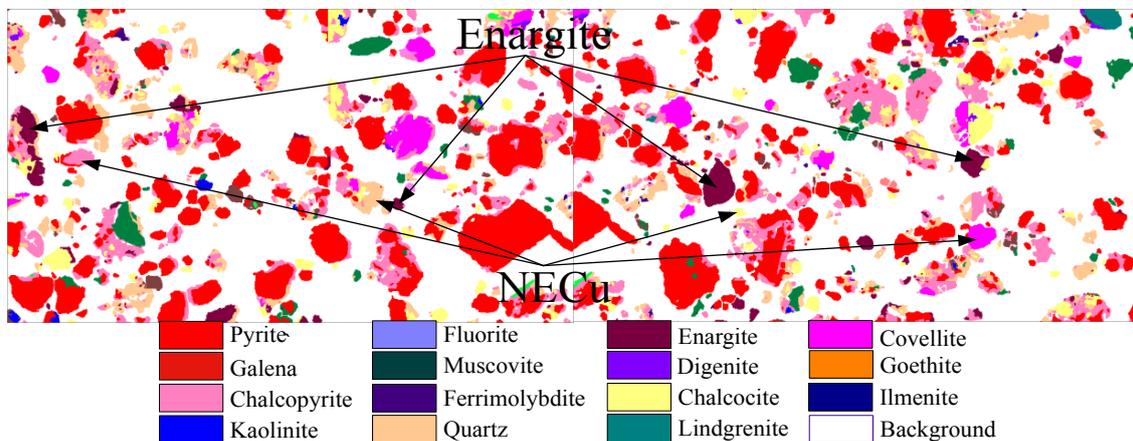
Fig. 4. MLA image of mineral constituents of the copper concentrates
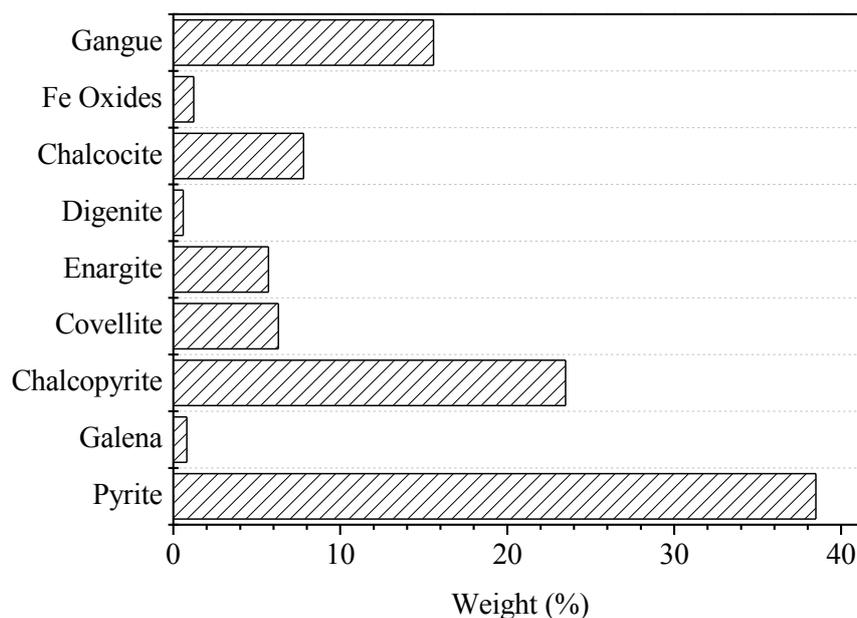
Fig. 5. The minerals weight distribution of the copper concentrate

The mineral liberation and association, as the most basic mineralogical characteristic, greatly affect the separation selectivity. The cumulative curves of the liberation of minerals of interest and the association were summarized in Figs. 6 and 7(a, b). The cumulative liberation has been widely used to report mineral liberation, which has the advantage of facilitating the comparison the liberation degree of minerals (Agorhom et al. 2013; Lastra and Paktunc, 2016). It was observed that pyrite was mostly liberated among these minerals of interest with 36% liberated particles (over 90% surface exposed) and 71% middling liberated (over 60% surface exposed). The majority of unliberated pyrite was associated with NECu (66.4%), while the association of unliberated pyrite with enargite was negligible (1.4%). It is reasonable to assume that the depression of pyrite in flotation circuits would reduce NECu recovery, not causing reduction on the recovery of enargite, which is advantageous to the separation of enargite from NECu minerals. Only 28% of enargite occured as liberated grains, namely a small proportion of enargite that was exposed and ready for flotation. Fig. 7(a) showed 56.7% of the unliberated enargite was associated with NECu, 12.1% associated with pyrite. The significant association of enargite with NECu would be problematic for separating them. NECu minerals were poorly liberated, in particular digenite.

The modal mineralogy reveals the complexity of mineral composition of the copper concentrate in consideration of many kinds of NECu minerals. It is obvious that the separation of enargite from these NECu minerals is more difficult than from a single chalcopyrite. The results of mineral liberation and association data indicate that regrinding of the copper concentrate is necessary for liberating enargite and NECu minerals. It should be mentioned that the depression of pyrite in an alkaline environment may enhance the separation of enargite from NECu minerals.
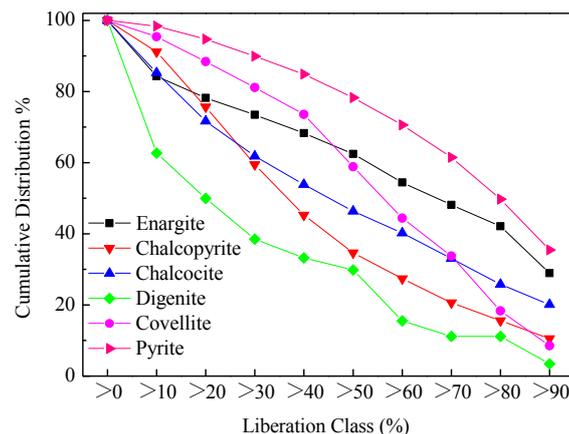
Fig. 6. The cumulative liberation distributions of major minerals of the copper concentrate

3.2. Flotation results

Based on the mineralogical analyses, a series of regrinding tests were performed to examine whether regrinding caused favorable flotation responses for separation of enargite from NECu minerals.

In this study, the complex copper concentrate was reground for 5 and 12 min to obtain the size distribution of 70% passing 38 μm and 80% passing 38 μm respectively, the particle size of regrinding products was seen in Fig. 2. Regrinding of the complex copper concentrate liberated more enargite and weakened the association between enargite and NECu minerals (Fig. 7(c, d)). Recoveries of arsenic and NECu and the separation selectivity calculated as the ratio of arsenic recovery to NECu recovery were used to evaluate the flotation responses. The pulp pH, NaClO concentration, conditioning time and flotation time were respectively fixed at pH 11.6, 0.5% (v/v), 10 min and 4 min except for special statement. The results were shown in Fig. 8(a). The NECu recovery displayed a gradual upward trend after regrinding, which was likely due to that more NECu particles were liberated and then floated. The arsenic recovery was significantly promoted after regrinding 5 min, then decreased slightly after regrinding 12 min. The possible reason for this phenomenon could be moderate regrinding that liberated more enargite particles in medium size which have high floatability, excessive regrinding that generated fine enargite particles which have low floatability. Tayebi-Khorami et al. (2017) also reported enargite is more ground readily than the other copper

sulfide minerals, and reporting to the fine size fractions. The separation selectivity has a similar changing trend to arsenic recovery. There is minor separation selectivity under unregrinding, followed by a large increase with regrinding 5 min and then decreasing after regrinding 12 min.
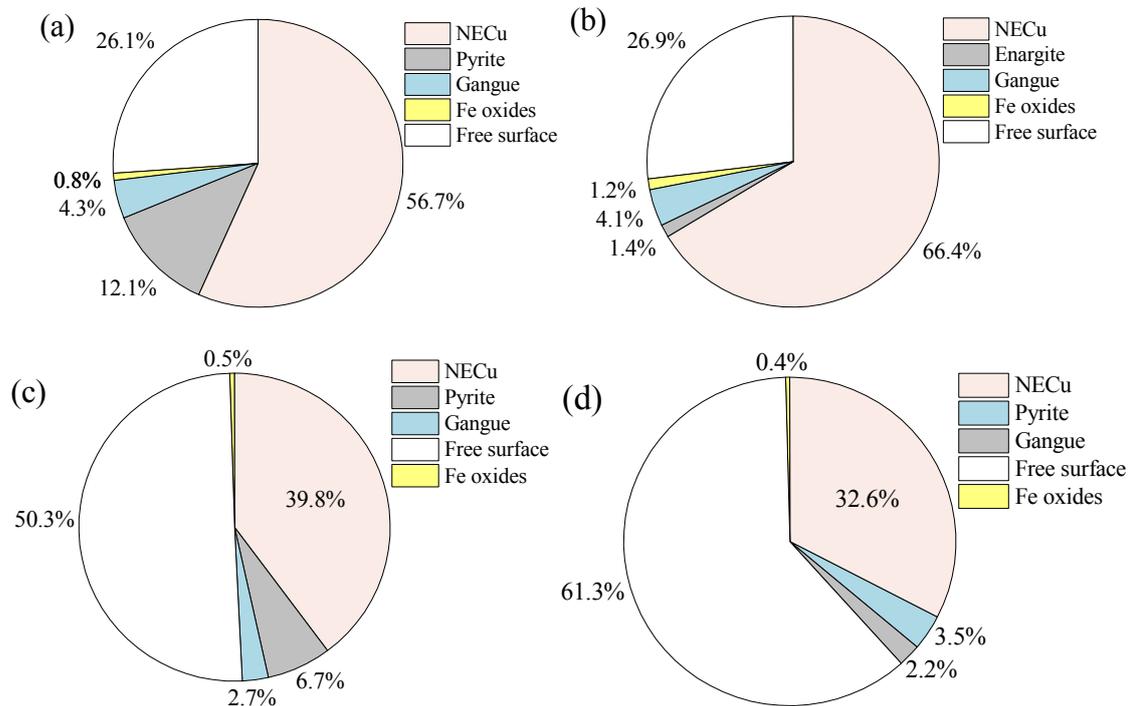
Fig. 7. Mineral association for enargite in the copper concentrate(a) and regrinding products(regrinding 5min (c), 12 min (d)), and for pyrite (b) in the copper concentrate

Control of the pulp pH is essential for the flotation of sulfide minerals. Fig. 8(b) shows that the pulp pH has a significant impact on recovery of both arsenic and NECu. The recovery of arsenic and NECu are quite low, less than 30%, at pH varying from 5.2 to 10.5. The recovery of NECu increased slowly with increasing the pulp pH toward more alkaline conditions. However, the recovery of arsenic increased significantly when the pulp pH reached to 11.6 where the separation selectivity reached to the maximum. Kantar (2002) investigated the floatability of enargite as a function of solution pH in the presence of hydrogen peroxide in a single mineral system. They found the flotability of enargite decreased gradually with increasing the solution pH, which is inconsistent with our finding. This obvious difference could be caused by the influence of large amounts of dissolved ions in a real ore system and galvanic interactions between sulfide minerals. It also reflected that the results obtained from a single mineral system may not be applied well in a real ore system. Besides, Haga et al. (2012) also studied the pulp pH on the flotation behavior of enargite. They reported enargite mineral was easily floated at pH 4 and 11.

The flotation experiments were carried out to study the effect of various concentrations of NaClO on the floatability of enargite and NECu minerals. The results were presented in Fig. 8(c). The recovery of arsenic and NECu was 57.8% and 60.7% respectively without the addition of NaClO, and the value of separation selectivity was only 0.95. The recovery of NECu was dropped dramatically after NaClO oxidation treatment at the concentration of 0.5% (v/v). Further increase of NaClO concentration slightly decreased the recovery of NECu. On the other hand, the recovery of arsenic increased gradually in low NaClO concentrations (< 0.5%) and then decreased in higher NaClO concentrations. It indicates that enargite was also depressed at strongly oxidizing conditions. Plackowski et al. (2014) investigated the surface species formed on enargite surfaces at electrochemically oxidizing conditions by XPS analysis. They reported Cu(II) species of $CuSO_4$ and $Cu(OH)_2$ and As_2O_3 were found on the mineral surface. The depression of enargite at strongly oxidizing conditions may be due to the formation of these hydrophilic species.

Hirajima et al. (2017) reported the conditioning time played an important role in the selective flotation of chalcopyrite from molybdenite with H_2O_2 oxidation. Insufficient conditioning time caused an unsatisfying oxidation of chalcopyrite and a poor separation selectivity of chalcopyrite from molybdenite. Therefore, a series of flotation experiments were performed to determine the appropriate conditioning time. As expected, the recovery of NECu decreased continuously with increasing the conditioning time (Fig. 8(d)). The recovery of arsenic increased slightly with an increase of the conditioning time from 5 min to 10 min. With the conditioning time prolonging to 30 min, however, the recovery of arsenic decreased to 49%. This phenomenon demonstrated the difference of oxidation rate between enargite and NECu minerals. After the oxidation treatment, there are still some NECu minerals that were floated during the flotation process, which revealed that not all of four kinds of NECu minerals were more oxidized than enargite.
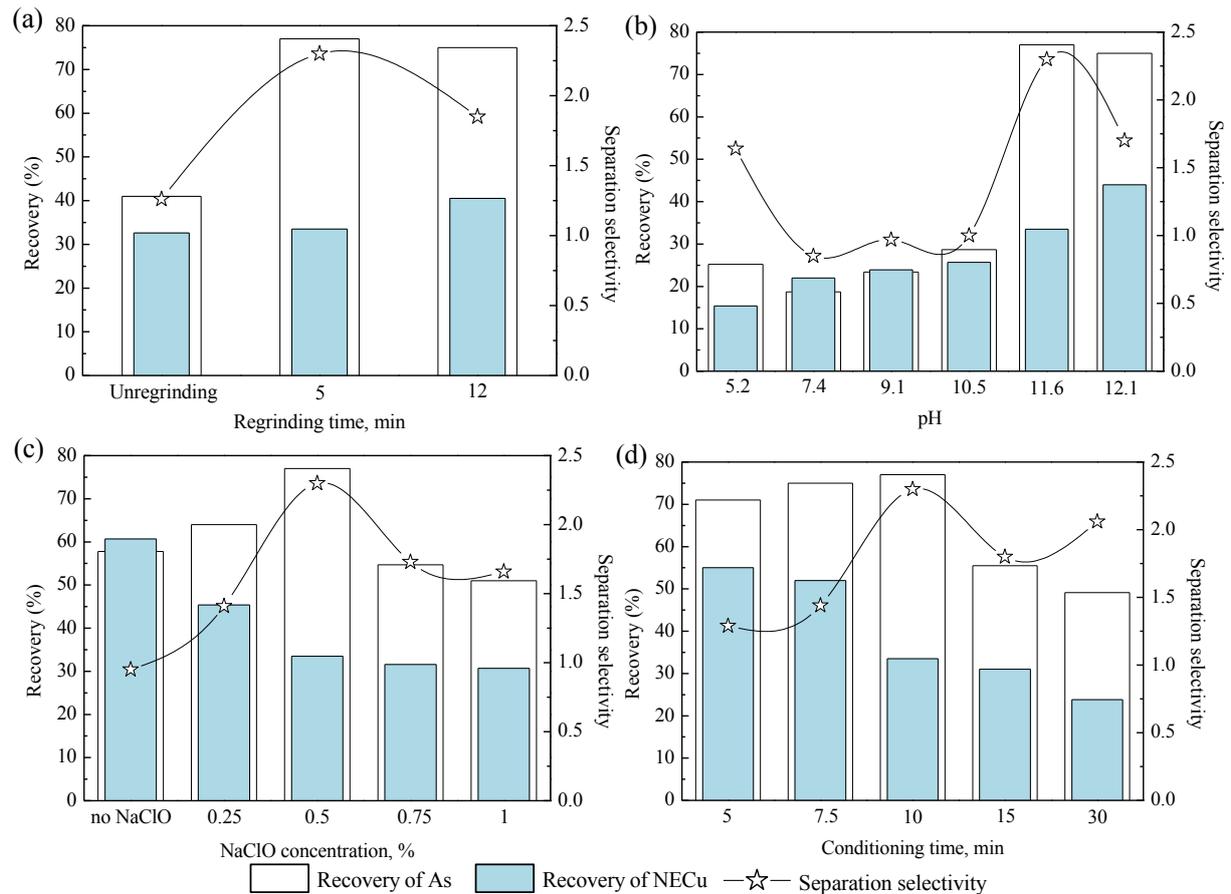
Fig. 8. The effect regrinding (a), pH (b), NaClO concentration (c), conditioning time (d) on separation of enargite from NECu minerals

A flotation recovery of arsenic and NECu curve as a function of flotation time is shown in Fig. 9. Flotation concentrates were collected every 1 min within 5 min of total flotation time to product five individual flotation concentrates. The recovery of arsenic and NECu of each concentrate is presented in Fig. 9. The line at 45° implies no selectivity between arsenic and NECu, while being away from the red line indicating the selective separation of arsenic from NECu. The flotation results in the absence of EDTA showed higher recovery of arsenic is observed at the first minute and second minute (43% for the first minute and 21% for the second minute), followed by a sharp decrease in arsenic recovery in the next 3 min. On the other hand, the value of separation selectivity for arsenic and NECu was respectively 3.5 and 2.3 at first minute and second minute while no selectivity for the next 3 min. The results indicate 2 min of flotation time show a more favorable result for separation of arsenic from NECu.

Ethylene diamine tetra-acetic acid(EDTA) can remove metal sulfides oxidation products and improve the floatability. In the study by Fornasiero et al. (2001) the effect of EDTA treatment on the

separation of chalcocite, covellite or chalcopyrite from enargite in an oxidation system of hydrogen peroxide at pH 11 was investigated. They observed surface oxidation products can be removed from both non-arsenic copper sulfide minerals and enargite resulting in high flotation recoveries at a high EDTA concentration. In the present study, flotation recovery of both NECu and arsenic increased after EDTA treatment indicating that the surface oxidation products were dissolved from both NECu minerals and enargite, which corresponds with the observation of Fornasiero et al. (2001). In addition, the recovery of NECu obviously has a higher increase compared to arsenic after EDTA treatment, which reflects that NECu minerals were more oxidized than enargite in the conditioning stage. Another important observation is that the separation selectivity between enargite and NECu minerals was largely lost after EDTA treatment at the first and second minute, which demonstrates the selective oxidation of NECu minerals in oxidizing conditions.
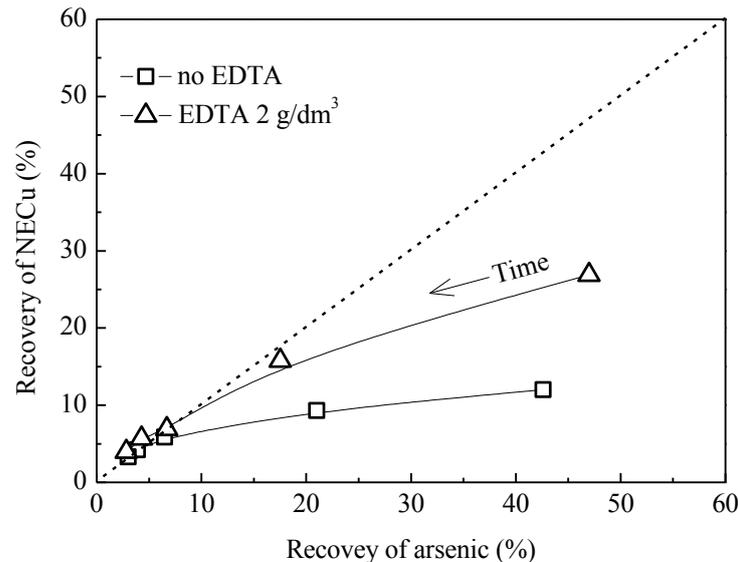
Fig. 9. Flotation recovery of arsenic and NECu as a function of flotation time. Flotation conditions: regrinding 5 min, pH 11.6, 0.5% (v/v) NaClO and conditioning time 10 min

3.3. EDTA extraction

Fig. 10 shows the Em values for Cu, Fe and As determined by EDTA extraction at different treatment stages. The extracted copper originates from surface oxidation products of NECu minerals and enargite, but mainly NECu minerals, while the extracted arsenic originates from only enargite. As for iron, the extraction results are more complex due to the presence of grinding media. It is difficult to determine whether the extracted iron derives from the oxidation of the iron bearing minerals or grinding media oxidation (Rumball and Richmond, 1996). It can be seen that the amount of extracted copper is higher than iron and arsenic. Tayebi-Khorami et al. (2018) reported the similar observation by extracting the arsenic bearing ore in Tampakan deposit. The Em values for Cu, Fe and As indicate that the feed (i.e. the arsenic bearing copper concentrate) is moderately oxidized before and after regrinding and deeply oxidized after conditioning.

There is upward trend in the Em value for copper, indicating NECu minerals were more and more oxidized as the process in Fig. 3 continues. The amount of extracted iron increased through regrinding, which may be due to the oxidation of iron bearing minerals or grinding media in the regrinding circuit. Interestingly, the amount of extracted iron decreased after conditioning. It can be due to the further oxidation of the iron species to the higher level, such as ferrous salts are oxidized to ferric salts which may be insoluble due to adsorption of EDTA rather than dissolution by EDTA.

Enargite oxidation was determined across the total treatment circuit by comparing the Em value of the extracted arsenic. The level of enargite oxidation was low after regrinding, and almost no change after the conditioning stage. It is suggested that enargite is more resistant to oxidized compared to NECu minerals.
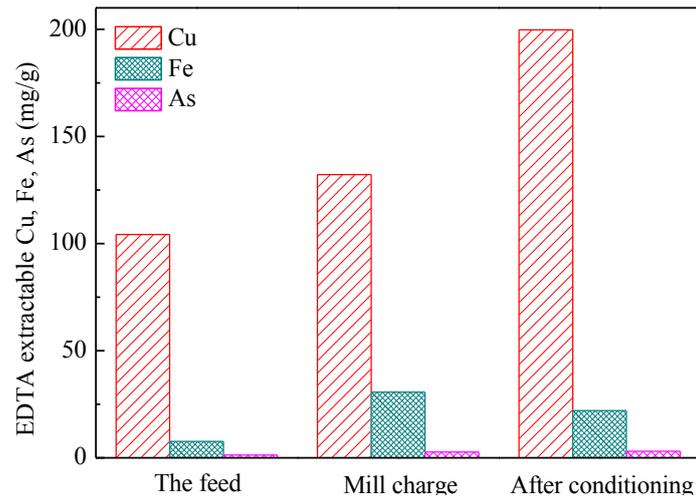
Fig. 10. EDTA extraction results from different treatment stages

3.4. Conceptual flowsheet

Based on the results of this study, a conceptual flowsheet for the separation of enargite from the complex copper concentrate is presented in Fig. 11. Briefly, the process involves the following steps.

- The complex copper concentrate as the feed is reground in a ball mill to liberate enargite and NECu minerals.
- In the rougher flotation for Cu-As separation, the pulp pH is adjusted to 11.6 with lime and the concentration of NaClO is set as 0.5% (v/v). The conditioning time and flotation time depend on the amount of ore used in flotation experiments. Then a high-arsenic copper concentrate and a low-arsenic copper concentrate are produced.
- The NECu minerals need to be further rejected through the cleaner flotation. The final high-arsenic copper concentrate can be treated via hydrometallurgical processing to achieve the transformation of enargite to non-arsenic copper sulfides.
- The low-arsenic copper concentrate is further reground (achieving a size distribution of 83% passing 38 μm) to liberate more enargite to decrease the arsenic grade in the final low-arsenic copper concentrate, which can be directly sent to copper smelter without any penalty.
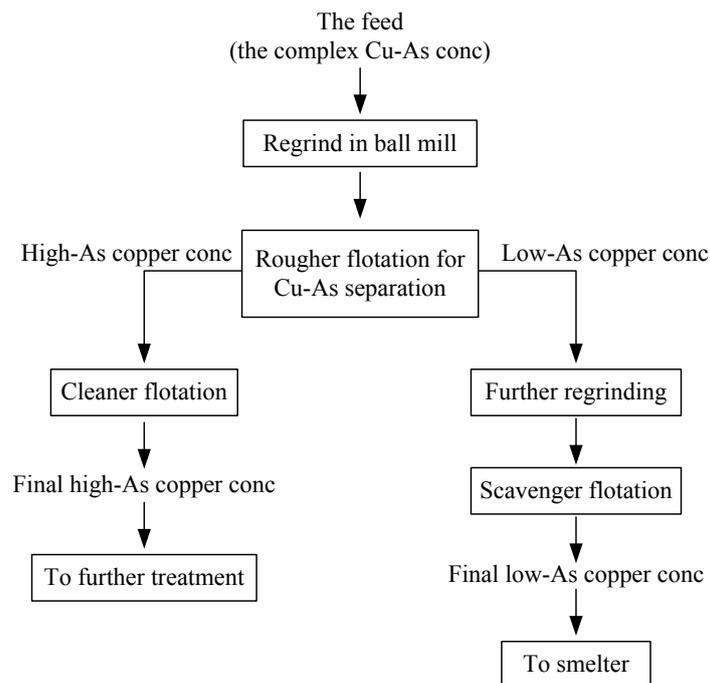
Fig. 11. Proposed conceptual flowsheet for separation enargite from NECu minerals

Following the conceptual flowsheet, a verification flotation experiment for separation enargite from NECu minerals was performed. The MLA images and minerals weight distribution of the final high-As and low-As copper concentrates were presented in Fig. 12. In the low-As copper concentrate, enargite content was decreased to 1.09 wt.% and the grade of arsenic and copper was respectively 0.2 wt.% and 17.4 wt.%. It is also observed that chalcopyrite content was decreased to 3.7 wt.%, and chalcocite and digenite were not presented in the final high-As copper concentrate containing 6.5 wt.% of As and 44.6 wt.% of Cu, which indicates that chalcopyrite, chalcocite and digenite were oxidized and depressed in the flotation circuit. However, the contents of enargite and covellite were respectively increased to 34.2 wt.% and 40 wt.%, which indicates enargite and covellite were not well oxidized and therefore the floatability of enargite and covellite did not decrease. From the analysis of flotation results, we deduce that the oxidation of these minerals follows the order: chalcopyrite (chalcocite, digenite)> enargite (covellite).
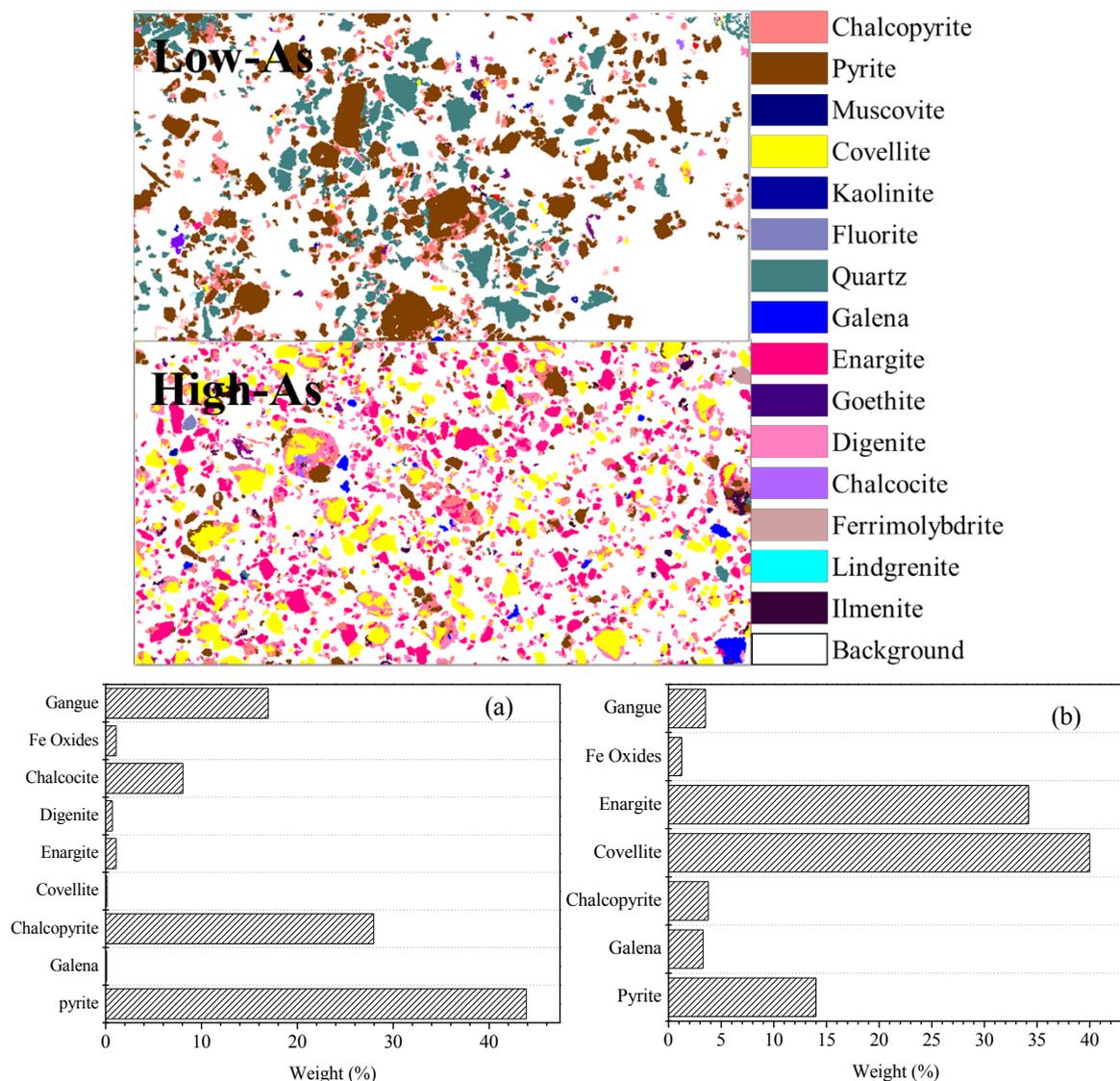
Fig. 12. The MLA images and minerals weight distribution of the final low-As (a) and high-As (b) copper concentrates

4.   Conclusions

This study investigated the separation of enargite from the complex copper concentrate by selective surface oxidation. The main findings in this research can be summarized as follows:

- The mineralogical characteristics of the arsenic–bearing copper concentrate were analysed by MLA. It is found that four kinds of NECu minerals are presented in the copper concentrate, which indicates the difficulty of complete separation of enargite from NECu minerals. The degree of liberation for enargite and NECu minerals is low.
- The flotation experiments demonstrated the selective surface oxidation is a promising treatment to separate enargite from NECu minerals.
- The Em values for Cu, Fe and As indicate that the arsenic bearing copper concentrate is moderately oxidized before and after regrinding and deeply oxidized after conditioning. The possible mechanism for separation of enargite from NECu minerals is that enargite is more resistant to oxidized in compared to NECu minerals. The oxidation of these minerals follows the order: chalcopyrite (chalcocite, digenite)> enargite (covellite).

Acknowledgments

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