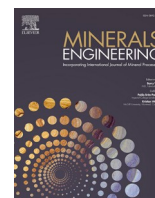# Extraction of copper from complex carbonaceous sulfide ore by direct high-pressure leaching

	Godirilwe Labone Lorraine, Magwaneng Refilwe S., Sagami Riku, Haga Kazutoshi, Batnasan Altansukh, Aoki Shogo, Kawasaki Takashi, Matsuoka Hidekazu, Mitsuhashi Kohei, Kawata Masanobu, Shibayama Atsushi
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Extraction of copper from complex carbonaceous sulfide ore by direct high-pressure leaching

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ABSTRACT

The increase of impurities and complexity of copper ores are among the recent challenges in the mining industry. Complex carbonaceous sulfide ores are extremely difficult to treat due to their mineralogical complexity and impurities of organic carbon and carbonates. This study focuses on the development of a hydrometallurgical process for efficient copper extraction from complex carbonaceous sulfide ore which contains chalcopyrite, carbonates (dolomite and calcite), and carbonaceous gangue minerals. Characterization of the ore sample and leach residues was conducted using XRD and EPMA analysis, while ICP-OES was used for the determination of total dissolved metals in solution. High-pressure leaching of complex carbonaceous sulfide ore in oxygenated sulfuric acid solution was performed and the influence of leaching parameters such as sulfuric acid concentration, temperature, total pressure, and pulp density was studied. The extraction of copper increased with increasing temperature, sulfuric acid concentration, and total pressure. On the other hand, an increase in pulp density resulted in a decline in copper extraction due to an increased slurry viscosity and resistance in the diffusive mass transfer of reactants. Selective dissolution of copper from iron can be achieved by controlling free acidity in the pregnant leach solution (PLS). Under these leaching conditions: 100 g/L, 1 M H_2SO_4, 160 °C, 1.0 MPa total pressure, the highest copper and iron extractions achieved were 97.55% and 95.37%, respectively. Precipitation of copper from the PLS by NaSH sulfidization was investigated and more than 99.9% of copper was recovered at a Cu: NaSH molar ratio of 1:1.8.

1. Introduction

The complex carbonaceous sulfide ore is categorized under the sediment-hosted stratiform copper deposits which account for about 20–25% of the world's copper production and reserves (Hitzman et al., 2005; Misra, 2000). Carbonaceous sulfide ores host polymetallic minerals characterized by carbonates (dolomite, calcite, magnesite, etc.) and carbonaceous materials (inorganic/elemental carbon and organic carbon) (Chimonyo et al., 2020). These deposits often contain substantial mineral grades of economic importance. However, the beneficiation of these deposits is extremely difficult due to their mineralogical complexity and lack of advanced processing technologies (Krausmann et al., 2009; Mudd, 2012; Calvo et al., 2016). In recent years, the depletion and decline of copper ore grades have encouraged the research

and development of beneficiation technologies that can concentrate and recover copper more efficiently from complex ores that contain harmful and high amounts of impurities. Efficient processing of these complex ores is beneficial in sustaining the world's growing demand for copper.

The treatment of primary copper ores by the pyrometallurgical process is responsible for about 80% of the world's copper production (Schlesinger et al., 2011). However, this process has several restrictions to treat other copper sulfide ores with organic and inorganic materials, silica, arsenic, and polymetallic (zinc, lead, cobalt, and PGE) (Liao et al., 2015; Konieczny et al., 2013; Flores et al., 2020). Flotation of carbonaceous sulfide ore is a challenge due to the fine-grained intergrowth of valuable minerals with impurities of organic carbon and carbonates (Liao et al., 2015; Matuska et al., 2018). High reagent consumption has also been associated with gangue minerals present in these complex ores

(Liu et al., 2016; Gredelj et al., 2009). Konieczny et al. (2013) noted that the presence of carbonaceous matter in the ore lowers copper recovery and leads to an increase of impurities such as Pb, As and organic matter in flotation concentrates. Carbon contaminant in copper concentrates results in challenges in the downstream processes and has been reported to cause smelting issues such as thermal imbalances and reduction in strength of sinters, which makes process control difficult (Gupta, 2017). A previous study (Magwaneng et al., 2019) showed that when carbonaceous sulfide ore of 2.08 wt% Cu was processed through flotation, only an average of about 60 % of Cu was recovered, owing to the presence of naturally hydrophobic organic and inorganic carbon in the ore. A separation efficiency of 65.75% was achieved between copper and organic carbon. These marginal results bring the need to further investigate alternative routes to efficiently recover copper from the complex carbonaceous sulfide ore.

Hydrometallurgical processing is widely being explored as an alternative route for metal extraction because of its great potential to process complex and low-grade ores with reduced environmental impact. A few studies have been conducted on the processing of complex sulfide copper ores and carbonaceous copper ores. Liao et al. (2015) studied the calcification roasting methodology on complex polymetallic sulfide copper concentrate. To improve the dissolution efficiency of valuable metals, the sulfide concentrate was roasted in the presence of calcium oxide before leaching using sulfuric acid. The calcification roasting process produced little emission of SO_2 as 97% of sulfur was retained as calcium sulfate. Liu et al. (2012) investigated the leaching kinetics of copper from low-grade copper ore containing calcium-magnesium carbonate in an ammoniacal leaching medium. When leaching carbonaceous ore, an ammoniacal leaching medium is occasionally preferred over an acid medium because it does not react with carbonates and siliceous gangue in the ore. Chmielewski et al. (2009) also utilized an ammoniacal leaching medium when investigating pressure leaching of a shale-enriched material. However, the disadvantages associated with the use of ammonia include various health and environmental concerns, operational issues such as the limitation of ammonia reuse, its volatility at high temperatures, and the limited Eh-pH stability fields of its metal complexes. (Eksteen et al., 2017) Another leaching method that is widely considered is bioleaching, when the bioleaching method was used with *Acidianus brierleyi*, the presence of carbonaceous matter was found to enhance the bioleaching of copper from chalcopyrite concentrates (Konadu et al., 2020). However, Kostudis et al. (2015) illustrated that bioleaching using acidophilic bacteria at pH values below 4 is greatly impeded by the high acid consumption of the abundant carbonate content in the copper ore. Nonetheless, when using heterotrophic microorganisms and glutamic acid in neutral conditions as a possible alternative to recover copper from Kupferschiefer, low copper recoveries up to 44 % were still obtained. The heap bioleaching method has successfully been applied on the polymetallic black schist ore originating from Terrafame, Finland and numerous studies have been conducted on the ore. Riekkola-Vanhanen (2013) and Arpalahti and Lundström (2018) found that the black schist ore leach according to electrochemistry, however, chalcopyrite leaching from the ore behaved differently, resulting in low copper recoveries. Bhatti et al. (2012) also found relatively low copper recovery compared to other metals, when the black schist ore sample was subjected to chemical and bacterial leaching and attributed it to chalcopyrite passivation.

Numerous research has been conducted on the Lubin copper deposit which is regarded as the most complex and hardest-to-treat ores, mined, and beneficiated at KGHM (Lubin Plant) in Poland (Matuska et al., 2018; Konieczny et al., 2013; Chmielewski et al., 2009; Chmielewski et al., 2011; Muszer et al., 2013; Chmielewski, 2015). The Lubin copper deposit is characterized by the presence of carbonate gangue and a highly complex mineralogical composition (Muszer et al., 2013; Chmielewski, 2015). Matuska et al. (2018) applied direct pressure leaching on the complex copper sulfide concentrate from Lubin Concentrator (ZWR Lubin) with oxygenated aqueous H_2SO_4 solutions and achieved Cu

extraction of 96% after 4 hrs. Atmospheric leaching was considered as one of the affordable ways to process Lubin ores, but to achieve high metal recoveries, prolonged leaching time of at least 7 hrs in oxygenated sulfuric acid and ferric ions solution was necessary (Chmielewski et al., 2011). Similarly, Muszer et al. (2013) studied pressure leaching of copper concentrate produced by Lubin Concentrator in oxygenated sulphuric acid solutions, where the major copper sulfides (chalcopyrite, bornite, and chalcocite) underwent phase conversion to covellite (CuS), which was easier to leach and allowed the transport of the leaching medium to other metals disseminated in the mineral phase.

One of the options to recover copper from the pregnant leach solution is by precipitation using sulfide reagents such as sodium hydrosulfide (NaSH), sodium sulfide (Na_2S), or hydrogen sulfide (H_2S). Sulfide precipitation is known to have good selectivity for metal removal, fast reaction rates, and low solubility of the precipitated metal sulfide (Lewis, 2010; Deng et al., 2019). The copper sulfide precipitate produced can subsequently be recovered through smelting. Therefore, sulfide precipitation offers a great potential to treat pregnant leach solutions obtained after leaching complex sulfide ores. Industrial processes such as the PLATSOL^TM, SART, and Terrafame processes are known to incorporate sulfide precipitation in their circuits. Several studies (Eksteen et al., 2017; Lewis, 2010; Wang et al., 2014) have successively utilized the sulfide precipitation method to recover copper from solution. Wang et al. (Wang et al., 2014) selectively precipitated 100% of Cu over Fe and Zn from the AMD sample by adding more than 20 mg/L of NaSH directly into the AMD sample. Aracena et al. (Aracena et al., 2019) utilized the NaSH precipitation method to efficiently precipitate 99.0% of copper from pregnant solution produced by ammoniacal leaching, to produce high purity chalcanthite hydrate ($CuSO_4 \cdot 5H_2O$), while Eksteen et al. (Eksteen et al., 2017) added NaSH powder to the pregnant liquor at a Cu: S^{2-} molar ratio of 1: 1 and successively recovered 99.1% of copper as CuS precipitate from glycine solution.

This study focuses on the application of a direct high-pressure leaching system for efficient dissolution of copper from complex carbonaceous sulfide ore which contains chalcopyrite, carbonates, and organic carbon. The oxidative pressure leaching method is effective in providing intensive leaching of finely disseminated copper sulfides from the carbonate-organic matrix, in a short leaching time, as well as providing the possibility of arsenic stabilization as a solid residue. Sulfuric acid which is readily available from existing pyrometallurgical plants is used as a leaching medium. The effect of other key parameters such as temperature, total pressure, and pulp density on copper leaching efficiency was evaluated. The separation efficiency of copper and iron is highly considered in this process, because of the known codissolution of copper and iron in acidic media and the subsequent challenges caused by iron contamination in the downstream processes. To selectively precipitate copper over iron and other dissolved impurities from the leachate, sodium hydrosulfide (NaSH) sulfidization method was used. The outcome of this research will contribute valuable insight into the leaching of complex carbonaceous sulfide ore which contains a substantial amount of copper.

2. Material and methods

2.1. Material

A copper ore sample from Southeast Asia was used in the leaching experiments. The chemical composition of the ore is indicated in Table 1. The sample was dissolved in aqua regia, and chemical analysis was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine the metal content. The sulfur content was determined by the ion chromatography method. Organic carbon was determined by the deduction method after the measurement of total carbon and inorganic carbon. Total carbon was determined by oxidatively decomposing the ore sample in a pyrolysis reactor of an electric furnace at 1000 °C with pure oxygen injection of 300 ml/min.

Table 1

Chemical composition of the complex carbonaceous sulfide ore.

Element	Al	Ca	Cu	Fe	Mg	SiO_2	S	As	Org. C	Inorg. C
Grade (wt.%)	4.55	12.16	2.08	5.37	3.91	24.60	1.92	41 ppm	0.98	4.55

The amount of carbon dioxide generated and absorbed was used to calculate the total amount of carbon in the sample. Inorganic carbon was measured by acidification of the ore sample with hydrochloric acid in the presence of nitrogen gas flow in a rubber stoppered flask fitted with an absorption apparatus. The amount of carbon dioxide absorbed was used to calculate the total inorganic carbon. Other elemental components were determined using X-ray fluorescence spectrometry (XRF) (Cu Kα, Ni filters). Mineralogical analysis of the ore was performed using an X-ray diffractometer (XRD, Rigaku RINT 2200 V) and the results are shown in Fig. 1. The main gangue minerals observed were quartz (SiO_2), dolomite ($CaMg(CO_3)_2$), and calcite ($CaCO_3$).

2.2. Experimental procedure

2.2.1. High-Pressure leaching

Leaching experiments were carried out in a stainless-steel autoclave (Nitto Koastu, Japan) equipped with a Teflon vessel (200 ml), heating mantle, temperature controller, and a variable speed stirrer (Fig. 2). The slurry samples were prepared by mixing 5 – 20 g of the ore sample with 50 ml of sulfuric acid solution (0.2 – 1 mol/L) to achieve different pulp densities. The optimum particle size of −106 μm was used throughout the experiments. The autoclave system, enclosing the slurry sample was heated to the desired set temperature (100 – 180 °C). Once the intended temperature was reached, oxygen (O_2) gas was injected into the slurry vessel at a controlled total pressure ($P_{total} = P_{vapor} + P_{oxygen}$) of 0.5 – 2.0 MPa. The stirring speed was kept constant at 750 rpm. The solution pH and Eh were measured before and after experiments using TPS WP-80 pH/ORP meter with double junction Ag/AgCl/ saturated KCl probe. After the set reaction time, the autoclave system was cooled, and the obtained slurry solution was filtered. The copper and iron concentrations in the PLS were determined using ICP-OES. Solid residues were dried overnight in an oven (60 °C) and analyzed by XRD. Additionally, the mineralogical transformation of the solid residues was studied by an electron probe micro-analyzer (EPMA) using JEOL-JXA-8230. The leaching tests were repeated three times.
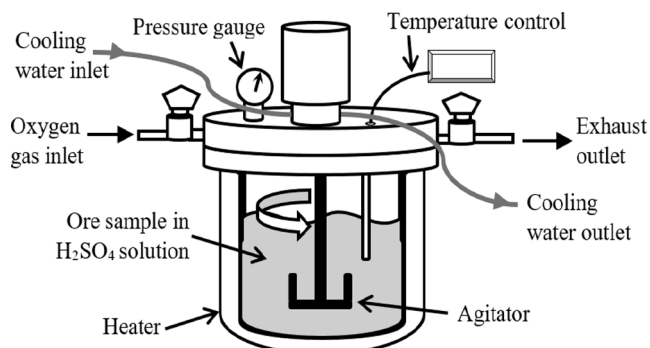

Fig. 2. Illustrative setup of an autoclave for high-pressure oxidative acid leaching.

2.2.2. Determination of free acidity

The free acidity of the PLS solution was determined by direct titration to a pre-determined pH point, in the absence of a complexing agent. The analyte solution was prepared using distilled water and 0.1 mol/L sulfuric acid solution to attain a pH of 3.0. The analyte solution was set over a magnetic stirring unit with a pH meter mounted into the solution. Exactly 1.0 ml of the PLS was added to the analyte. The starting point of the burette containing 0.05 mol/L sodium carbonate (Na_2CO_3) was noted. Titration was then carried out by adding the Na_2CO_3 solution into the analyte up to the pre-determined endpoint of the initial pH (3.0). The final burette reading was recorded to determine the total volume of Na_2CO_3 solution added. The titration tests were run three times and the average values were used to calculate free acidity. Free acidity was determined by utilizing the reaction of 1 mol of Na_2CO_3 with 1 mol of H_2SO_4 (equation 1) and free acidity in 1.0 ml of PLS was calculated by equation 2.

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + H_2O + CO_2 \tag{1}$$
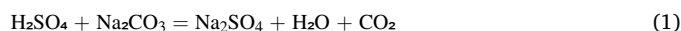
$$\text{Free acidity [FA] (g/L)} = Na_2CO_3 \text{ (ml)} \times 98.08 \ H_2SO_4 \text{ (g/mol)} \times 0.05 \text{ (mol/L)} \ Na_2CO_3 \tag{2}$$
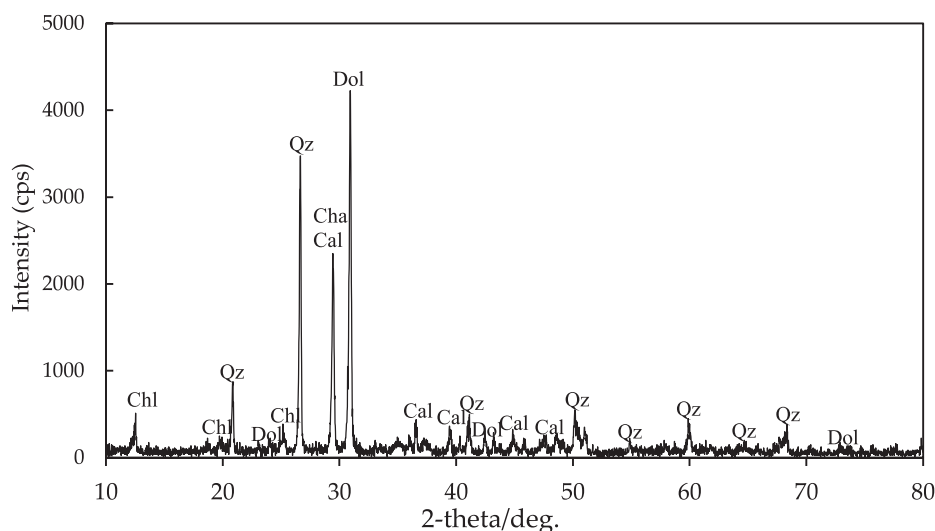
Fig. 1. The results of XRD analysis of complex carbonaceous sulfide ore. **Dol**: Dolomite ($CaMg(CO_3)_2$), **Cal**: Calcite ($CaCO_3$), **Chl**: Chlorite (($MgFeAlSi)O_{10}(OH)_8$), **Qz**: Quartz (SiO_2), **Cha**: Chalcopyrite($CuFeS_2$).

2.2.3. Precipitation of copper by NaSH sulfidization

Precipitation tests by NaSH sulfidization were conducted in 5 ml centrifugal tubes using a high-speed mixer (Eyela, CM-1000). A NaSH solution of 0.1 mol/L was prepared and dosed in relation to the total moles of copper in the pregnant leach solution. The precipitation tests were conducted at room temperature with a fixed shaking speed of 800 rpm. The effects of Cu:NaSH molar ratio (1:1, 1:1.2, 1:1.4, 1:1.6, 1:1.8 and 1:2) and shaking time (1, 5 and 10 min) were investigated. The concentrations of Cu and Fe in the residual solution were determined using ICP-OES. The precipitates were filtered and dried before XRD analysis was performed to characterize the sulfide precipitate generated. The pH and oxidation–reduction potential (ORP) were measured before and after precipitation tests. The precipitation tests were repeated three times.

3. Results and discussion

3.1. High-Pressure leaching

3.1.1. Effect of sulfuric acid (H₂SO₄) concentration

The effect of H_2SO_4 concentration on the leaching behavior of copper and iron is shown in Fig. 3, which shows that the extraction of metals generally increases as the H_2SO_4 concentration is increased. Thus, showing that sulfuric acid concentration has a significant role in the extraction of copper from the complex carbonaceous sulfide ore. Other studies of similar mineralogical components also showed that an increase in acid concentration yielded a positive effect on the leaching of chalcopyrite (Cerda et al., 2017; Chetty, 2018; Dávila-Pulido and Uribe-Salas, 2014; Ntengwe, 2010). Fig. 3 shows that Cu was selectively leached over Fe at a sulfuric acid concentration of 0.6 mol/L, but as the sulfuric acid concentration further increased, the extraction of Fe increased sharply, minimizing the copper/iron selectivity. The key observation at this condition was hydrolysis of ferric iron into jarosite which was separated with the solid residue (Fig. 4). The highest copper and iron extraction percentages achieved were 97.55% and 95.37% respectively at a sulfuric acid concentration of 1.0 mol/L. The mean standard error for Cu and Fe extractions was estimated to be 2.7% and 3.5%, respectively. The Cu and Fe concentration in the pregnant leach solution was 2.43 g/L and 5.35 g/L respectively. Despite the appreciable amount of iron dissolved at 1.0 mol/L H_2SO_4, the direct leaching of copper in complex carbonaceous sulfide ore is still a viable option because of the high copper dissolution of 97.55%. Therefore, 1.0 mol/L
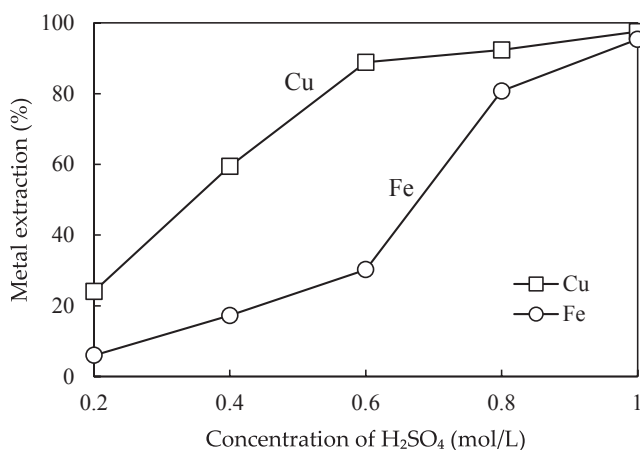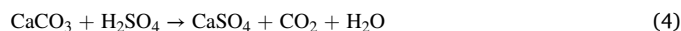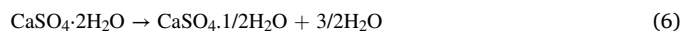
H_2SO_4 was used for the subsequent leaching experiments.

Table 2 shows the change in slurry pH before and after leaching with respect to the different sulfuric acid concentrations. For all the investigated sulfuric acid concentrations, the slurry pH increased after the leaching tests. This indicates that the consumption of sulfuric acid is necessary for the reactions of chalcopyrite and carbonate minerals (calcite, dolomite) as in Eqs. (3)–(5).

$$4CuFeS_2 + 17O_2 + 2H_2SO_4 \rightarrow 4CuSO_4 + 2Fe_2(SO_4)_3 + 2H_2O \quad (3)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \quad (4)$$

$$CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow CaSO_4 + MgSO_4 + 2CO_2 + 2H_2O \quad (5)$$

The XRD analysis was done on the leach residues obtained after leaching tests of different H_2SO_4 concentrations (Fig. 4). The intensity of quartz peaks remained unaltered in all the leach residues. The diffraction peaks of bassanite ($CaSO_4.1/2H_2O$) were observed in leach residues of 0.2 – 0.4 mol/L H_2SO_4 tests. Bassanite is usually formed when gypsum ($CaSO_4 \cdot 2H_2O$) is transformed through energy-intensive dehydration (equation 6). At higher H_2SO_4 concentrations (0.6 – 1.0 mol/L), the main component in the leach residues was calcium sulfate ($CaSO_4$) generated by equations 4 and 5. Hydronium jarosite ($H_3O(Fe_3(SO_4)_2(OH)_6)$) peaks were only noted in residue samples of 0.6 and 0.8 mol/L H_2SO_4 concentrations. Equation 7 shows the formation of hydronium jarosite through hydrolysis of the ferric sulfate.

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4.1/2H_2O + 3/2H_2O \quad (6)$$

$$3Fe_2(SO_4)_3 + 14H_2O \rightarrow 2H_3O(Fe_3(SO_4)_2(OH)_6) + 5H_2SO_4 \quad (7)$$
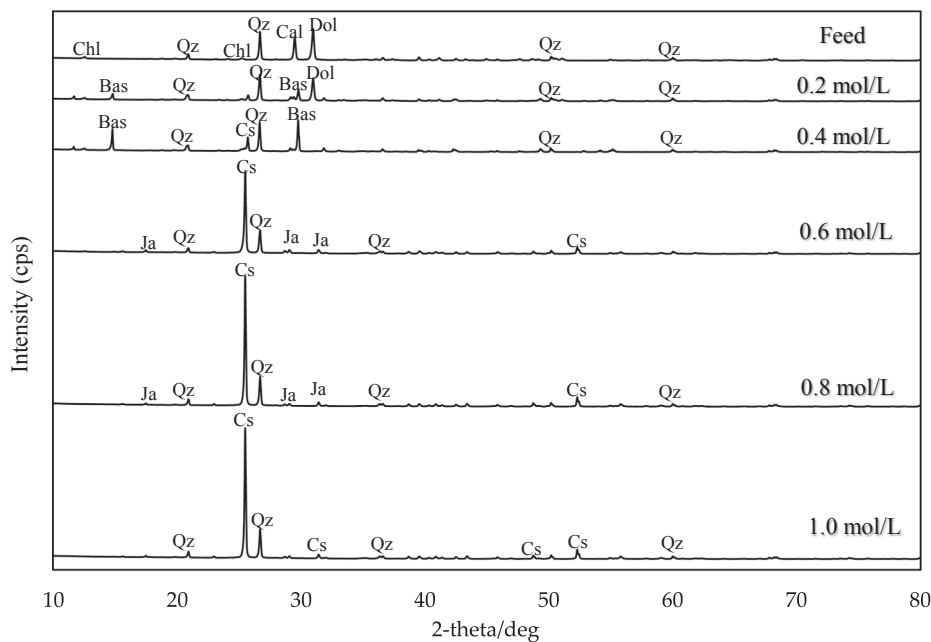
3.1.2. Effect of pressure

The influence of total pressure on copper dissolution from complex carbonaceous sulfide ore was studied by varying the total pressure between 0.5 (without oxygen supply) to 2.0 MPa (with oxygen supply). Other parameters were kept constant at stirring speed 750 rpm, temperature 160 °C, particle size −106 μm, pulp density 100 g/L, and H_2SO_4 concentration of 1.0 mol/L. It is evident in Fig. 5 that an increase in total pressure results in a significant increase in the extraction of copper. Oxygen plays a significant role in the leaching of chalcopyrite as a direct oxidizing agent (Eq. (3)) (Antonijević et al., 2004; Córdoba et al., 2009; Dutrizac, 1994). This is demonstrated by a sharp increase in copper leaching percentage from 10.55% without oxygen supply (0.5 MPa) to more than 90% with oxygen supply (1.0 MPa). However, a further increase in the total pressure from 1.0 MPa to 2.0 MPa, did not show any significant improvement in the dissolution of copper.

Fig. 5 also reveals the difference in the leaching behavior of iron and copper. Iron dissolution from the carbonaceous sulfide ore was not hindered by the lack of oxygen supply (0.5 MPa), reaching a high of 96.72% while Cu dissolution was highly dependent on oxygen, and remained low (10.55%) in the absence of oxygen. The mean standard error for Cu and Fe extractions was estimated to be 2.4% and 3.4%, respectively. Likely, other iron-bearing minerals in the ore, other than chalcopyrite, such as chlorite ($(MgFeAlSi)O_{10}(OH)_8$) dissolved and thus increased solely the extraction of iron. This is supported by the disappearance of chlorite diffraction peaks in Fig. 6 under the total pressure of 0.5 MPa, indicating its dissolution in the leachate. The slight copper dissolution in the absence of an oxidizing reagent is likely by Eq. (8) (Nicol et al., 2010).

$$CuFeS_2 + 2H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2H_2S \quad (8)$$
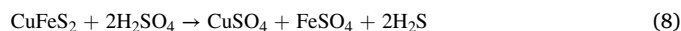
The XRD analysis of the solid residues formed under leaching at different total pressure conditions is shown in Fig. 6. In all the investigated conditions (non-oxidative and oxidative), no diffraction peaks of dolomite and calcite were observed, indicating their dissolution and re-precipitation as calcium sulfate via Eqs. (4) and (5).


Fig. 3. Effect of sulfuric acid concentration on the copper and iron extraction behaviors. (Conditions: −106 μm p.s., 100 g/L p.d., 60 min, 750 rpm, 160 °C, 1.0 MPa t.p.). Where, p.s. = particle size, p.d. = pulp density, and t.p. = total pressure.

Fig. 4. The XRD patterns of solid residues at different H_2SO_4 concentrations (Conditions: –106 μm p.s., 100 g/L p.d., 60 min, 750 rpm, 160 °C, 1.0 MPa total pressure). **Qz**: Quartz, **Cal**: Calcite, **Dol**: Dolomite, **Chl**: Chlorite, **Bas**: Bassanite, ($CaSO_4.1/2H_2O$), **Cs**: Anhydrite/ Calcium Sulfate, ($CaSO_4$), **Ja**: Jarosite, ($H_3O(Fe_3(SO_4)_2(OH)_6)$).

Table 2
Change in slurry pH before and after leaching.

H_2SO_4 concentrationmol/L	Slurry pH before leaching	after leaching
0.2	0.81	5.79
0.4	0.63	1.68
0.6	0.44	0.85
0.8	0.27	1
1	0.13	0.42
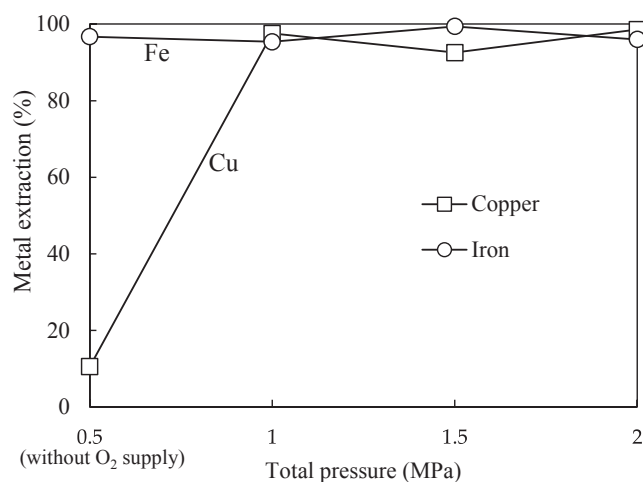
Fig. 5. Effect of total pressure on copper and iron extraction behaviors. (Conditions: 1.0 mol/L H_2SO_4, –106 μm p.s., 100 g/L p.d., 60 min, 750 rpm, 160 °C).

3.1.3. Effect of temperature

The effect of temperature on the conversion of copper and iron was investigated at different temperatures (100–180 °C) and the results are shown in Fig. 7. An increase in temperature increased copper and iron dissolutions simultaneously. At 180 °C, the highest copper extraction of 98.26% was obtained, with Fe extraction of 94.1%. The mean standard error for Cu and Fe extractions was estimated to be 1.4% and 1.5%, respectively. The significant role of temperature on the metals leaching efficiency is attributed to the promoted acceleration of the thermal motion of molecules and the increased surface contact between single particles because of increased kinetic energy from heating (Liao et al., 2015).

A gradual increase in copper extraction was noted when the temperature was increased from 100 to 160 °C, during which a temperature increase of 20 °C, accordingly yielded an increase of about 20% in copper extraction. However, a further increase in temperature to 180 °C, did not yield a significant improvement in copper dissolution. This clearly shows that the leaching of chalcopyrite at early stages (from 100 to 160 °C) is highly dependent on temperature, which Matuska et al. (2018) attributed to the gradual solid conversion of chalcopyrite as it is transformed to covellite before leaching can occur, noting that at higher temperatures, this conversion is significantly faster. McDonald and Muir (2007a, 2007b) also confirmed that at higher temperatures, the sulfide content is entirely converted to sulfate resulting in higher leaching rates. At lower temperatures (100 °C), the extraction of iron seems to be prevalent than that of copper because of the rapid dissolution tendencies of iron (Qiu et al., 2007). Other similar studies affirmed that increasing the reaction temperature can increase the dissolution efficiency of metals during leaching (Chen et al., 2014; Choubey et al., 2018; Gok et al., 2013; Han et al., 2017; Hidalgo et al., 2018; Lampinen et al., 2015; Mojtahedi et al., 2020).

3.1.4. Effect of pulp density

To observe the effect of pulp density on the copper and iron extraction, leaching experiments were performed with pulp densities ranging from 100 to 400 g/L under the conditions of –106 μm particle size, 1.0 mol/L H_2SO_4 concentration, 1.0 MPa total pressure, 160 °C, and stirring speed of 750 rpm. The results plotted in Fig. 8 show that the copper and iron extractions significantly decreased with an increase in pulp density. The highest copper and iron extractions of 97.55% and 95.37% were obtained with a pulp density of 100 g/L respectively. The mean standard error for Cu and Fe extractions was estimated to be 1.4% and 1.6%, respectively.

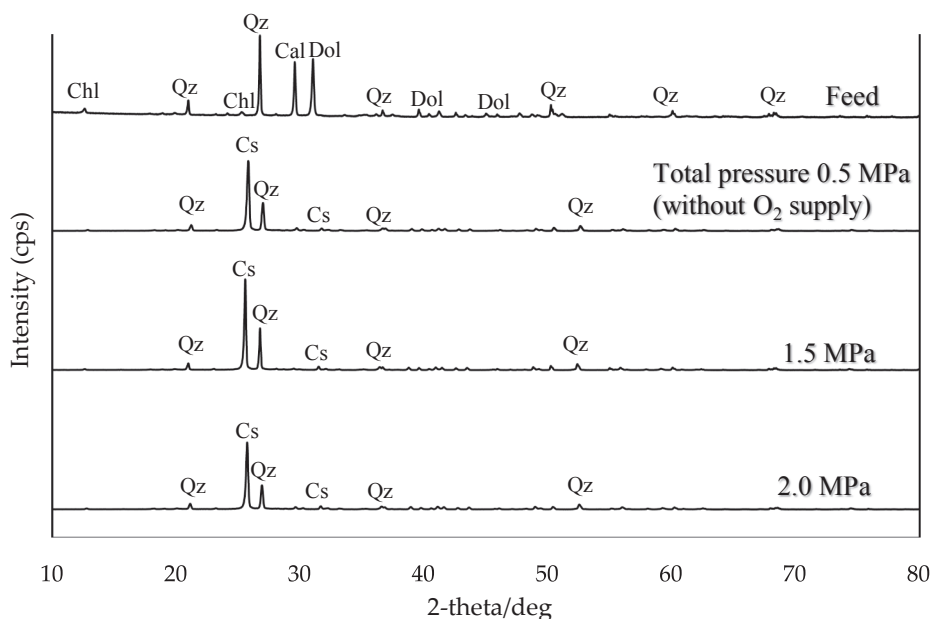A good leaching selectivity of copper over iron was observed at a

Fig. 6. The XRD patterns of the feed and solid residues obtained at different total pressure leaching conditions (1.0 mol/L H_2SO_4, –106 μm p.s., 100 g/L p.d., 60 min, 750 rpm, 160 °C). **Qz**: Quartz, **Cal**: Calcite, **Dol**: Dolomite, **Cs**: Anhydrite/ Calcium Sulfate, **Chl**: Chlorite.
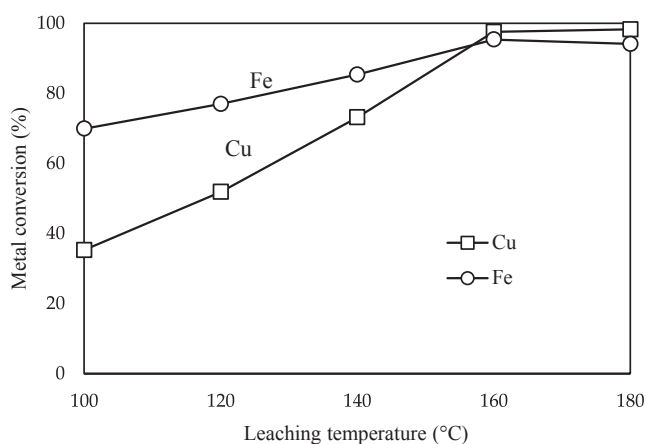

Fig. 7. Effect of temperature on the leaching of copper and iron from complex carbonaceous sulfide ore (Conditions: 1.0 mol/L H_2SO_4, –106 μm p.s., 100 g/L p.d., 60 min, 750 rpm, 1.0 MPa t.p.).

Fig. 8. Effect of pulp density on the leaching of copper and iron from complex carbonaceous sulfide ore (Conditions: 1.0 mol/L H_2SO_4, –106 μm p.s., 160 °C, 60 min, 750 rpm, 1.0 MPa total pressure).

pulp density of 200 g/L. With a further increase in pulp density (300 – 400 g/L), the extractions of copper and iron were significantly reduced to less than 1%. The results suggest that a high pulp density increases the slurry viscosity and hinders the well mixing of reactants, so due to high resistance in diffusive mass transfer, the metal leaching rate is negatively affected (Rao et al., 2015). At an increased pulp density, the amount of reactant may be insufficient to achieve high metal extractions, this is further investigated and shown in Fig. 10.

Fig. 9 shows the XRD patterns of the feed and solid residues obtained after leaching at different pulp densities. The presence of quartz is common in all the solid residues, while at lower pulp densities (100 – 200 g/L) the dominating species is calcium sulfate ($CaSO_4$) which may have formed via equations 4 and 5.

At pulp densities of 300 and 400 g/L, undissolved calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) were noted, new peaks of wollastonite ($Ca_3Si_3O_9$) were also observed at these pulp densities. At 200 g/L pulp density, hydronium jarosite was observed in the leach residue sample. The precipitation of iron as hydronium jarosite (equation 7) resulted in a good separation efficiency of copper and iron as observed in Fig. 8. The
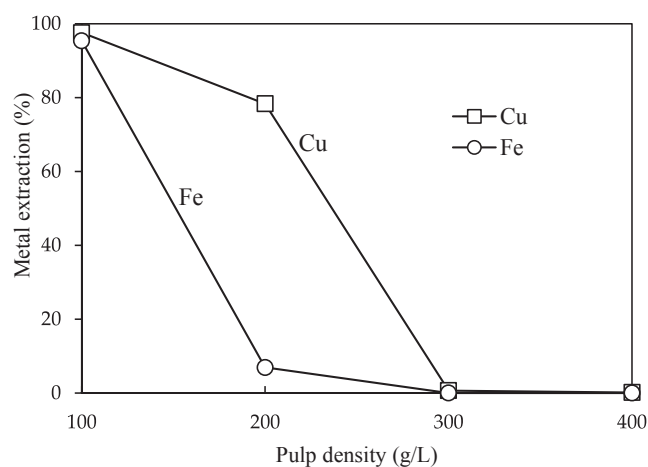
obtained residues such as quartz, calcium sulfate, and calcite have elevated pH values and therefore are environmentally stable. The carbonate minerals such as calcite have been utilized as a neutralizing agent in acidified AMD water environments, thus providing environmental sustainability (Sasaki et al., 2013; Olds et al., 2013). Jarosite has also been found to play an important role in the removal of trace elements from acidic AMD waters by adsorption and co-precipitation and thus can be used as an adsorbent (Asta et al., 2009; Johnston et al., 2012).

A high pulp density is important as it allows a high metal concentration in the PLS that is efficient for further upgrade processes such as solvent extraction. Fig. 10 shows the change in metal extractions as the H_2SO_4 concentration was increased from 1.0 mol/L to 3.0 mol/L utilizing a slurry sample of 300 g/L pulp density. The highest percentage of copper leached was 70.2% at an H_2SO_4 concentration of 1.5 mol/L. A further increase in sulfuric acid concentration did not improve the dissolution of copper but maintained an extraction percentage of around 60%. Iron dissolution increased with increasing sulfuric acid concentration, achieving a high of 86% at an acid concentration of 3.0 mol/L.
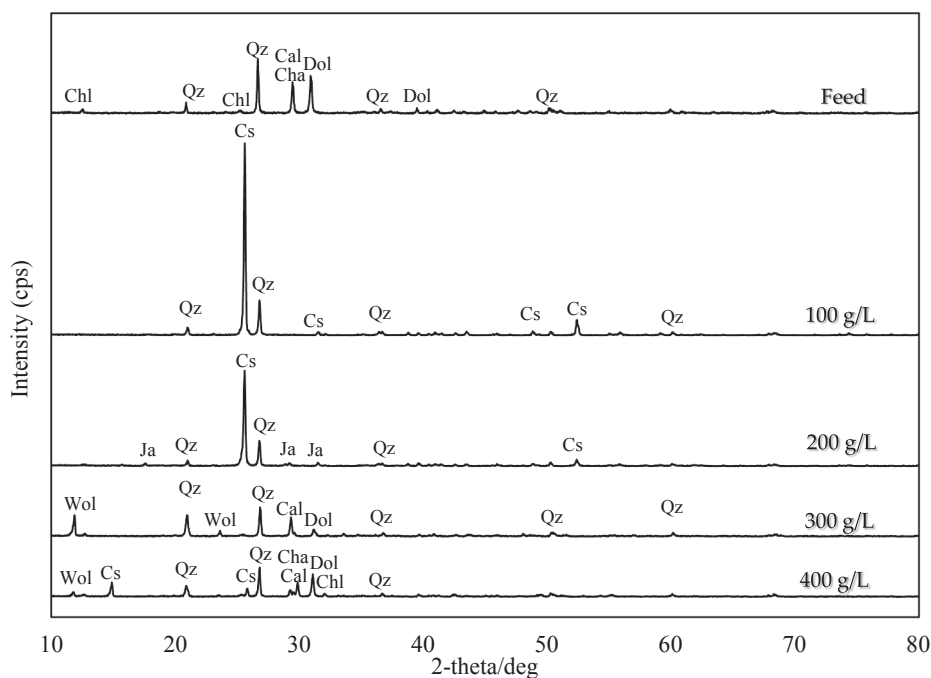
Fig. 9. XRD patterns of the feed and solid residues obtained after leaching at different pulp densities (Conditions: 1.0 mol/L H_2SO_4, −106 μm p.s., 160 °C, 60 min, 750 rpm, 1.0 MPa total pressure). **Qz:** Quartz, **Cha:** Chalcopyrite, **Wol:** Wollastonite ($Ca_3Si_3O_9$), **Cal:** Calcite, **Dol:** Dolomite, **Cs:** Calcium sulfate, **Chl:** Chlorite, **Ja:** Jarosite.
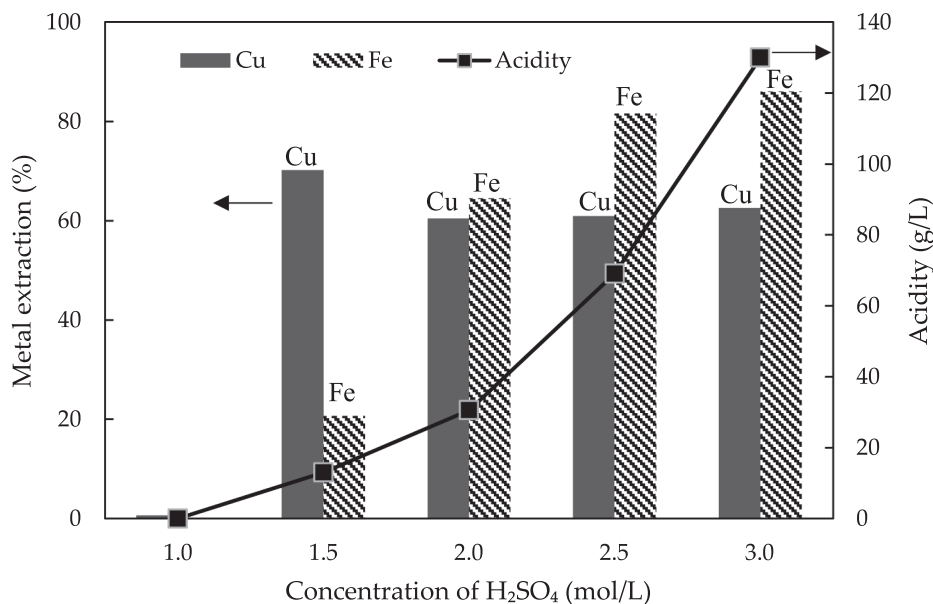
Fig. 10. Effect of H_2SO_4 concentration on copper and iron extraction behaviors. (Conditions: 300 g/L p.d., 60 min, 750 rpm, 160 °C, 1.0 MPa t.p.).

Fig. 10 also shows that as the sulfuric acid concentration was increased, the residual acidity in the PLS also increased, but the extraction of copper did not improve. Therefore, the decrease in copper extraction as the pulp density is increased is not attributed to the insufficient amount of sulfuric acid required for leaching.

Change in slurry pH before and after leaching of the slurry sample of 300 g/L pulp density as well as the metal concentration in the pregnant leach solution is displayed in Table 3. When the H_2SO_4 concentration was 1.0 mol/L, the slurry pH changed from an acidic pH of −0.05 to a neutral pH of 6.40, while the copper and iron dissolution was nil. This is due to the rapid acid consumption and depletion by the carbonates and clay minerals present in the system. An increase in acid concentration to

Table 3
Change in slurry pH before and after leaching of 300 g/L p.d. slurry sample at different sulfuric acid concentrations and the metal concentration in the PLS.

H_2SO_4 concentration, mol/L	Slurry pH before leaching	Slurry pH after leaching	Cu in PLS, g/L	Fe in PLS, g/L
1.0	−0.05	6.40	0	0
1.5	−0.18	1.51	5.19	2.97
2.0	−0.30	1.09	4.55	9.04
2.5	−0.39	0.70	4.44	11
3.0	−0.46	0.42	4.59	13.5

1.5 mol/L supported copper dissolution yielding the highest copper concentration in solution of 5.19 g/L and the lowest iron concentration of 2.97 g/L. Thereby, a good selectivity of copper over iron during leaching can be achieved using a high pulp density of 300 g/L.

The leach residue from 300 g/L pulp density and 2 mol/L H_2SO_4 leaching experiment were analyzed using EPMA (Fig. 11) to examine the hindering factor that results in the inefficient dissolution of copper. When using mapping analysis, Si and Ca were observed around the undissolved chalcopyrite in the leach residue. In various analyzed areas of the residue, the majority of the observed chalcopyrite was not corroded and found embedded in quartz, which is one of the main gangue minerals in the ore. This confirms that a high pulp density significantly increased the viscosity of the slurry and resulted in poor mixing of the reactants. As a result of the decreased acid to solid contact, the chalcopyrite locked in quartz remained un-leached resulting in low copper extraction. XRD analysis (Fig. 12) confirmed the presence of quartz and calcium sulfate in the leach residue.

3.1.5. Effect of free acidity

The effect of free acidity was examined with respect to the dissolution behavior of copper and iron, and the results are displayed in Fig. 13. A relationship between free acidity and the leaching efficiency of copper and iron was established in all the investigated pulp densities. The copper extraction reached its maximum when free acidity was about 10 g/L, then slightly decreased, and remained constant with further increase of free acidity. Contrary to copper, the iron leaching efficiency increased with increasing free acidity and attained its maximum level when the free acidity was approximately 40 g/L. The error estimates of free acidity on metal extractions at 100, 200, and 300 g/L pulp densities are 5.6%, 7.7%, and 5.1%, respectively. The free acidity trends with respect to the metals leaching efficiencies, strongly suggest that the selective leaching of copper and iron from the carbonaceous ore is possible and can be controlled by adjusting the free acidity of the leachate. When free acidity is adjusted to 10 g/L, copper can be dissolved in solution while iron remains in the solid residue. It can thus be concluded that free
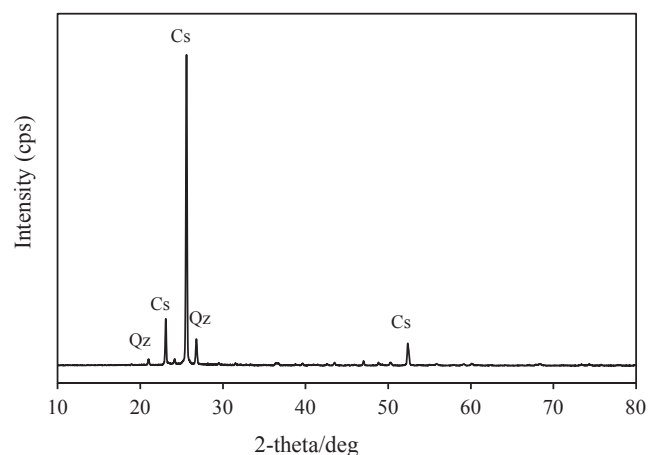

Fig. 12. XRD pattern of the solid residue obtained after direct leaching (conditions: 300 g/L p.d., 2.0 mol/L H_2SO_4, 60 min, 750 rpm, 160 °C, 1.0 MPa t.p.). **Qz:** Quartz, **Cs:** Calcium sulfate.

acidity is an important parameter in the leaching process of copper from the complex carbonaceous sulfide ore.

Fig. 14 (a) shows a linear correlation between log[Fe] concentration and log[free acidity] in the pregnant leach solution, with a good correlation coefficient of 0.929. The relationship between Fe concentration in the PLS and free acidity can thus be presented as in Eq. (9). This implies that the extraction of Fe from the complex carbonaceous sulfide ore is dependent on the free acidity of the slurry. On the contrary, there was no correlation found between Cu concentration in the PLS and free acidity. A relationship was also established between free acidity and H_2SO_4 acid concentration used for leaching at different pulp densities (Fig. 14 (b)). Such a relationship is important as it allows for the determination of H_2SO_4 consumption, especially when dealing with carbonate minerals. When utilizing a slurry sample of 100 g/L pulp
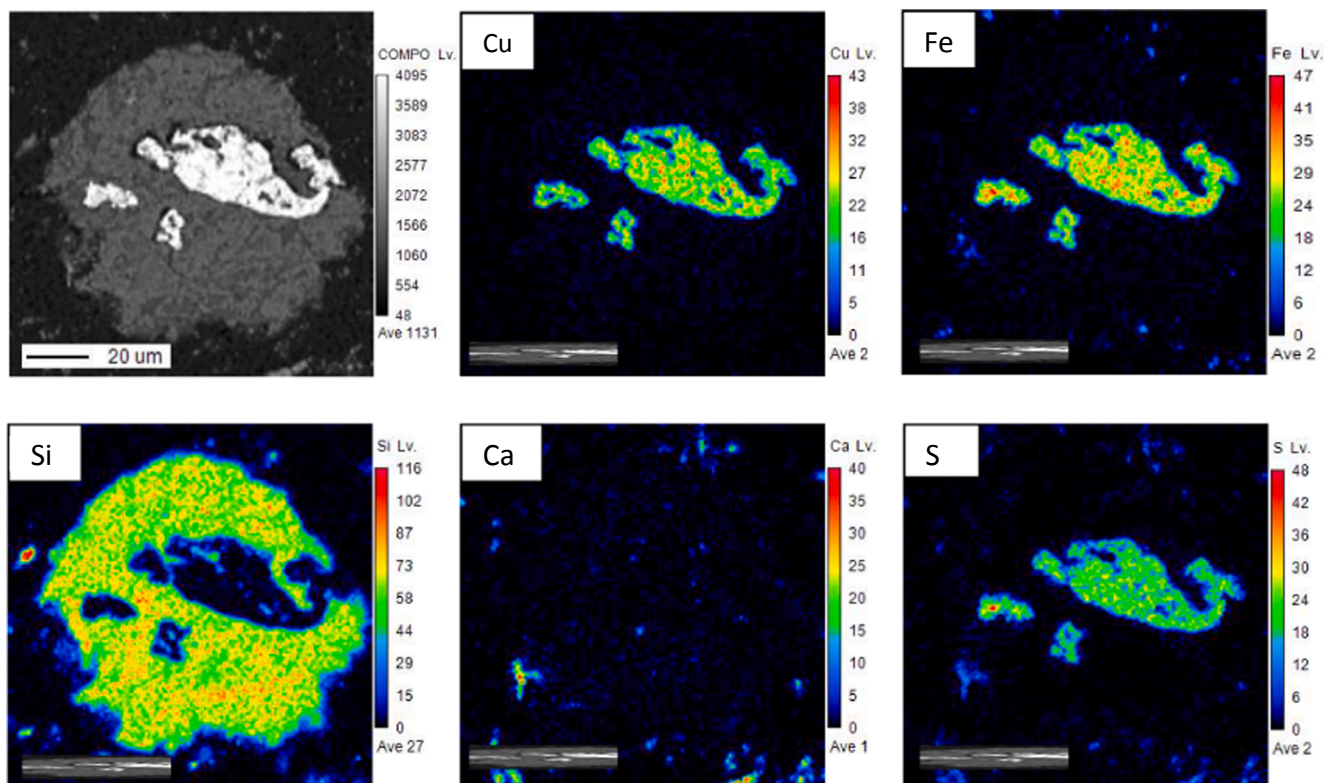

Fig. 11. EPMA results showing the elemental mapping of the leach residue (Conditions: 300 g/L p.d., 2.0 mol/L H_2SO_4, 60 min, 750 rpm, 160 °C, 1.0 MPa t.p.).
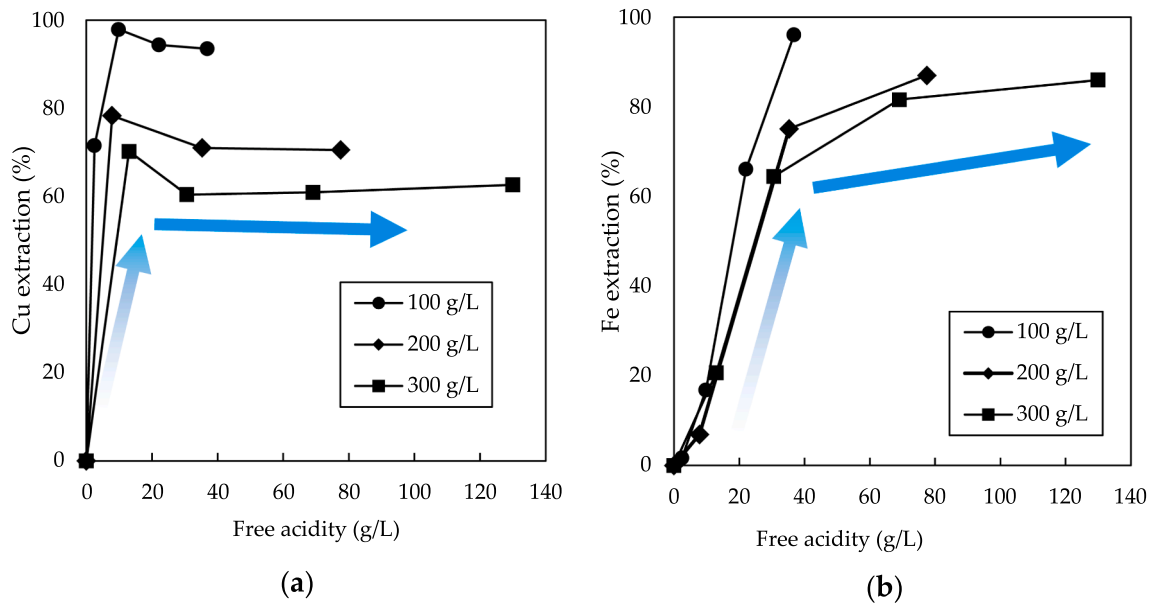
Fig. 13. The effect of free acidity on dissolution behavior of (a) copper and (b) iron. (0.2 – 3.0 mol/L H$_2$SO$_4$ concentration, 1.0 MPa t.p., 160 °C, 100 – 300 g/L p.d., 60 min).
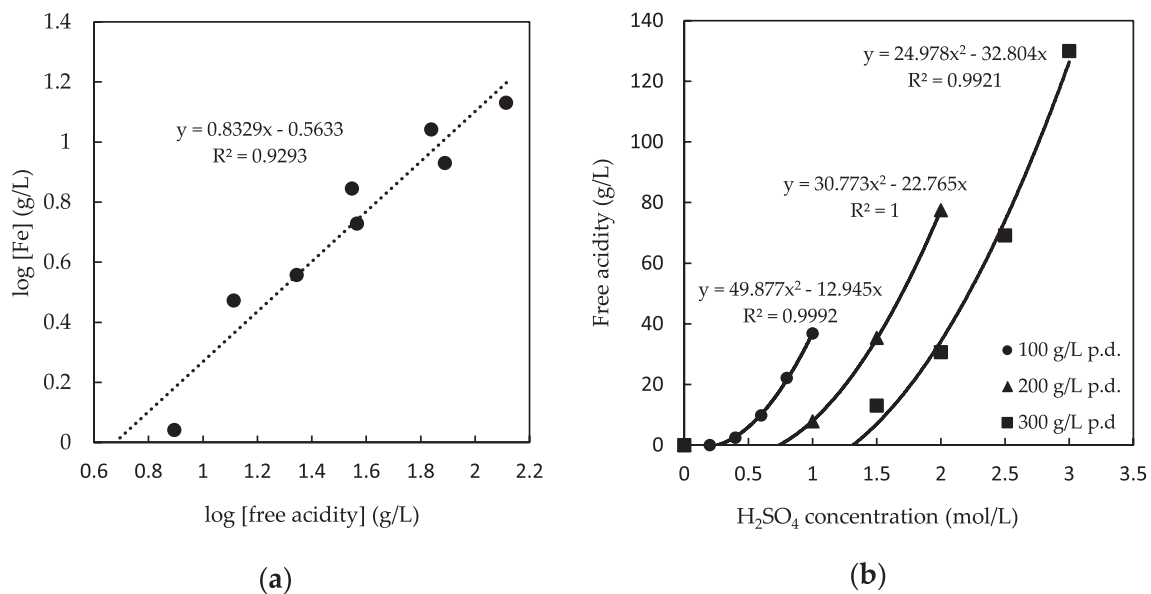

Fig. 14. (**a**) The correlation of log [Fe] (g/L) as a function of log [free acidity] (g/L) in the pregnant leach solution (0.2 – 3.0 mol/L H$_2$SO$_4$ concentration, 1.0 MPa t. p., 160 °C, 100 – 300 g/L p.d., 60 min); (**b**) The correlations of free acidity and H$_2$SO$_4$ concentration (mol/L) (1.0 MPa t.p., 100 – 300 g/L p.d., 160 °C, 60 min).

density, free acidity can be expressed as in equation 10. Since a relationship exists between Fe concentration in the PLS and free acidity (Eq. (9)), a direct relationship of Fe concentration in the PLS and sulfuric acid concentration used for leaching can be deduced by a combination of equations 9 and 10. This indicates that Fe tenors in the PLS can be controlled directly through adjustment of the sulfuric acid concentration used for leaching. Therefore, a means for iron precipitation and removal with the solid residue during leaching may be possible. The Fe concentrations obtained from experimental results were found to agree with those calculated from Eq. (9) and the derived equations from Fig. 14(b) with an error margin of less than 2 g/L Fe.

$$\log [Fe] = 0.833 \log[Free\ acidity] - 0.563 \tag{9}$$

$$Free\ acidity\ (g/L) = 49.877[H_2SO_4]^2 - 12.945[H_2SO_4] \tag{10}$$

3.2. Precipitation of copper by NaSH sulfidization

To recover the dissolved copper from the leachate, sodium hydrosulfide (NaSH) sulfidization method was used to selectively precipitate copper over iron and other impurities. Using NaSH, copper is mostly precipitated as copper sulfide (synthetic covellite) via equation 10, while iron remains in the residual solution. Leachate (Cu: 3.08 g/L and Fe: 5.28 g/L) obtained from a direct high-pressure leaching experiment of 100 g/L pulp density, 1.0 mol/L H$_2$SO$_4$, 160 °C, and 60 min was used for these precipitation tests.

$$2CuSO_4 + 2NaSH \rightarrow 2CuS + Na_2SO_4 + H_2SO_4 \tag{10}$$
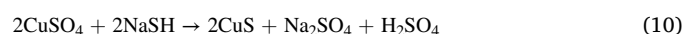
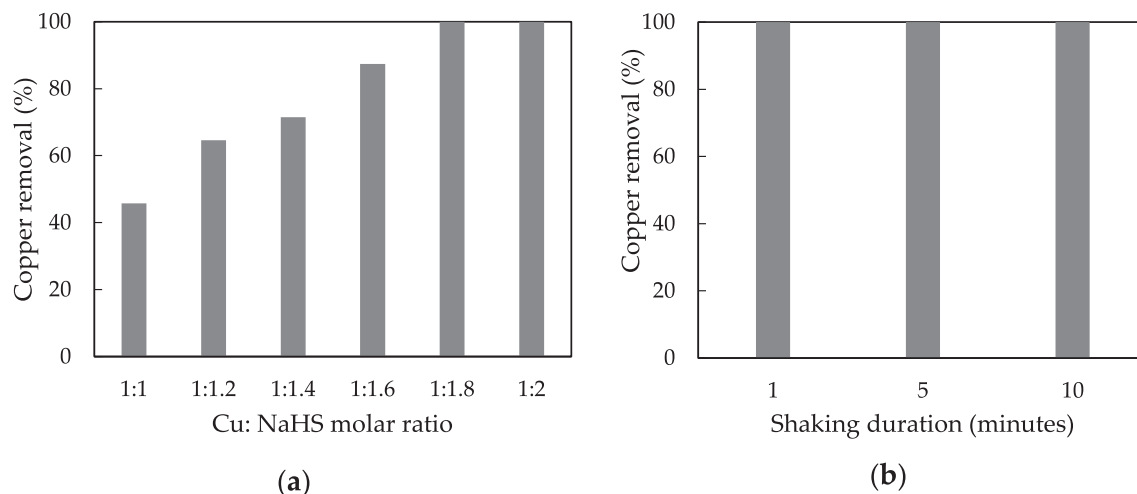Fig. 15 (a) shows the results of copper precipitation rate from the

Fig. 15. Copper removal after precipitation as a function of (a) Cu: NaSH ratio at room temperature, shaking speed, 800 rpm, and shaking duration, 10 min. (b) Shaking duration at room temperature, Cu: NaSH molar ratio, 1:1.8 and shaking speed, 800 rpm.

leachate at different NaSH molar ratios and a constant shaking time of 10 min. The precipitation rate of copper gradually increased with increasing NaSH addition. A low copper precipitation rate of about 45% was observed at the Cu: NaSH molar ratio of 1:1. Copper was not detected in the residual solution at Cu: NaSH molar ratios of 1:1.8 and 1:2, it indicates that more than 99.9% of copper was precipitated. Fig. 15 (b) shows a consistent copper precipitation rate of more than 99.9% under all the investigated shaking times (1, 5, and 10 min). Therefore, the shortest residence time can be recommended to achieve a good separation of copper from iron during copper precipitation. At Cu: NaSH = 1:1.8, shaking time: 10 min, the pH slightly declined from 1.129 to 1.080 due to the acidic conditions enhanced by equation 10. The oxidation–reduction potential (ORP) was measured before and after precipitation of copper to be 527 and −94 mV respectively, indicating a greatly reducing ORP for precipitation of copper.

The obtained copper precipitate (Cu: NaSH = 1:1.8, shaking time: 10 min) was analyzed to determine its chemical composition. The copper and iron content were determined to be 61.2% and 1.21% respectively, indicating a very low iron co-precipitation of about 1.05%. XRD pattern (Fig. 16) confirmed that the generated precipitate is copper sulfide.

4. Conclusion

A metallurgical process for selective extraction of copper and iron from complex carbonaceous sulfide ore using high-pressure leaching and sulfide precipitation methods was studied. The main findings from this study are highlighted below:

(i) The evaluation of leaching parameters showed that an increase in temperature, sulfuric acid concentration, and total pressure increase the extraction of copper and iron from the complex carbonaceous sulfide ore. Cu was selectively extracted over Fe at 0.6 mol/L H_2SO_4, due to iron precipitating as jarosite, however, a further increase in H_2SO_4 concentration diminished the Cu/Fe selectivity.

(ii) An increase in pulp density resulted in a significant decline in copper extraction. EPMA analysis of the solid residue obtained from leaching a sample of 300 g/L pulp density in 2.0 mol/L H_2SO_4, showed unreacted chalcopyrite embedded/locked in the quartz phase. This indicates that a high pulp density significantly increases the viscosity of the slurry which hinders efficient mixing of the reactants, consequently resulting in low copper extraction.
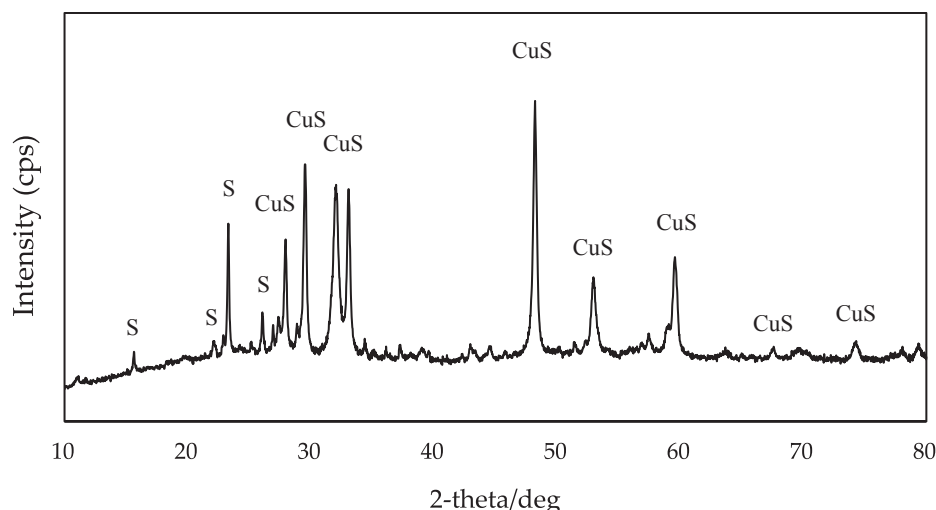

Fig. 16. The XRD pattern of the precipitate generated by NaSH sulfidization (Cu: NaSH = 1:1.8, shaking time: 10 min). **CuS**: copper sulfide, **S**: sulfur.

(iii) Free acidity analysis showed that the maximum copper and iron extractions were achieved when free acidity was approximately 10 g/L and 40 g/L, respectively, confirming that selective dissolution/separation of copper and iron can be achieved through efficient control of free acidity in the pregnant leach solution.

(iv) The concentration of iron (g/L) in the pregnant leach solution was found to be dependent on free acidity. A linear relation between log[Fe] concentration and log[free acidity] was established as follows: log [Fe] = 0.833 log[Free acidity] − 0.563. Relationships were also established between free acidity and H_2SO_4 acid concentration used for leaching at different pulp densities.

(v) Under optimized high-pressure leaching conditions, a high copper extraction of over 97% was achieved with a copper concentration of 2.43 g/L in the PLS.

(vi) Over 99.9% copper was precipitated from the PLS using NaSH sulfidization, at a Cu: NaSH molar ratio of 1:1.8.

CRediT authorship contribution statement

Labone L. Godirilwe: Investigation, Formal analysis, Validation, Visualization, Writing – original draft. **Refilwe S. Magwaneng:** Investigation, Methodology, Formal analysis, Writing – review & editing. **Riku Sagami:** Investigation, Conceptualization, Methodology, Formal analysis. **Kazutoshi Haga:** Conceptualization, Methodology, Writing – review & editing, Project administration. **Altansukh Batnasan:** Data curation, Writing – review & editing. **Shogo Aoki:** Formal analysis. **Takashi Kawasaki:** Resources, Conceptualization, Writing – review & editing. **Hidekazu Matsuoka:** Resources, Conceptualization, Writing – review & editing. **Kohei Mitsuhashi:** Resources, Conceptualization, Writing – review & editing. **Masanobu Kawata:** Resources, Conceptualization, Writing – review & editing. **Atsushi Shibayama:** Conceptualization, Methodology, Writing – review & editing, Project administration, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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