

–PhD Thesis–

**Development of Copper Recovery Processes from
Low-Grade-Copper Resources by Flotation and
High-Pressure Oxidative Leaching**

浮選および加圧酸浸出を用いた低品位銅資源から
の銅回収プロセスの開発

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Abstract:

Due to the long-term mining activity and economic growth of countries in the world, the depletion of high-grade copper ore has gradually been happening during the last several decades. With the decreasing of copper grade, the content of the copper ores becomes complex due to the increasing of impurities such as clay minerals and refractory ores. In addition, mine tailings are generally produced as a byproduct during the beneficiation of a copper ore, namely by flotation. The old mine tailings have higher copper grade than that of naturally occurring copper ore (world average: 0.4 %). Due to the lower grade and complex mineralization of copper ore and mine tailings, it becomes difficult to apply the conventional pyrometallurgical method to recover copper from that kind of resources. On the other hand, it can be expected that the demand for copper metal and copper-bearing products will be increased in the coming years. Hence, it becomes more important to address the processing of low-grade copper resources, especially low-grade copper ores and mine tailings by advanced flotation and hydrometallurgical method. In this research, the flotation and high-pressure oxidative leaching were developed for recovery of copper from the low-grade copper resources. This PhD thesis is composed of six (6) chapters, each of them dealing with different aspects of development the approaches for recovery of the copper from low-grade copper resources.

Thesis Summary:**Chapter 1: Introduction**

This chapter introduces the general overview of the low-grade copper ores and mine tailings, the conventional copper producing process and the previous research on the low-grade copper ore resources. Fundamental technologies for the recovery of copper from ores by flotation and hydrometallurgical processes are discussed throughout this dissertation.

Chapter 2: Direct Leaching of the Low-Grade Copper Ore

This chapter describes the direct atmospheric and high-pressure oxidative leaching (HPOL) of low-grade ores (copper grade: 0.4 mass%, CuFeS_2 as the main copper mineral) under a variety of sulfuric acid concentrations (0–1.0 M). It can be seen from the results that both copper and iron dissolution rates were low (< 20 %) under the atmospheric conditions, due to the formation of elemental sulphur onto the unreacted copper particles. However, a maximum copper leaching rate of 98 % achieved under the optimal HPOL conditions, whereas the copper concentration in the pregnant leach solution (PLS) was only 0.06 g/L, that lower copper concentration causes difficulty in the subsequent process, namely solvent extraction.

Chapter 3: Flotation and the Combination of Flotation with High-Pressure Oxidative Leaching Using Low-Grade Copper Ores

This chapter presents the results for the recovery of copper from the low-grade copper ore using flotation followed by HPOL. The effects of various flotation parameters, such as time, collector (Potassium Amyl Xanthate: PAX) dosage, slurry pH and air injection rate on beneficiation of copper from the sample were studied. The recovery of copper reached 93.1 % while a copper grade improved to 18.1 from 0.4 mass% under the collector-less optimal flotation conditions. The enrichment ratio of copper in the concentrate was 45. The concentrate obtained from the flotation of low-grade copper ore was used in HPOL study. The maximum efficiency of copper dissolution from the concentrate into water under HPOL was 98.4 %. As a result, copper concentration in the PLS reached 15.0 g/L under the optimized HPOL conditions. A process flow for the recovery of copper from the low-grade copper ores is proposed based on this result.

Chapter 4: Leaching and Kinetic Study on Pressure Oxidation of Chalcopyrite in H₂SO₄

Solution and the Effect of Pyrite on the Chalcopyrite Leaching

This chapter investigates the leaching of copper from chalcopyrite in H₂SO₄ solution at pressure oxidative conditions and kinetics of copper dissolution. Leaching variables that affect the rate of copper dissolution from chalcopyrite are particle size (-38 μm, +38–75 μm, and +75–100 μm), agitation speed (300–900 rpm), total pressure (0.8–2.0 MPa), temperature (160–180 °C) and sulfuric acid concentration (0.1–2.0 M). Under the optimal conditions, copper extraction of 94.5 % was achieved after 90-min leaching, while a dissolution of iron at 4.2 % was obtained. The kinetic study showed that the dissolution of chalcopyrite is represented by a shrinking core model with chemical reaction controlling mechanism given as $(1 - (1 - \alpha)^{1/3})$. The activation energy (E_a) for the leaching reaction was calculated to be 42.4 kJ/mol. The reaction order with respect to total pressure was about 8.0, which indicates that total pressure, i.e., oxygen partial pressure in an autoclave is the most important factor in controlling the dissolution of chalcopyrite in H₂SO₄ solution under pressure oxidative leaching conditions. The effect of Fe/Cu mole ratio (1–20 mol/mol, adjusted by addition of pyrite) on chalcopyrite leaching from a copper ore was investigated. The results show that the sulfuric acid produced during pyrite oxidation promotes the chalcopyrite dissolution.

Chapter 5: Application of Flotation and High-Pressure Oxidative Leaching Processes to

Mine Tailings

This chapter discusses the possibility of applying the developed flotation and HPOL processes for recovery of copper from mine tailings. The grade of copper reached to be 0.65 from the initial 0.34 mass% and its recovery was 78.4 % under the optimal flotation conditions. It was revealed that both grade and recovery of copper increased with the addition of sulfurizing reagent (NaHS). The results of HPL using the concentrate of mine tailings obtained by flotation under the optimal conditions shown that the copper dissolution of 94.4 % was achieved in an H₂O media. The solvent extraction of pregnant leach solution obtained from the optimal HPOL indicated that 91.3 % copper was recovered in the stripped solution under the determined optimum conditions, at which the copper concentration reached to be 44.8 g/L. Finally, it was verified that the application of the

combined method consistency of flotation, HPOL, and solvent extraction is possible to recover copper from mine tailings and low-grade copper ores.

Chapter 6: Conclusion

This chapter provides a summary of findings from each chapter and recommendations for future research based on the obtained results and observations for recovery of copper from low-grade copper resources. Finally, an advanced copper recovery process from the low-grade copper resources was proposed by a combination method of flotation-HPOL.

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List of Abbreviations

HPOL: High-Pressure Oxidative Leaching

PAX: Potassium Amyl Xanthate

PLS: Pregnant Leach Solution

MIBC: Methyl Iso Butyl Carbinol

XRD: X-Ray Diffractometer

XRF: X-Ray Fluorescence Spectrometer

ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometry

SEM-EDS: Scanning Electron Microscope Energy-Dispersive X-Ray Spectroscopy

SX: Solvent Extraction

List of Symbols

Leaching:

- R_M** : Metal leaching rate (%)
- C_L** : Metal concentration in pregnant leach solution (mg/L)
- C_F** : Metal concentration in feed (mg/kg)
- V_L** : Volume of pregnant leach solution (L)
- m_F** : Dry mass of the feed (kg)

Flotation:

- Y** : Yield (%)
- I** : Enrichment ratio
- R** : Recovery (%)
- F** : Weight of feed (g)
- C** : Weight of concentrate (g)
- f** : Metal grade in the feed (mass%)
- c** : Metal grade in the feed (mass%)
- t** : Metal grade in tailings (mass%)

Kinetics study:

- α** : The fraction reacted (%)
- k_r and k_d** : The kinetic constants
- t** : The reaction time (min)
- k** : Rate constant
- A** : Pre-exponential factor (s^{-1})
- E_a** : Activation energy (kJ/mol)
- R** : Gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)
- T** : Absolute temperature ($^{\circ}C$)
- P_{Total}** : Total pressure (MPa)

Solvent extraction:

- E_i** : Extraction percent (%)
- S_i** : Stripping ratio (%)
- $[i]_{aqueous}$** : Concentrations of the element i in aqueous (g/L)
- $[i]_{raffinate}$** : Concentrations of the element i in raffinate solutions (g/L)
- $[i]_{Cu-rich}$** : Concentrations of the element i in Cu-rich solutions (g/L)
- $[i]_{Cu-loaded}$** : Concentrations of the element i in Cu-loaded organic phase (g/L)

Chapter 1: Introduction

Copper (Cu), one of the most widely used base metal in the world in many forms during the course of human development. It can be cold-rolled down to one-thousandth inch in thickness, and its length can be increased as much as 5000 times by cold drawing [1]. Today, it is primarily used in construction, electronics, machinery, and consumer goods due to copper is a soft, malleable, and ductile metal with very high thermal and electrical conductivity.

Copper found in the free metallic state in nature is called "native copper" (Fig. 1.1) [2]. It is found throughout the world as a primary mineral in basaltic lavas. As a mineral, native copper is found only in small quantities throughout the world, but there are a few areas that are rich in findings [1]. Most copper in nature combines with a number of elements, and more than 150 copper minerals have been identified, although only a small number of these are of economic importance [3]. Currently, porphyry copper deposits are currently the world's main source of copper which contributes 50–60 % of world copper production [3]. As the image of porphyry deposit shown in Fig. 1.2 [4], copper minerals can be divided into three groups (Table 1.1) which are primary sulfides, oxide ores, and secondary sulfides.

- Primary or hypogene minerals including bornite, chalcopyrite, and enargite, are formed relate to hydrothermal processes.
- The second group is the copper oxide, typically formed from weathering of copper sulfides, and its typical minerals are cuprite, malachite, chrysocolla, and covellite.
- The third group is named secondary sulfide, such as chalcocite and covellite, and it is formed from copper leached from near-surface sulfides.

Estimates suggest at least 90 % of copper is derived from sulfide deposits [3]. Of the sulfide minerals, chalcopyrite (CuFeS_2) is by far the most important accounting for approximately half of all copper production [3].



Fig. 1.1 Photograph of the native copper (source: <https://en.wikipedia.org/wiki/Copper>).

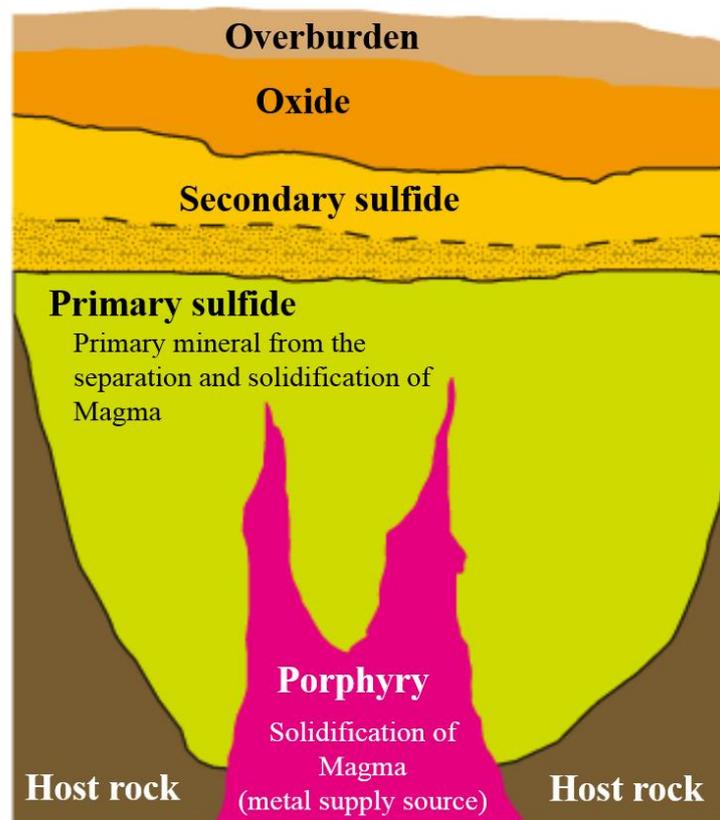


Fig. 1.2 Image of porphyry copper deposit.

(source: http://mric.jogmec.go.jp/kouenkai_index/2012/briefing_120906_2.pdf)

Table 1.1 Classification of the copper ores and its typical minerals.

Classification	Typical minerals	
	Name	Formula
Copper oxides	Cuprite	Cu_2O
	Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$
Secondary sulfides	Chalcocite	Cu_2S
	Covellite	CuS
Primary sulfides	Chalcopyrite	CuFeS_2
	Bornite	Cu_5FeS_4
	Enargite	Cu_3AsS_4

1.1 Copper production processes

As mentioned above, there are three (3) main copper ore types in porphyry deposits, i.e., copper oxide ores, primary sulfide ores, and secondary sulfide ores. For extracting copper from the different types of copper minerals, the conventional copper production can be divided into two (2) processes, namely **hydrometallurgical** and **pyrometallurgical** method.

1.1.1 Oxide ores

Oxide ores and some of the Cu_2S ores are generally processed via a hydrometallurgical process which is shown in [Fig. 1.3](#) [5]. This process uses aqueous (water-based) solutions to extract and purify copper from oxide ores at ordinary temperatures, which is usually in three steps, i.e., **heap leaching, solvent extraction, and electrowinning**.

Heap Leaching is the process of using percolating chemical solutions to leach out metals. Following mining, transporting, and crushing to a consistent gravel or golf ball-size, the crushed ore is piled into a heap on top of an impenetrable layer on a slight slope. The leaching reagent (dilute sulfuric acid) is sprayed through sprinklers on top of the heap pile and allowed to trickle down through the heap, where it dissolves the copper from the ore. The resulting “pregnant” leach solution of sulfuric acid and copper sulfate is collected in a small pool.

The second step is **solvent extraction**, in which consists of extraction and stripping (back

extraction). General, two immiscible (un-mixing) liquids, i.e., aqueous and organic, are stirred for separating copper from the impurities base on the solubility of each metal in two phase. The pregnant leach solution is mixed vigorously with a solvent for a required time allowing copper transport from leach solution into the solvent (organic phase). Then, the two-phase is separated into the aqueous phase with impurities remaining and organic phase with Cu-loaded. The obtained Cu-loaded organic phase is then mixed with an acid solution for extracting copper back to the aqueous phase and making a Cu-rich solution, which will feed to the next step. The leftover leach solution is then recycled by adding additional acid and sending it back to the sprinklers in the heap leaching process [5].

The last step is called **electrowinning**, a type of electrolysis. An electrical current passes through an inert anode (positive electrode) and through the copper solution from the previous step, which acts as an electrolyte. Positively-charged copper ions (called cations) come out of solution and are plated onto a cathode (negative electrode) which consists of 99.99 % pure copper [5].

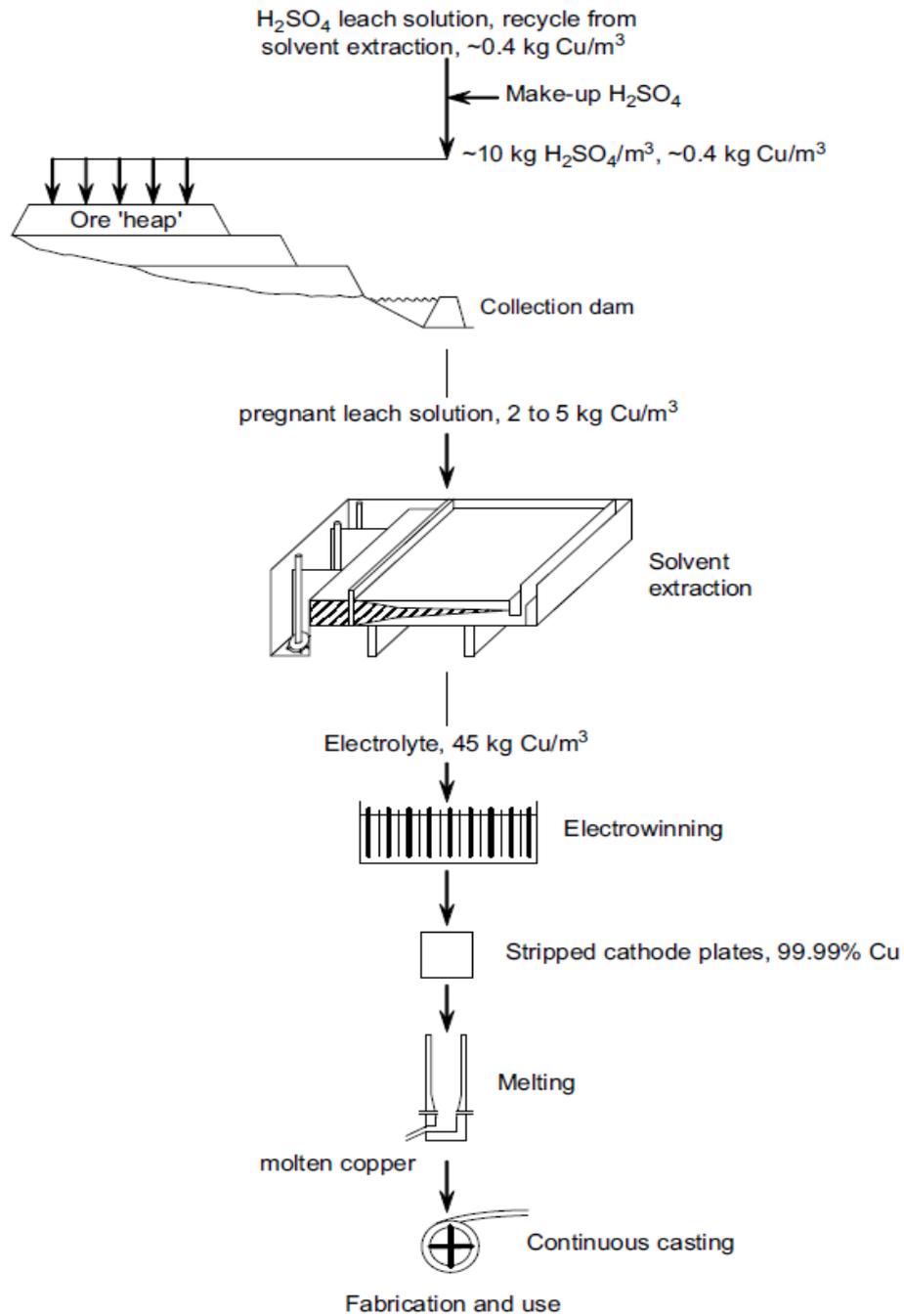


Fig. 1.3 Flowsheet for leaching oxide and Cu₂S ores.

(source: Schlesinger, M. E., King, M. J., Sole, K. C., and Davenport, W. G.: Extractive metallurgy of copper, Elsevier, (2011))

1.1.2 Sulfide ores

Sulfide ores are generally processed using pyrometallurgical processes as well as given in [Fig. 1.4 \[5\]](#). This process uses a series of physical steps and high temperatures to extract and purify copper from copper sulfide ores, which including four (4) basic steps: **flotation, thickening, smelting, and electrolysis [5]**.

After the sulfide ores are crushed, the liquid is added to make it a slurry. The slurry is a mix of valuable copper ore minerals and “worthless” rock, which also called gangue. The slurry is placed in a tank and a process called **flotation** is used to separate the copper minerals from the gangue minerals. The froth of copper-rich bubbles at the top of the tank is then skimmed off for further processing. The gangues which sink to the bottom of the tank will be removed or disposed of as mine tailings [\[5\]](#).

The next stage after flotation is the **thickening** stage. The bubbles break and solids from the froth solution settle at the bottom of the tank, which is called thickener. The solids are then filtered to remove excess water, which can be reused in processing additional batches of sulfide ore. The final product of the thickening stage, namely copper concentrate, contains around 30 % copper, and then will be sent to the smelter [\[5\]](#).

At the smelter, high temperatures are used to further purify the ore in a series of **smelting** steps. The copper concentrate is first sent through the smelting furnace to be heated up to 1260 °C and converted into a molten liquid. The heated liquid is poured into a slag-settling furnace. This step produces a combination of matte which consists of copper 58–60 % and other impurities. The molten matte is then taken to another furnace called a converter to burn off the remaining iron and sulfur. The product is referred to as blister copper, which contains 98 % copper, and taken to the anode smelter. The blister copper is yellow, and it turns a blue–green color when the oxygen in the copper is burned off in the anode smelter. The resulting product, molten anode copper, is poured into molds called anode-casting wheels. Finally, the cooled anode consists of 99 % pure copper is produced, and feed to the subsequent step [\[5\]](#).

Electrolysis is the final process for purifying sulfide ore into copper cathodes. An electric current is applied for leaving the positively-charged copper ions (called cations) from the anode (positive electrode) to the electrolyte solution, and finally to be plated on the cathode (negative electrode).

Other metals and impurities also leave from the anode, and drop to the bottom of the tank or stay in the electrolytic solution. These impurities are collected and may be refined to recover other metals such as silver and gold. After 14 days of electrolysis, the anodes have gradually disappeared, and the copper cathodes contain 99.99 % pure copper. The cathodes are taken out of the tank and rinsed with water to prevent further reaction. The finished copper cathodes can then be made into wires, plates, tubes, and other copper products [5].

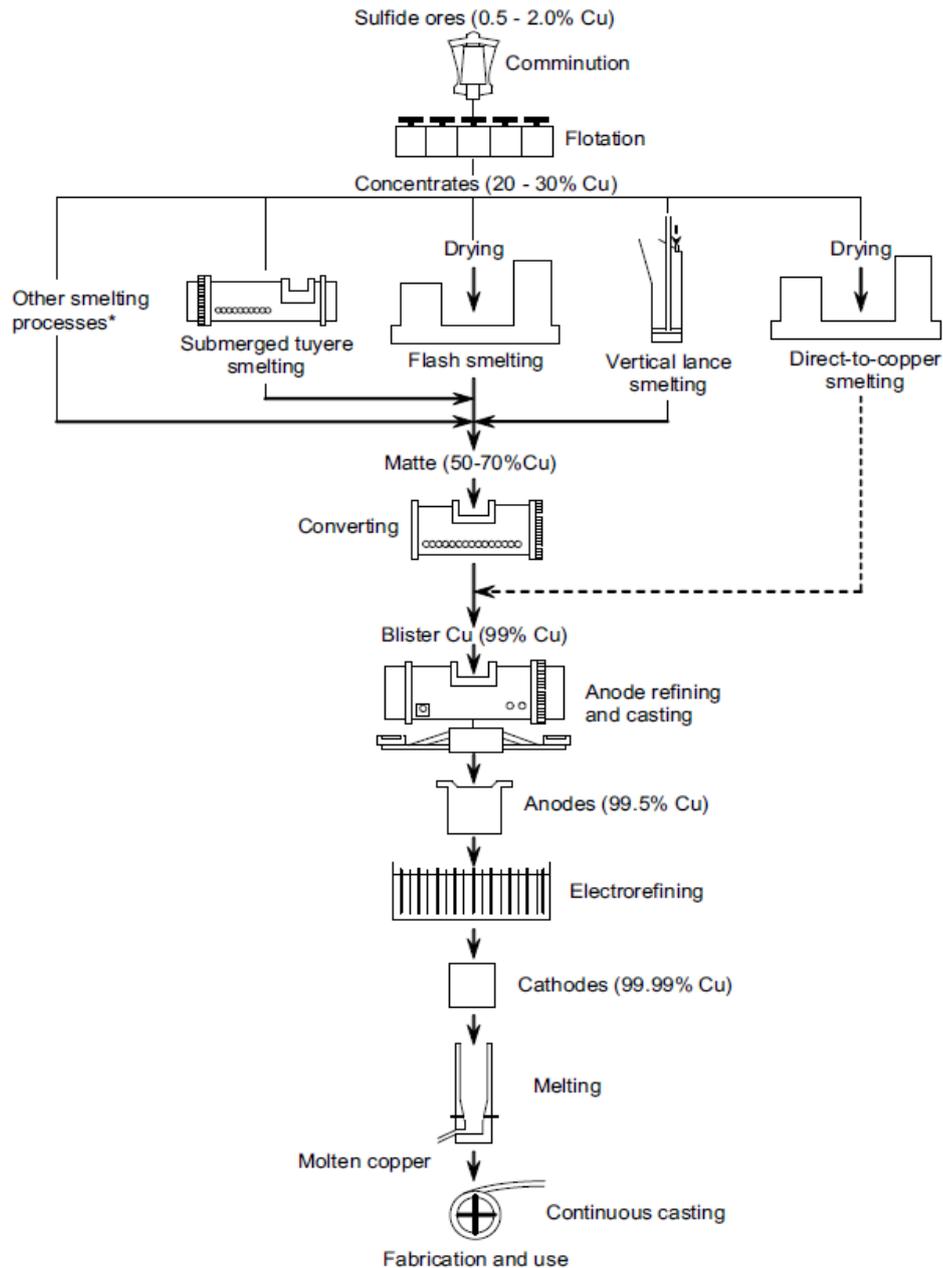


Fig. 1.4 Main processes for extracting copper from sulfide ores.

(source: Schlesinger, M. E., King, M. J., Sole, K. C., and Davenport, W. G.: Extractive metallurgy of copper, Elsevier, (2011))

1.2 About the low-grade copper ore

1.2.1 Current situation of copper ores and the generation of low-grade copper ore

As one of the most important base metal, the demand for copper increased in recent years. [Fig. 1.5](#) shows the world copper production in 19th through 20th centuries [[5-7](#)]. It can be seen that world copper production increased significantly from 1810 to 2010, in which copper-mining supply doubled between 1994 and 2014. In addition, [Fig. 1.6](#) presents selling prices of copper from 1956 to 2010 [[3](#)]. It shows that the constant dollar price fell until 2002 then rose rapidly. The actual price also rose rapidly after 2002, and the record highs come around 2007. These high prices are due to the huge demand for copper in China. The copper demand can be expected that will continue increasing and the price will do not stable, due to the rapid industrialization and infrastructure development in China and other developing countries.

Due to the long-term mining activity and economic growth of countries in the world, there are simply fewer high-grade copper deposits being discovered, i.e., the depletion of high-grade copper ores and low-impurity copper sources general occurs in recent years. Now, the key factors affecting the production of new copper are declining of ore grades (with fewer high-grade discoveries), and not enough new mine production to meet demand. The [Fig. 1.7](#) provides a graphic view of the decline in world average copper grades since 1985, plus the declining grade forecasts based on new mines under construction [[8](#)]. The grade declines have been particularly acute in Chile, which produces about 38% of the world's mined copper. For example, the world's largest copper mine and producer of 9.5% of the world's global copper supply at Escondida, the average copper content of mined ore has fallen from 1.72 % in 2007 to 0.97 % at the end of 2011 which is a drop of nearly 43 % in four (4) years [[8](#)]. Now, the world average copper grade is reported as low as 0.5 % [[9](#)]. In addition, with the decreasing of copper grade, the content of the copper ores becomes more complex due to the increasing of impurities such as clay minerals and refractory ores.

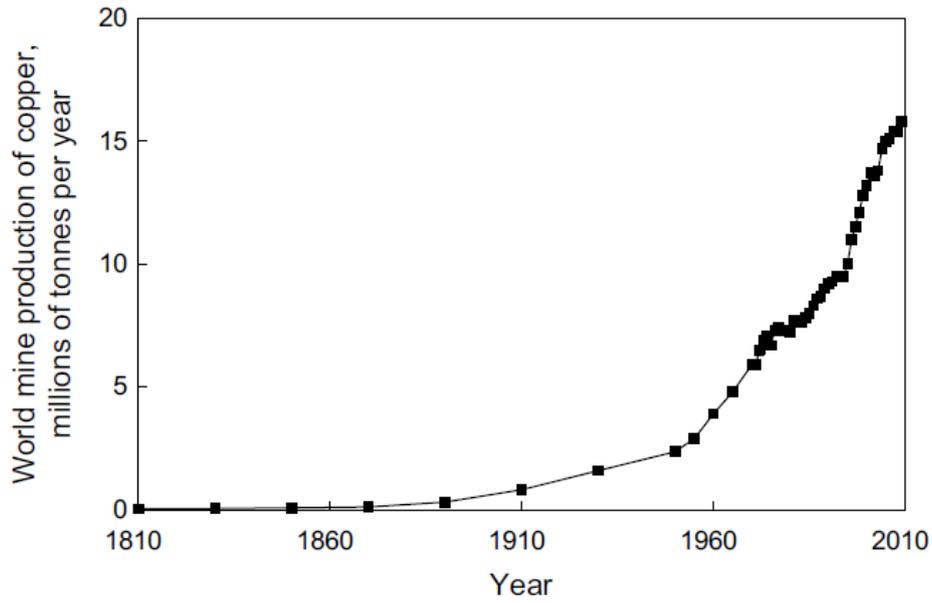


Fig. 1.5 World mine production of copper in the 19th through 21st centuries.

(source: Schlesinger, M. E., King, M. J., Sole, K. C., and Davenport, W. G.: Extractive metallurgy of copper, Elsevier, (2011))

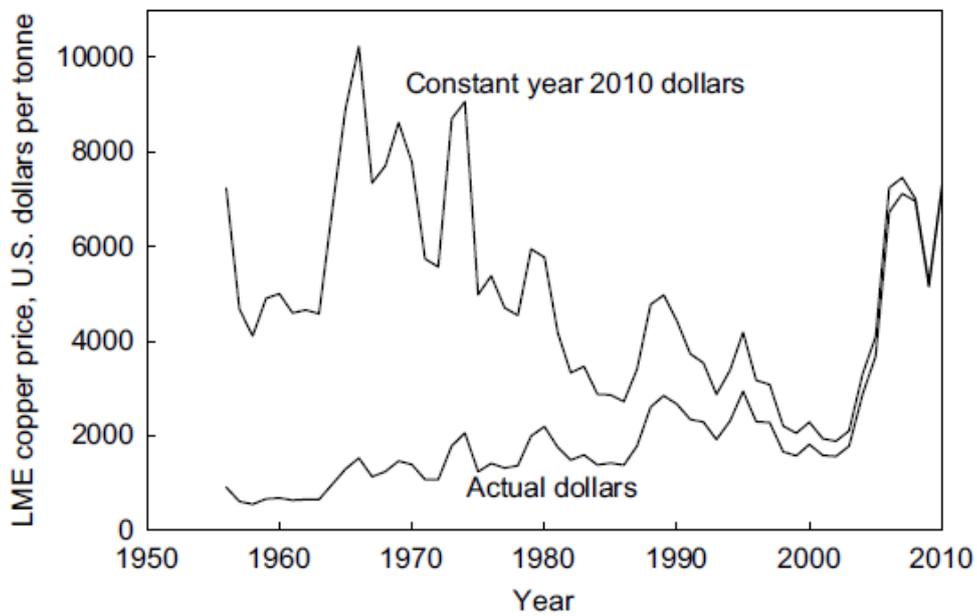


Fig. 1.6 London Metal Exchange cash price for Grade A copper since 1956.

(source: Schlesinger, M. E., King, M. J., Sole, K. C., and Davenport, W. G.: Extractive metallurgy of copper, Elsevier, (2011))

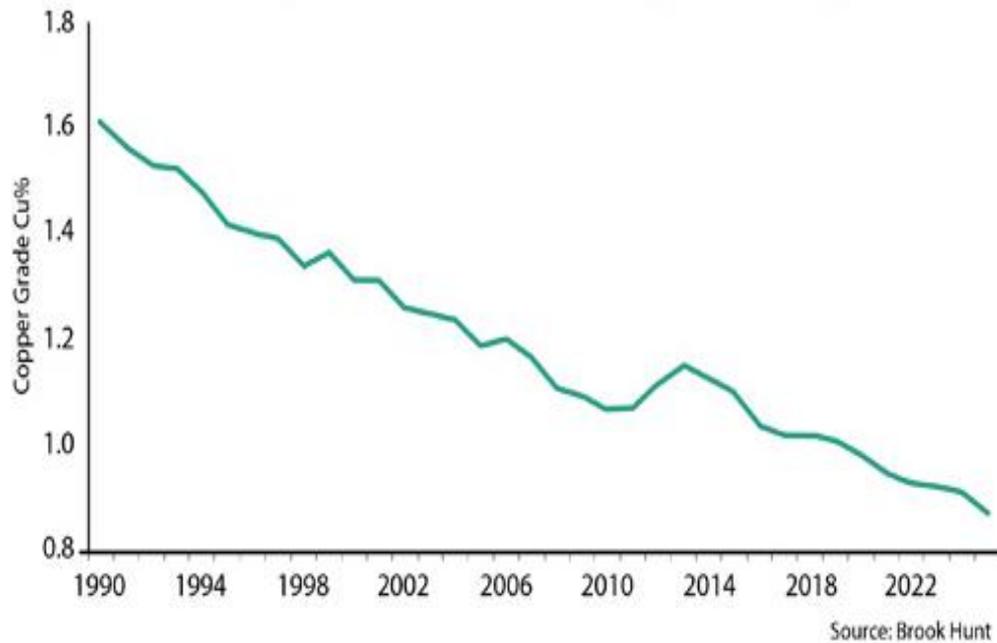


Fig. 1.7 Industry head grade trends.

(source: <http://www.oracleminingcorp.com/copper/>)

1.2.2 Why recovery copper from the low-grade copper ore?

As introduced before, among the copper sulfides, chalcopyrite (CuFeS_2) is the predominant mineral used to produce metallic copper [10]. In recent years, much attention has been focused on chalcopyrite as the chief copper sulfide mineral due to two reasons: 1) it is the most abundant copper mineral in nature, and 2) it is one of the most refractory sulfide copper minerals under hydrometallurgical conditions, owing to the formation of a stable passivation layer on the chalcopyrite surface [11]. At present, approximately 80–85 % of the world copper production is accomplished with the conventional pyrometallurgical method/technology, which consists of flotation, smelting and refining and electro-refining routes [12–15].

Currently, with the depletion of the high-grade copper deposits, the grade of the copper ores is becoming more and more low. In addition, the content of copper ores is getting more complex than that of high-grade copper ores due to the increasing of impurities and refractory minerals. On the other hand, it can be expected that the demand for copper will be increased in the coming years. However, it becomes more difficult to extract copper from this kind of copper resources, i.e., low-grade copper ores, by the conventional pyrometallurgical methods (Fig. 1.8) due to environmental

regulations relevant to the emission of sulfur dioxide and the requirement for high-grade feeds for the pyrometallurgical processes [16]. The hydrometallurgical routes are becoming more active and growing worldwide interest in the copper production [17–22]. There are many studies related to the development of hydrometallurgical routes to extract copper from oxidized and copper sulfide ores by atmospheric leaching, pressure leaching and biological leaching processes [23–26]. Some researchers have concluded that both direct atmospheric and biological leaching of copper from its ore is extremely slow due to the formation of an elemental, sulfur passivation layer on the surface of unreacted particles [27]. In addition, huge amounts of acid are required in the copper leaching from the low-grade copper ores, especially it contains large amounts of carbonates or siliceous gangue minerals as impurities such as silicate which make difficulty on the separation process and produce many residues. On the other hand, copper concentration in the leach liquor/pregnant leach solution (PLS) is much lower when acid leaching is applied for copper extraction from low-grade ores and it causes difficulty in subsequent processes such as solvent extraction (SX) and electrowinning (EW). For those reasons, it becomes necessary to recover copper from the low-grade copper ores by developing the production technologies for facing the demand for copper in coming years.

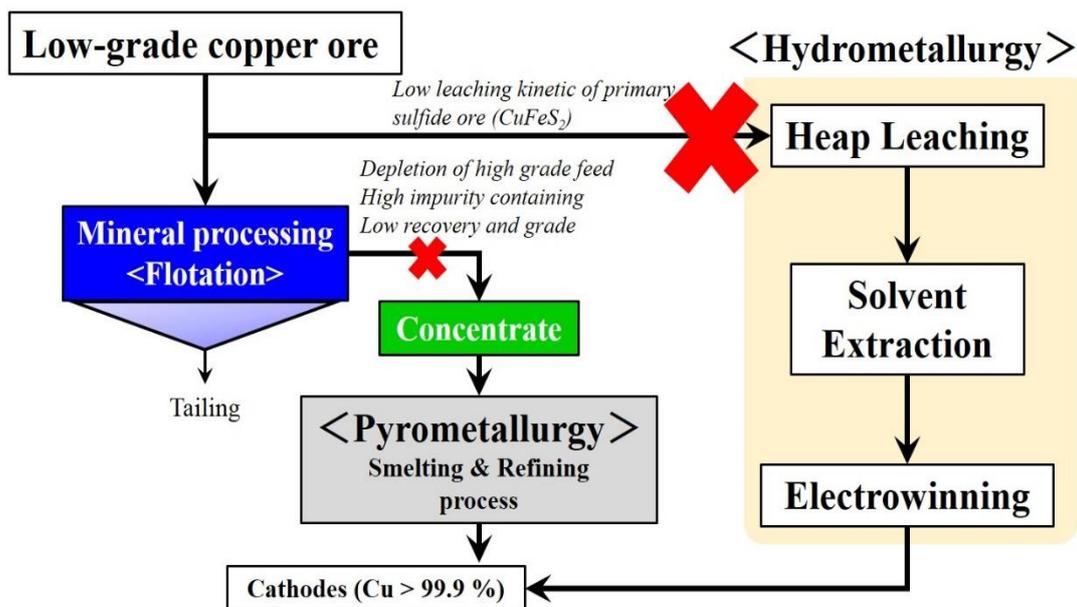


Fig. 1.8 The issues of applying the traditional copper production processes to low-grade ore.

1.3 About the mine tailings

1.3.1 Generation of mine tailings and the normal treatment of it

Mine tailings (**Fig. 1.9**) are the materials left over after the process of separating and beneficiation the valuable fraction from the worthless fraction of an ore, namely flotation. Mine tailings consist of host rock (gangue minerals) and some of the value contents which could not recovery in the flotation process. There are several methods used to dispose of mine tailings such as the discharge of it into rivers and streams which is still practiced at sometimes, and the dumping of coarse dewatered tailings onto land [28]. In addition, it is common practice in underground mines, in which the method of working requires the filling of mined-out areas, to return the coarser fraction of the mill tailings underground [28]. For an operation that is close to the sea, submarine tailings disposal is an alternative to conventional tailings disposal provided the governmental regulations permit disposal in such approach [28].



Fig. 1.9 Image of mine tailings and tailings dam.

1.3.2 Why recovery copper from the mine tailings?

As a by-product of flotation process, the mine tailings always treated by the methods mentioned in **section 1.3.1**. However, there are still some issues are raised by tailings management.

- A large amount of land area is required for the mine tailings treatment.

- Tailings piles are not stable, and experience land-slides.
- Dry tailings dam contains small particles that are picked up by wind, transported and deposited on communities nearby.
- The dust in high enough concentration to cause serious health problems.
- When rain falls on the tailings, it leaches away materials that can create water pollution. As a result, high acidic water leaks from the tailings and disrupted aquatic life downstream.

For that, the disposal of the mine tailings is becoming one of the most important challenges for the mining industry.

In recent years, due to the depletion of the high-grade copper ores, more and more low-grade copper ores are mined for production of metallic copper. Presently about 60% of global copper mine production comes from massive, low-grade porphyry open pit deposits [29]. Due to an increased exploration of copper ore and the discovery of more low-grade deposits, it can be predicted that more mine tailings will be produced in the coming years. It is reported that the low-grade ores and tailings can account for up to three-quarters of the total reserves of certain metals. In addition, mine tailings still contain valuable components such as copper, and the old mine tailings sometimes have higher copper grade than that of original world average copper minerals which are about 0.4 %. Therefore, the mine tailings constitute a potential future copper resource. New or improved technologies can allow the value contained in tailings, which was lost in earlier processing, to be recovered, or commodities considered waste in the past can become valuable in a new economic order. Reducing or eliminating tailings dumps or dams by retreating them also reduces the environmental impact of the waste. Therefore, it becomes necessary to recover copper from the mine tailings by developing the processes technologies.

1.4 Introduction of technologies used in this thesis

1.4.1 Flotation

1.4.1.1 Fundamental of flotation

Froth flotation is a highly versatile method for physically separating particles based on differences in the ability of water-wetting in a mineral/water slurry. If a mixture of hydrophobic and hydrophilic particles are suspended in water, and the air is bubbled through the suspension, then

the hydrophobic particles will tend to attach to the air bubbles and float to the surface, as shown in **Fig. 1.10**. The froth layer that forms on the surface which has been heavily loaded with the hydrophobic mineral will be removed as a separated product. The hydrophilic particles will have much less tendency to attach to air bubbles, and so it will remain in suspension and be flushed away. Flotation is currently used for many diverse applications, with a few examples being: separating sulfide minerals from silica gangue (and from other sulfide minerals); separating potassium chloride (sylvite) from sodium chloride (halite); separating coal from ash-forming minerals; removing silicate minerals from iron ores; separating phosphate minerals from silicates; and even non-mineral applications such as de-inking recycled newsprint. It is particularly useful for processing fine-grained ores that are not amenable to conventional gravity concentration.

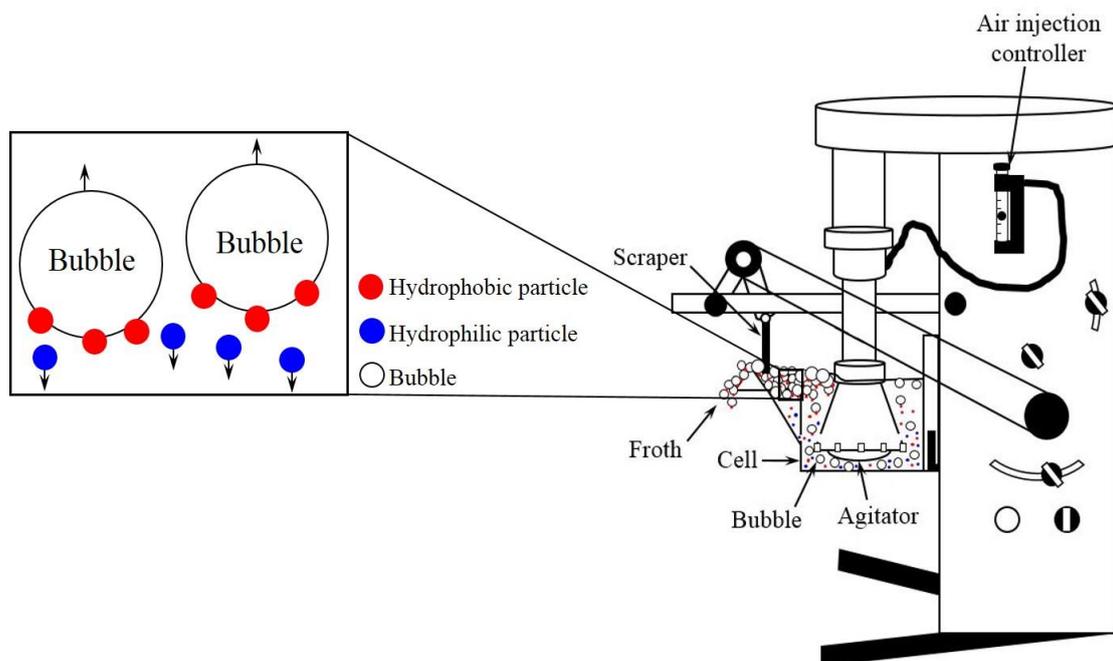


Fig. 1.10 Image of the flotation.

1.4.1.2 Flotation reagent

Reagents are the most important part of the flotation process. In developing a treatment process, much time, energy and attention are spent on the selection of reagents to give the most effective separation and concentration results. In commercial plants, the control of reagent additions is the most important part of the flotation strategy. Modern classification of the reagents is based on the

function of a particular reagent. On this basis, reagents are divided into **collectors**, **frothers**, **regulators**, and depressants.

1.4.1.2.1 Collector

Collectors are reagents that are used to selectively adsorb onto the surfaces of particles. They form a monolayer on the particle surface that essentially makes a thin film of non-polar hydrophobic hydrocarbons. The collectors greatly increase the contact angle so that bubbles will adhere to the surface. Collectors can generally be classified into three categories, i.e., nonionic, anionic, and cationic. Nonionic collectors are simple hydrocarbon oils. Anionic and cationic collectors consist of a polar component that selectively attaches to mineral surfaces, and a non-polar component that projects out into the solution making the surface hydrophobic. Collectors can either chemically bond to the mineral surface with high selectivity (chemisorption), or be held on the surface by physical forces (physical absorption).

1.4.1.2.2 Frother

Frothers are compounds that act to stabilize air bubbles, so that they will remain well-dispersed in the slurry, and will form a stable froth layer that can be removed before the bubbles burst. The most commonly used frothers are alcohols, particularly MIBC (Methyl Isobutyl Carbinol, or 4-methyl-2-pentanol, a branched-chain aliphatic alcohol) or any of a number of water-soluble polymers based on propylene oxide (PO) such as polypropylene glycols.

1.4.1.2.3 pH regulator

The pH regulator is the reagent for adjusting the slurry pH. For example, in general minerals develop a positive surface charge under acidic conditions and a negative charge under alkaline conditions. Since each mineral changes from negatively-charged to positively-charged at some particular pH, it is possible to manipulate the attraction of collectors to their surfaces by pH adjustment. There are also other, more complex effects due to pH that change the way that particular collectors adsorb on mineral surfaces. Sulfhydryl collectors such as xanthate ions compete with OH^- ions to adsorb on mineral surfaces, and so adsorption is a function of pH. This

makes it possible for sulfhydryl collectors to be used to progressively separate specific minerals. The pH where the xanthate ion wins the competition with OH⁻ ions depends both on the concentration of xanthate in solution, and on the specific sulfide mineral present.

1.4.1.2.4 Sulfurizing reagent

The sulfurizing reagent is one kind of activator, and it is contributing to modify the mineral surfaces for improving the flotability. Sodium sulfide is used as a common sulfurizing reagent, and it can be dissociated in solution as shown in [Eqs. 1.1–1.4](#) [28].



Since the dissociation constants of [Eqs. 1.3 and 1.4](#) are extremely low and that of [Eq. 1.2](#) is high, the concentration of OH⁻ ions increase at a faster rate than that of H⁺ ions and the pulp becomes alkaline. Hydrolysis and dissociation of sodium sulfide release OH⁻, S²⁻, and HS⁻ ions into solution and these can react with and modify the mineral surfaces. Sulfurizing causes sulfur ions to pass into the crystal lattice of the oxidized minerals, giving them a relatively insoluble sulfide surface coating and allowing them to be floated by collectors.

1.4.2 Leaching

1.4.2.1 Fundamental of leaching

Leaching is a primary extractive operation in hydrometallurgical processing, by which a metal of interest is transferred from naturally occurring minerals into an aqueous solution. In essence, it involves the selective dissolution of valuable minerals, where the ore, concentrate or matte is brought into contact with an active chemical solution known as a leach solution. The transfer of a metal from the ore to the leach solution constitutes a transfer from a solid to a liquid phase. Because the dissolution is selective, most of the unwanted components in the ore are unaffected by the leaching process and remain in the solid state, which is called residue. Consequently, the metal is separated when the solids are separated from the solution after the leaching process has been

completed, and the solution that is produced is termed a pregnant leach solution or leach liquor. Leaching can broadly be classified into two types, namely non-oxidative and oxidative leaching. Non-oxidative leaching involves a chemical dissolution process using water, acid or an alkali as a reagent. Oxidative leaching involves the use of oxidizing agents such as O_2 , Cl_2 , Fe^{3+} , and Cu^{2+} etc.

1.4.2.2 High-pressure oxidative leaching

The technical advantages of the autoclave and/or pressure-leaching ([Fig. 1.11](#)) is that experiment can be conducted over atmospheric leaching stem from a combination of elevated operating temperature and oxygen overpressure, both of which increase reaction kinetics. Increased operating temperatures above the ambient boiling point can only be achieved by increasing pressure. The use of high-pressure oxidative leaching is becoming more prevalent as ores are becoming increasingly complex, but it's interesting to note that this technology has been used successfully for 75 years, in a number of different applications and on every continent. This robust process has been adapted to operate in acid, neutral, and alkaline pH as well as under strongly oxidizing, neutral or reducing conditions. Pressure leaching of sulfide ores is complicated by many items such as sulfur viscosity and the passivation of reactive surfaces. The pressure-oxidative leaching can be classified into low ($< 100\text{ }^\circ\text{C}$), medium ($140\text{--}180\text{ }^\circ\text{C}$) and high-temperature ($> 200\text{ }^\circ\text{C}$) regimes. "Low" temperature conditions are generally not used in sulfide pressure leaching as this temperature range is conducive to the formation of liquid elemental sulfur. This liquid sulfur has a very high viscosity at these temperatures resulting in excessive agitator power requirements as well as coating reactive particles surfaces reducing metal extraction. So that, the medium temperature which is around $180\text{ }^\circ\text{C}$ is becoming more and more popular in the high-pressure leaching area.



Fig. 1.11 Image of the Autoclave (source: <http://www.ucl.ac.uk/en/ag1200features.html>).

1.4.3 Solvent extraction and stripping

1.4.3.1 Solvent extraction

Solvent extraction, also known as Liquid–liquid extraction (LLE) and partitioning, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent [30]. It is an extraction of a substance from one liquid into another liquid phase. It consists of transferring one (or more) solute(s) contained in a feed solution to another immiscible liquid (solvent). The solvent that is enriched in solute(s) is called extract. The feed solution that is depleted in solute(s) is called the raffinate. The principle of solvent extraction is illustrated in Fig. 1.12. The vessel (a separatory funnel) contains two layers of liquids, one that is generally aqueous solution (aq) and the other generally an organic solvent (org) also known as extractants. In the example shown in Fig. 1.12, the organic solvent is lighter (i.e., has a lower density) than aqueous, but the opposite situation is also possible. The target substance, which initially dissolved in only one of the two liquids, eventually distributes between the two phases. In case of copper, the typical reaction of the copper in aqueous phase extracted by extractant to form a complex soluble in organic solvents can be written as Eq. 1.5:



Finally, a Cu-loaded organic will be produced and sent to the next process named stripping.

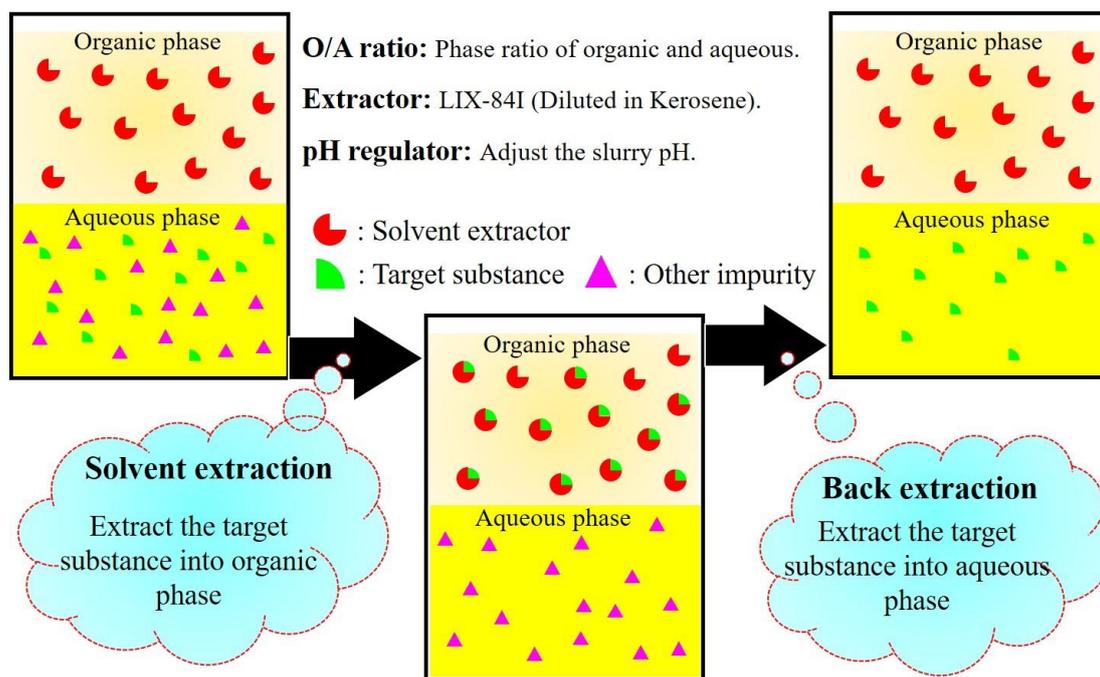


Fig. 1.12 Image of the solvent extraction.

1.4.3.2 Stripping

In order to recover the substance loaded in the organic phase back to aqueous again, the stripping process and/or back extraction general conducted after the extraction process. A general procedure is as follows: the loaded solvent is contacted with a suitable strip solution (e.g., acid, base, etc.) at an appropriate phase ratio until equilibrium is attained (Fig. 1.12). The aqueous phase is then removed, fresh strip solution is added to the organic phase, and the procedure repeated. This process is continued until all (or as much as possible) of the metal has been stripped from the organic phase.

1.5 Contents of this thesis

This PhD thesis is organized into six (6) chapters, each of them dealing with different aspects of development the approaches for recovery of the copper from low-grade copper resources.

Chapter 1 introduces the conventional copper producing process and the general overview of the low-grade copper ores and mine tailings. The fundamental technologies for the recovery of copper

from ores by flotation and hydrometallurgical processes are discussed throughout this dissertation.

Chapter 2 describes the possibility of copper recovery from the low-grade ores (copper grade: 0.4 mass%, CuFeS_2 as the main copper mineral) using direct atmospheric and high-pressure oxidative leaching (HPOL). The effect of sulfuric acid concentrations (0–1.0 M) on direct leaching of low-grade copper ore was investigated.

Chapter 3 presents the results for the recovery of copper from the low-grade copper ore using flotation followed by HPOL. Firstly, the effects of various flotation parameters, such as time, collector (PAX) dosage, slurry pH and air injection rate on beneficiation of copper from the sample were studied. Then, the concentrate obtained under the optimal flotation conditions from low-grade copper ore was used in HPOL study. The leaching efficiency of copper from the concentrate into solution under HPOL was discussed under a variety conditions such as total pressure, leaching time, temperature, and sulfuric acid concentration. As a result, a process flow for the recovery of copper from the low-grade copper ores is proposed based on this result.

Chapter 4 investigates the leaching of copper from chalcopyrite in H_2SO_4 solution at pressure oxidative conditions and kinetics of copper dissolution. Leaching variables that affect the rate of copper dissolution from chalcopyrite are particle size ($-38 \mu\text{m}$, $+38-75 \mu\text{m}$ and $+75-100 \mu\text{m}$), agitation speed (300–900 rpm), total pressure (0.8–2.0 MPa), temperature (160–180 °C) and sulfuric acid concentration (0.1–2.0 M) were studied. The leaching kinetic analysis of chalcopyrite was conducted using the result obtained from each experiment and a shrinking core model. Then, the effect of Fe/Cu mole ratio (1–20 mol/mol, adjusted by addition of pyrite) on chalcopyrite leaching from a copper ore was investigated for understanding the influence of pyrite on chalcopyrite leaching and its dissolution mechanism.

Chapter 5 discusses the possibility of applying the developed flotation and HPOL processes for recovery of copper from mine tailings. First, flotation under the various flotation time, slurry pH, and sulfurizing reagent were carried out for obtaining the optimal conditions. Then, in order to

achieve an efficient copper dissolution process, the HPOL using the concentrate of mine tailings obtained by flotation under the optimal conditions was performed with varying the parameters such as sulfuric acid concentration, total pressure, temperature, and pulp densities. Finally, the pregnant leach solution obtained from the optimal HPOL of the concentrate of mine tailings, was fed to solvent extraction for separating copper from other impurities such as iron. Subsequently, the stripping was conducted using the Cu-loaded organic phase for making Cu-rich solutions. As a result, the application of the combined method consistency of flotation, HPOL, and solvent extraction for recovery copper from mine tailings was evaluated.

Chapter 6 provides a summary of findings from each chapter and recommendations for future research based on the obtained results and observations for recovery of copper from low-grade copper resources. Finally, an advanced copper recovery process from the low-grade copper resources was proposed by a combination method of flotation-HPOL.

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Chapter 2: Direct Leaching of the Low-Grade Copper Ore

2.1 Introduction

Copper is one of the important non-ferrous metals which has a lot of commercial applications in a wide range of industries such as medicine, construction, machinery, electrical and electronics and telecommunication [1]. Chalcopyrite (CuFeS_2) is the most abundant and the most refractory copper sulfide mineral which accounts for about 70 % of the copper reserves in the world [2]. At present, a large portion of the copper is produced from chalcopyrite ore via flotation followed by the pyrometallurgical method [3–5]. Due to the long-term mining activity and economic growth of countries in the world, the reduction of copper grade and depletion of high-grade copper ore have gradually been happened during last several decades [6–7]. With the decreasing of copper grade, the content of the copper ores becomes complex due to the increasing of impurities such as clay minerals and refractory ores. For those reasons, it becomes more difficult to apply the conventional pyrometallurgical method to treatment of the low-grade copper ores [6–7]. On the other hand, the copper market continually constrained on the stable supply because the increasing of demand for copper in recent years and the low-grade ores and tailings can account for up to three-quarters of the total reserves of certain metals [8–10]. Hence, it becomes important to address the utilization of common secondary resources especially low-grade ores by the development of the processing technology. Recently, much attention has been focused on the hydrometallurgical route, particularly acid leaching, which suggests a viable alternative approach to extract copper from low-grade sulfide ores, complex ores and tailings [11–14]. There are many studies related to the development of hydrometallurgical routes to extract copper from oxidized and copper sulfide ores by atmospheric leaching, pressure leaching and biological leaching processes [15–18].

In this chapter, the leaching efficiency of copper from low-grade copper ore was investigated using atmospheric leaching and high-pressure oxidative leaching (HPOL) processes, respectively. The effects of sulfuric acid concentration on the leaching efficiency of copper from the low-grade copper ore were studied.

2.2 Experimental

2.2.1 Sample

A low-grade copper ore (Fig. 2.1) from Chile was used in this study. The sample was firstly prepared by a jaw crusher (P-1, Fritsch Japan Co., Ltd) and a disc mill (P-13, Fritsch Japan Co., Ltd) followed by a Sieve Shaker (AS200 digit, Retsch Japan Co., Ltd) to a size fraction of under 160 μm . The average particle size of the sample was 27 μm (D_{50}) which estimated by a wet type size distribution analyzer (Microtrac MT3300II) as shown in Fig. 2.2. The chemical composition of the low-grade copper ore was determined by an inductively coupled plasma-optical emission spectrometry (ICP-OES, SII NanoTechnology Inc., Chiba, Japan) and X-Ray Fluorescence Spectrometer (XRF, Rigaku ZSX Primus II). As shown in Table 2.1, the sample consists of 0.4 mass% copper (Cu), 4.6 mass% iron (Fe) and 38.3 mass% silicon (Si), and small amounts of a number of other elements, including aluminium (Al), calcium (Ca), potassium (K), magnesium (Mg) and sulfur (S). The mineral composition of the ore was identified by X-Ray Diffractometer (XRD, Rigaku RINT-2200V) and XRD pattern of the sample is given in Fig. 2.3. The main mineralogical constituents of the low-grade copper ore are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), chlorite ($(\text{Mg}, \text{Fe})_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$), quartz (SiO_2), and chalcopyrite (CuFeS_2). The chalcopyrite was certified as the main copper minerals in the low-grade copper ore sample.

a) Original low-grade copper ore



b) Powder of the low-grade copper ore



Fig. 2.1 Photograph of a) original and b) powder of the low-grade copper ore used in this chapter.

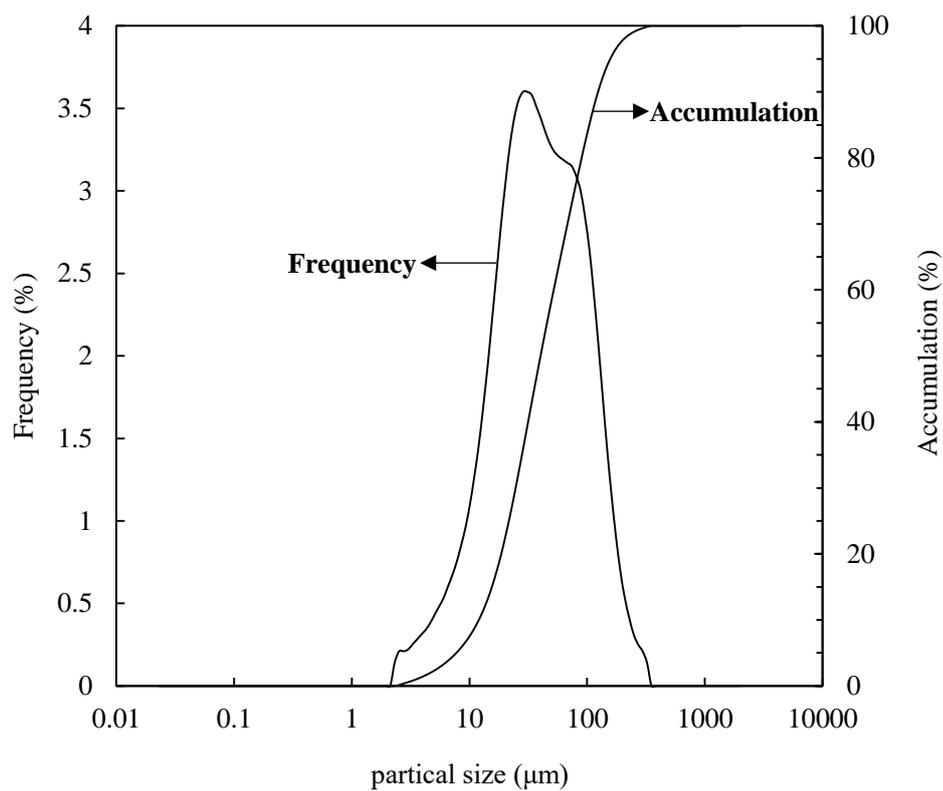


Fig. 2.2 Size distribution of the low-grade copper ore.

Table 2.1 Chemical compositions of the low-grade copper ore.

Chemical contents (mass%)								
Elements	Al	Ca	Cu	Fe	K	Mg	Si	S
Grade	1.8	1.4	0.4	4.6	1.3	2.7	38.3	4.5

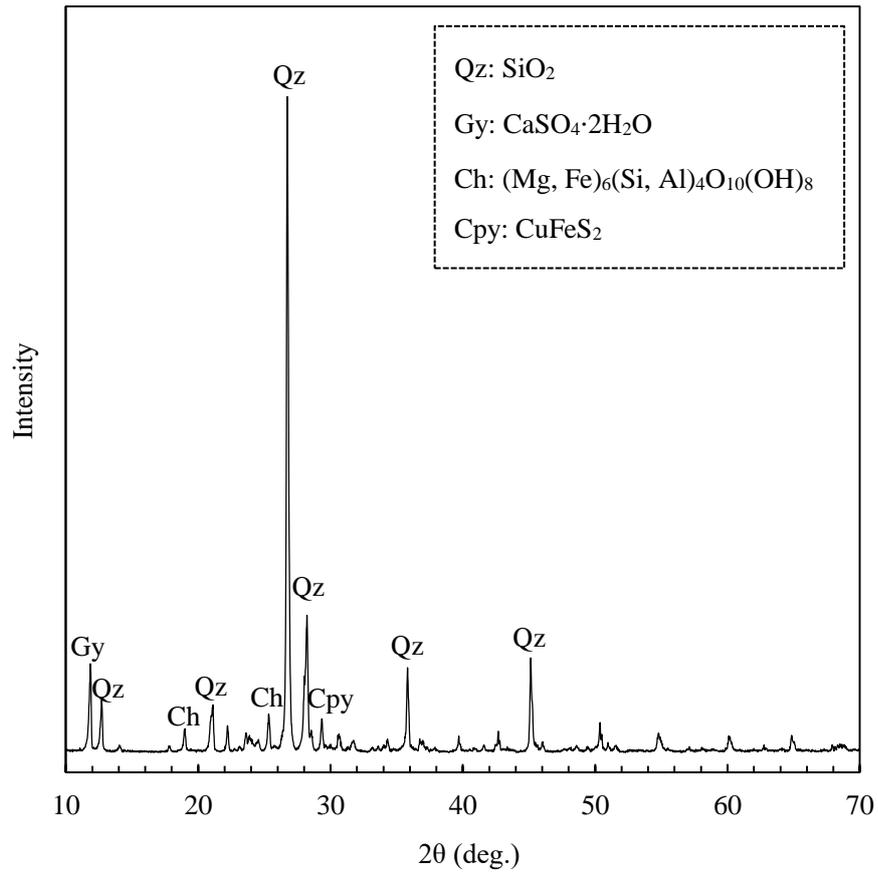


Fig. 2.3 XRD pattern of a low-grade copper ore.

2.2.2 Reagent

The reagent used in this chapter was shown in [Table 2.2](#). The sulfuric acid (H_2SO_4) and oxygen (O_2) was used as an oxidizer in the direct leaching experiments.

Table 2.2 List of the chemical reagents used in this chapter.

Experiments	Name	Maker	Formula
Atmospheric leaching	Sulfuric acid	Kanto Chemical Co., Inc.	H_2SO_4
High-pressure oxidative leaching	Sulfuric acid Oxygen	Kanto Chemical Co., Inc. Aiba Shouten Inc.	H_2SO_4 O_2

2.2.3 Procedure

2.2.3.1 Direct atmospheric leaching of low-grade copper ore

Froth concentrate from the flotation of low-grade copper ore sample was dissolved in a sulfuric acid (H_2SO_4) solution placed in a beaker (see [Fig. 2.4](#)). As the procedure shown in [Fig. 2.5](#), all experiments were carried out under various acid concentrations (0–10 M (mol/L)) at a fixed temperature (90 °C), fixed leaching time (60 min), pulp density 10 %, and adjusted stirring speed (700 rpm). After the experiment, solid residue and pregnant leach solution (PLS) were separated by filtration.

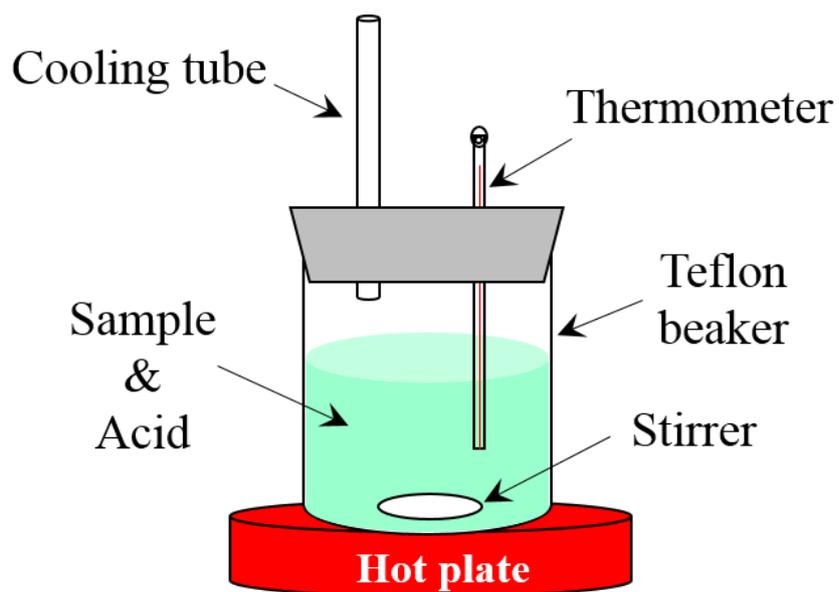


Fig. 2.4 Illustration of the atmospheric leaching.

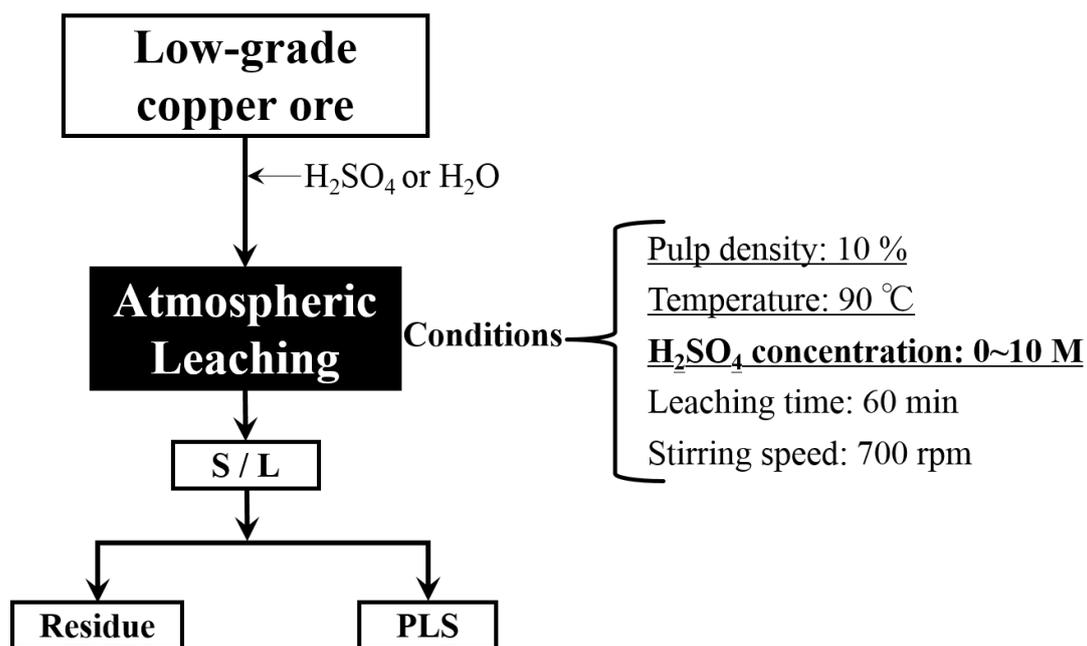


Fig. 2.5 Procedure of the atmospheric leaching.

2.2.3.2 Direct high–pressure oxidative leaching of low–grade copper ore

High–pressure oxidative leaching (HPOL) experiments were conducted in an autoclave (Fig. 2.6, Nitto Koastu, Japan) using the low–grade copper ore. The procedure of the high–pressure oxidative leaching experiments was shown in Fig. 2.7. The autoclave is equipped with 200 mL of a Teflon vessel, inlet/discharge lines for oxygen and excess gasses, pressure and temperature sensors as well as an electrical heating system. A schematic illustration of the autoclave is shown in Fig. 2.6. A 5 g sample of the low–grade copper ore was transferred into a vessel with 50 mL distilled water or sulfuric acid solution with concentration ranging from 0 to 1.0 M. The vessel containing slurry was placed into the autoclave and experimental parameters were set to their nominal values throughout the leaching experiments as follows: when temperature reached at desired value (170 °C), oxygen gas was injected to the slurry into the vessel with controlling the total pressure (2.0 MPa), and allowed the oxidation reaction for 60 min. After the oxidation reaction is completed, turn off the oxygen gas supply followed by cooling down the slurry to below 50 °C and purge the autoclave with excess oxygen gas and vapor through the discharge line. The oxidized slurry was filtrated to separate solid residue and pregnant leach solution for analyses.

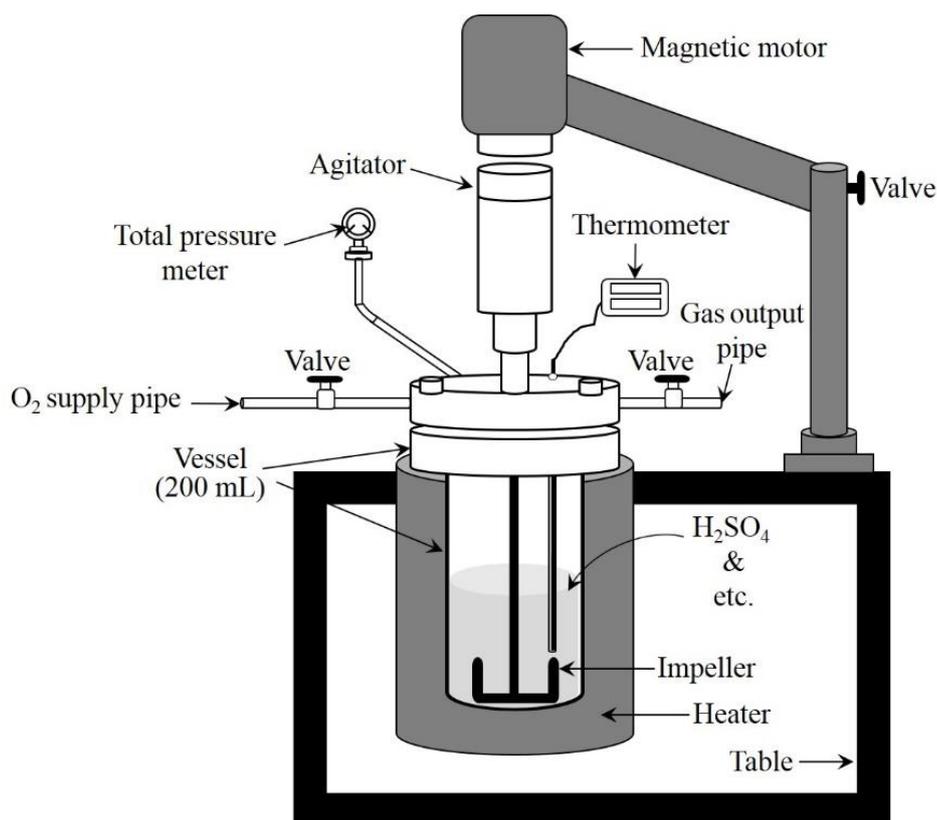


Fig. 2.6 A schematic illustration of an autoclave for high-pressure oxidative leaching.

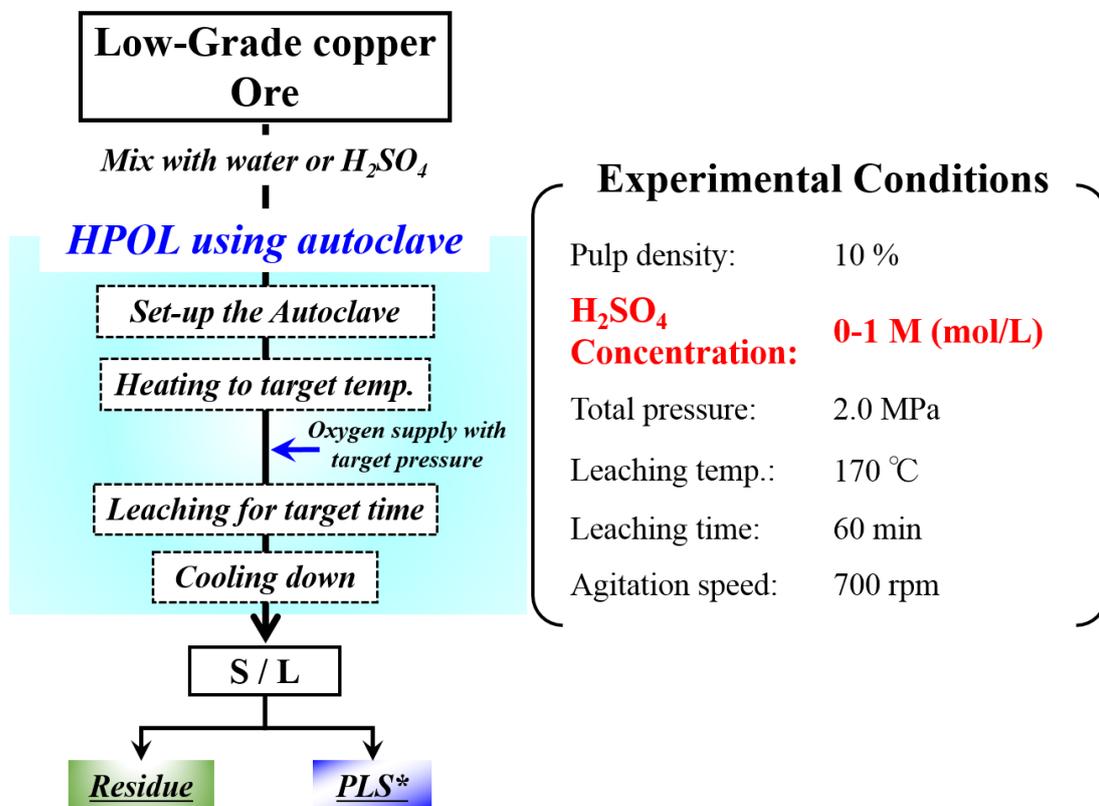


Fig. 2.7 Procedure of the high-pressure oxidative leaching.

2.2.4 Characterization and analyses

In this chapter, all solution (PLS: Pregnant Leach Solution) analysis was conducted using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP–OES, SII NanoTechnology Inc., Chiba, Japan). In addition, the mineral composition of the solid samples was identified by X–Ray Diffractometer (XRD, Rigaku RINT–2200V) and Scanning Electron Microscope Energy Dispersive X–ray Spectrometry (SEM–EDS). The leaching rate of each metal from the low–grade copper ore into the sulfuric acid solution was calculated by [Eq. 2.1](#) as shown below.

$$\text{Metal leaching rate: } R_M (\%) = \frac{C_L \cdot V_L}{C_F \cdot m_F} \times 100 \quad (2.1)$$

Where C_L and C_F is the concentration of metal in PLS (mg/L) and feed (mg/kg), respectively. V_L is the volume of PLS (L) and m_F is the dry mass of the feed (kg).

2.3 Results and discussion

2.3.1 Direct atmospheric leaching–effect of sulfuric acid concentration

Under the atmospheric oxidative condition, a sample of the froth concentrate was dissolved in various concentrations (0–10 M) of sulfuric acid (H_2SO_4) solutions at the temperature of 90 °C, and agitation speed of 700 rpm for 1 hour. As shown in [Fig. 2.8](#), the leaching efficiencies of copper and iron dissolution from the copper concentrate did not exceed 12 % and 18 % respectively with sulphuric acid solutions. The solid residue obtained from the atmospheric leaching with sulfuric acid was analyzed by SEM–EDS. It can be seen from [Fig. 2.9](#) that the surface of minerals in the froth concentrate was coated by sulfur–passivating layer. For that reason, it could be concluded that some of the chalcopyrite (CuFeS_2) dissolved into the pregnant leach solution (PLS) at an early stage and after that the formation of passivation layers of elemental sulfur (S^0) on the chalcopyrite may impede the leaching kinetics of copper from its concentrate.

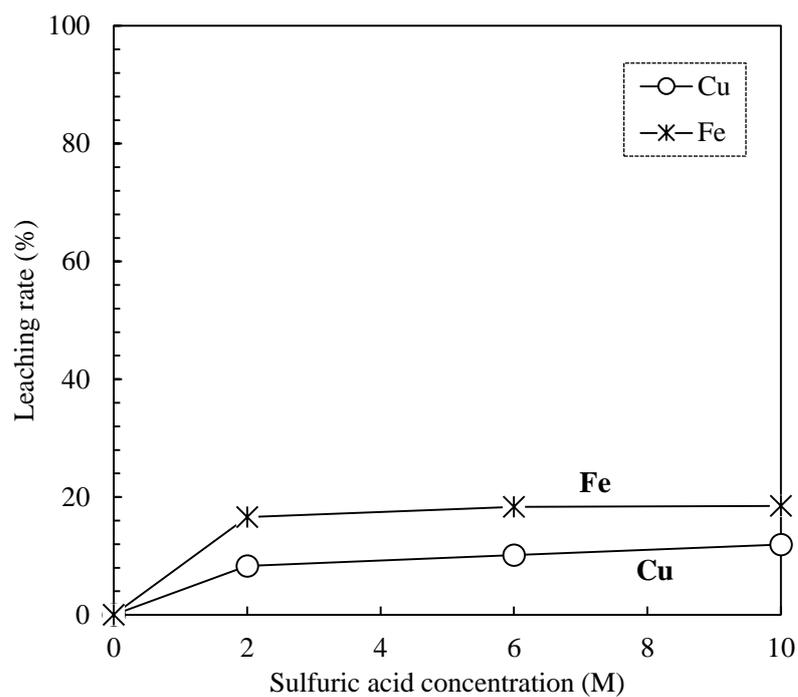


Fig. 2.8 Leaching efficiency of copper and iron as a function of acid concentration.

(H_2SO_4 concentration: 0–10 M, pulp density: 10 %, temperature: 90 °C, leaching time: 60 min and agitation speed: 700 rpm at atmospheric pressure)

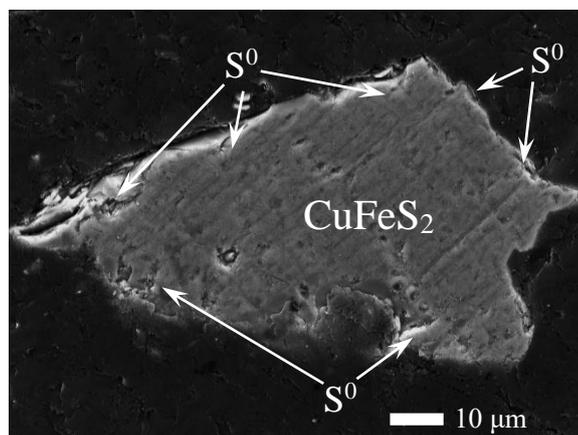


Fig. 2.9 SEM-EDS image of the solid residue obtained from atmospheric sulfuric acid leaching at 90 °C for 60 min leaching.

(Whitish areas show the sulfur (S^0) passivation layer)

2.3.2 Direct high–pressure oxidative leaching–effect of sulfuric acid concentration

The effect of sulfuric acid concentration on the copper and iron dissolution were conducted in the range of 0 (water)–1.0 M. The other conditions were fixed at a pulp density of 10 %, leaching temperature of 170 °C, leaching time of 60 min, agitation speed of 700 rpm and total pressure of 2.0 M. It can be seen from the results shown in [Fig. 2.10](#) that the copper and iron dissolution was 9.6 % and 2.3 %, respectively, under the sulfuric acid concentration of 0 M, i.e., water, which is similar to that rates under atmospheric leaching conditions ([Fig. 2.8](#)). In addition, both the copper and iron leaching rate depend significantly on the sulfuric acid concentration in the range of 0–1.0 M. The copper dissolution rate increased up to 95.7 % with the increases sulfuric acid of 0.3 M, and there are no much changes when the sulfuric acid concentration further increased to 1.0 M. On the other hand, the iron leaching rate reached to be 84.6 % when the sulfuric acid concentration was 1.0 M. It is observed that the dissolution of copper from the low–grade copper ore, in which chalcopyrite consists as the major copper mineral, is a sulfuric acid consumption reaction.

The pregnant leach solution obtained after high–pressure leaching under the different sulfuric acid concentration and the concentration of the element in it was shown in [Fig. 2.11](#) and [Table 2.3](#), respectively. It can be seen that color of the pregnant leach solution changed from no–color and/or white (sulfuric acid concentration: 0–0.5 M) to yellow (sulfuric acid concentration: 1.0 M), may be due to that both the copper and iron concentration is lower at lower acid concentration, whereas the iron concentration was quite high under 1.0 M acid concentration. As the concentration is shown in [Table 2.3](#), both the concentration of copper and iron increased with the increasing of sulfuric acid concentration similar to the variety of the leaching rates. The maximum copper and iron concentration in the pregnant leach solution was 0.49 g/L and 5.5 g/L, respectively. That is the reason why the pregnant leach solution change from no–colour to yellow. However, even the leaching rate of copper achieved to be about 100 %, the concentration of it in the pregnant leach solution is too lower to link with the subsequent process such as solvent extraction. So that, it suggested that a pretreatment process to upgrading the copper grade and decreasing the impurities concent is necessary for achieving a significant copper recovery from the low–grade copper ore.

The residues obtained by high–pressure leaching under a variety sulfuric acid concentration and its XRD patterns were given in [Fig. 2.12](#) and [2.13](#), respectively. It can be seen from the [Fig. 2.12](#)

that the colour of the residues varying from original brown (sulfuric acid concentration: 0–0.1 M) to yellow (sulfuric acid concentration: 0.2–0.5 M), and finally to be white (sulfuric acid concentration: 1.0 M). In order to know the mineral composition of the residues, the XRD analysis were conducted using the residues obtained after high–pressure oxidative leaching of the low–grade copper ore under the sulfuric acid concentration in a range of 0–1.0 M. As the results shown in [Fig. 2.13](#), the peaks of chlorite ((Mg, Fe)₆(Si, Al)₄O₁₀(OH)₈) disappeared due to the iron in it was dissolved under high–pressure leaching conditions in a high acidity medium. By the same time, the peaks of jarosite ((H₃O)Fe₃(SO₄)₂(OH)₆) appeared when the sulfuric acid concentration over 0.1 M because of the dissolved iron from both chalcopyrite and chlorite reprecipitated at examined conditions. However, the peaks of jarosite disappeared when the high–pressure leaching was conducted under the sulfuric acid concentration of 1.0 M. The changes of the pH and ORP of the slurry before and after high–pressure leaching was given in [Table 2.4](#).

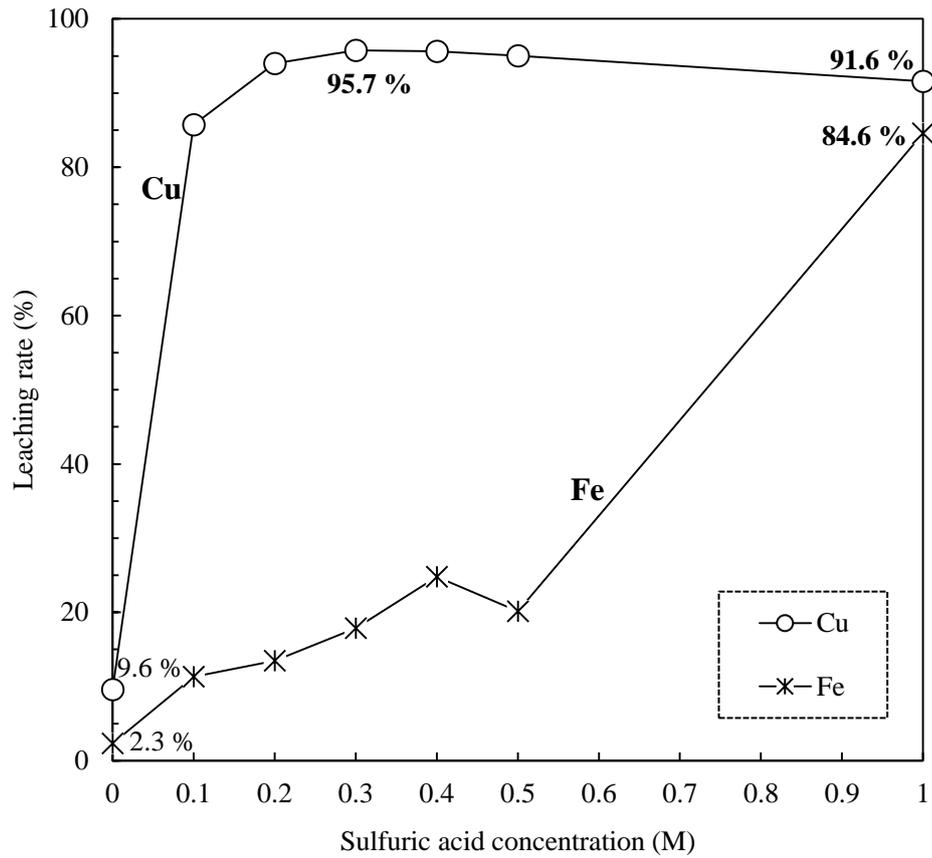


Fig. 2.10 Leaching efficiency of copper and iron as a function of acid concentration.

(H₂SO₄ concentration: 0–1.0 M, pulp density: 10 %, temperature: 170 °C, leaching time: 60 min,
and agitation speed: 700 rpm at total pressure 2.0 MPa)



Fig. 2.11 Pregnant leach solutions obtained after high-pressure oxidative leaching under the condition of 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 M.

Table 2.3 Element concentration in the pregnant leach solutions.

Sulfuric acid concentration (M)	Elements concentration (g/L)	
	Cu	Fe
0	0.06	0.18
0.1	0.44	0.76
0.2	0.48	0.90
0.3	0.49	1.20
0.4	0.49	1.70
0.5	0.50	1.50
1.0	0.45	5.50



Fig. 2.12 Photograph of the low-grade copper ore and residues obtained after high-pressure oxidative leaching under the condition of 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 M.

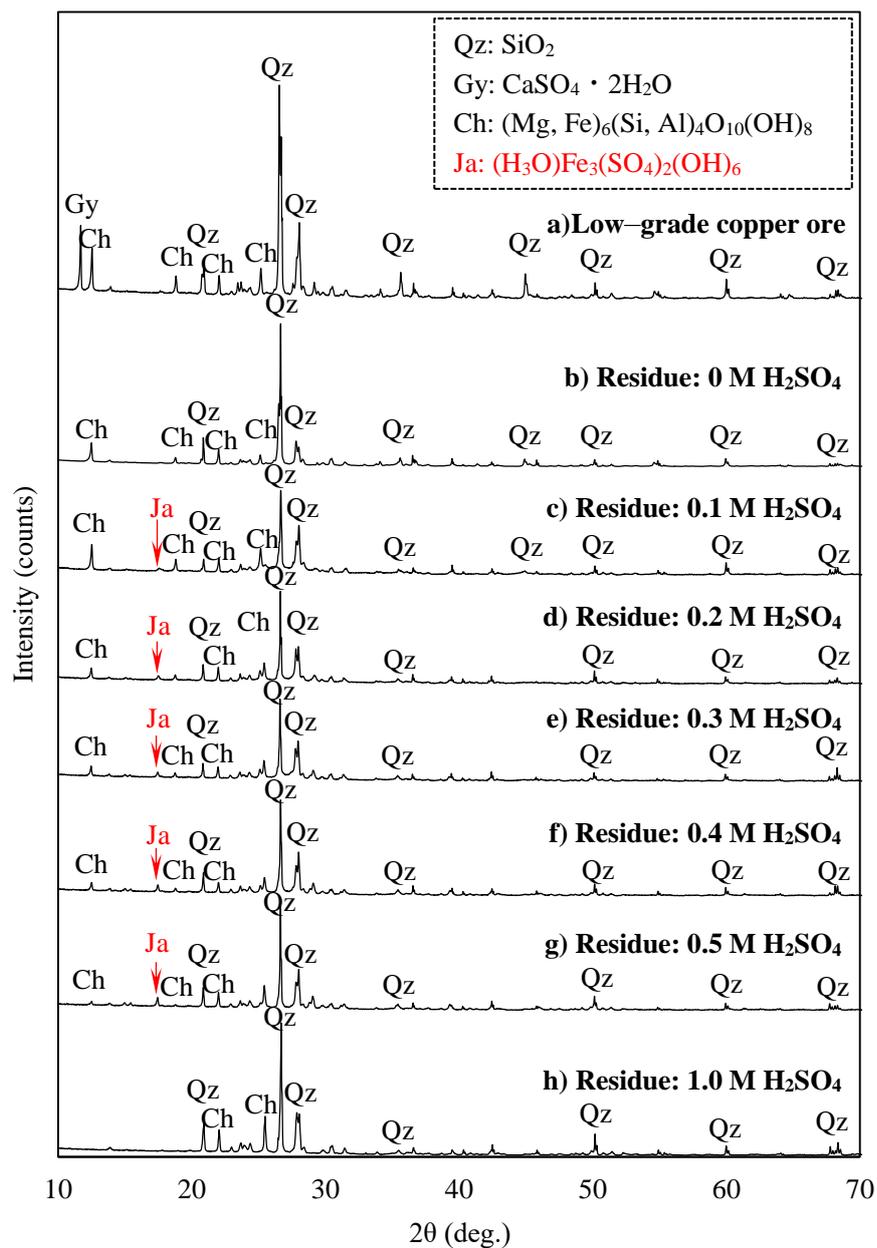


Fig. 2.13 XRD patterns of a) low-grade copper ore and residue obtained under the condition of b) 0 M, c) 0.1 M, d) 0.2 M, e) 0.3 M, f) 0.4 M, g) 0.5 M, and h) 1.0M. (H_2SO_4 concentration: 0–1.0 M, pulp density: 10 %, temperature: 170 °C, leaching time: 60 min and agitation speed: 700 rpm, and total pressure: 2.0 MPa)

Table 2.4 Changes in the slurry pH and ORP before and after high-pressure oxidative leaching.

Sulfuric acid concentration (M)	pH		ORP	
	before	after	before	after
0	8.31	6.33	241.77	360.87
0.1	1.22	1.67	658.47	640.77
0.2	0.98	1.33	676.17	662.37
0.3	0.79	1.58	688.37	672.97
0.4	0.70	1.03	693.57	679.17
0.5	0.68	0.90	695.07	684.47
1.0	0.39	0.62	709.17	697.37

2.4 Conclusion

In this chapter, the copper recovery from low-grade copper ores was investigated using direct atmospheric and high-pressure oxidative leaching. The findings can be summarized as follows.

- (1) The leaching efficiencies of copper and iron dissolution from the low-grade copper ores were 12 % and 18 %, respectively, under the atmospheric leaching conditions, due to the formation of passivation layers of elemental sulfur (S^0) onto the unreached copper particles, which impede the leaching kinetics of copper from the low-grade copper ores.
- (2) A maximum dissolution rate of copper 98 % achieved under the sulfuric acid concentration of 0.3 M using high-pressure oxidative leaching, while the iron leaching rate reached around 26 %. However, the copper concentration in the pregnant leach solution was only 0.06 g/L, that lower copper concentration causes difficulty in the subsequent process, namely solvent extraction.

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Chapter 3: Flotation and the Combination of Flotation with High-Pressure Oxidative Leaching Using Low-Grade Copper Ore

3.1 Introduction

As introduced in **Chapter 1**, the reduction of copper grade and depletion of high-grade copper ore have gradually been happened during last several decades [1–2], because of the long-term mining activity and economic growth of countries in the world. With the decreasing of copper grade, the content of the copper ores becomes complex due to the increasing of impurities such as clay minerals and refractory ores. For those reasons, it becomes more difficult to apply the conventional pyrometallurgical method to the treatment of the low-grade copper ores [1–2]. On the other hand, the copper market continually constrained on the stable supply because the increasing of demand for copper in recent years and the low-grade ores and tailings can account for up to three-quarters of the total reserves of certain metals [3–5]. Hence, it becomes important to address the utilization of common secondary resources especially low-grade ores by the development of the processing technology. Recently, much attention has been focused on the hydrometallurgical route, particularly acid leaching, which suggests a viable alternative approach to extract copper from low-grade sulfide ores, complex ores and tailings [6–9]. There are many studies related to the development of hydrometallurgical routes to extract copper from oxidized and copper sulfide ores by atmospheric leaching and biological leaching processes [10–13]. However, some researchers including the results obtained in **Chapter 1** have concluded that both direct atmospheric and biological leaching of copper from its ore is extremely slow due to the formation of an elemental, sulfur passivation layer on the surface of unreacted particles [14], and there are few references to the copper leaching from the low-grade copper resources using high-pressure oxidative leaching. Hence, in order to recover the copper from the low-grade copper ore efficiently a high-pressure oxidative leaching was selected as a major approach in this research. In addition, huge amounts of acid are required in the copper leaching from the low-grade copper ores, especially it contains

large amounts of carbonates or siliceous gangue minerals as impurities such as silicate which make difficulty on the separation process and produce many residues. On the other hand, copper concentration in the leach liquor/pregnant leach solution (PLS) is much lower when acid leaching is applied for copper extraction from low-grade ores and it causes difficulty in subsequent processes such as solvent extraction (SX) and electrowinning (EW).

Froth flotation is widely used to beneficiate and selectively separate copper ores. Therefore, it is essential to develop the hydrometallurgical processes for the extraction of copper from low-grade copper ores in combination with flotation as a pre-treatment process for upgrading the copper grade and reducing the impurity content. However, low-grade copper ores cannot be economically beneficiated by the conventional flotation process due to the fine particle size distribution of the ores. Therefore, an efficient approach, which could give reasonably high copper recovery, high copper grade and low impurity content, has been attracting much attention from researchers in this field. For those reasons, this study aims to develop an efficient method for the recovery of copper from low-grade copper ores by flotation followed by the leaching process.

In this Chapter, the effects of flotation parameters, particularly collector dosage (PAX), frother (MIBC), pH, contact time on the flotation performance of a low-grade copper ore were investigated. Leaching efficiency of copper from the froth concentrate obtained by the flotation of the low-grade copper ore was investigated using high-pressure oxidative leaching (HPOL) process. As a result of this Chapter, an efficient method has been proposed to recover copper from a low-grade copper ore by flotation followed by high-pressure oxidative leaching (HPOL).

3.2 Experimental

3.2.1 Sample

A low-grade copper ore (Fig. 2.1) from Chile was used in this study, which is same with the material used in Chapter 2. The sample was firstly prepared by a jaw crusher (P-1, Fritsch Japan Co., Ltd) and a disc mill (P-13, Fritsch Japan Co., Ltd) followed by a Sieve Shaker (AS200 digit, Retsch Japan Co., Ltd) to a size fraction of under 160 μm . The average particle size of the sample was 27 μm (D_{50}) which estimated by a wet type size distribution analyzer (Microtrac MT3300II). The chemical composition of the low-grade copper ore was determined by an inductively coupled

plasma–optical emission spectrometry (ICP–OES, SII NanoTechnology Inc., Chiba, Japan) and X–Ray Fluorescence Spectrometer (XRF, Rigaku ZSX Primus II). As shown in [Table 3.1](#), the sample consists of 0.4 mass% copper (Cu), 4.6 mass% iron (Fe) and 38.3 mass% silicon (Si), and small amounts of a number of other elements, including aluminium (Al), calcium (Ca), potassium (K), magnesium (Mg) and sulfur (S). The mineral composition of the ore was identified by X–Ray Diffractometer (XRD, Rigaku RINT–2200V) and XRD pattern of the sample is shown in [Table 3.1](#). The main mineralogical constituents of the sample are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), chlorite ($(\text{Mg, Fe})_6(\text{Si, Al})_4\text{O}_{10}(\text{OH})_8$), quartz (SiO_2), and chalcopyrite (CuFeS_2).

Table 3.1 Chemical compositions of the low–grade copper ore.

Elements	Chemical contents (mass%)							
	Al	Ca	Cu	Fe	K	Mg	Si	S
Grade	1.8	1.4	0.4	4.6	1.3	2.7	38.3	4.5
Major mineral phase	SiO_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $(\text{Mg, Fe})_6(\text{Si, Al})_4\text{O}_{10}(\text{OH})_8$, and CuFeS_2							

3.2.2 Reagent

The reagents used in this chapter were shown in [Table 3.2](#). The collector (PAX), frother (MIBC), and pH regulator ($\text{Ca}(\text{OH})_2$, H_2SO_4) was used in flotation, and the sulfuric acid (H_2SO_4) and oxygen (O_2) was used as an oxidizer in the high–pressure oxidative leaching experiments, respectively.

Table 3.2 List of the chemical reagents used in this chapter.

Experiments	Type	Name	Maker	Formula
Flotation	Collector	Potassium Amyl Xanthate (PAX)	Kanto Chemical	$\text{KC}_6\text{H}_{11}\text{OS}_2$
	Frother	Methyl Iso Butyl Carbinol (MIBC)	–	$\text{C}_6\text{H}_{13}\text{O}$
	pH regulator	Calcium hydroxide	Kanto Chemical	$\text{Ca}(\text{OH})_2$
		Sulfuric acid	Kanto Chemical	H_2SO_4
HPOL		Sulfuric acid	Kanto Chemical	H_2SO_4
		Oxygen	Aiba Shouten	O_2

3.2.3 Procedure

3.2.3.1 Flotation of low-grade copper ore

All the flotation tests were carried out using a laboratory mechanical flotation machine (237FL, Mekhanobr–tekhnik Corp.) equipped with a plastic flotation cell (500 mL) as shown in [Fig. 3.1](#). The most common reagent for traditional copper flotation such as collector of potassium amyl xanthate (PAX, $\text{C}_5\text{H}_{11}\text{OCSSK}$), frother of methyl isobutyl carbinol (MIBC, $\text{C}_6\text{H}_{14}\text{O}$) and pH regulator of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and sulfuric acid (H_2SO_4) were used in this study. As the procedure shown in [Fig. 3.2](#), the low-grade copper ore samples were first introduced into the flotation cell with 500 mL water under constant stripping (1000 rpm) to prepare a slurry of 10 % pulp density. pH of the slurry was then adjusted to target pH ranging from pH 4 to pH 10 using 1 M H_2SO_4 and 1 M $\text{Ca}(\text{OH})_2$ solutions and conditioning continued for 5 min. After adjusted the pH of the slurry, appropriate amounts of PAX as a collector and MIBC as frother were added to the cell and stirring continued for 5 min. Then, a certain amount (0.8–1.7 L/min) of air was injected into the cell throughout the flotation. Froth layer at the top of the cell during the flotation was gathered in the collection chamber by an auto-scraper. The collected froth concentrate and tailing of flotation were dried at 70 °C into an electric drying oven for 1 day and analyzed by ICP–OES, XRF and XRD.

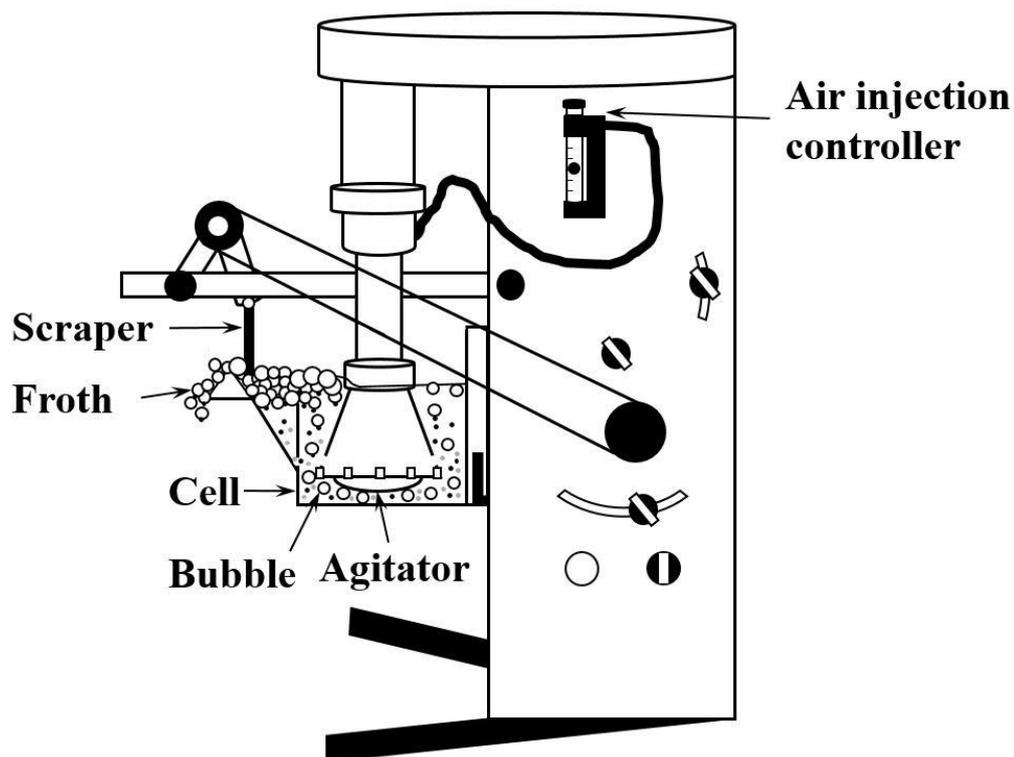


Fig. 3.1 Laboratory mechanical flotation machine.

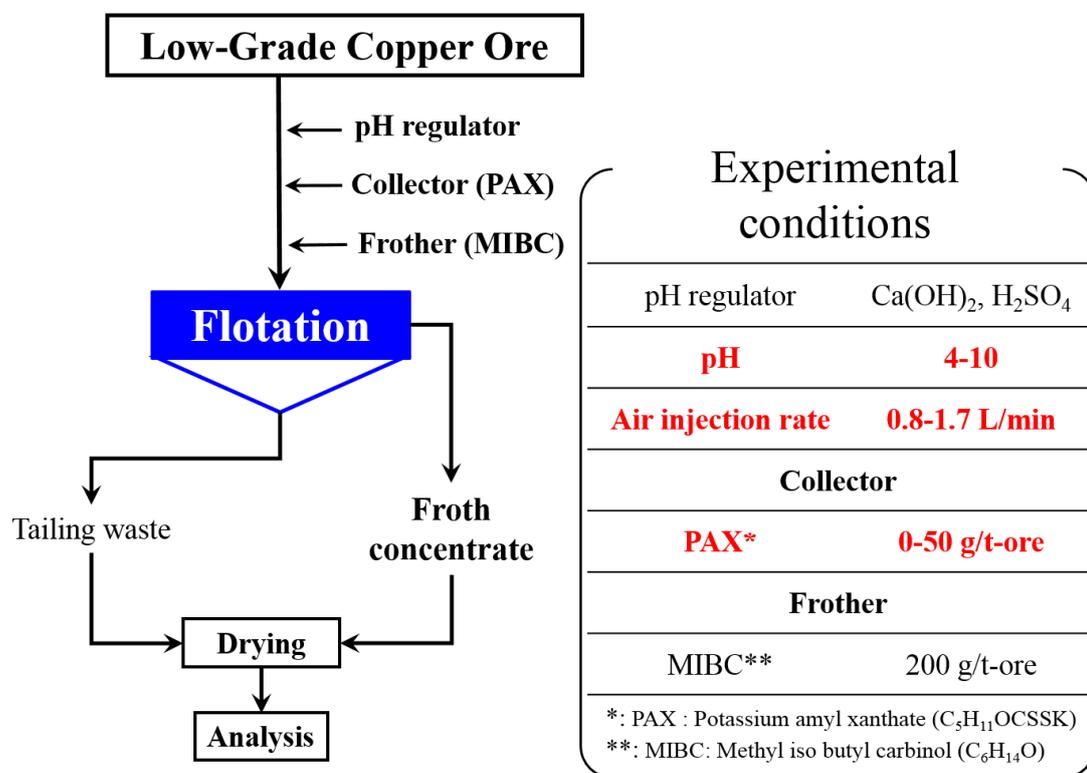


Fig. 3.2 Procedure of the flotation experiments.

3.2.3.2 High-pressure oxidative leaching of concentrate of low-grade copper ore

High-pressure oxidative leaching (HPOL) experiments were conducted in an autoclave (Fig. 2.6, Nitto Koastu, Japan) using the froth concentrate obtained from the flotation of the low-grade copper ore. The procedure of the high-pressure oxidative leaching experiments using the concentrate was shown in Fig. 3.3. A 5 g sample of the froth concentrate was transferred into a vessel with 50 mL distilled water or sulfuric acid solution with concentration ranging from 0.5 to 1.0 M. The vessel containing slurry was placed into the autoclave and experimental parameters were set to their nominal values throughout the leaching experiments as follows: when temperature reached at desired value (100, 160, 170 and 180 °C), oxygen gas was injected to the slurry into the vessel with controlling the total pressure (0.8, 1.5, 2.0, and 2.5 MPa), and allowed the oxidation reaction at varying times from 60 to 180 min. After the oxidation reaction is completed, turn off the oxygen gas supply followed by cooling down the slurry to below 50 °C and purge the autoclave with excess oxygen gas and vapor through the discharge line. The oxidized slurry was filtrated to separate solid residue and pregnant leach solution for analyses.

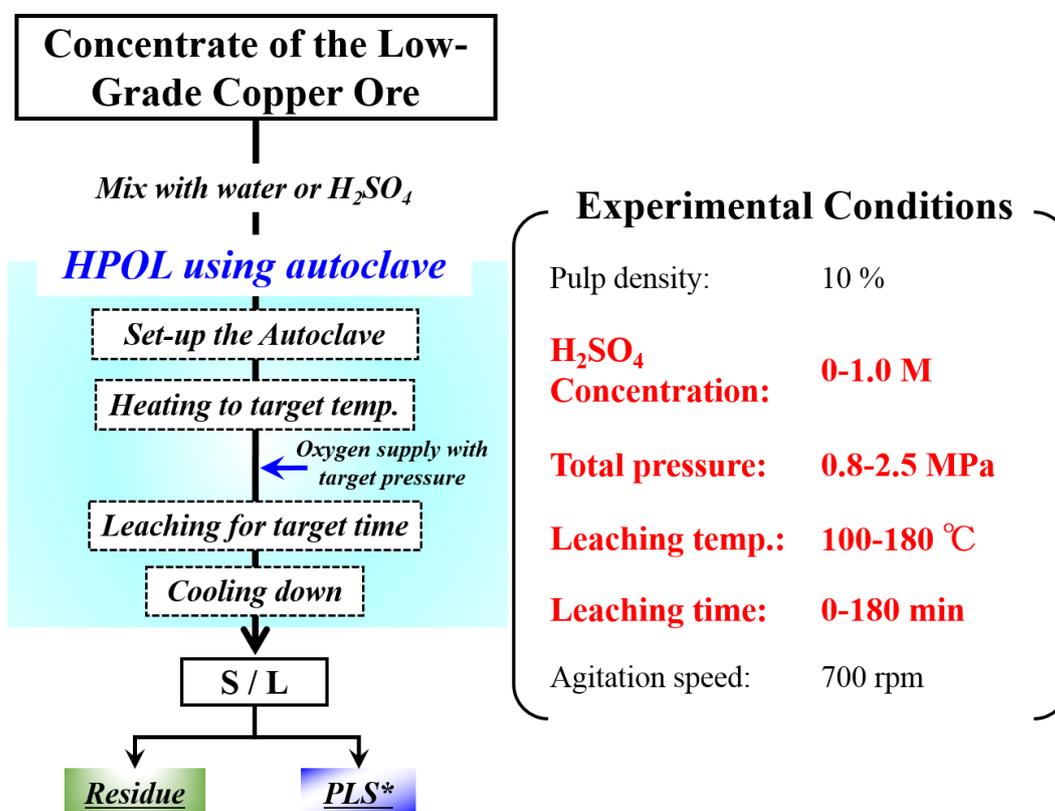


Fig. 3.3 Procedure of the high-pressure oxidative leaching experiments.

3.2.4 Characterization and analyses

In this chapter, all solution analysis was conducted using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP–OES, SII NanoTechnology Inc., Chiba, Japan). In addition, the mineral composition of the solid samples was identified by X–Ray Diffractometer (XRD, Rigaku RINT–2200V).

The yield (Y), enrichment ratio (I) and recovery (R) of each metal from the low–grade copper ore were evaluated by [Eqs. 3.1–3.3](#).

$$\text{Yield: } Y (\%) = \frac{c}{F} \times 100 \quad (3.1)$$

$$\text{Enrichment ratio: } I = \frac{c}{f} \quad (3.2)$$

$$\text{Recovery: } R (\%) = \frac{c (f - t)}{f (c - t)} \times 100 \quad (3.3)$$

Where Y is the yield, I is an enrichment ratio, and R is the recovery of each metal. F and C are the weight of the feed and concentrate, f , c , and t are the metals grade in feed, concentrate and tailing, respectively.

The leaching rate of each metal from the concentrate of low–grade ore into the water or sulfuric acid solution was calculated by [Eq. 3.4](#) as shown below.

$$\text{Metal leaching rate: } R_M (\%) = \frac{C_L \cdot V_L}{C_F \cdot m_F} \times 100 \quad (3.4)$$

Where C_L and C_F is the concentration of metal in PLS (mg/L) and feed (mg/kg), respectively. V_L is the volume of PLS (L) and m_F is the dry mass of the feed (kg).

3.3 Results and discussion

3.3.1 Flotation of low–grade copper ore

3.3.1.1 Effect of flotation time

The effect of flotation time on the copper beneficiation and recovery from a low–grade copper ore was investigated by varying the time from 5 to 20 min. Other conditions, namely pulp density, slurry pH, collector (PAX) dosage, frother (MIBC) dosage, and air injection rate, were kept constant at 10 %, pH of 8, 50 g/t–ore, 200 g/t–ore, and 0.8 L/min. The experimental results presented in [Fig. 3.4](#) and [Table 3.3](#) showed that the grade, recovery and enrichment ratio of copper

is increased with increasing of flotation time from 5 to 10 min. The maximum grade, recovery and enrichment ratio of copper from the low-grade copper ore were 7.1 mass%, 87.8 %, and 22.6 after 10-min flotation. An increase in the flotation time further up to 20 min resulted in a 3.2 % and 10.4 decreases in the copper grade and enrichment ratio, respectively, while the copper recovery did not change obviously. The yield of the low-grade ore sample is increased with increasing the flotation time while there are no changes like other flotation results (Table 3.3). The increment of the yield may be related to the flotation of impurity minerals such as clay minerals and silicates present in a low-grade copper ore. As a result, flotation time was selected to be 10 min as an optimal condition for the further flotation experiments.

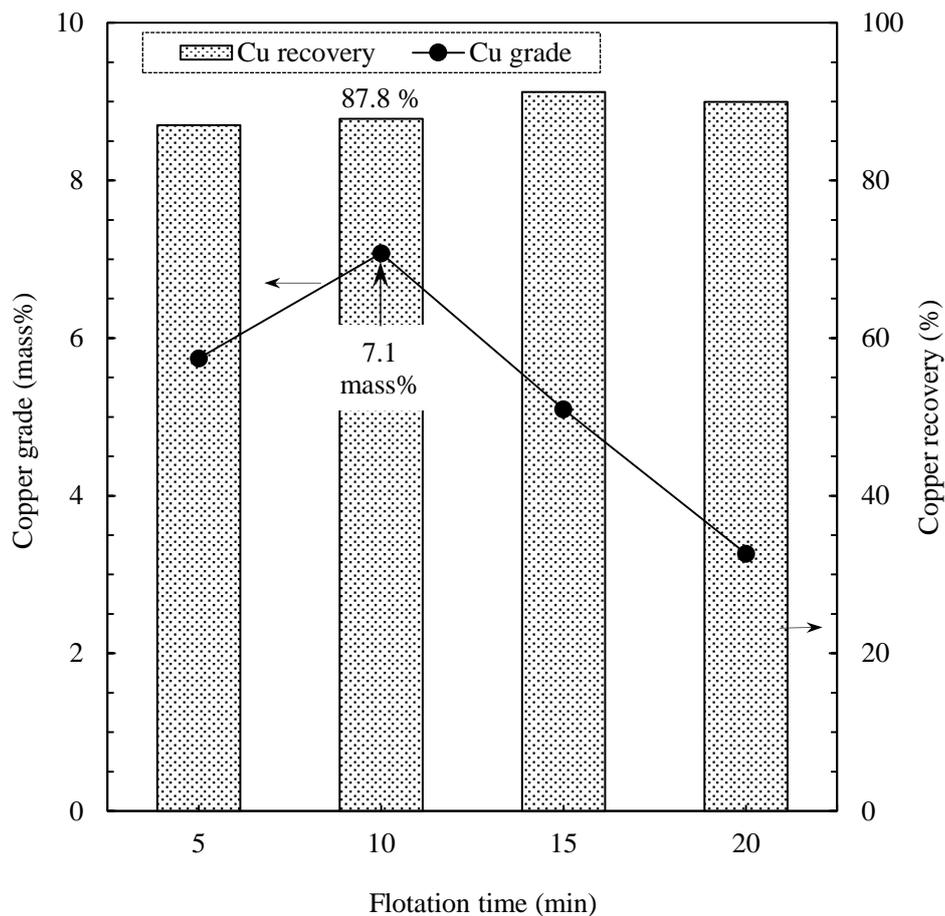


Fig. 3.4 The copper grade and recovery as a function of flotation time.

(Flotation time: 5–20 min, pulp density: 10 %, slurry pH: 8, PAX: 50 g/t-ore, MIBC: 200 g/t-ore, and air injection rate: 0.8 L/min)

Table 3.3 Effect of flotation time on copper enrichment ratio and yield.

Flotation time (min)	Contents	
	Cu enrichment ratio	Yield (%)
5	18.31	3.19
10	22.56	3.81
15	16.24	4.66
20	10.41	6.22

3.3.1.2 Effect of collector (PAX) and its dosage

The flotation experiments were conducted under the fixed conditions as follows: pulp density of 10 %, frother (MIBC) dosage of 200 g/t–ore, air injection rate of 0.8 L/min at natural pH (pH 8) and flotation time of 10 min when collector (PAX) dosage varied from 0 to 50 g/t–ore. The results of the flotation experiment shown in [Fig. 3.5](#) indicated the maximum copper grade of 11.1 mass%, maximum copper enrichment ratio of 24.7, and copper recovery of 78.6 % when performed the flotation without PAX. These findings are in good agreement with other published results [15]: low–grade ore i.e. chalcopyrite is floatable without a collector due to its self–induced/ collector–less flotation ability in the pulp potential ranges. Self–induced/collector–less flotation is an influential property of this type ore to promote the copper recovery and reduce the reagent consumption. With the increase of PAX dosage to a 50 g/t–ore, copper grade in the froth concentrate decreased to 6.4 mass%, and copper recovery and yield increased to 90.5 % and 5.5 %, respectively ([Fig. 3.5](#) and [Table 3.4](#)). It is expected that the availability of extra collector molecules in the feed enhances the hydrophobicity of particles promoting the bubble–particle attachments that represent an increase of yield [16]. The tendency of the grade of iron in concentrate and the recovery of iron from the low–grade copper ore were quite similar to the both of grade and recovery of copper.

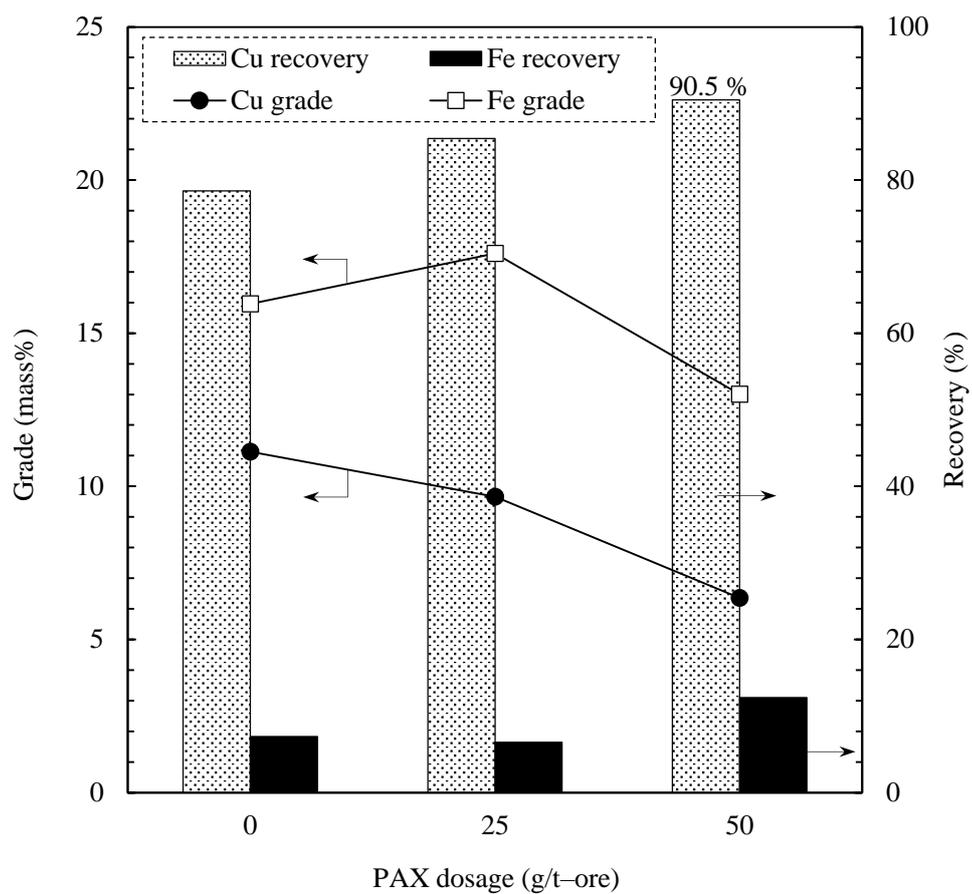


Fig. 3.5 The grade and recovery of copper and iron as a function of PAX dosage.

(PAX dosage: 0–50 g/t-ore, flotation time: 10 min, pulp density: 10 %, slurry pH: 8, MIBC: 200 g/t-ore, and air injection rate: 0.8 L/min)

Table 3.4 Effect of PAX dosage on copper enrichment ratio and yield.

PAX dosage (g/t-ore)	Contents	
	Cu enrichment ratio	Yield (%)
0	24.74	2.77
25	21.47	2.34
50	14.12	5.52

3.3.1.3 Effect of slurry pH

The flotation tests were performed under varying slurry pH ranging from pH 4 to pH 10 when other fixed parameters were: pulp density of 10 %, collector (PAX) dosage of 0 g/t-ore, frother (MIBC) dosage of 200 g/t-ore, air injecting rate of 0.8 L/min, and flotation time of 10 min. 1.0 M H₂SO₄ and 1.0 M Ca(OH)₂ were used as a pH regulator. The results obtained were presented in [Fig. 3.6](#) and [Table 3.5](#). When the slurry pH increased from pH 4 to pH 10, the grade of copper reached to 16.7 mass% from 9.4 mass%, whereas the recovery of copper and yield were decreased to 74.7 % and 2.3, from 83.1 % and 3.9, respectively. The grade of iron decreased with increasing the pH of slurry from pH 4 to pH 6, and increased further with increasing the pH of the slurry. The results obtained are verified that high pH value of the slurry has a positive effect on copper beneficiation due to the depression effect of pyrite (FeS₂) and gangue minerals including silicate (SiO₂) [17–19].

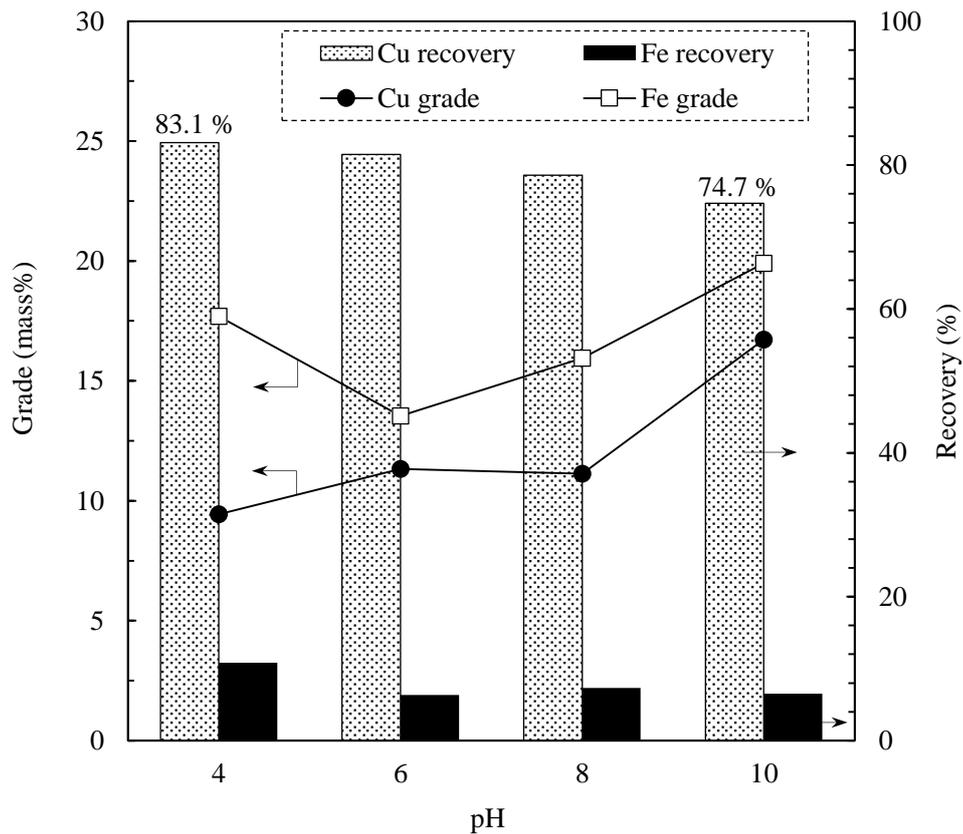


Fig. 3.6 The grade and recovery of copper and iron as a function of slurry pH.

(Slurry pH: 4–10, PAX: 0 g/t-ore, flotation time: 10 min, pulp density: 10 %, MIBC: 200 g/t-ore, and air injection rate: 0.8 L/min)

Table 3.5 Effect of slurry pH on copper enrichment ratio and yield.

Slurry pH	Contents	
	Cu enrichment ratio	Yield (%)
pH 4	19.25	3.94
pH 6	23.09	3.28
pH 8 (natural pH)	22.69	2.77
pH 10	34.09	2.33

3.3.1.4 Effect of air injection rate

The flotation experiments were carried out at air injection rates varied from 0.8 to 1.7 L/min with other variables like pulp density, collector (PAX) dosage, frother (MIBC) dosage, and pH range were fixed at 10 %, 0 g/t-ore, 200 g/t-ore, and pH 10 for 10-min flotation. The results of these flotation experiments were summarized in [Fig. 3.7](#) and [Table 3.6](#). The copper grade and enrichment ratio of copper decreased to 12.6 mass% from 16.7 mass% and to 31 from 42, whereas its recovery increased up to 91.0 % from 74.7 %, respectively, when the air injection rate is increased from 0.8 to 1.0 L/min. This result revealed that the formation of froth is lower ([Fig. 3.8](#)) due to the burst of bubbles before they reach the overflowing lip under an air injection rate of 0.8 L/min which resulting in a low copper recovery (74.7 %) [20]. The high copper recovery of 91.0 % and a low copper grade of 12.6 mass% with the air injection of 1.0 L/min are due to the formation of froth and its relatively faster flow as well as lightly loaded stabilized hydrophobic particles [20]. However, the air injection rate increased further until 1.7 L/min, the copper grade and its enrichment ratio increased to 18.2 mass% and 45.5, respectively, while the recovery of copper did not change much (>93 %) than that value with air injection of 1.0 L/min. The reason for that was shown in [Fig. 3.8](#). It seems that this observation may be related to the greater froth depth and stability of bubbles formed through sufficient particle attachment.

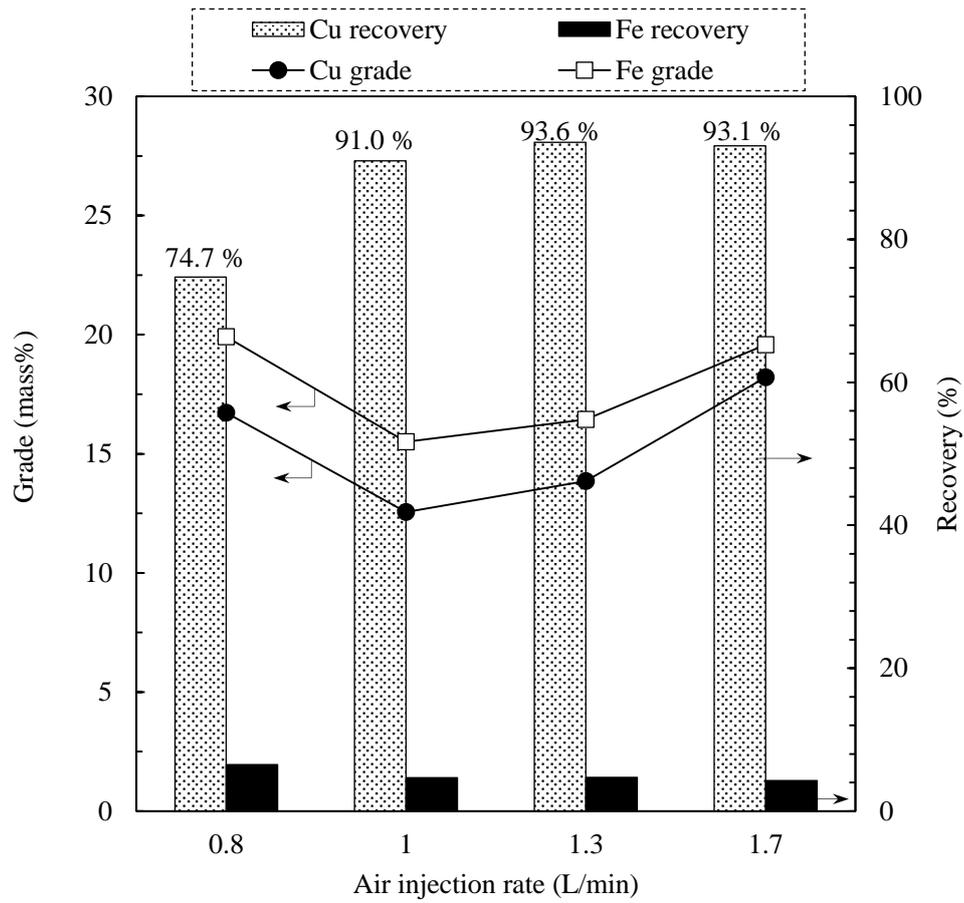


Fig. 3.7 The grade and recovery of copper and iron as a function of air injection.

(Air injection rate: 0.8–1.7 L/min, slurry pH: 10, PAX: 0 g/t-ore, flotation time: 10 min, pulp density: 10 %, and MIBC: 200 g/t-ore)

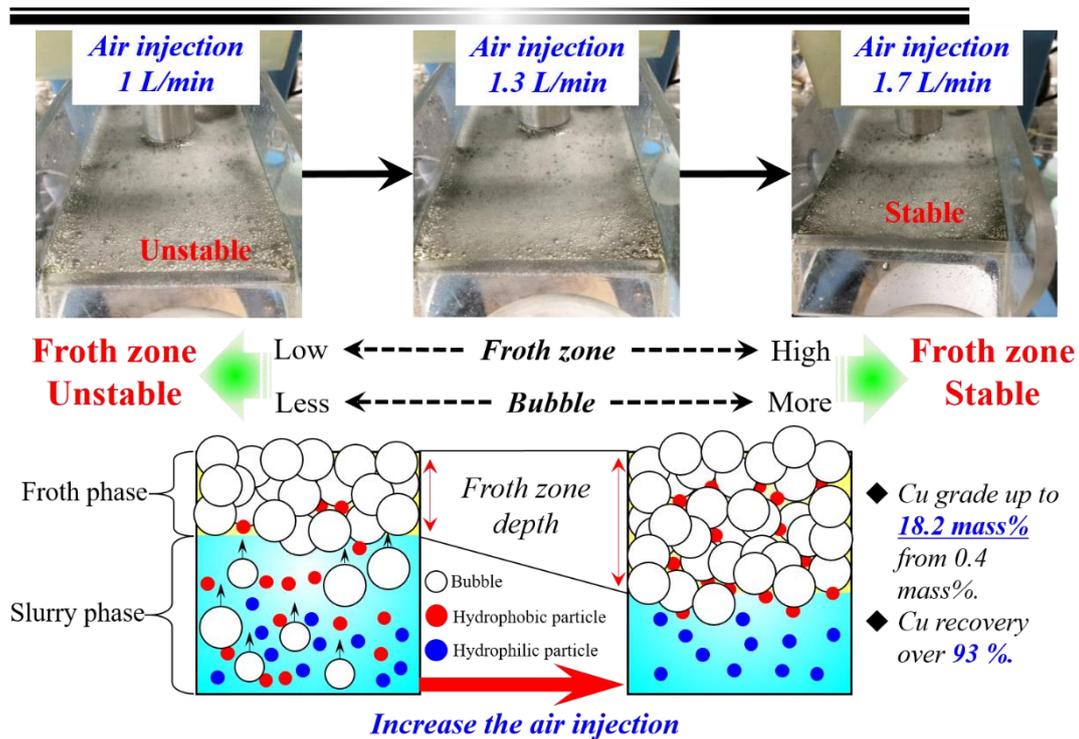


Fig. 3.8 The observation of the bubbles and discussion as a function of air injection.

(Air injection rate: 0.8–1.7 L/min, slurry pH: 10, PAX: 0 g/t–ore, flotation time: 10 min, pulp density: 10 %, and MIBC: 200 g/t–ore)

Table 3.6 Effect of air injection rate on copper enrichment ratio and yield.

Air injection rate (L/min)	Contents	
	Cu enrichment ratio	Yield (%)
0.8	41.79	2.04
1.0	31.38	2.13
1.3	34.63	2.33
1.7	45.51	1.52

3.3.1.5 The beneficiation of copper from the low-copper grade ore under optimum flotation conditions

As a result of a batch flotation experiments described in **section 3.3.1.1–3.3.1.4**, the optimal flotation conditions were determined and the results are summarized in **Table 3.7**. Under the optimal flotation conditions, flotation experiment was performed and the results obtained are presented in **Table 3.8**. It was revealed that the grade of copper achieved to be 18.2 % with enrichment ratio of 45.5 when the recovery of copper was 93.1 %. The XRD patterns of low-grade copper ore and its froth concentrate obtained from flotation under the optimized condition are shown in **Fig. 3.9**. Main mineral constituents in the froth concentrate are chalcopyrite (CuFeS_2), quartz (SiO_2), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), chlorite ($(\text{Mg, Fe})_6(\text{Si, Al})_4\text{O}_{10}(\text{OH})_8$) and pyrite (FeS_2). The peak of pyrite (FeS_2) was not detected by XRD of low-grade copper ore because of its low-grade and detection limitation of the equipment.

The froth concentrate containing 18.2 mass% Cu and 19.6 mass% Fe was further used for extraction of copper with distilled water and diluted sulfuric acid solutions using atmospheric and high-pressure oxidative leaching.

Table 3.7 The optimum conditions for recovery of copper from a low-grade copper ore.

Parameters	Conditions	Cu recovery (%)	Cu grade (mass%)
Pulp density	10 %		
PAX dosage	0 g/t-ore		
MIBC dosage	200 g/t-ore	93.1	18.2
pH	10		
Air injection rate	1.7 L/min		
Flotation time	10 min		

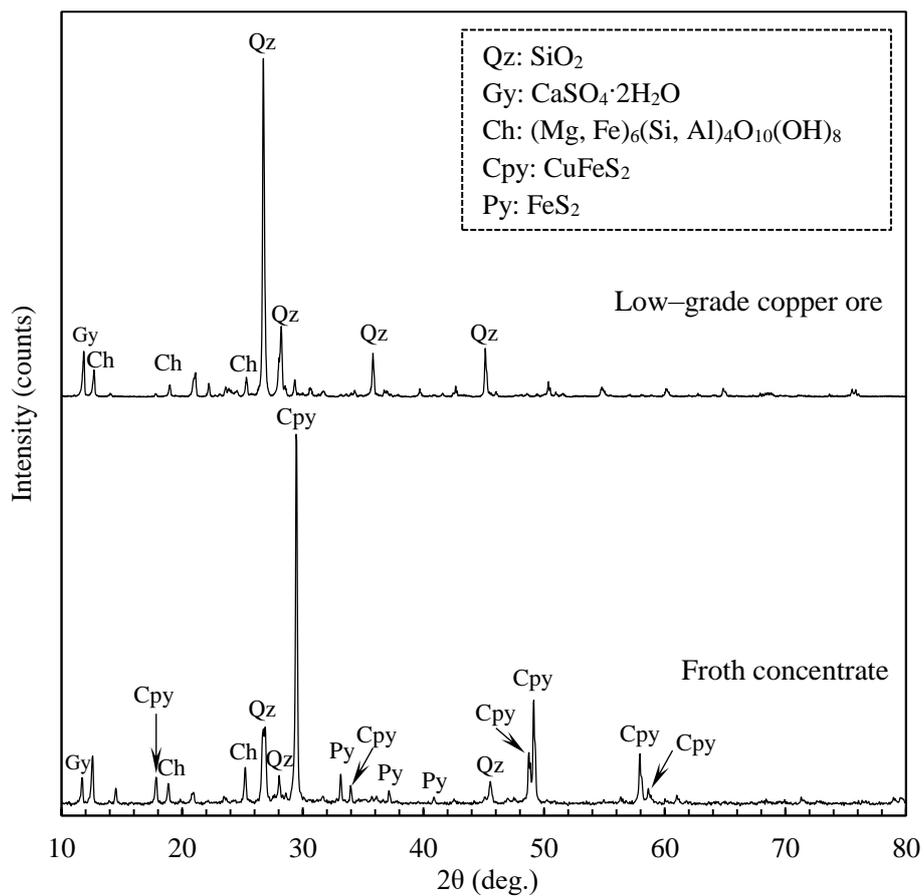


Fig. 3.9 XRD patterns of low-grade copper ore and its concentrate.

Table 3.8 Chemical compositions of low-grade copper ore and its concentrate.

Sample	Grade (mass%)					
	Al	Ca	Cu	Fe	K	Mg
Low-grade copper ore	1.8	1.4	0.4	4.6	1.3	2.7
Froth concentrate	2.2	0.8	18.2	19.6	0.8	2.2

3.3.2 High-pressure oxidative leaching of concentrate of low-grade copper ore

3.3.2.1 Effect of total pressure

The effect of total pressure (oxygen and vapor pressure) on the copper and iron dissolution was conducted in the range of 0.8 (without oxygen supply)–2.5 MPa. The other conditions were fixed at a pulp density of 10 %, leaching temperature of 170 °C, leaching time of 60 min, agitation speed of 700 rpm and sulfuric acid concentration of 1.0 M. It can be seen from the results shown in [Fig. 3.10](#) that both copper and iron dissolution depend significantly on the total pressure in the range of 0.8–1.5 MPa. The copper and iron leaching rate reached 52.2 and 40.7 %, respectively, under the total pressure of 1.5 MPa, whereas their rates were 7.8 and 5.5 % at the total pressure 0.8 MPa, which is similar to that rates under atmospheric leaching conditions ([Fig. 2.8](#)), when the total pressure was 0.8 MPa (without oxygen gas addition in the system). It is observed that as a result of oxygen gas supply, sulfide minerals entirely oxidized to sulfate under the high-pressure oxidation conditions at 170 °C promoting the dissolution of copper, and resulted in the higher copper leaching rate. However, a further increase in the total pressure from 1.5 to 2.5 MPa does not produce a substantial increase in the dissolution rate of copper and iron. These results are in agreement with the observation made some researchers who concluded that due to surface saturation by oxygen, leaching is not affected by oxygen partial pressure after a certain pressure [[17, 21](#)]. When the total pressure was 2.0 MPa, a maximum copper dissolution rate of 59.7 % was achieved within 60 minutes leaching. Thus total pressure of 2.0 MPa was selected in subsequent experiments.

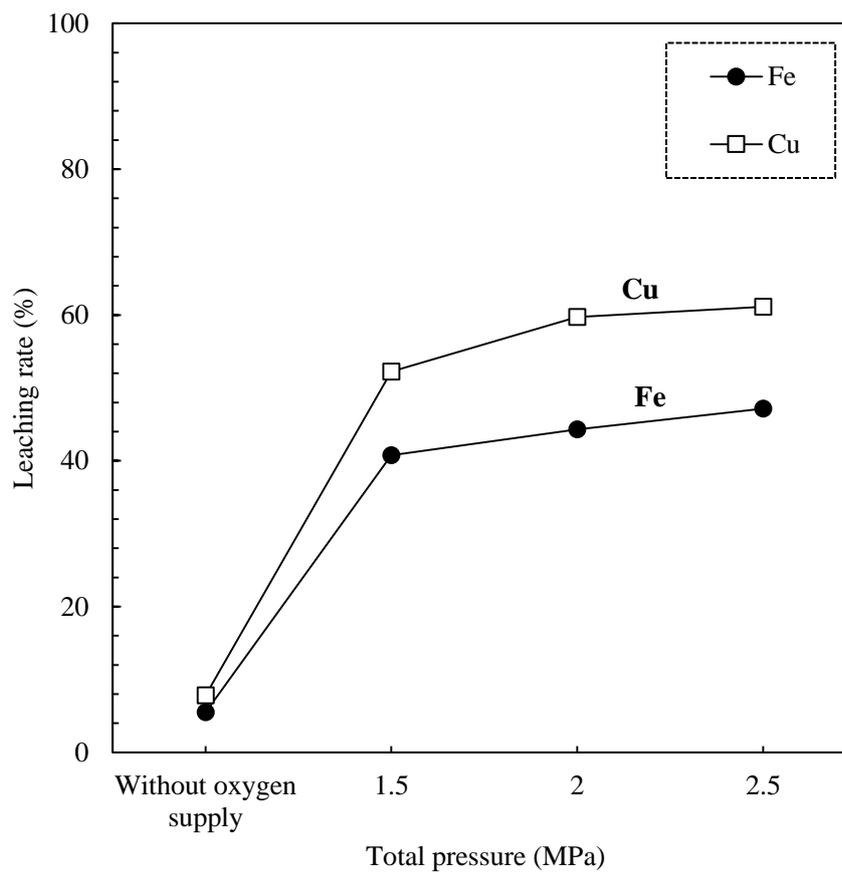


Fig. 3.10 The leaching efficiency of copper and iron as a function of total pressure.

(Total pressure: 0.8 (without oxygen supply)–2.0 MPa, H_2SO_4 concentration: 1.0 M, leaching time: 60 min, pulp density: 10 %, temperature: 170 °C, and agitation speed: 700 rpm)

3.3.2.2 Effect of temperature

The influence of the temperature ranging between 100–180 °C on the copper and iron leaching rate was studied under certain conditions while the sulfuric acid concentration of 1.0 M, pulp density of 10 %, leaching time of 60 min, agitation speed of 700 rpm, and a total pressure of 2.0 MPa. As shown in **Fig. 3.11**, the temperature has a large effect on the leaching of copper and iron. A linear relationship between temperature and copper leaching rate was found. With increasing the temperature from 100 to 180 °C, the copper leaching rate was raised from 17.7 to 61.1 %. It suggested that the dissolution of copper from chalcopyrite (CuFeS_2) is a high temperature dependent process.

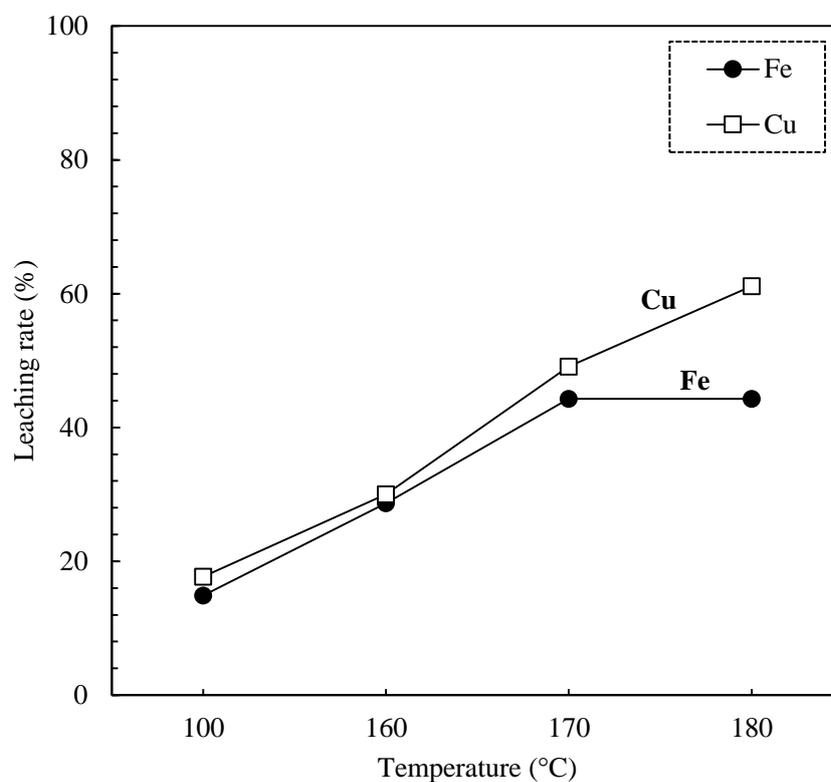


Fig. 3.11 The leaching efficiency of copper and iron as a function of temperature.

(Temperature: 100–180 °C, H_2SO_4 concentration: 1.0 M, leaching time: 60 min, total pressure: 2.0 MPa, pulp density: 10 %, and agitation speed: 700 rpm)

3.3.2.3 Effect of sulfuric acid concentration

To determine the efficiency of copper dissolution, the copper concentrate of low-grade copper ore was leached with distilled water and different concentrations of sulfuric acid solutions ranging from 0.5 to 1.0 M. The leaching experiments were conducted under different leaching times from 0 to 180 min while other parameters like pulp density, total pressure in an autoclave, agitation speed and temperature were fixed at 10 %, 2.0 MPa, 700 rpm, and 180 °C. The results of copper dissolution with distilled water and with different concentrations of sulfuric acid solutions at varying leaching times are shown in **Fig. 3.12 (a)**. It is interesting that an excellent copper leaching rate (93.4 %) achieved after 120 min and the maximum (98.3 %) copper dissolution obtained after 180-min leaching with distilled water, while the iron dissolution did not exceed 5.4 % (**Fig. 3.12 (b)**). The efficiency of copper dissolution decreased with increasing the sulfuric acid concentration and reached the minimum dissolution of 70.8 % with 1.0 M H₂SO₄ solution under the leaching conditions. It was observed that the sulfuric acid concentration gave an opposite effect on the dissolution of copper from the copper concentrate. On the contrary, the efficiency of iron dissolution from the concentrate increased with increasing the sulfuric acid concentration, and the iron dissolution rate reached 67.7 and 70.0 % after 120-min and 180-min leaching, respectively, when the sulfuric acid concentration was 1.0 M (**Fig. 3.12 (b)**). The reduction of copper dissolution from the concentrate in the sulfuric acid solution may be induced by the solubility of oxygen in a sulfuric acid solution containing copper and iron sulfates and the salting-out effect of the sulfuric acid solution [22].

It was observed that after high-pressure oxidative leaching with distilled water under the optimal conditions, pH of slurry decreased to pH 1.47 while an initial slurry pH was 6.1. The major mineral phase in the solid residue is hematite (Fe₂O₃) as identified by XRD analysis (**Fig. 3.13**). When using 0.5 and 1.0 M sulfuric acid solutions in the leaching, the initial pH values of slurries of pH 0.72 and pH 0.49 were increased to pH 0.9 and pH 0.8, respectively. The XRD patterns of solid residues from 0.5 and 1.0 M sulfuric acid leaching showed the quartz, chalcopyrite, and hydronium jarosite ((H₃O)Fe₃(SO₄)₂(OH)₆) peaks (**Fig. 3.13**). It can clearly be seen that the results are in agreement with the literature [23–24] data presented in **Fig. 3.14** showing areas of stability of various compounds in the Fe–S–O system as a function of temperature and pH. It can be said that

the hematite is favorite around pH 1.5 at the setting temperature of 180 °C and the major iron phase of the solid residue transport to jarosite when the pH decreasing under pH 1. It is evident from the **Figs. 11–13** that chalcopyrite was remained in the solid residues of the sulfuric acid leaching and confirmed the decrease of the efficiency of copper dissolution in the acid solution under the high–pressure oxidative leaching conditions. As a result, it is concluded that the higher extraction of copper (98.4%) from the froth concentrate of low–grade copper ore with water (i.e., without sulfuric acid) can be achieved by using high–pressure oxidative leaching (HPOL) process.

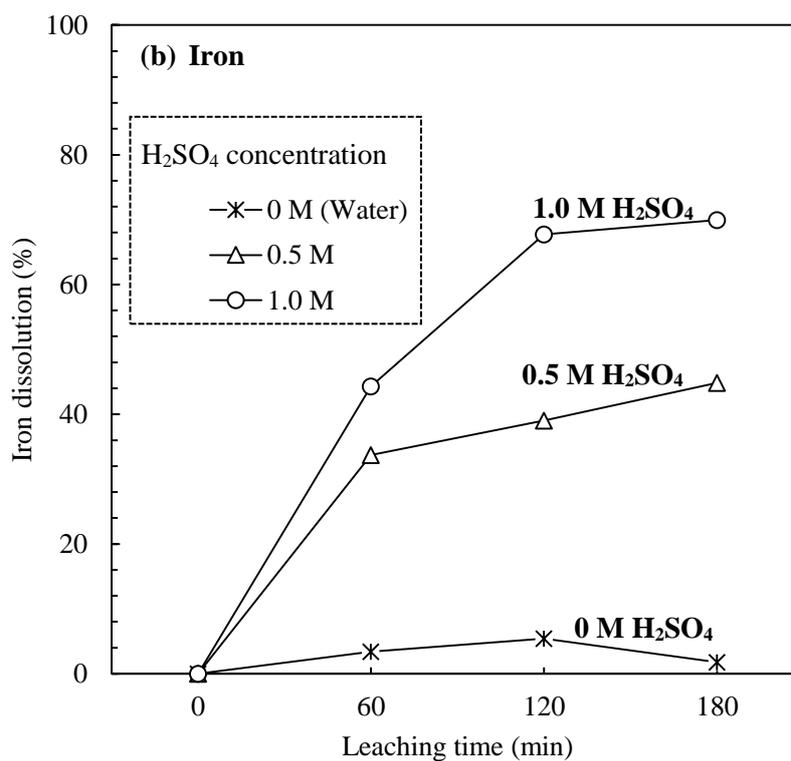
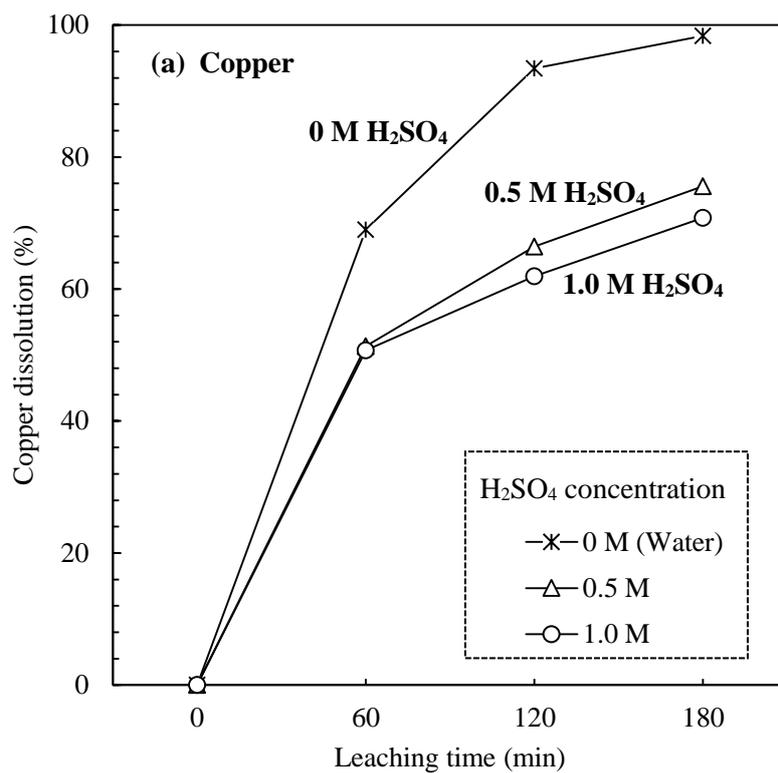


Fig. 3.12 Leaching efficiency of (a) copper and (b) iron as functions of leaching media and leaching time.

(Dissolution: distilled water and H₂SO₄ solution (0.5–1.0 M), leaching time: 0–180 min, total pressure: 2.0 MPa, pulp density: 10 %, temperature: 180 °C, and agitation speed: 700 rpm)

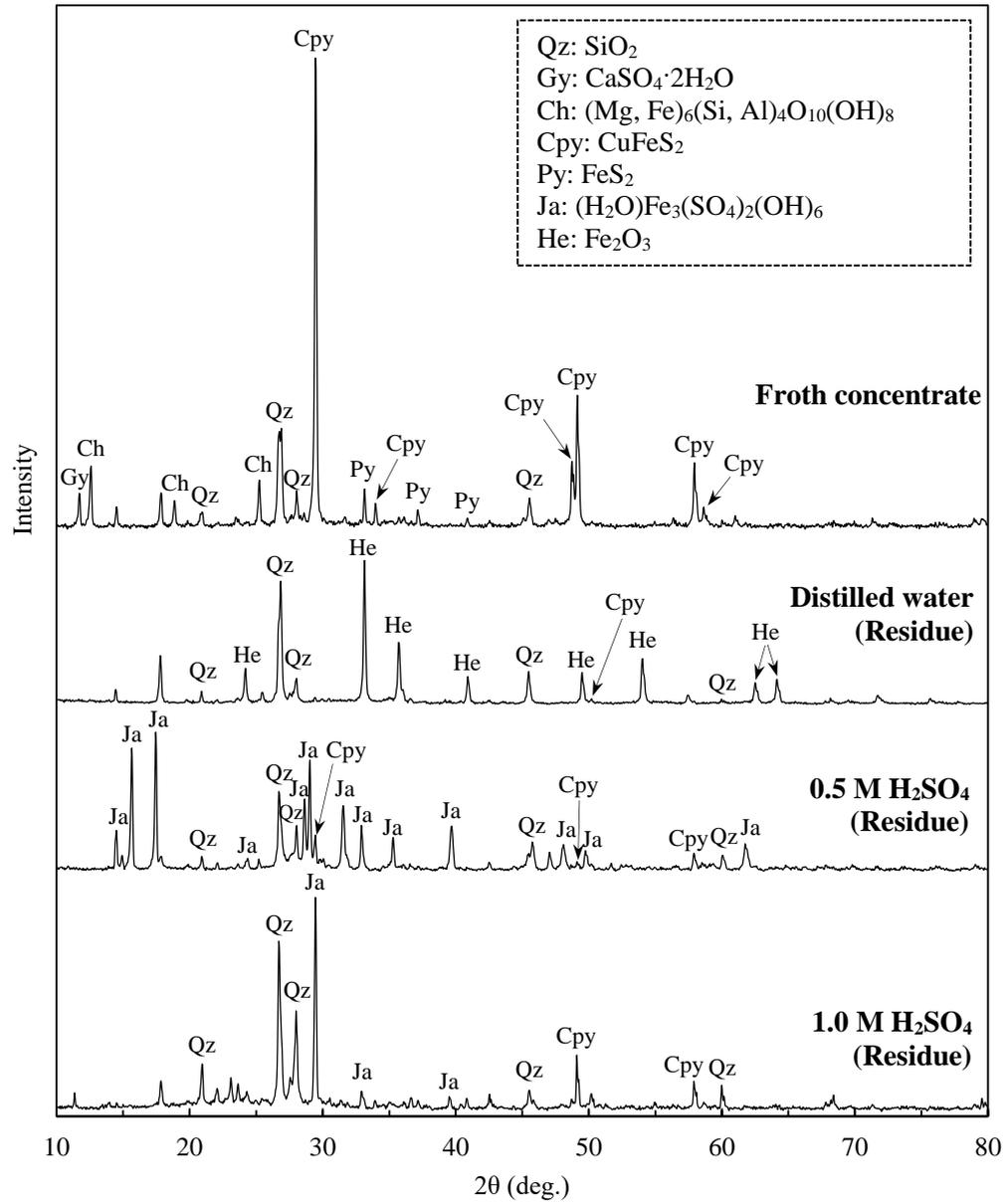


Fig. 3.13 XRD patterns of the froth concentrate and residues after high-pressure oxidative leaching.

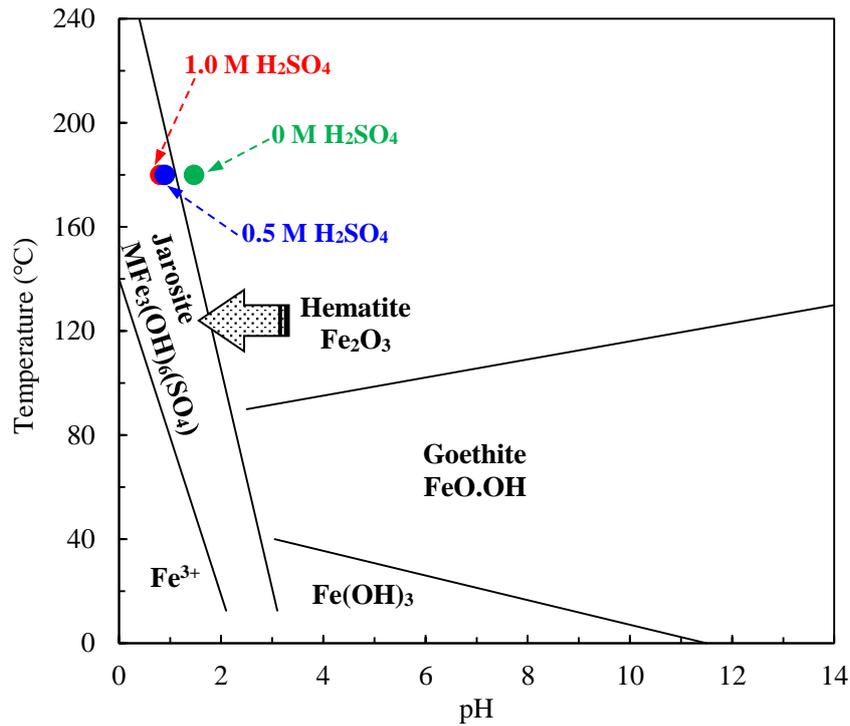


Fig. 3.14 Areas of stability of various compounds in the Fe–S–O system.

3.2.2.4 Application of optimal high–pressure oxidative leaching for copper extraction

The results of numerical experiments as described sections suggested that the optimum high–pressure oxidative leaching conditions for copper extraction from the froth concentrate were found to be as shown in **Table 3.9**. Under the optimum high–pressure oxidation conditions, 98.5 % of copper was leached with distilled water and the obtained pregnant leach solution contained 15.0 g/L copper (**Table 3.9**).

The mechanism of copper dissolution from the froth concentrate, which contains chalcopyrite as main copper mineral, can be described by **Eq. 3.5**. It means that sulfur in chalcopyrite entirely oxidized to sulfate under the high–pressure (2 MPa) oxidative conditions at 180 °C in the presence of oxygen gas, resulting in an excellent copper dissolution (> 90 %).

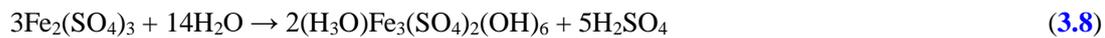


It can be seen from **Eq. 3.5** that the oxidation of chalcopyrite is an acid consuming reaction, and complete dissolution (> 98 %) of copper from the froth concentrate in distilled water was achieved under the high–pressure oxidative conditions. It is obvious that pyrite in the froth concentrate can be a source of sulfuric acid as presented below:



Oxygen gas (O_2) supply in the slurry promotes the oxidation of minerals such as pyrite and chalcopyrite, and the generation of sulfuric acid can dissolve copper efficiently from the concentrate under the high–pressure and high–temperature conditions. Hence, it can be said that the presence of pyrite in the sample has a significant effect on the production of sulfuric acid to dissolve copper from the sample.

Furthermore, XRD measurement confirmed the formation of hematite (Fe_2O_3) and hydronium jarosite ($(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$) in the solid residues after the high–pressure oxidative leaching with distilled water and with sulfuric acid solution due to undergo hydrolysis of ferric ions (Fe^{3+}) in aqueous solution (Fig. 3.14) by the following reactions (Eqs. 3.7 and 3.8).



It is observed that the formation of hematite and jarosite by HPOL of the chalcopyrite with distilled water and the sulfuric acid solution depends not only on the leaching medium, but also on the pH value of slurry.

Based on the experimental results, a flowchart is proposed for the recovery of copper from low–grade copper ore, as seen in Fig. 3.15. The copper grade in the froth concentrate reached 18.1 from 0.4 mass% under the optimal flotation conditions, when the recovery of copper was 93.1 %. The vast majority of copper (> 98.4% Cu) was leached from the froth concentrate in distilled water under the high–pressure oxidation leaching (HPOL) conditions after flotation of the low–grade copper ore. The concentration of copper in the pregnant leach solution (PLS) from HPOL reached to be 15.0 g/L. On the other hand, more than 98 % of iron was removed from the copper concentrate by the high–pressure oxidation leaching (HPOL) process, and it precipitated as hematite in the solid residue. As a result, a selective and highest copper recovery (> 91 %) was achieved by a combination process of flotation–high–pressure oxidative leaching (HPOL).

Table 3.9 The optimum high–pressure oxidative leaching conditions for recovery of copper from froth concentrate.

Parameters	Conditions	Cu leaching rate, %	Cu concentrate, g/L
H ₂ SO ₄ concentration	0 M (Water)		
Temperature	180 °C		
Total pressure	2.0 MPa	98.4	15.0
Pulp density	10 %		
Leaching time	180 min		

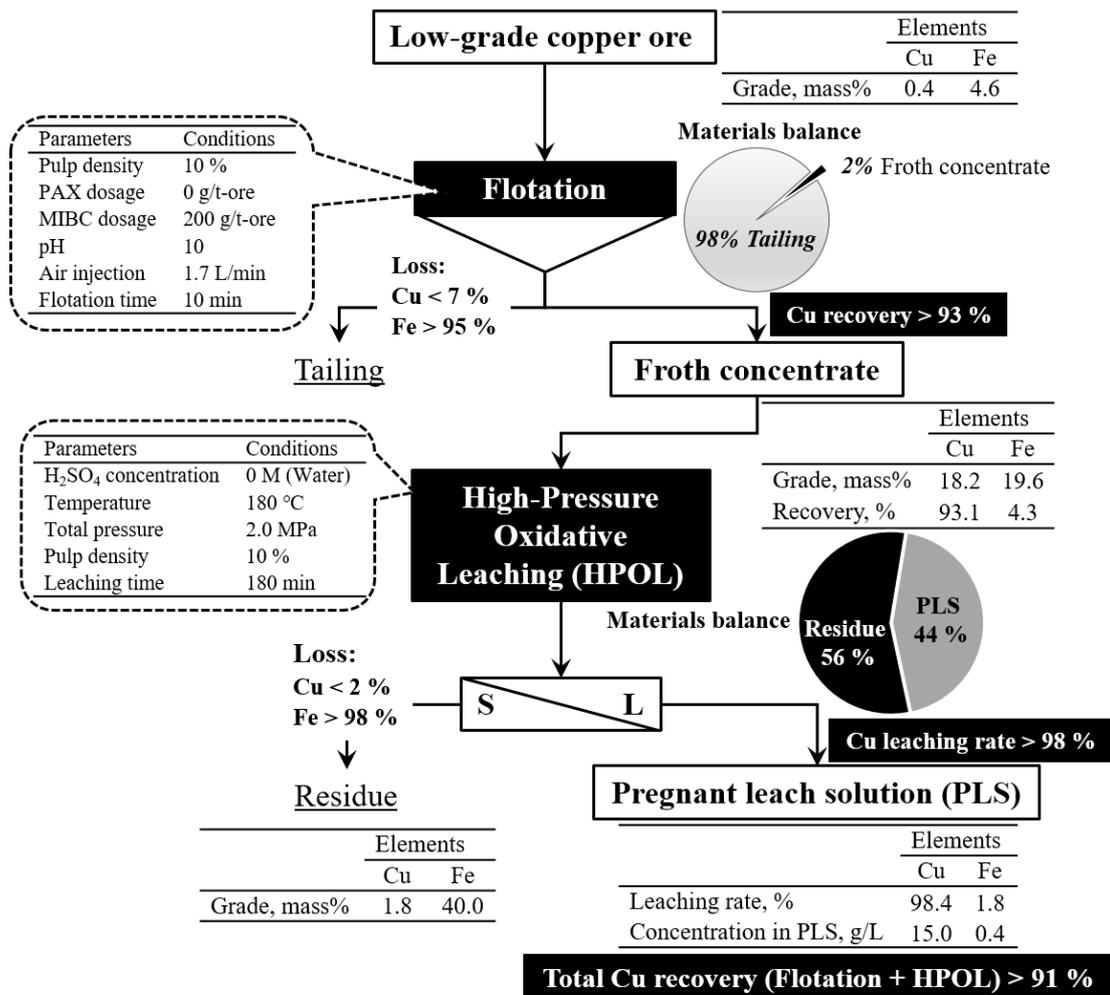


Fig. 3.15 A flowchart for the copper recovery from the low–grade copper ore.

3.4 Conclusion

This chapter focused on the development of a hydrometallurgical process for recovering copper from a low-grade copper ore by a combined process of flotation and high-pressure oxidative leaching. Experimental results obtained can be concluded as bellow.

(1) Flotation process: A collector-less flotation was suggested for beneficiation of copper from the low-grade copper ore due to its high self-induced ability under the flotation condition. The copper grade in the froth concentrate reached 18.1 from 0.4 mass% with an enrichment ratio of 45 under the optimal flotation conditions, while the recovery of copper was 93.1%.

(2) Leaching process: Experimental results revealed that the copper dissolution from the froth concentrate did not exceed 11.9% under atmospheric leaching with sulfuric acid solution. However, about 98.4% of copper could be dissolved from the froth concentrate in distilled water by high-pressure oxidative leaching. The copper concentration in the pregnant leach solution reached to be 15.0 g/L. Moreover, over 98% of iron in copper concentrate was removed and precipitated as hematite in the residue under the optimized conditions.

(3) The presence of pyrite (FeS_2) in the sample has a positive effect on copper leaching process, and it can be a source of sulfuric acid (H_2SO_4) production under the high-pressure oxidative leaching conditions promoting the copper dissolution.

(4) It can be concluded that the leaching media, pressure (oxygen supply), temperature, and acidity of the slurry are the important valuables for the dissolution of copper, and the formation of hematite and jarosite throughout the copper leaching from chalcopyrite (concentrate of low-grade copper ore) in the presence of aqueous solutions under high-pressure oxidative leaching conditions. A selective (iron removal rate >98%) and efficient copper extraction (Cu leaching rate >98%) process are proposed for the recovery of copper (total Cu recovery >91%) from the low-grade copper ore using flotation followed by high-pressure oxidative leaching.

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Chapter 4: Leaching and Kinetic Study on Pressure Oxidation of Chalcopyrite in H₂SO₄ Solution and the Effect of Pyrite on the Chalcopyrite Leaching

4.1 Introduction

Among the copper sulfides, chalcopyrite (CuFeS₂) is the predominant mineral used to produce metallic copper [1]. In recent years, much attention has been focused on chalcopyrite as the chief copper sulfide mineral due to two reasons: 1) it is the most abundant copper mineral in nature, and 2) it is one of the most refractory sulfide copper minerals under hydrometallurgical conditions, owing to the formation of a stable passivation layer on the chalcopyrite surface [2]. At present, approximately 80–85 % of the world copper production is accomplished with the conventional pyrometallurgical method/technology, which consists of flotation, smelting and refining and electrorefining routes [3–6]. Due to environmental regulations relevant to the emission of sulfur dioxide and the requirement for high-grade feeds for the pyrometallurgical processes [7], the hydrometallurgical routes are becoming more active and growing worldwide interest in the copper production [8–13].

The hydrometallurgical process offers great potential for treating complex sulfide concentrates, especially chalcopyrite concentrate, and it results in increased metal recoveries and reduced air pollution hazards [5]. In addition, the chalcopyrite concentrate may often contain significant levels of precious metals such as gold (Au) and silver (Ag) by-products. The hydrometallurgical process provides a potential way and an option to separate the precious metals into solid residue and to expose the gold and silver particles from the base metal sulfides for subsequent treatment [14–15]. Nevertheless, direct leaching of chalcopyrite has some problems due to the low solubility of chalcopyrite without the presence of an oxidant, the formation of precipitation, and the disposal of a large amount of iron that dissolves along with the copper [16–18]. Therefore, many studies have

been investigated using various leaching/oxidizing reagents such as ferric and cupric ions, bacteria, oxygen, etc. in sulfuric and chloride media under atmospheric or pressure leaching conditions at elevated temperatures [19–35]. Unfortunately, the kinetics of copper dissolution from chalcopyrite is very slow due to the formation of the passivation layer on the surface of chalcopyrite particles by oxidation of sulfide to elemental sulfur under oxidative conditions. Some authors suggested that the problem of low extraction might be overcome by effective extraction methods such as pressure oxidative leaching in an autoclave system [36–43]. Turan et al. (2015) [18] investigated the dissolution of chalcopyrite concentrate using ammonium persulfate in an autoclave system and they concluded that a 57.04 % of copper extraction was achieved under the optimized conditions. Baba et al. (2014) [2] studied the leaching kinetics of chalcopyrite in NH_3 medium and proposed a surface chemical reaction mechanism as the rate determining step for the chalcopyrite dissolution process. Gok et al. (2014) [44] reported that a high efficiency of copper recovery (98 %) from chalcopyrite concentrate was obtained under a low pressure (0.6 MPa) condition at 120 °C within 120 min in nitrous-sulfuric acidic solution. However, sulfuric acid (H_2SO_4) is preferred over all other leaching reagents with regard to cost, environmental friendliness, ease of its regeneration during electro-winning and can be easily combined with the conventional solvent extraction–electro-winning methods [45]. Additionally, there are a few references to the chalcopyrite leaching with dilute sulfuric acid in the absence of another oxidant.

The hydrometallurgical processes that have been developed for the pressure oxidative leaching of chalcopyrite can be classified into low (< 100 °C), medium (140–180 °C) and high-temperature (> 200 °C) regimes [31]. Low-temperature regime leaching employs ultra-fine grinding to enhance the kinetics and even that it is a quite slow process. At high temperature, leaching kinetics are rapid; the entire sulfide content is converted to sulfate leading to substantially higher oxygen consumption and producing higher free acid levels [32]. Therefore, the medium temperature pressure leaching process becomes more important to extract copper from chalcopyrite and the process development for chalcopyrite dissolution is much emphasized.

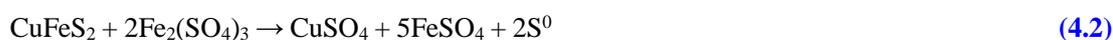
Moreover, pyrite and chalcopyrite, the most common and exploitable sulfide minerals, usually occur together and in contact with each other. Due to the companionship of pyrite with chalcopyrite

in nature the effect of pyrite on the dissolution of chalcopyrite is necessary to investigate, and the co-treatment of these minerals might be advantages from an economic point of view.

In this chapter, leaching behavior and kinetics of copper from chalcopyrite in sulfuric acid solution under pressure oxidative conditions at medium temperature were investigated. The effects of various parameters, which are particle size (-38 μm , +38–75 μm , and +75–100 μm), agitation speed (300–900 rpm), total pressure (0.8–2.0 MPa), temperature (160–180 $^{\circ}\text{C}$), sulfuric acid concentration (0.1–2.0 M) and Fe/Cu mole ratio (1–20 mol/mol) were systematically studied in broad ranges in the absence of common oxidants such as nitrous and hydrogen peroxide. The optimal pressure oxidative leaching conditions were accomplished for nearly complete extraction of copper from chalcopyrite.

4.1.1 Chemical reactions and kinetic model

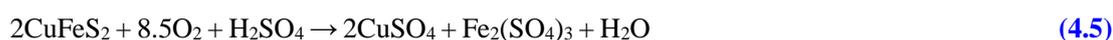
Based on the literature data for oxidation of chalcopyrite in acidic medium, the following chemical reactions were chosen to study the $\text{CuFeS}_2\text{-H}_2\text{SO}_4\text{-H}_2\text{O-O}_2$ system [32].



Under high oxidative conditions (oxygen supply), sulfuric acid is generated by reacting elemental sulfur with oxygen (Eq. 4.3), while the ferrous sulfate converts to ferric sulfate by oxidation (Eq. 4.4).

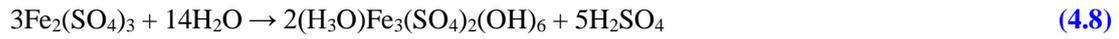


Therefore, oxidation of chalcopyrite at medium temperature (around 180 $^{\circ}\text{C}$) can be described by the following equations (Eqs. 4.5 and 4.6).



The ferric sulfate generated is hydrolyzed at these temperatures (around 180 $^{\circ}\text{C}$) forming hematite, hydronium jarosite or basic ferric sulfate dependent upon the free acidity in the system as follows (Eqs. 4.7 and 4.8):





Some researchers have studied the activation energies and kinetics of the oxidative dissolution of chalcopyrite in different medium and their results obtained are summarized in [Table 4.1](#) [3, 21, 23, 34, 43–44, 46–49].

Accordingly, the dissolution of chalcopyrite can be explained by a shrinking core model which is expressed by the following equation ([Eq. 4.9](#)).



This kinetic model predicts the mechanism of leaching process to be either surface reaction controlled, diffusion controlled or a mixed controlled containing diffusion and surface reaction components, which simultaneously take place.

If the reaction rate is controlled by a surface reaction, then the integrated rate expression becomes [Eq. 4.10](#):

$$1 - (1 - \alpha)^{\frac{1}{3}} = k_r t \quad (4.10)$$

If the reaction rate is controlled by diffusion through a product layer, the integrated rate equation is as follows ([Eq. 4.11](#)):

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = k_d t \quad (4.11)$$

In the expression, α is the fraction reacted, k_r and k_d are the kinetic constants, t is the reaction time, respectively.

Additionally, the value of activation energy (E_a) can be calculated by Arrhenius plot, i.e. $\ln k$ vs $1000/T$ as plot shown in [Eq. 4.12](#).

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4.12)$$

Where k is rate constant, A is a pre-exponential factor, E_a is activation energy, R is gas constant and T is absolute temperature.

Table 4.1 Reported kinetic models and activation energies for leaching of chalcopyrite with different media.

Leaching medium	Kinetic model	Temp. (°C)	E_a (kJ/mol)	Reference
H ₂ SO ₄ + NaCl	Diffusion	90–120	15.22	[43]
K ₂ Cr ₂ O ₇ + H ₂ SO ₄	Diffusion	50–97	24	[23]
K ₂ + NH ₄	Diffusion	35–60	30.3	[46]
NaNO ₂ + H ₂ SO ₄	Diffusion	80–120	34.06	[44]
HNO ₃ + H ₂ O ₂	Diffusion	25–60	42.26	[49]
FeCl ₃ + HCl	Surface reaction	70–100	92.8	[47]
H ₂ O ₂ + H ₂ SO ₄	Surface reaction	25–50	60	[3]
K ₂ Cr ₂ O ₇ + H ₂ SO ₄	Surface reaction	30–80	49	[21]
K ₂ Cr ₂ O ₇ + H ₂ SO ₄	Surface reaction	25–60	50	[48]
FeCl ₃ + HCl	Mixed control model	30–90	15.98	[34]

4.2 Experimental

4.2.1 Sample

The three (3) different ore samples, namely chalcopyrite ore with pyrite content (Sample A), chalcopyrite ore without pyrite content (Sample B), and pyrite ore (Sample C) were used in this study. The ore samples were firstly crushed by a jaw crusher (P-1, Fritsch Japan Co., Ltd) and a disc mill (P-13, Fritsch Japan Co., Ltd), and then screened by a sieve shaker (AS200 digit, Retsch Japan Co., Ltd) in three size fractions: $-38\ \mu\text{m}$, $+38-75\ \mu\text{m}$, and $+75-100\ \mu\text{m}$. The chemical compositions of the ore samples were determined by an inductively coupled plasma-optical emission spectrometry (ICP-OES, SII NanoTechnology Inc., Chiba, Japan) and the contents of main elements (Cu and Fe) are presented in [Table 4.2](#). The mineralogical studies on each ore samples were conducted by X-ray diffraction (XRD, Rigaku RINT-2200V) analyses. XRD patterns confirmed the presence of chalcopyrite (CuFeS_2), quartz (SiO_2), greenalite ($\text{Fe}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$), and pyrite (FeS_2) as main mineral constituents of the samples A, B, and C, respectively ([Fig. 4.1](#)).

Table 4.2 Chemical composition of each sample.

Sample name	Elements (mass%)	
	Cu	Fe
Sample A (chalcopyrite ore with pyrite content)	15.8	22.7
Sample B (chalcopyrite ore without pyrite content)	0.4	4.6
Sample C (pyrite ore)	0.1	44.5

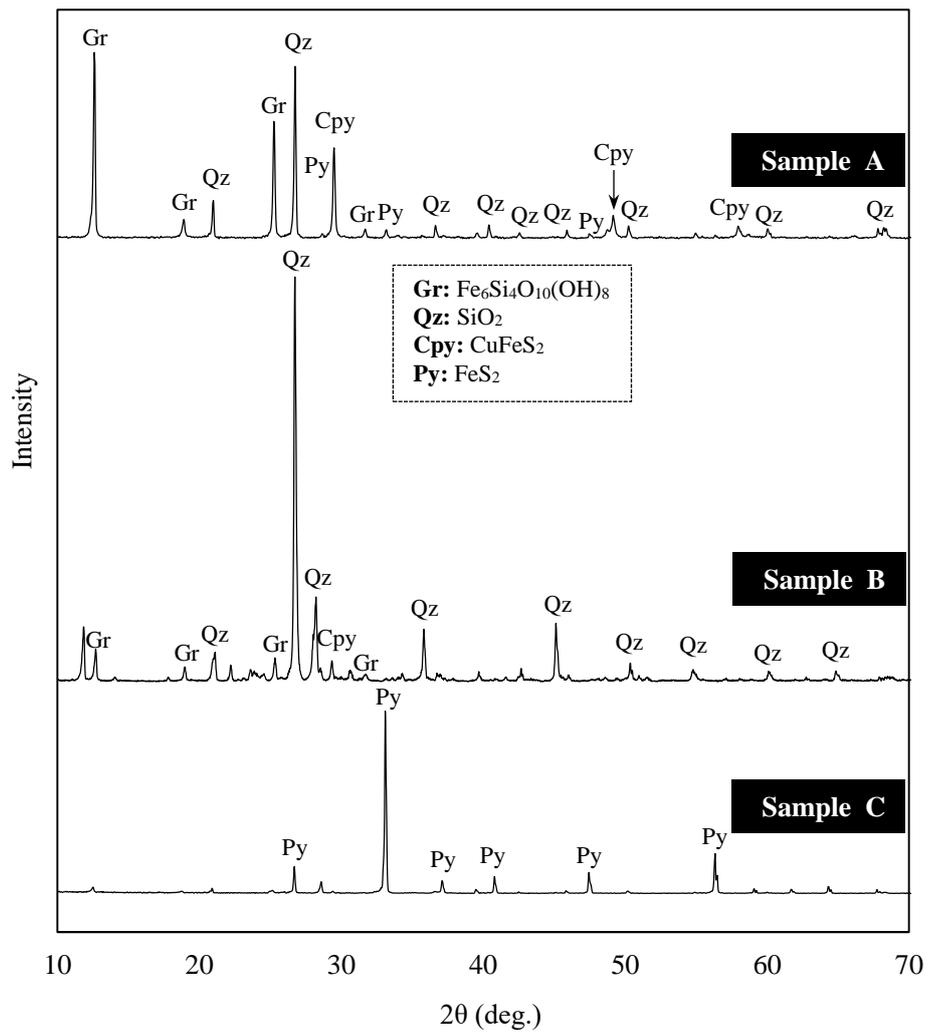


Fig. 4.1 XRD patterns of each sample.

4.2.2 Reagent

The reagents used in this chapter were shown in [Table 4.3](#). The sulfuric acid (H_2SO_4) and oxygen (O_2) was used as an oxidizer in the high-pressure oxidative leaching experiments.

Table 4.3. List of the chemical reagents used in this chapter.

Experiments	Name	Maker	Formula
High-pressure oxidative leaching	Sulfuric acid	Kanto Chemical	H_2SO_4
	Oxygen	Aiba Shouten	O_2

4.2.3 Procedure

All high-pressure oxidative leaching (HPOL) experiments were conducted using a stainless steel autoclave (NITTO KOASTU) with a Teflon vessel (200 mL) as shown in [Fig. 2.6](#). As the procedure of the pressure oxidative leaching shown in [Fig. 4.2](#), a 5 g of ore sample with different particle size fractions ($-38 \mu\text{m}$, $+38-75 \mu\text{m}$, and $+75-100 \mu\text{m}$) was placed into a Teflon vessel with a total volume of 200 ml and added 50 mL of water or known concentrations of sulfuric acid solution (0.1–2.0 M, KANTO CHEMICAL CO., INC.) controlling the pulp density of 10 %. The vessel containing a slurry sample was then put into the autoclave and started the agitation by using a magnetic impeller at speeds ranging from 300 to 900 rpm. The charged slurry/feed into an autoclave was heated to the required temperature (160–180 °C) and pure oxygen gas was injected into the vessel to maintain the target total pressure (sum of vapor and oxygen partial pressure: 0.8–2.0 MPa), and then the reaction continued for a period ranging from 0 to 90 min. After completion of high-pressure oxidation leaching (HPOL), the feed into the vessel was cooled down by an electric fan and filtered through a $0.45 \mu\text{m}$ membrane to obtain pregnant leach solution (PLS) and solid residue, which are for the chemical and mineralogical analysis using ICP–OES, XRD and SEM–EDS, respectively.

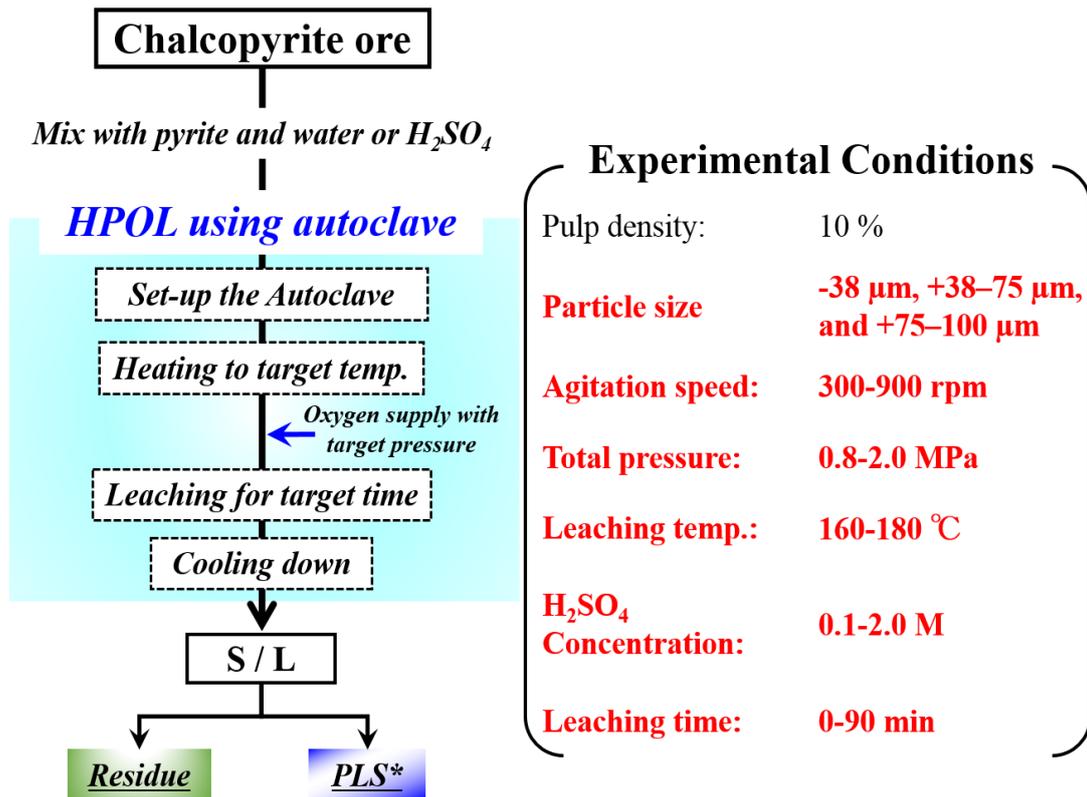


Fig. 4.2 Procedure of the high-pressure oxidative leaching experiments.

4.2.4 Characterization and analyses

In this study, all solution (PLS: Pregnant Leach Solution) analysis was conducted using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, SII NanoTechnology Inc., Chiba, Japan). In addition, the mineral composition of the solid samples was identified by X-Ray Diffractometer (XRD, Rigaku RINT-2200V) and Scanning Electron Microscope Energy Dispersive X-ray Spectrometry (SEM-EDS).

The leaching rate of each metal from the chalcopyrite ore into the water or sulfuric acid solution was calculated by [Eq. \(4.13\)](#) as shown below.

$$\text{Metal leaching rate: } R_M (\%) = \frac{C_L \cdot V_L}{C_F \cdot m_F} \times 100 \quad (4.13)$$

Where C_L and C_F is the concentration of metal in PLS (mg/L) and feed (mg/kg), respectively. V_L is the volume of PLS (L) and m_F is the dry mass of the feed (kg).

4.3 Results and discussion

4.3.1 Effect of particle size

To determine the effect of particle size on the copper leaching rate from chalcopyrite, experiments were performed with three different size fractions ($-38\ \mu\text{m}$, $+38-75\ \mu\text{m}$, and $+75-100\ \mu\text{m}$) at an agitation speed of 500 rpm, total pressure of 2.0 MPa, sulfuric acid concentration of 1.0 M, temperature of $180\ ^\circ\text{C}$, and pulp density of 10 %. The results are shown in Fig. 4.3, from where it can be seen that the smaller size of the particles ($-38\ \mu\text{m}$) has the faster copper dissolution rate of 63.3 % after 90 min leaching. The results are shown in Fig. 4.3. It can be seen that for the smaller particles ($-38\ \mu\text{m}$), extremely faster and higher copper dissolution rate is achieved due to the quickly interaction of particles with the solvent molecules/the increase of the surface area of solid particles and a leaching efficiency of 63.3 % for copper (Cu) could be obtained at 90 min. The leaching efficiency of copper from a chalcopyrite ore sample having a particle size of $+38-75\ \mu\text{m}$ was coincident with that of $-38\ \mu\text{m}$ particles which were 63 % and 60 %, respectively. In addition, for the particles upper $75\ \mu\text{m}$ ($+75-100\ \mu\text{m}$), the maximum leaching efficiency of copper was 53 % under the condition because of the reduction in the surface area of solids. However, there are not big differences found between the leaching efficiency of copper from larger particle size fraction of $+75-100\ \mu\text{m}$ (53 %) and smaller particles of $-75\ \mu\text{m}$ (60 %). Therefore, the particle size of $+75-100\ \mu\text{m}$ was selected for further study to minimize the impact on the filter operation.

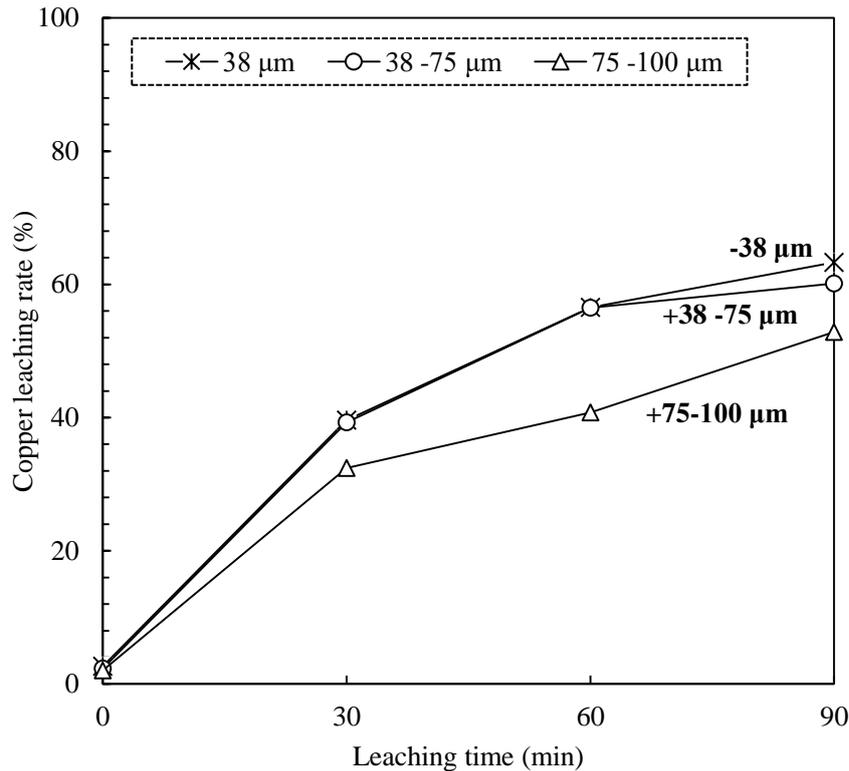


Fig. 4.3 The effect of particle size on copper leaching rate.

(particle size: -38, +38–75, and +75–100 μm, agitation speed: 500 rpm, total pressure: 2.0 MPa, H₂SO₄ concentration: 1.0 M, temperature: 180 °C and pulp density: 10 %)

4.3.2 Effect of agitation speed

The influence of agitation speed on the dissolution of copper from the sample A (chalcopyrite ore with pyrite content) was studied under different speeds: 300, 500, 700, and 900 rpm. The other conditions were fixed at a pulp density of 10 %, the temperature of 180 °C, the sulfuric acid concentration of 1.0 M, the total pressure of 2 MPa, and particle size of +75–100 μm for 90 min.

It was observed from the results shown in Fig. 4.4 that the agitation speed has a significant effect on the dissolution rate of copper, suggesting the diffusion control of the leaching process. The efficiency of copper dissolution increased from 29.8 to 62.8 % with increasing the agitation speed from 300 to 700 rpm. It suggested that an agitation speed of 700 rpm is the most efficient speed for the solid–liquid mass transfer/oxygen mass transfer into the vessel in an autoclave (three–phase mass transfer). However, the copper leaching rate decreased from 62.8 to 51.0 % with a further increase of an agitation speed to 900 rpm in consequence of the weak interactions between particles and solvent molecules under strong agitation. It can be seen that the leaching trend of copper from

the sample at different agitation speeds shows similar characteristics. Aydogan et al. (2006) [23] studied the chalcopyrite leaching in the $\text{H}_2\text{SO}_4+\text{K}_2\text{Cr}_2\text{O}_2$ system and they concluded that the leaching rate of copper increases with increasing stirring speed up to 400 rpm, but further increase in the agitation speed leads to decline the leaching rate of copper significantly. The decreasing of copper leaching rate may be due to the reduced concentrations of reactants such as O_2 and H^+ on chalcopyrite surface with the over agitation speed. Therefore, the agitation speed was chosen as 700 rpm for further studies.

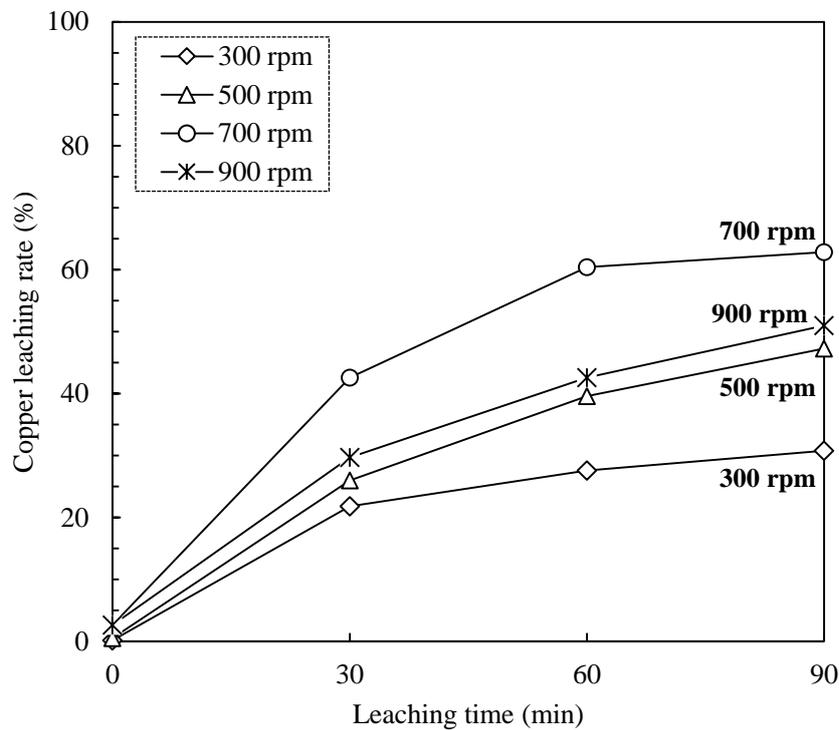


Fig. 4.4 The effects of agitation speed on copper leaching rate.

(agitation speed: 300–900 rpm, particle size: +75–100 μm , total pressure: 2.0 MPa, H_2SO_4 concentration: 1.0 M, temperature: 180 $^\circ\text{C}$, and pulp density: 10 %)

4.3.3 Effect of total pressure

The effect of total pressure, P_{Total} (sum of the vapor, P_V and oxygen partial pressure, P_O) on the rate of copper dissolution from sample A was investigated in the pressure (P_{Total}) range between 0.8 (without oxygen supply) and 2.0 MPa at an agitation speed of 700 rpm, pulp density of 10 %, temperature of 180 $^\circ\text{C}$, sulfuric acid concentration of 1.0 M, and particle size of 75–100 μm for 90

min. The results presented in [Fig. 4.5](#) showed that that copper from chalcopyrite did not dissolve (copper leaching rate < 1 %) into the solution in the absence of oxygen supply ($P_{Total} = P_V = 0.8$ MPa) under the condition. The XRD patterns of the solid residues after high-pressure oxidative leaching under the different pressure conditions were shown in [Fig. 4.6](#). It can be seen that intensities of chalcopyrite peaks remain nearly unaltered under the leaching condition in the absence of oxygen supply, i.e., the total pressure of 0.8 MPa. This result suggests that the lower dissolution rate of copper ore with pyrite content (sample A) is associated with the slow oxidation of chalcopyrite. Some researchers reported that the formation of elemental sulfur (S^0) might impede the leaching kinetics of chalcopyrite by forming a passivation layer on the unreacted chalcopyrite particles. The formation of elemental sulfur was not revealed by the XRD analysis due to the detection limit of the equipment. However, SEM-EDS analysis ([Fig. 4.7](#)) detected the presence of copper, iron, and sulfur phases in the residue sample, suggesting the formation of sulfur containing copper and iron compounds according to [Eqs. 4.5 and 4.6](#) and insufficient dissolution of chalcopyrite. Under the leaching condition, the total pressure ($P_{Total} = P_V + P_O$) of the reaction was maintained at a constant 1.5 MPa by introducing pure oxygen, and nearly 45.0 % of copper dissolution was achieved within 90 min. It can be seen that a further increase in the total pressure up to 2 MPa resulted in an increase in the efficiency of copper dissolution, and the maximum copper dissolution reached was 79.5 %. Results suggested that the efficiency of copper leaching from chalcopyrite depends significantly on the total pressure especially oxygen partial pressure (P_O) in an autoclave. It is predicted that increase in oxygen supply causes a rapid increase of total pressure in an autoclave and leads to the formation of iron sulfate and iron oxide compounds based on the oxidation of chalcopyrite. Diffraction peaks of hematite (Fe_2O_3) and jarosite ($H_3O(Fe_3(SO_4)_2(OH)_6)$) on the XRD patterns of the solid residues from the chalcopyrite leaching at 1.5 MPa and 2 MPa are proved this prediction ([Fig. 4.6](#)). Hence it can be concluded that oxygen supply is the most important factor for dissolution of chalcopyrite under the pressure oxidation condition due to the formation of iron sulfate and iron oxide compounds. As a result, a 2 MPa was selected as the optimal total pressure (P_{Total}) in the autoclave for further studies.

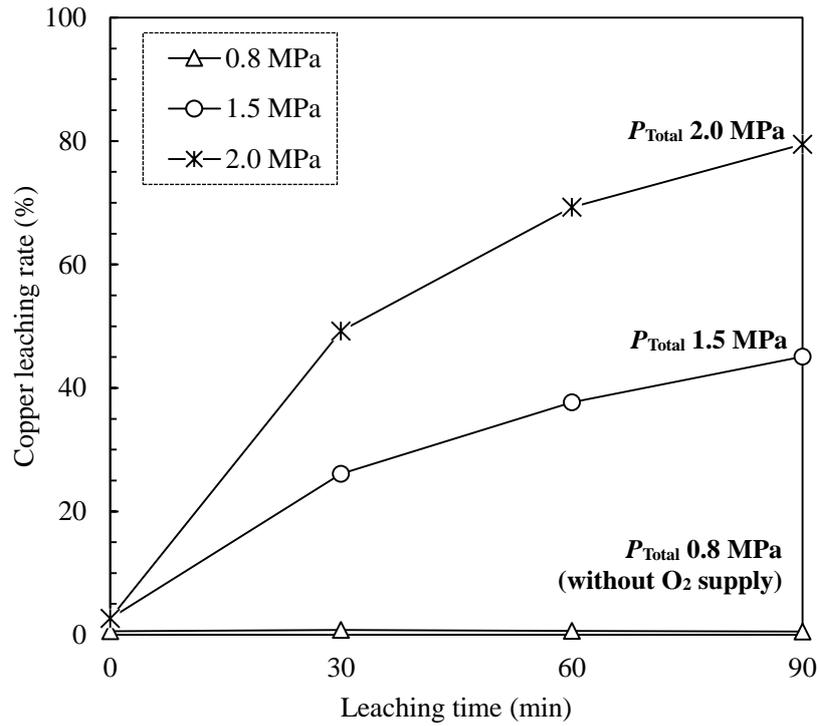


Fig. 4.5 The effects of total pressure on copper leaching rate.

(total pressure: 0.8, 1.5, and 2.0 MPa, agitation speed: 700 rpm, particle size: +75–100 μm ,

H_2SO_4 concentration: 1.0 M, temperature: 180 $^\circ\text{C}$, and pulp density: 10 %)

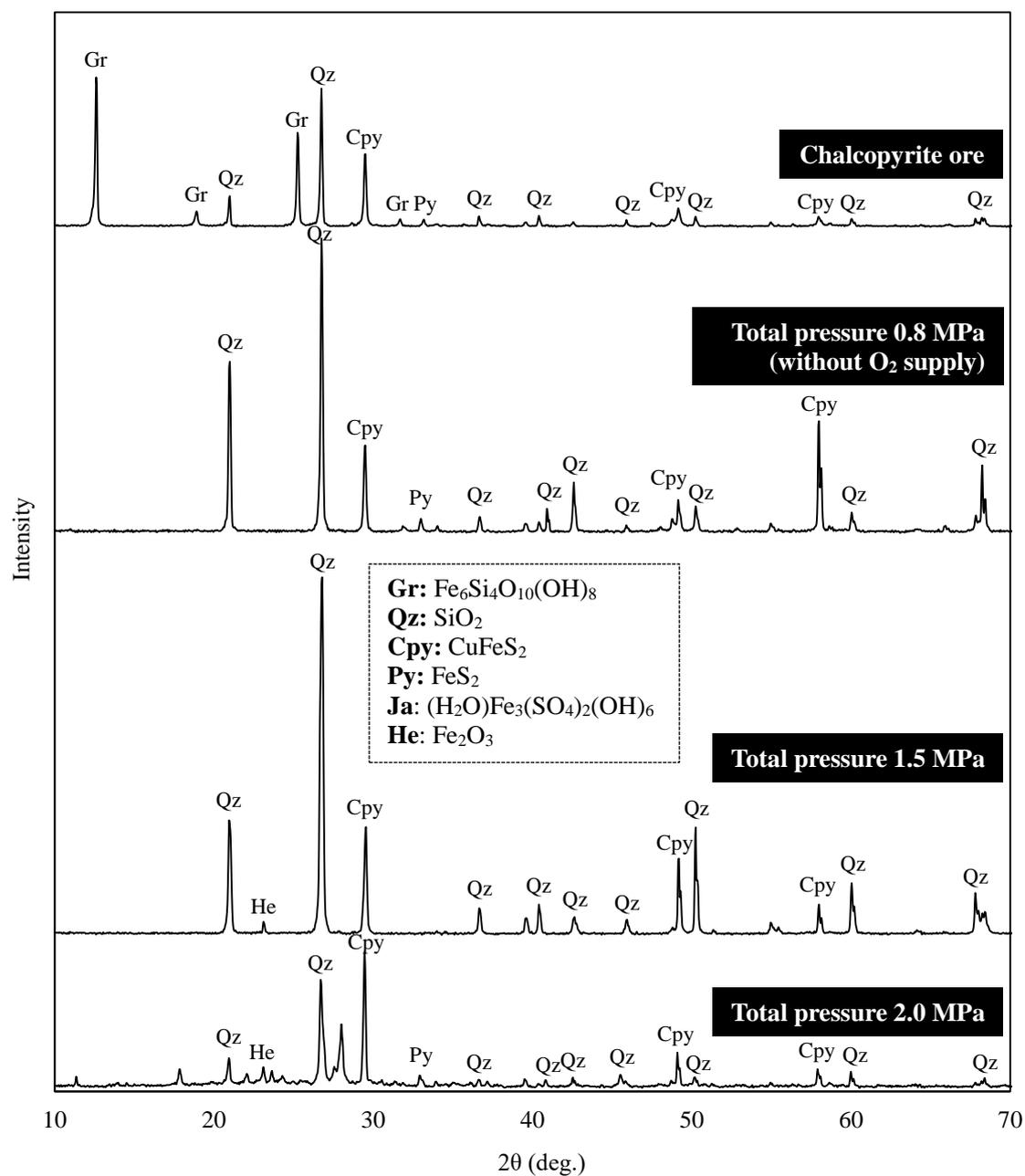


Fig. 4.6 XRD patterns of initial feed and residues obtained from various total pressure leaching.

Pressure: 0.8 MPa, 1.5 MPa, and 2.0 MPa, 700 rpm at 180 °C for 90 min.

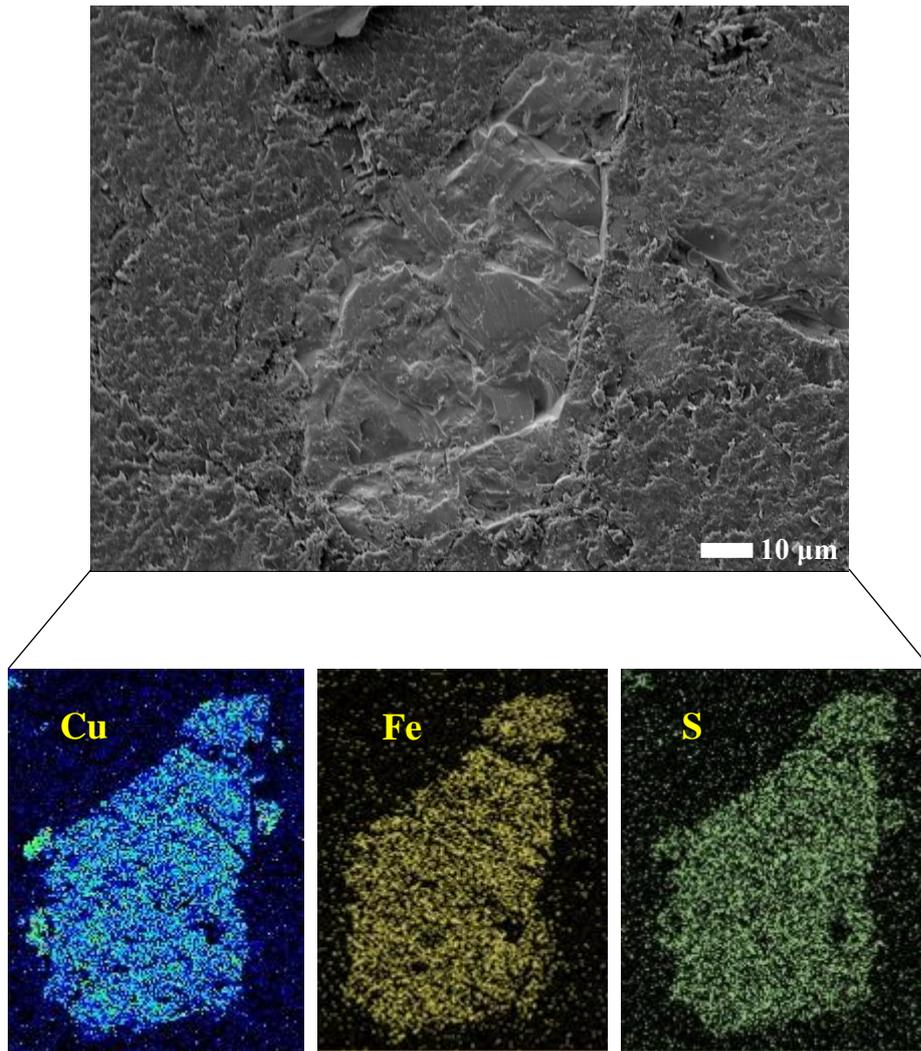


Fig. 4.7 SEM observation of the residue sample obtained from the leaching under the total pressure of 0.8 MPa for 90 min.

4.3.4 Effect of temperature

In order to study the influence of temperature on the copper dissolution from sample A (chalcopyrite ore with pyrite content), pressure oxidative leaching experiments were performed at various temperatures ranging from 160 to 180 °C with 1.0 M sulfuric acid, 10 % pulp density, 75-100 µm particle size, and 700 rpm agitation speed at 2 MPa pressure for 90 min. The results summarized in [Fig. 4.8](#) and results showed that an increase in temperature affects the leaching rate of copper from chalcopyrite. Particularly, the copper extraction increases from 43.0 to 62.8 % with increasing the temperature from 160 to 180 °C in 90 min. The temperature dependence of leaching rate in chalcopyrite was earlier determined by Berry et al. (1978) [50], and they noticed that the rate of reaction doubles for every 10 °C rise in temperature. As a result, it is observed that under the pressure–oxidative conditions, the increase in the leaching rate is not consistent with the reference data, however, the dissolution of chalcopyrite with the dilute sulfuric acid solution is a temperature dependent process. It suggests that the determination of the dissolution kinetics and mechanism of chalcopyrite with a H₂SO₄ solution under the pressure oxidative leaching conditions is needed to develop the hydrometallurgical process for chalcopyrite ores.

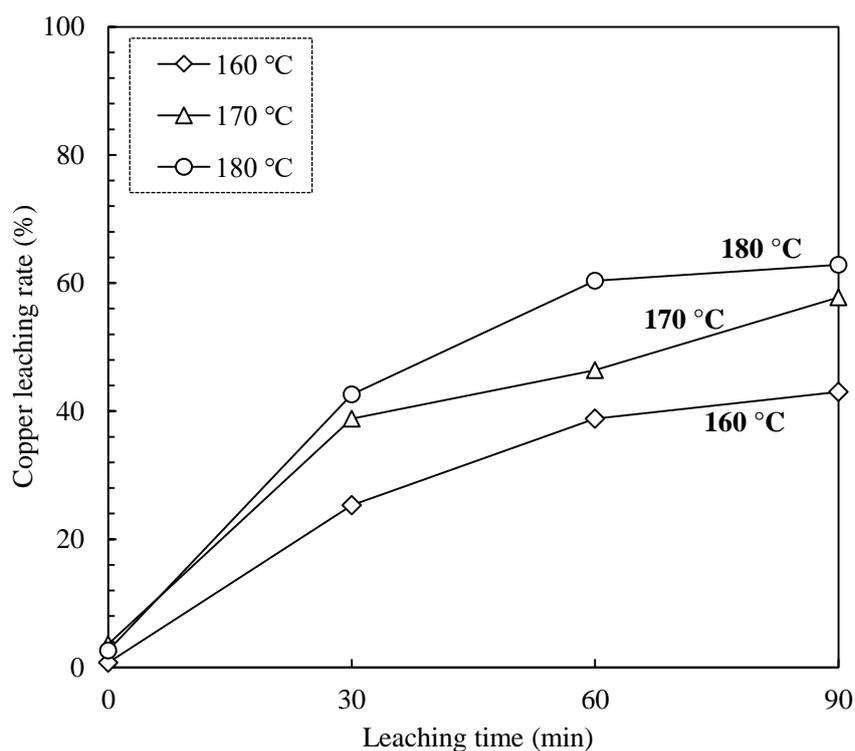


Fig. 4.8 The effects of temperature on copper leaching rate.

(Temperature: 160, 170 and 180 °C, H₂SO₄ concentration: 1.0 M, total pressure: 2.0 MPa, agitation speed: 700 rpm, particle size: +75–100 μm, and pulp density: 10 %)

4.3.5 Effect of sulfuric acid concentration

The effect of sulfuric acid concentration on the dissolution of copper from sample A was investigated with respect to leaching time. The leaching experiments were conducted under different sulfuric acid concentrations in the range of 0.1–2.0 M at the total pressure of 2.0 MPa, leaching time of 90 min, agitation speed of 700 rpm, pulp density of 10 %, the temperature of 180 °C, and particle size of 75–100 μm. Results obtained from these experiments are plotted as shown in **Figs. 4.9 and 4.10**. It can be seen from **Fig. 4.9** that over 94.5 % of copper is dissolved from the chalcopyrite with 0.1 M sulfuric acid solution in 90-min leaching. However, the efficiency of copper dissolution significantly decreases from 94.5 to 39.9 % with the increasing sulfuric acid concentration from 0.1 to 2.0 M due to the salting-out effect which is caused a decrease in oxygen solubility in the aqueous solution [51]. On the other hand, this observable trend of copper dissolution may be attributed to the competitive adsorption of sulfate and oxygen molecules to block the active surface sites [52]. As shown in **Fig. 4.10**, the efficiency of iron dissolution

increases with increasing sulfuric acid concentration due to the high solubility of the ferric sulfate in a high acid solution, and the dissolution rate of iron not change much when the acid concentration was over 1.0 M. A comparison between the XRD patterns of an initial chalcopyrite sample and the solid residues after pressure–oxidative leaching with various H_2SO_4 concentrations is shown in Fig. 4.11. The XRD analysis exhibited the disappearance of the characteristic peaks of chalcopyrite and the appearance of the corresponding peaks of hematite (Fe_2O_3), verifying the complete dissolution of chalcopyrite and the formation of hematite in the 0.1 M and 0.3 M sulfuric acid solution under the pressure oxidation conditions. It is also revealed that the peaks of chalcopyrite reappeared when the sulfuric acid concentration is increased further due to the decrease in the copper dissolution rate from chalcopyrite. Interestingly, when the sulfuric acid concentration is over 0.3 M, the peaks of hematite disappeared due to the dissolution rate of iron which increased with the increasing acid concentration to 2.0 M.

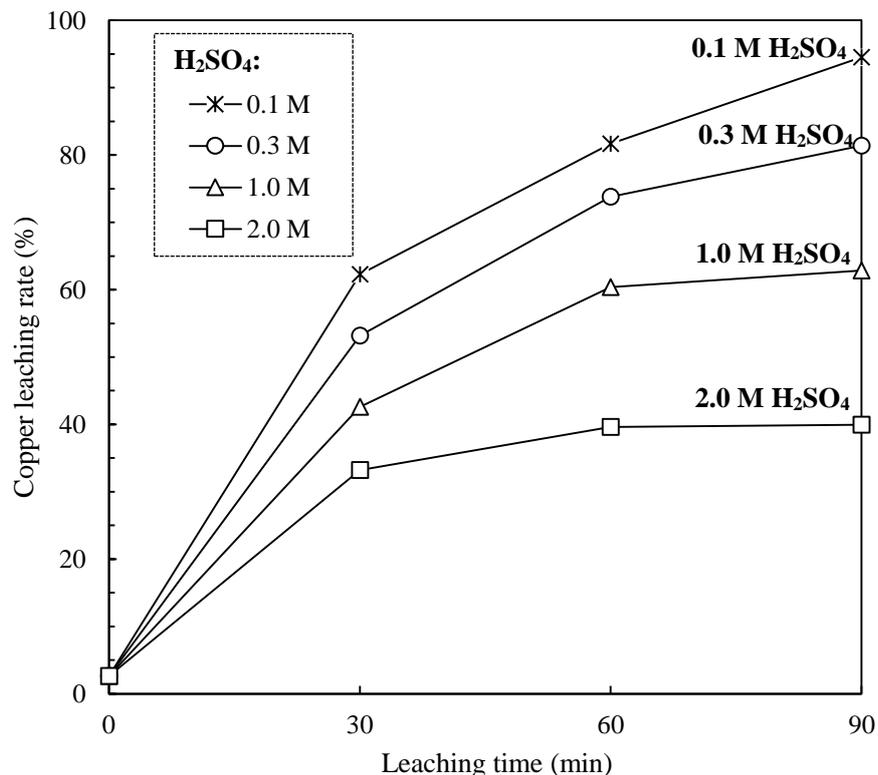


Fig. 4.9 The effects of sulfuric acid concentration on copper leaching rate.

(H_2SO_4 concentration: 0.1–2.0 M, total pressure: 2.0 MPa, agitation speed: 700 rpm, particle size: +75–100 μm , temperature: 180 $^\circ\text{C}$, and pulp density: 10 %)

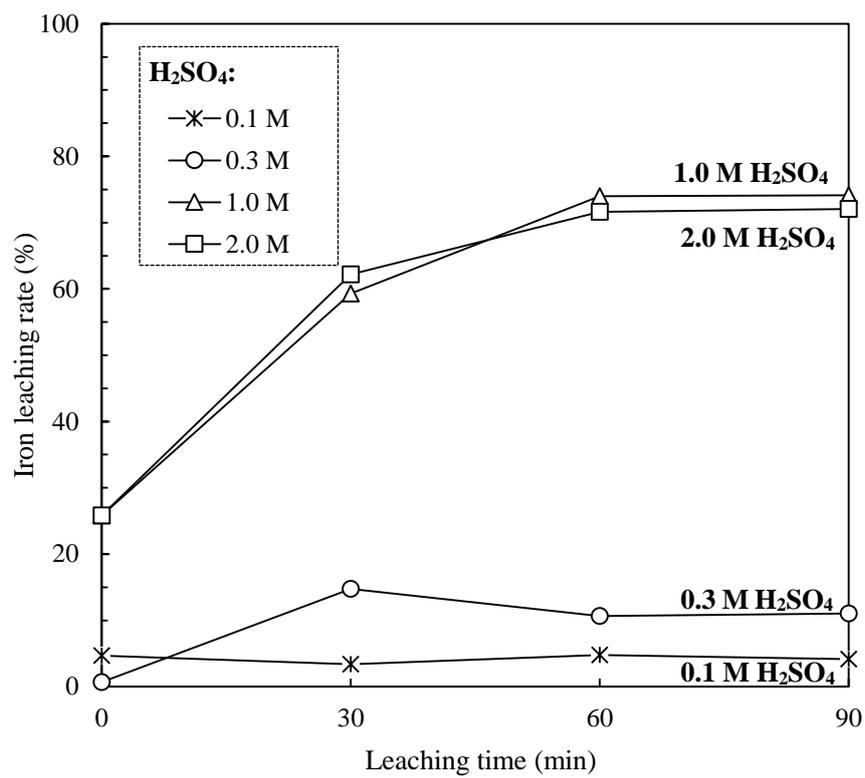


Fig. 4.10 The effects of sulfuric acid concentration on iron leaching rate.

(H₂SO₄ concentration: 0.1–2.0 M, total pressure: 2.0 MPa, agitation speed: 700 rpm, particle size: +75–100 μm, temperature: 180 °C, and pulp density: 10 %)

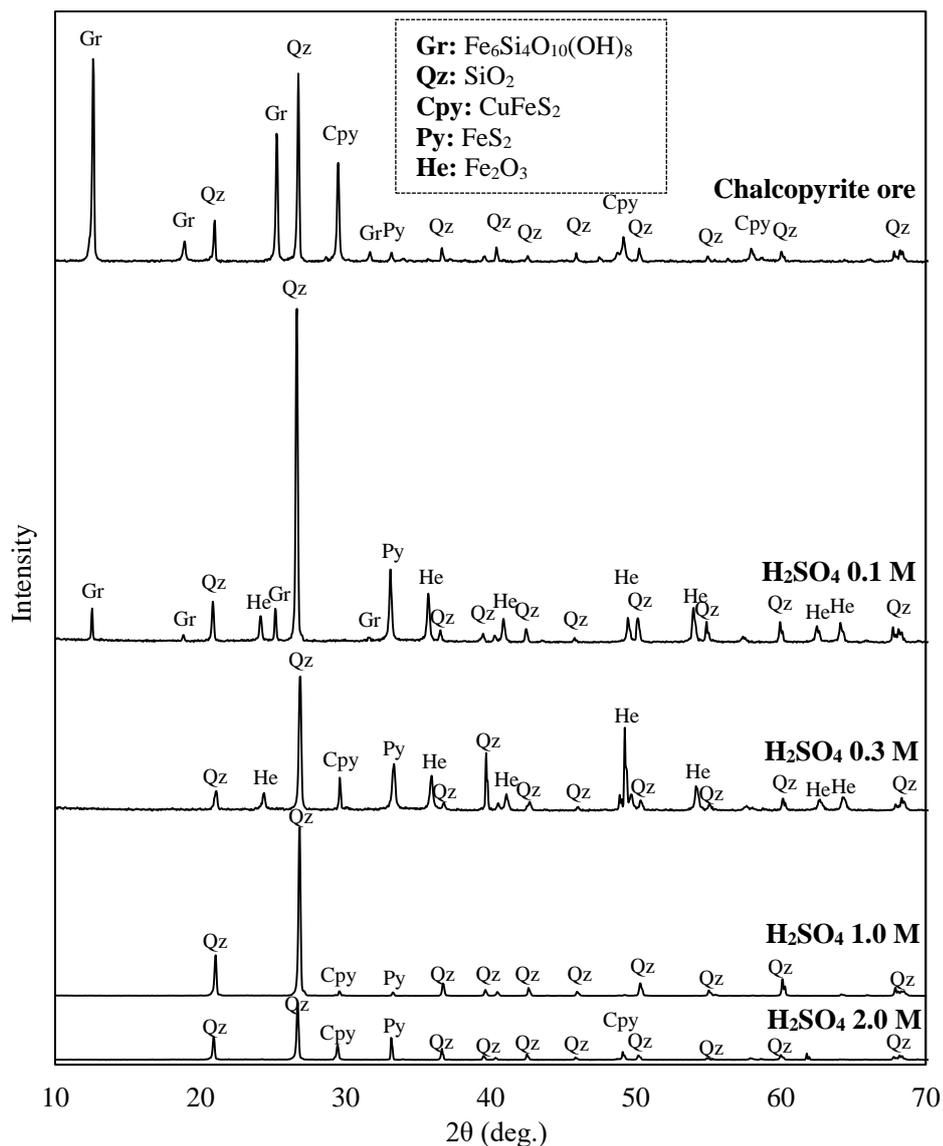


Fig. 4.11 XRD patterns of an initial feed and residues obtained from the pressure–oxidative leaching studies under the different H_2SO_4 concentrations.

(H_2SO_4 concentration: 0.1–2.0 M, total pressure: 2.0 MPa, agitation speed: 700 rpm, particle size: +75–100 μm , temperature: 180 $^\circ\text{C}$, and pulp density: 10 %)

4.3.6 Dissolution kinetics of chalcopyrite under pressure oxidation leaching condition

In order to determine the mechanism of chalcopyrite leaching in sulfuric acid conditions, experimental data obtained were analyzed by using shrinking core models, particularly surface chemical reaction model and product layer diffusion model. The apparent rate constants and correlation coefficients were calculated using Eqs. 4.10 and 4.11 by the best fit to the experimental data obtained from the leaching studies under different particle size, total pressures, temperatures, and H₂SO₄ concentrations (Figs. 4.3, 4.5, 4.8, and 4.9), respectively. The results obtained from regression and correlation analysis using the dissolution kinetics models are summarized in Table 4.4. Results show that the linear correlation coefficients between total pressure, temperature, and H₂SO₄ concentration against the time period of leaching are over 0.99, 0.94, and 0.94, respectively, except than the 2.0 M H₂SO₄ leaching when fit the data using product layer diffusion controlled model. Whereas the surface chemical reaction model is used for analysis, the linear correlation coefficients between total pressure, temperature, and H₂SO₄ versus time for leaching are 0.96, 0.83, and 0.83, respectively. Results suggest that there are no large differences between the diffusion controlled model and chemical reaction model on the linear correlation coefficients (Table 4.4). In order to study the effect of temperature on reaction rates, the activation energy (E_a) of the chalcopyrite dissolution was estimated by the Arrhenius equation (Eq. 4.12) using the apparent rate constants of the diffusion controlled model (k_d) and chemical reaction controlled model (k_r) estimated previously (Table 4.4). Fig. 4.12 displays the Arrhenius plots of $\ln k$ versus $1000/T$ for the chalcopyrite dissolution by fitting the diffusion and chemical reaction models. The activation energy of diffusion model and chemical reaction model derived from the Arrhenius plot are 80.21 and 42.44 kJ/mol, respectively (Fig. 4.12). A high activation energy of 80.21 kJ/mol indicates that chalcopyrite leaching maybe not controlled by diffusion model because it generally has a low activation energy value (< 20 kJ/mol) [53]. On the other hand, an activation energy (42.44 kJ/mol) obtained by fitting the chemical reaction model clearly confirms that chalcopyrite leaching process can be represented by chemical reaction model. The obtained activation energy for chalcopyrite dissolution of 42.44 kJ/mol is similar to previously reported values which were 49, 50, and 60 kJ/mol in different leaching media and different leaching conditions, namely, H₂SO₄-K₂Cr₂O₇ (30–80 °C), H₂SO₄-K₂Cr₂O₇ (25–60 °C) and H₂O₂-H₂SO₄ (25–50 °C) systems, respectively [21, 48,

3]. In addition, a linear dependence of the rate constant on the inverse particle radius is a fact in favor of the proposed surface reaction shrinking core model. However, it is necessary to confirm that how does the activation energy changes as a function of particle size in the future work, due to this research only calculated that at a size fraction of +75–10 μm . It can be expected that may be a higher activation energy could be found than that under particle size of +75–10 μm , which further supports that chalcopyrite leaching process can be represented by chemical reaction model. In order to determine the reaction order, a linear correlation plot between the logarithms of the slope of each line and the total pressure is created (Fig. 4.13). The empirical reaction order with respect to different total pressure (P_{Total}) by fitting the chemical reaction model is about 8.0. It indicates that the total pressure is the most important factor for the dissolution of copper from chalcopyrite during the leaching process.

Table 4.4 Apparent rate constants and correlation coefficients for shrinking core model under different conditions.

Conditions		Surface chemical reaction		Product layer diffusion	
		$1-(1-\alpha)^{1/3}$		$1-2/3\alpha-(1-\alpha)^{2/3}$	
		k_r, min^{-1}	R^2	k_d, min^{-1}	R^2
Particle size (μm)	-38	0.0044	0.9386	0.0007	0.9627
	+38-75	0.0003	0.9583	0.0007	0.9908
	+75-10	0.0019	0.9672	0.0004	0.9574
Total pressure (MPa)	0.8	-	-	-	-
	1.5	0.0044	0.9672	0.0014	0.9971
	2.0	0.0019	0.9583	0.0003	0.9984
Temperature ($^{\circ}\text{C}$)	160	0.0022	0.8954	0.0003	0.9799
	170	0.0030	0.8568	0.0006	0.9832
	180	0.0037	0.8290	0.0008	0.9392
H_2SO_4 concentration (M)	0.1	0.0072	0.9772	0.0024	0.9891
	0.3	0.0053	0.9193	0.0015	0.9911
	1.0	0.0037	0.8290	0.0008	0.9392
	2.0	0.0022	0.5960	0.0003	0.7804

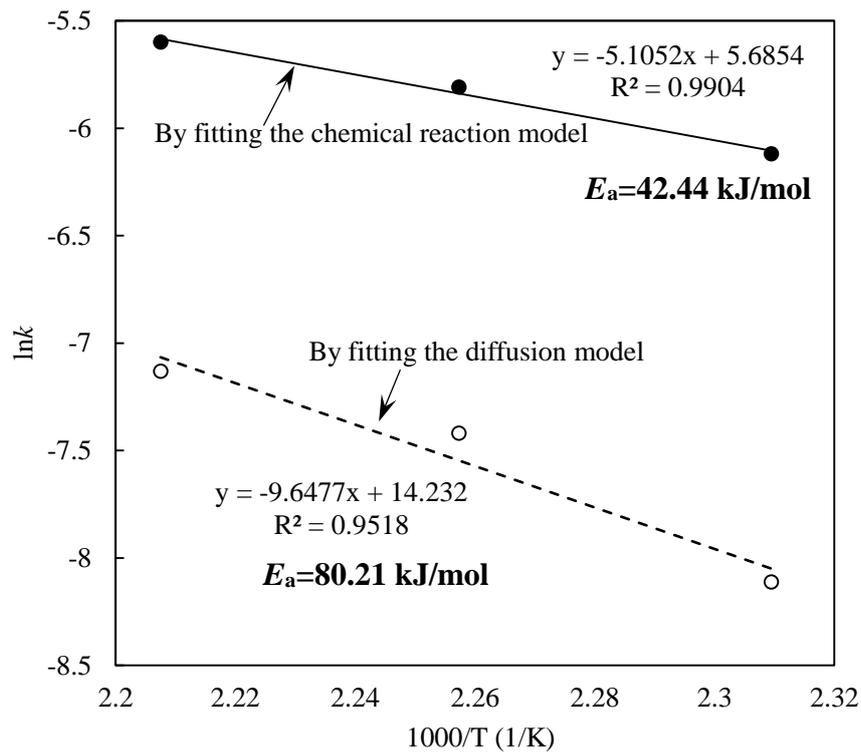


Fig. 4.12 Arrhenius plot for copper leaching from chalcopyrite in H_2SO_4 solution.

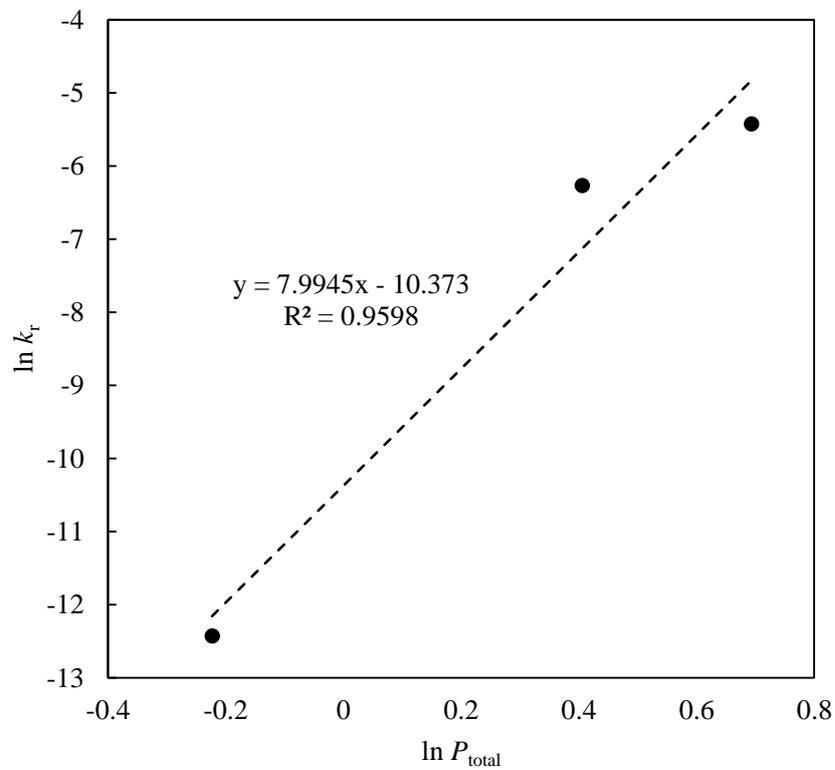


Fig. 4.13 The plot of $\ln k_r$ vs $\ln P_{Total}$ to estimate reaction order.

4.3.7 Effect of Fe/Cu mole ratio

Pyrite (FeS_2) and chalcopyrite (CuFeS_2) commonly occur together in copper sulfide minerals and pyrite is a source of sulfuric acid [32]. The sulfuric acid production from pyrite under the oxidative condition can be illustrated as follows (Eq. 4.14):



Therefore, this study is based on the assumption that if sulfuric acid forms during the pyrite oxidative process, that can further promote the dissolution of chalcopyrite without the addition of sulfuric acid solution into the reaction system. To verify this assumption proposed, high-pressure oxidative leaching experiments in the absence of sulfuric acid solution were firstly performed under a total pressure of 2.0 MPa, temperature of 180 °C, agitation speed of 700 rpm, and pulp density of 10 % for 60 min using copper ore samples with and without content of pyrite (Fig. 4.1, Table 4.2). Results showed that the leaching efficiency of copper from the sample A is several ten times higher than that of sample B (Table 4.5) due to the presence of pyrite in sample A (Table 4.2). It is observed that the copper dissolution rate of 77.2 % from sample A in the absence of a sulfuric acid solution is almost consistent with the result from the lower concentration of sulfuric acid leaching (Fig. 4.9). It suggests that the presence of pyrite has an efficient effect on copper dissolution.

In addition, to clearly identify the opposite effect of the presence of pyrite on copper dissolution, the copper ore sample without the content of pyrite (sample B) and pyrite ore sample (sample C) are used in a further leaching study. The ratio of moles of iron (Fe) to moles of copper (Cu) in sample B was varied in the range from 1 (without pyrite addition) to 20 (the sum of Fe from CuFeS_2 and added FeS_2 divided by the Cu from CuFeS_2) by adding the pyrite ore (sample C). The pressure oxidative leaching experiments were conducted under the same conditions in the absence of sulfuric acid solution as previous experiments and results obtained are plotted in Fig. 4.14. It can be seen that with an increase of the Fe/Cu mole ratio, copper dissolution rate increases significantly and about 90 % copper dissolution efficiency was achieved when Fe/Cu mole ratio was 20 under the condition. Whereas the efficiency of iron leaching from the sample increases slightly from 4 up to 15 % with increasing of Fe/Cu ratio. As a result, it can be concluded that the presence of pyrite in the leaching system has an obvious enhancing effect on copper dissolution from

chalcopyrite. It also implies that iron dissolution has no negative influence on the copper dissolution from the chalcopyrite/copper ore. **Fig. 4.15** shows the SEM–EDS of the solid residue obtained from the high–pressure oxidative leaching under the total pressure of 2.0 MPa, agitation speed of 700 rpm, the particle size of +75–100 μm , pulp density of 10 %, the reaction time of 60 min at a temperature of 180 $^{\circ}\text{C}$ when the Fe/Cu mole ratio was 1. From **Fig. 4.15**, it can be seen that a thin film of hematite was formed onto the chalcopyrite surface due to a chemical reaction via **Eq. 4.15**, which may occur under high–pressure oxidation condition in water system i.e. without sulfuric acid. The hematite is stable under low acid conditions and impeded the further dissolution of chalcopyrite from the sample, resulting in a lower copper leaching rate of 12.3 % under the conditions of Fe/Cu mole ratio 1.



However, when the pyrite was added into the reaction system for adjusting the Fe/Cu mole ratio, the maximum copper dissolution rate of 89.2 % was achieved under the optimized leaching conditions when Fe/Cu mole ratio was 20. The internal temperature profile inside the autoclave during oxidative leaching of copper ore sample with a Fe/Cu mole ratio of 20 under the optimized leaching condition is presented in **Fig. 4.16**. As shown in **Fig. 4.16**, the internal temperature inside the autoclave increased rapidly up to 188 $^{\circ}\text{C}$ with the introduction of pure oxygen gas in the leaching system in which the temperature was 170 $^{\circ}\text{C}$. The unexpectedly rapid increase in temperature into the leaching system is due to the generation of heat associated with the oxidation of pyrite (exothermic reaction) and the temperature inside the autoclave is reached at the preset temperature (180 $^{\circ}\text{C}$) of the experiment after completed the oxidation of pyrite by oxygen during 22 min. XRD patterns of residues obtained from the copper ore leaching with various Fe/Cu mole ratios under the optimized high–pressure oxidative conditions are shown in **Fig. 4.17**. It observed that the peak of chalcopyrite disappeared and the peaks of pyrite were not detected in the residue samples even if some pyrites added into the reaction system. It implies that under the optimized pressure oxidative conditions, both chalcopyrite and pyrite are oxidized forming ferric sulfate (**Eqs. 4.5 and 4.14**) that was further completely oxidized resulting in the formation of hematite according to **Eq. 4.7**. This implication was verified by XRD analysis of leach residue. Particularly, hematite characteristic peaks were identified by XRD analysis of the solid residues obtained from the copper

ore/chalcopyrite leaching when a Fe/Cu ratio was greater than 5. In order to verify the effect of pyrite on chalcopyrite dissolution, a comparison experiment was carried out between experiments conducted under two (2) optimized conditions: the Fe/Cu mole ratio of 20 (presence of pyrite) in water (H₂O) and Fe/Cu mole ratio of 1 (absence of pyrite) in 0.3 M sulfuric acid (H₂SO₄) using sample B (copper ore without pyrite content), while the other experimental parameters was fixed as follows: agitation speed of 700 rpm, total pressure of 2.0 MPa, temperature of 180 °C, pulp density of 10 %, and reaction time for 60 min. Results obtained are shown in [Table 4.6](#). It can be seen that the dissolution rate of copper in water and 0.3 M H₂SO₄ solution with and without pyrite addition is 89.2 and 95.7 %, respectively. These results confirm that pyrite is a source of the generation of sulfuric acid under the pressure–oxidative condition. Therefore pyrite addition through chalcopyrite leaching can promote the copper dissolution from chalcopyrite according to [Eq. 4.14](#). It is obvious that in the presence of oxygen, Fe²⁺ is oxidized to Fe³⁺ as illustrated in [Eq. 4.14](#) and then Fe³⁺ is hydrolysed to hematite as a precipitate ([Eq. 4.7](#)).

Table 4.5 The leaching efficiency of copper from chalcopyrite ore with/without the pyrite content under same leaching condition.

Sample	Leaching efficiency (%)	
	Cu	Fe
Sample A (chalcopyrite ore with pyrite content)	77.2	3.6
Sample B (chalcopyrite ore without pyrite content)	0.02	0.8

Table 4.6 A comparison of copper dissolution from sample B in water (H₂O) and 0.3 M sulfuric acid (H₂SO₄) solutions with and without the addition of pyrite.

Leaching media	Pyrite	Fe/Cu mole ratio (mol/mol)	Leaching efficiency (%)	
			Cu	Fe
Water (H ₂ O)	With	20	89.22	15.48
0.3 M H ₂ SO ₄	Without	1	95.74	17.85

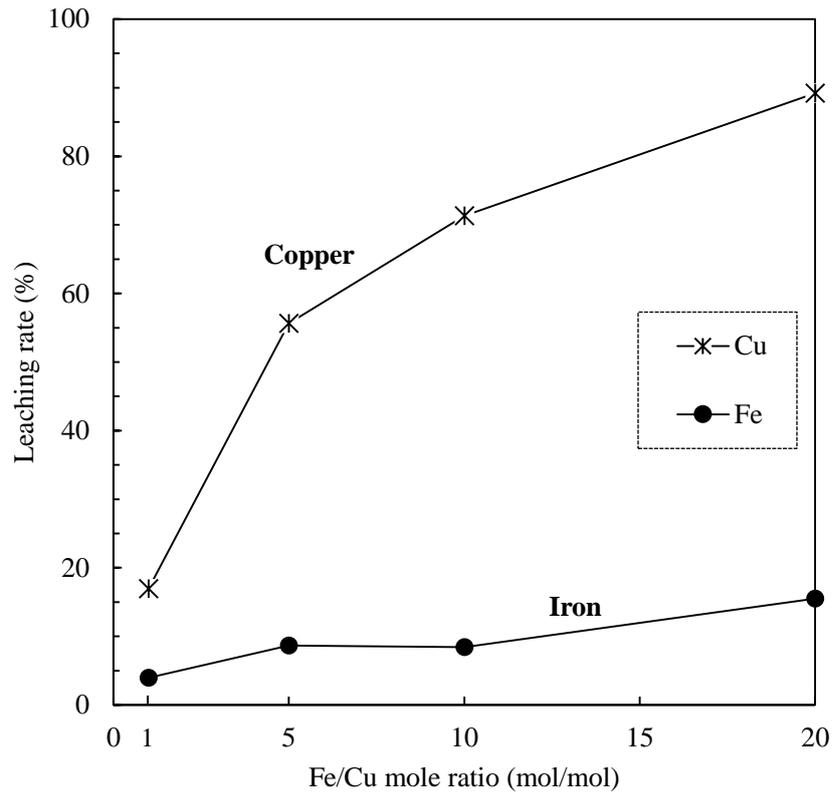


Fig. 4.14 The effects of Fe/Cu mole ratio on copper and iron leaching rates.

(Fe/Cu mole ratio: 1–20 mol/mol, H_2SO_4 concentration: 0 M, total pressure: 2.0 MPa, agitation speed: 700 rpm, particle size: +75–100 μm , reaction time: 60 min, temperature: 180 $^\circ\text{C}$, and pulp density: 10 %)

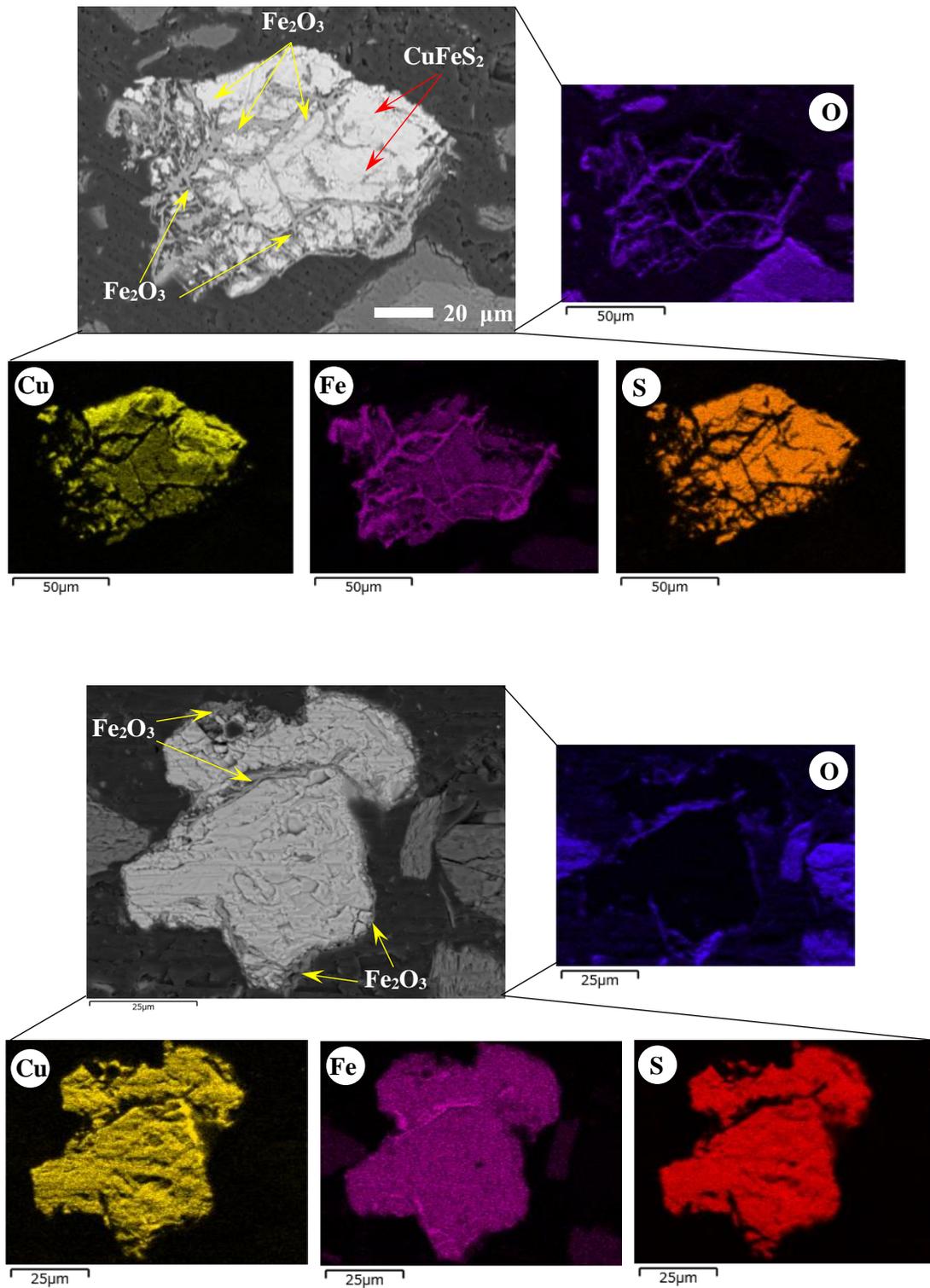


Fig. 4.15 SEM observation of the residue obtained from pressure-oxidative leaching.

(Fe/Cu mole ratio: 1, H_2SO_4 concentration: 0 M, total pressure: 2.0 MPa, agitation speed: 700 rpm, particle size: +75–100 μm , reaction time: 60 min, temperature: 180 $^\circ\text{C}$, and pulp density:

10 %)

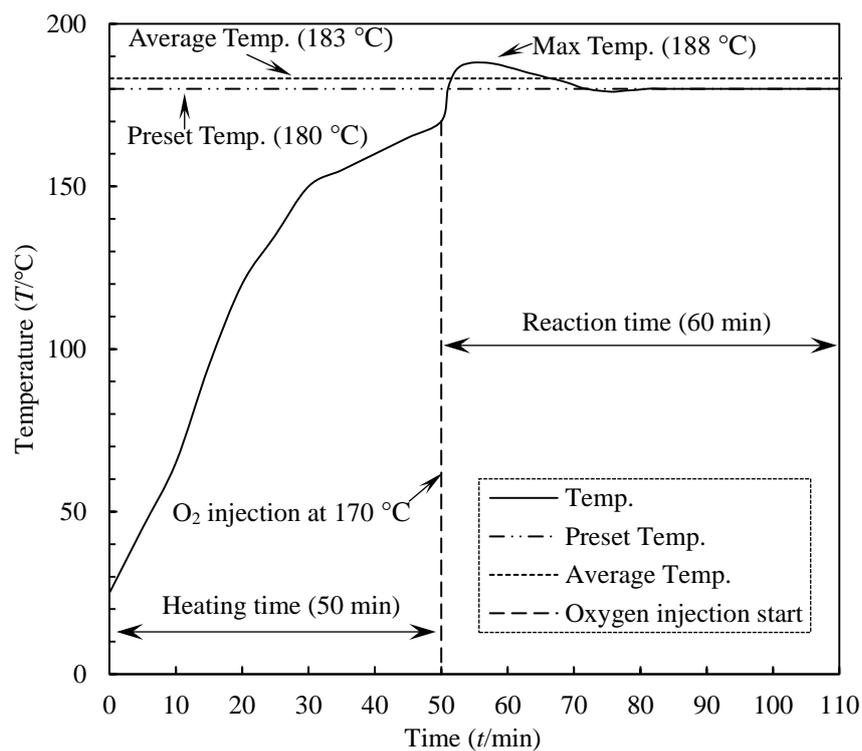


Fig. 4.16 Changes in temperature inside the autoclave during the heating and reaction periods.

(Oxygen gas was introduced at 10 °C before preset Temp. and oxidation reaction allowed for 60 min. The total pressure and pulp density were maintained at 2.0 MPa and 10 %, respectively)

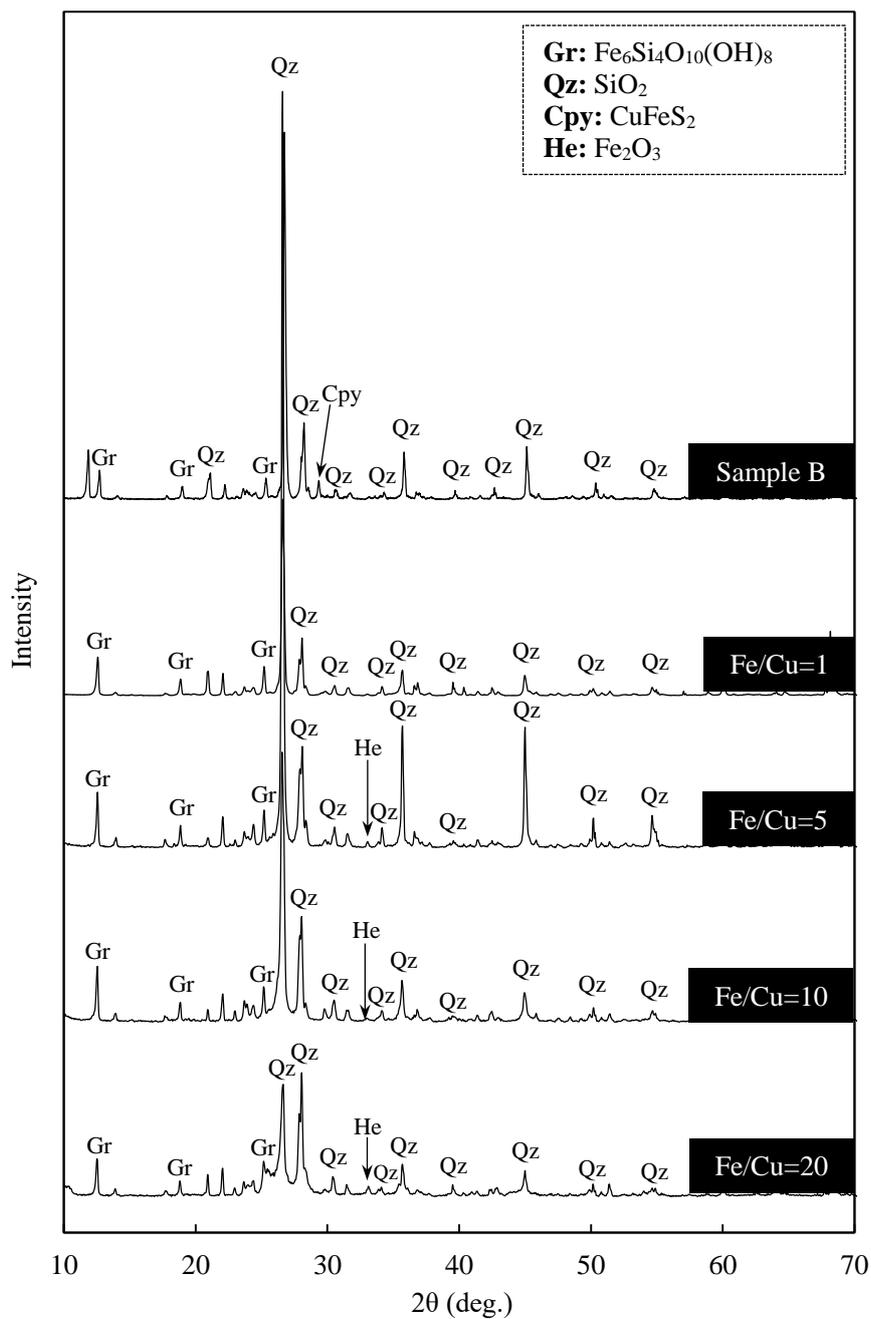


Fig. 4.17 XRD patterns of initial feed and residues obtained from pressure-oxidative leaching of sample B with various Fe/Cu mole ratios under optimized conditions.

(Fe/Cu mole ratio: 1–20 mol/mol, H_2SO_4 concentration: 0 M, total pressure: 2.0 MPa, agitation speed: 700 rpm, particle size: +75–100 μm , reaction time: 60 min, temperature: 180 $^\circ\text{C}$, and pulp density: 10 %)

4.4 Conclusion

Leaching and kinetics of copper dissolution from chalcopyrite ore in sulfuric acid (H_2SO_4) solution, as well as the effect of pyrite on the chalcopyrite leaching under pressure–oxidative conditions at medium temperature (160–180 °C), were investigated during this study. The results of this chapter can be summarized as follows:

- (1) The increasing the temperature, pressure, and agitation speed had a positive effect on the efficiency of copper dissolution from chalcopyrite in 1.0 M H_2SO_4 solution, whereas an increase of H_2SO_4 concentration resulted in an opposite effect. Under the optimal conditions, selective leaching for the recovery of copper from chalcopyrite ore was achieved. The maximum efficiency of copper dissolution reached 94.5 %, while the efficiency of iron dissolution was 4.5 %.
- (2) The kinetics of copper dissolution from chalcopyrite in H_2SO_4 solution under pressure–oxidative leaching conditions can be represented by the chemical reaction controlled model, i.e., $k_t = 1 - (1 - \alpha)^{1/3}$, and the activation energy was calculated to be 42.44 kJ/mol.
- (3) An excellent linear relationship from the plot of $\ln(k_r)$ versus $\ln(P_{Total})$ confirms the applicability of the kinetic model chosen for the analysis of experimental data in this work. The reaction order with respect to total pressure (P_{Total}) by fitting the chemical reaction model was approximately 8.0, which confirmed that the total pressure is the most important factor for the dissolution of copper from chalcopyrite ore under the conditions.
- (4) The pyrite addition has a significant effect on the dissolution of copper from chalcopyrite/copper ore due to the production of sulfuric acid from pyrite under pressure oxidative condition.

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Chapter 5: Application of the Flotation and High-Pressure Oxidative Leaching Processes to Mine Tailings

5.1 Introduction

Copper is one of the most important base metal and widely used as wire and conductor. In the earth's crust, copper is most commonly present as copper-iron-sulfide and copper-sulfide minerals, such as chalcopyrite (CuFeS_2) and chalcocite (Cu_2S) [1, 2]. About 80 % of the world's copper from ore originates in Cu-Fe-S minerals, especially chalcopyrite, which is the most refractory minerals and not easily dissolved in aqueous solutions [1-3]. For that reason, most majority of copper extracted from these copper minerals is usually by the pyrometallurgical process, i.e., flotation followed by smelting and refining [2, 4, and 5]. Generally, the mine tailings are produced as a byproduct during the beneficiation of copper ore namely froth flotation before the pyrometallurgical process. According to the literature data, the greatest flow of the mined material arises in the flotation process represents mine tailings in the range of 90-95 % [6-7]. These mine tailings usually treated with methods included the dumping of dewatered tailings onto land and discharge it into rivers and streams, the practice that is still done at some mines [8]. Apart from the visual effect on the landscape of tailings disposal, the major ecological effect is water pollution, which is usually arising from the discharge of water contaminated with solids, heavy metals, mill reagents, and sulfur compounds etc. [8-14]. Due to an increased exploration of copper ore and the discovery of more low-grade deposits, it can be predicted that more mine tailings will be produced in the coming years, which might cause more environmental problems and challenges. Regarding data from 1998, 44 % of copper is lost during flotation process [6, 15], which illuminate that the mine tailings still contain valuable components of copper. In addition, the old mine tailings sometimes have higher copper grade than that of original world average copper minerals which are about 0.4 %. Considering the current price of copper in the world, and predictions that the demand for the copper will increase, as well as a very low-grade copper content in the ore, which is being extracted today [6], it is very necessary to utilize the mine tailings constitute a potential future

copper resource. However, the mine tailings usually consist of clay minerals and pyrite etc., which makes it more complex and difficult to treat using the traditional pyrometallurgical technologies. In recent years, research and development in the hydrometallurgical process have intensified as an alternative to the pyrometallurgical route [16–18]. Some researchers have investigated the possibility of copper recovery from the mine tailings using direct atmospheric leaching in an acid solution [6, 19, and 20]. The result shows that the dissolution percentage of copper from the mine tailings is quite low (low than 55 %) and the copper concentration in the PLS is poor, and this limits the further recovery of copper from the liquid using such as solvent extraction. The purpose of the research study was to develop an effective copper recovery process for contributing to resolving the utilization of mine tailings as a potential copper resource by a hydrometallurgical process.

In this chapter, the possibility of applying the developed flotation and high–pressure oxidative leaching processes for recovery of copper from mine tailings was investigated. In order to upgrade the copper grade and reduce the impurities such as clay minerals, flotation of the mine tailings was conducted under the conditions of pH 4–10, sulfurizing reagent dosage 0–1000 g/t–ore, and floatation time 0–15 min. In addition, to achieve an excellent copper dissolution from the concentrate of mine tailings, which consist chalcopyrite as the major copper component, a high–pressure oxidative leaching (HPOL) was conducted using an autoclave under a variety of sulfuric acid concentration (0–0.5 M), total pressure (0.8–2.0 MPa), temperature (140–180 °C), and pulp density (100–400 g/L). Then, the solvent extraction of pregnant leaching solution (PLS) obtained under the optimal HPL conditions was carried out under various parameters of pH (0.1–2.0) and sulfuric acid concentration (0.5–1.5 M), for producing the Cu–rich solution. As a result of this chapter, an efficient method has been proposed to disposal mine tailings and recover copper from it by a combined hydrometallurgical process of flotation–HPOL–solvent extraction.

5.2 Experimental

5.2.1 Sample

A sample of mine tailings (**Fig. 5.1**) obtained from Bor Mining, Serbia was used as an initial feed to this study. As shown in **Table 5.1**, Cu (0.34 mass%), Al (8.12 mass%), Fe (8.96 mass%), S (11.23 mass%), and SiO₂ (57.84 mass%) are confirmed as main components in the mine tailings. The mineral composition of the material was identified by X-Ray Diffractometer (XRD, Rigaku RINT-2200V) and XRD patterns of the sample was shown in **Fig. 5.2**. The main mineralogical constituents of the mine tailings are quartz (SiO₂), pyrite (FeS₂), and kaolinite (Al₂Si₂O₅(OH)₄). The copper minerals were not detected in the mine tailings by the XRD analysis due to the limitation of the equipment. However, the SEM-EDS test confirmed that the chalcopyrite (CuFeS₂) was the major copper phase of the mine tailings.



Fig. 5.1 Photograph of the mine tailings.

Table 5.1 Chemical compositions of the mine tailings.

	Grade (mass%)				
	Cu	Fe	Al	S	SiO ₂
Mine tailings	0.34	8.96	8.12	11.23	57.84

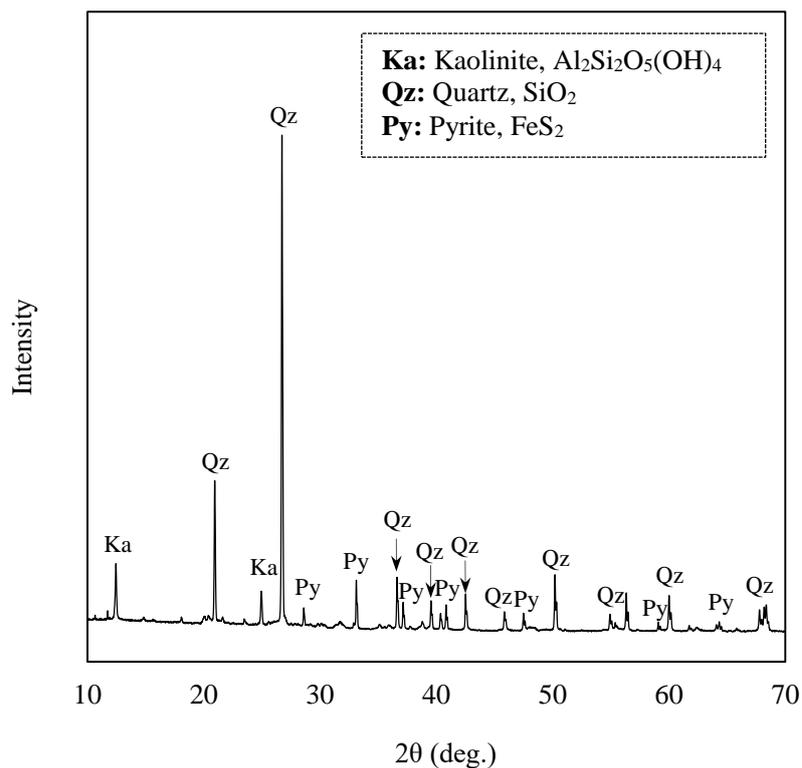


Fig. 5.2 The XRD patterns of mine tailings.

5.2.2 Reagent

The reagents used in this chapter were shown in [Table 5.2](#). The collector PAX, frother MIBC, sulfurizing reagent NaHS, and pH regulator sodium hydroxide and sulfuric acid were used in flotation experiments. In high-pressure oxidative leaching, the sulfuric acid (H_2SO_4) and oxygen (O_2) was served for an oxidizer to improve the leaching efficiency of copper. In addition, the pH regulator sodium hydroxide and pH indicator Methyl orange were employed for measuring the free acidity of the pregnant leach solutions. Finally, to recover copper from the pregnant leach solution, an extractant called LIX[®] 84I diluted by a kerosene and a back extractant of sulfuric acid were used in extraction and stripping, respectively.

Table 5.2 List of the chemical reagents used in this chapter.

Experiments	Type	Name	Maker	Formula
Flotation	Collector	Potassium Amyl Xanthate (PAX)	Kanto Chemical	$\text{KC}_6\text{H}_{11}\text{OS}_2$
	Frother	Methyl Iso Butyl Carbinol (MIBC)	–	$\text{C}_6\text{H}_{13}\text{O}$
	Sulfurizing reagent	Sodium hydrogen sulfide	Nagao Corp.	NaHS
	pH regulator	Sodium hydroxide	Kanto Chemical	NaOH
		Sulfuric acid	Kanto Chemical	H_2SO_4
HPOL	Oxidizer	Sulfuric acid	Kanto Chemical	H_2SO_4
	Oxidizer	Oxygen	Aiba Shouten	O_2
Free acidity	pH regulator	Sodium hydroxide	Kanto Chemical	NaOH
	pH indicator	Methyl orange	–	$\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$
SX	Extractant	LIX [®] 84I	BASF Corp.	–
	Dilutor	Kerosene	–	–
	pH regulator	Sodium hydroxide	Kanto Chemical	NaOH
	Back extractant	Sulfuric acid	Kanto Chemical	H_2SO_4

5.2.3 Procedure

5.2.3.1 Flotation of mine tailings

Experiments were carried out by using the floating machine shown in [Figure 5.3](#). As the flotation procedure is shown in [Fig. 5.4](#), 250 g mine tailings introduced into the cell with water and adjusted the pulp density to 250 g/L at an agitation speed of 1000 rpm and mixing time of 5 minutes. After the pH of the slurry fixed from pH 4–12 using NaOH, a sulfurizing reagent (NaHS) was added under constant agitation, and conditioned for 5 min. After that, an appropriate amount of collector (PAX: Potassium amyl xanthate ($\text{C}_5\text{H}_{11}\text{OCSSK}$)) was added into the cell, and conditioned for 5

min. Flotation was performed during 5–15 min after frother (MIBC) was added into the cell. The mineral and chemical composition analyses are carried out with X-ray diffraction and ICP (Inductively Coupled Plasma) after prepared the froth concentrate.



Fig. 5.3 Photograph of the flotation machine.

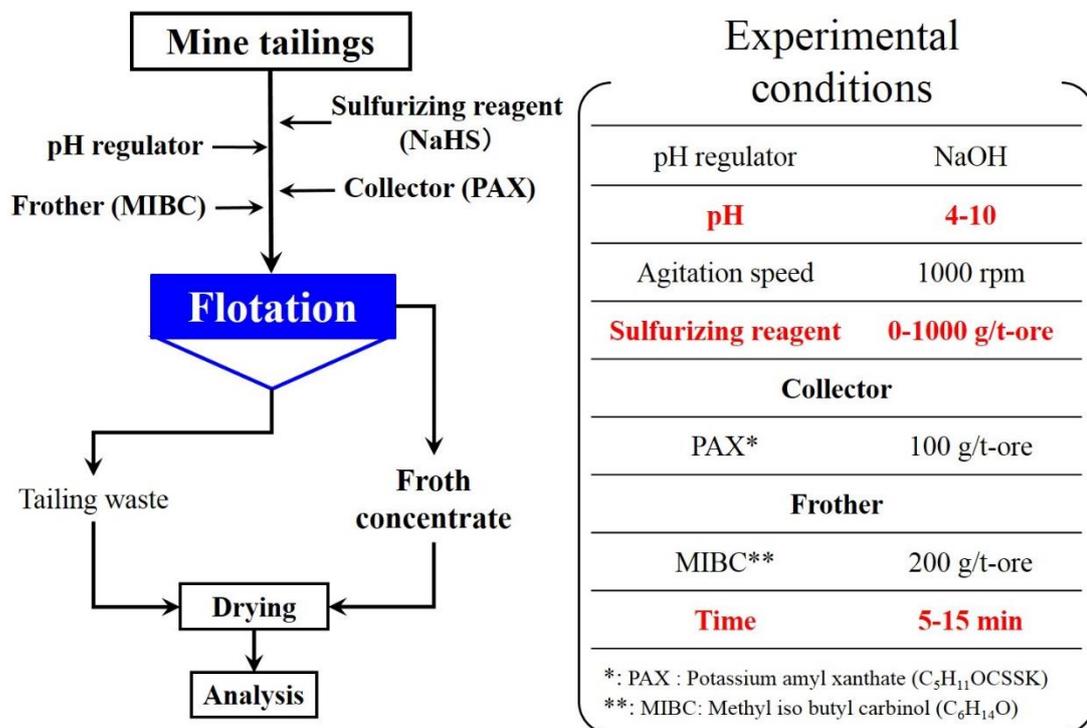


Fig. 5.4 Procedure of the flotation of mine tailings.

5.2.3.2 High-pressure oxidative leaching of concentrate of mine tailings

An autoclave (given in Fig. 5.5) which has a 2 L of Teflon beaker was used as a leaching reactor in HPOL experiments. To test the feed sample, the experiment was carried out as well as the procedure given in Fig. 5.6. A slurry of 50–200 g concentrates of mine tailings was prepared with 0.5 L distilled water or sulfuric acid solution (0.2–0.5 M) for adjusting the pulp density in the range of 100–400 g/L. The vessel containing slurry was placed into the autoclave, and the system was allowed to heat up to the desired set-point temperature (140–180 °C). When the temperature reached the target value, oxygen (O₂) gas was injected to the slurry into the vessel with a controlling total pressure (0.8–2.0 MPa), and the reaction was left to proceed until the required leaching duration of 60 min was attained. After cooling down the slurry to below 50 °C, the pH of the solution was recorded, and then the slurry was filtrated to separate solid residue and PLS which were analyzed using XRD, SEM–EDS, and ICP–OES, respectively. In addition, the free acidity of the PLS was determined by the titration using 1.0 M sodium hydroxide (NaOH) solution and 0.1 % Methyl Orange (C₁₄H₁₄N₃NaO₃S).

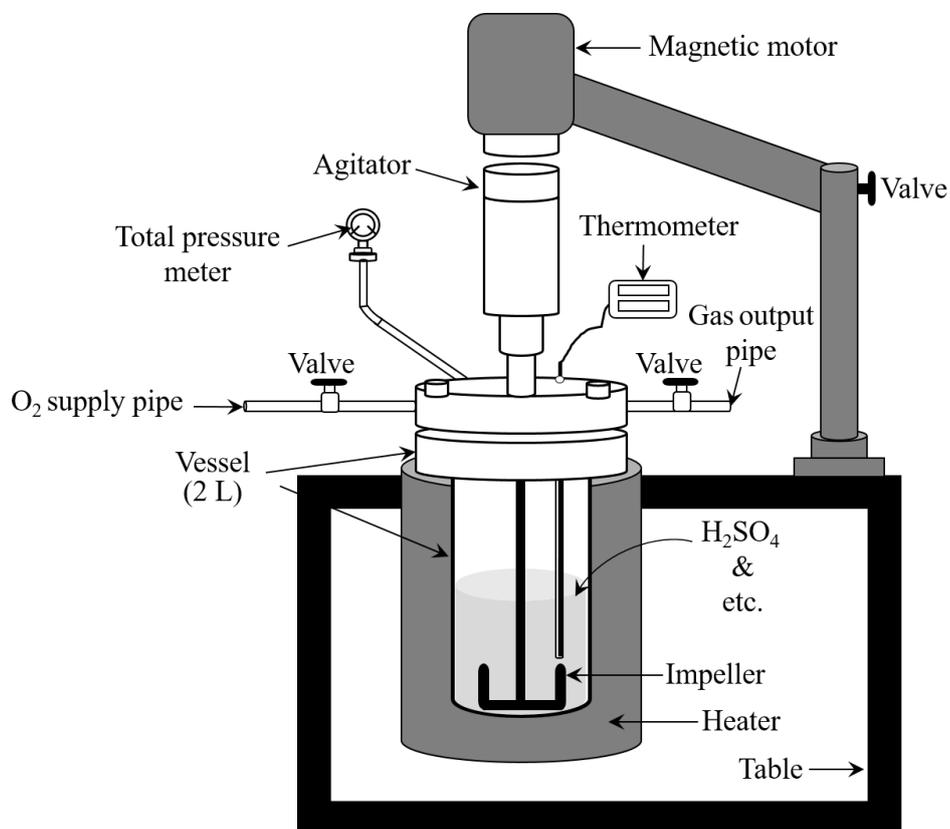


Fig. 5.5 A schematic illustration of an autoclave for high-pressure oxidative leaching.

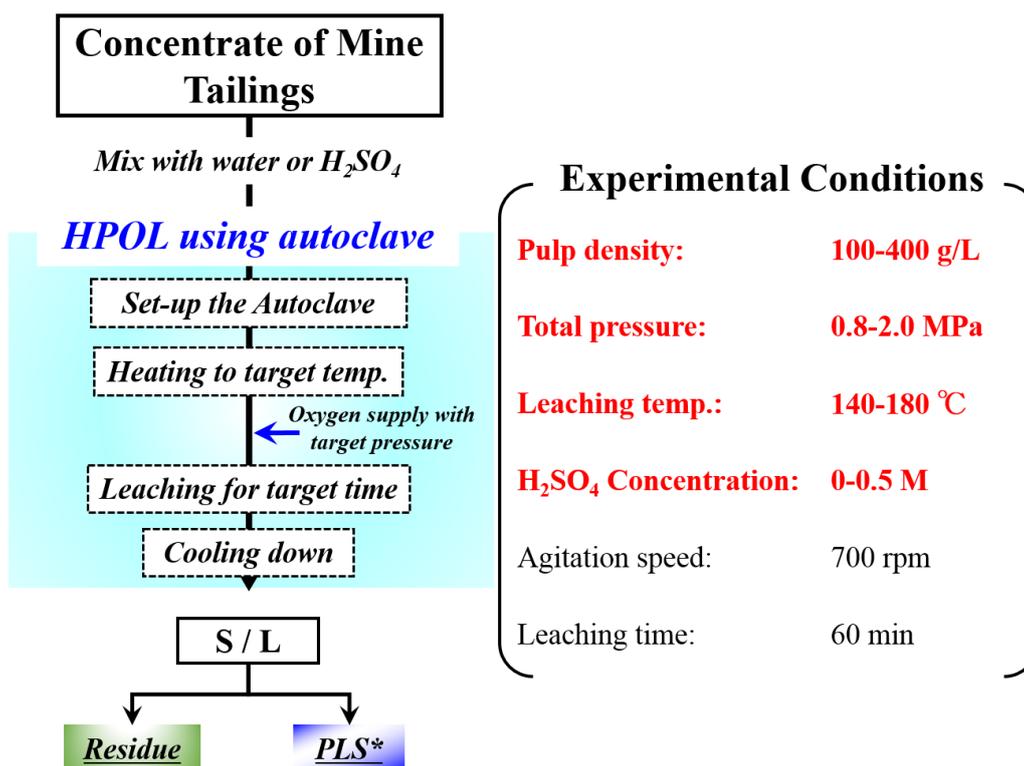


Fig. 5.6 Procedure of the high-pressure oxidative leaching of concentrate of mine tailings.

5.2.3.3 Solvent extraction and stripping

Solvent extraction of copper from the PLS obtained by HPOL of concentrate was carried out using LIX-84I (2-hydroxy-5-nonylacetophenone oxime) extractant which was diluted with kerosene at a certain phase ratio of 1. For each extraction (see Fig. 5.7), a 10 mL of solution and 2 mL of diluted extractant ($O/A = 0.2$) inserted into a plastic tube and mixed by an agitator at 600 rpm. After adjusting the pH (0.1–2.0) of the mixture to a desired value by a 1.0 M NaOH solution, the extraction reaction was allowed for 15 min. Once the reaction was finished, the solution was centrifuged for 5 min at 4000 rpm to ensure a rapid phase separation. The raffinate was analyzed by ICP-OES for determination of the metal extraction efficiency. Once the optimal condition for copper extraction was determined, the Cu-loaded organic was subjected to stripping experiments. The Cu-loaded organic was mixed with three (3) different sulfuric acid concentrations (0.5, 1.0, and 1.5 M) in a fixed phase ratio ($O/A = 5$) at 600 rpm. After 15-min contacting, the stripped

solution was removed and send to the ICP–OES analysis for calculation the stripping efficiency and copper concentration.

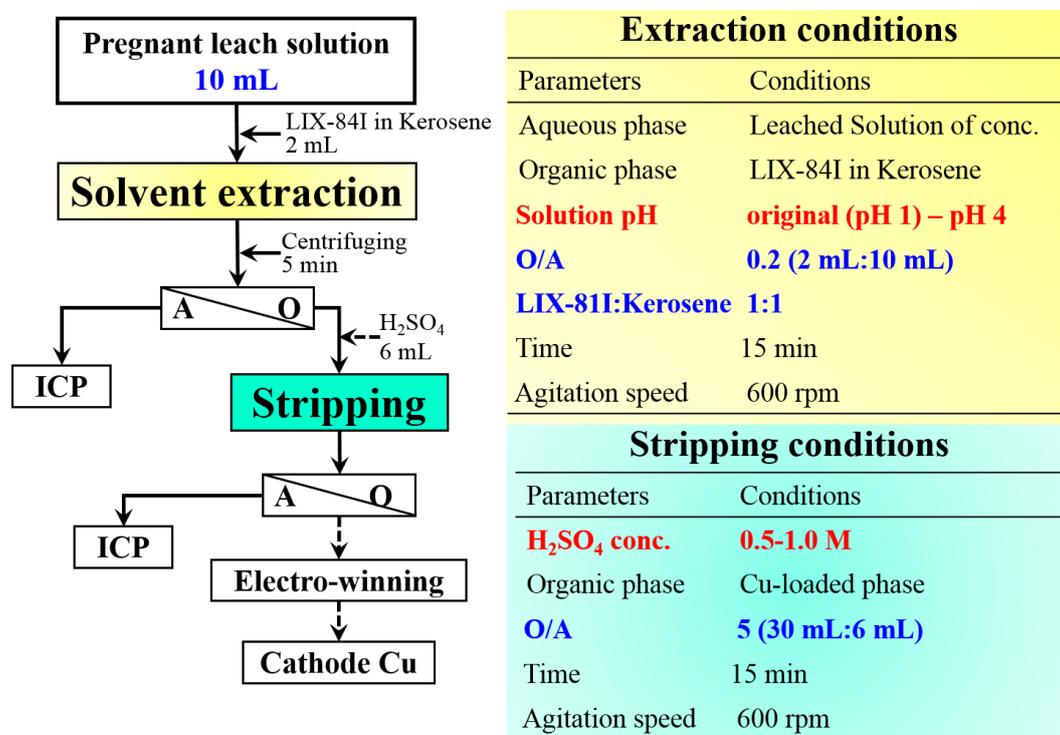


Fig. 5.7 Procedure of the solvent extraction and stripping of pregnant leach solution obtained under optimal high–pressure oxidative leaching of concentrate.

5.2.4 Characterization and analyses

In this chapter, all solution analysis was conducted using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP–OES, SII NanoTechnology Inc., Chiba, Japan). In addition, the mineral composition of the solid samples was identified by X–Ray Diffractometer (XRD, Rigaku RINT–2200V) and Scanning Electron Microscope Energy Dispersive X–ray Spectrometry (SEM–EDS).

The enrichment ratio (I) and recovery (R) of each metal from the low–grade copper ore were evaluated by [Eqs. 5.1–5.2](#).

$$\text{Enrichment ratio: } I = \frac{c}{f} \quad (5.1)$$

$$\text{Recovery: } R (\%) = \frac{c(f-t)}{f(c-t)} \times 100 \quad (5.2)$$

Where I is an enrichment ratio, and R is the recovery of each metal. F and C are the weight of the feed and concentrate, f , c , and t are the metals grade in feed, concentrate and tailing, respectively. The leaching rate of each metals from the concentrate of mine tailings into the water or sulfuric acid solution was calculated by [Eq. 5.3](#) as shown below.

$$\text{Metal leaching rate: } R_M (\%) = \frac{C_L \cdot V_L}{C_F \cdot m_F} \times 100 \quad (5.3)$$

Where C_L and C_F is the concentration of metal in PLS (mg/L) and feed (mg/kg), respectively. V_L is the volume of PLS (L) and m_F is the dry mass of the feed (kg).

The extraction percentage of each metals was calculated by [Eqs. 5.4 and 5.5](#):

$$E_i (\%) = ([i]_{\text{aqueous}} - [i]_{\text{raffinate}}) / [i]_{\text{aqueous}} \times 100 \quad (5.4)$$

$$S_i (\%) = [i]_{\text{Cu-rich}} / [i]_{\text{Cu-loaded}} \times 100 \quad (5.5)$$

Where E_i , S_i , $[i]_{\text{aqueous}}$, $[i]_{\text{raffinate}}$, $[i]_{\text{Cu-rich}}$, and $[i]_{\text{Cu-loaded}}$ are extraction percent, stripping ratio, concentrations of the element i in aqueous, raffinate solutions, Cu-rich solutions, and Cu-loaded organic phase, respectively.

5.3 Results and Discussion

5.3.1 Flotation of the mine tailings

5.3.1.1 Effect of slurry pH

The effect of slurry pH on flotation of the mine tailings was examined under the conditions of flotation time: 15 min, without NaHS addition, pulp density: 25 %, collector dosage (PAX): 100 g/t-ore, and frother dosage (MIBC): 200 g/t-ore, with varying the pH from natural 4 to 10 using 1.0 M NaOH solution. The results were given in [Figs. 5.8 and 5.9](#). It was revealed that the copper grade was increased to be 0.50 and 0.53 mass% when the slurry pH was controlled at natural 4 and 10, respectively, while the iron grade decreased from initial to 37.69 and 34.47 mass% maybe because of the depression effect of pH on the pyrite and clay minerals. In addition, the recovery of copper decreased with increasing pH from natural 4 to 10, while the recovery of iron did not change much. At natural pH (pH 4), the copper grade and iron reached 0.53 and 34.5 mass%, while the recovery of them were 79 and 91 %, respectively. For that reason, the natural pH 4 was selected as the optimal pH for the flotation of mine tailings.

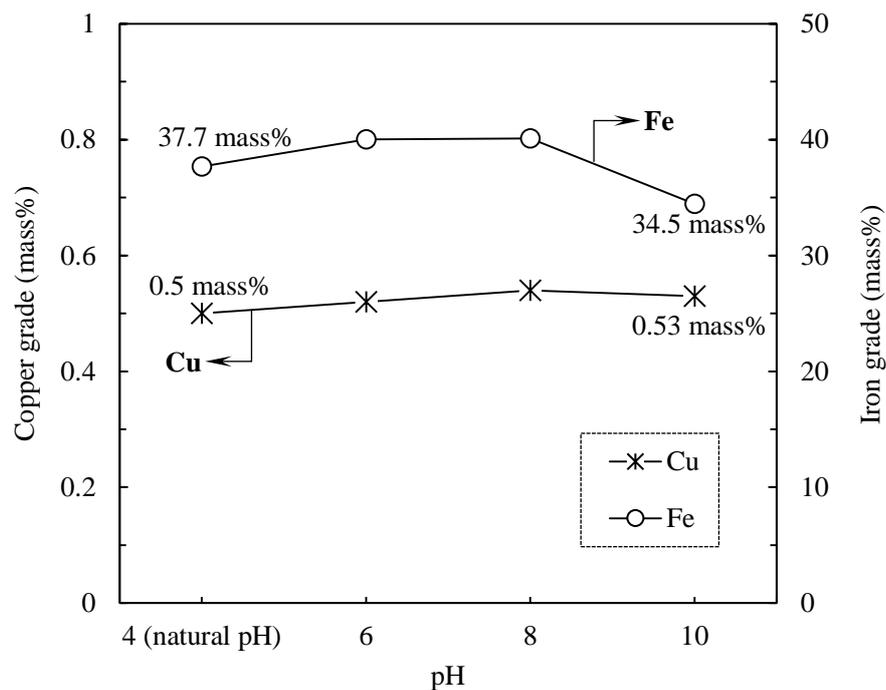


Fig. 5.8 The grade of copper and iron as a function of slurry pH.

(pH: natural 4–10, flotation time: 15 min, NaHS addition: 0 g/t–ore, pulp density: 25 %, collector dosage (PAX): 100 g/t–ore, and frother dosage (MIBC): 200 g/t–ore)

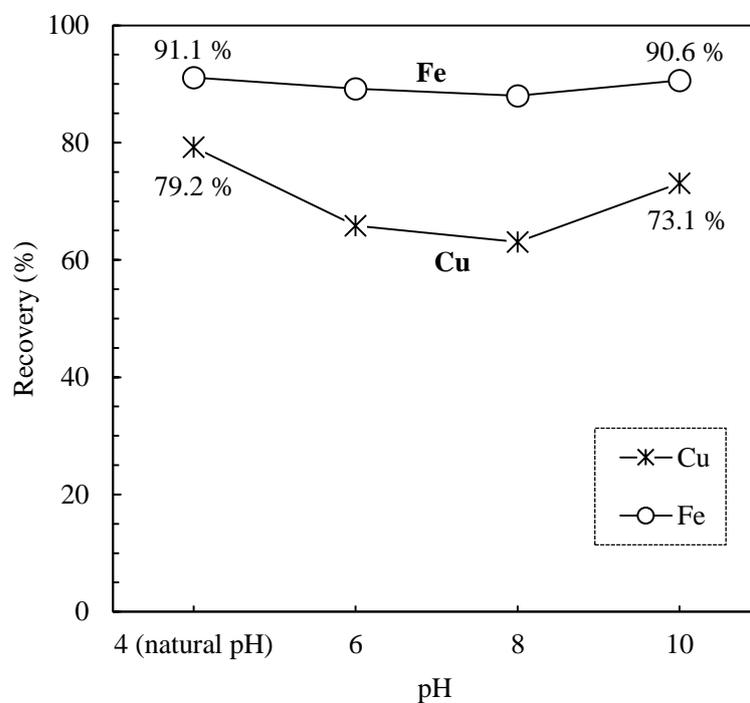


Fig. 5.9 Recovery of copper and iron as a function of slurry pH.

(pH: natural 4–10, flotation time: 15 min, NaHS addition: 0 g/t–ore, pulp density: 25 %, collector dosage (PAX): 100 g/t–ore, and frother dosage (MIBC): 200 g/t–ore)

5.3.1.2 Effect of flotation time

The effect of time on the flotation of mine tailings was conducted with a variety of the time ranging from 5 to 10 min. The other conditions were fixed at natural pH (pH 4), without NaHS addition, pulp density: 25 %, PAX: 100 g/t-ore, and MIBC: 200 g/t-ore. The results were shown in Figs. 5.10 and 5.11. Both the copper and iron recovery increased with increasing the flotation time from 5 to 15 min, whereas the grade of copper and iron decreased. When the flotation time was 15 min, the recovery of copper and iron reached 83 and 92 %, while the grade of them were 0.5 and 32 mass%, respectively. Therefore, flotation time of 15 min was selected as the optimal condition for the subsequent experiments.

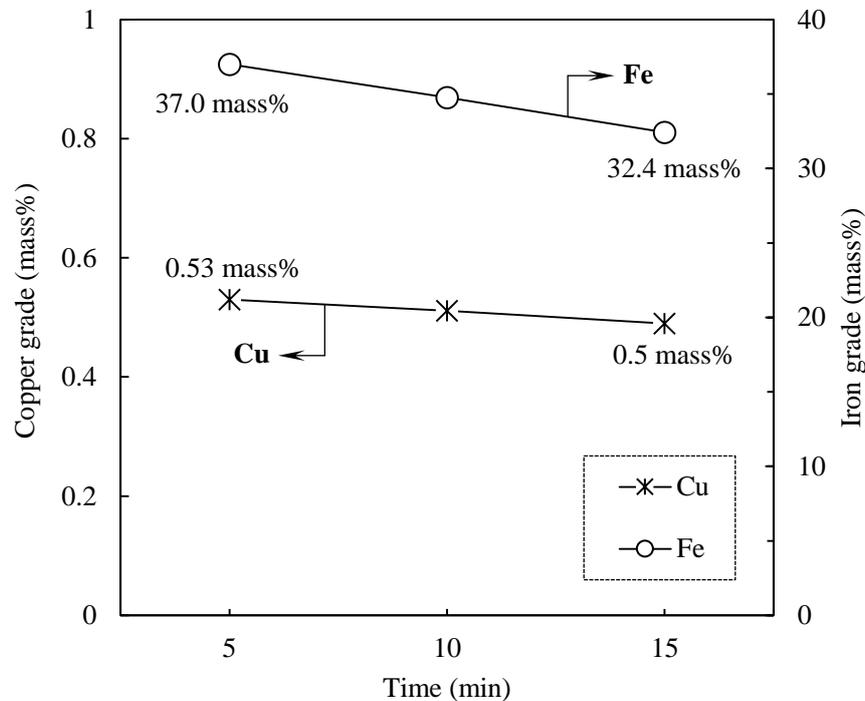


Fig. 5.10 The grade of copper and iron as a function of flotation time.

(flotation time: 5–15 min, natural pH (4), NaHS addition: 0 g/t-ore, pulp density: 25 %, collector dosage (PAX): 100 g/t-ore, and frother dosage (MIBC): 200 g/t-ore)

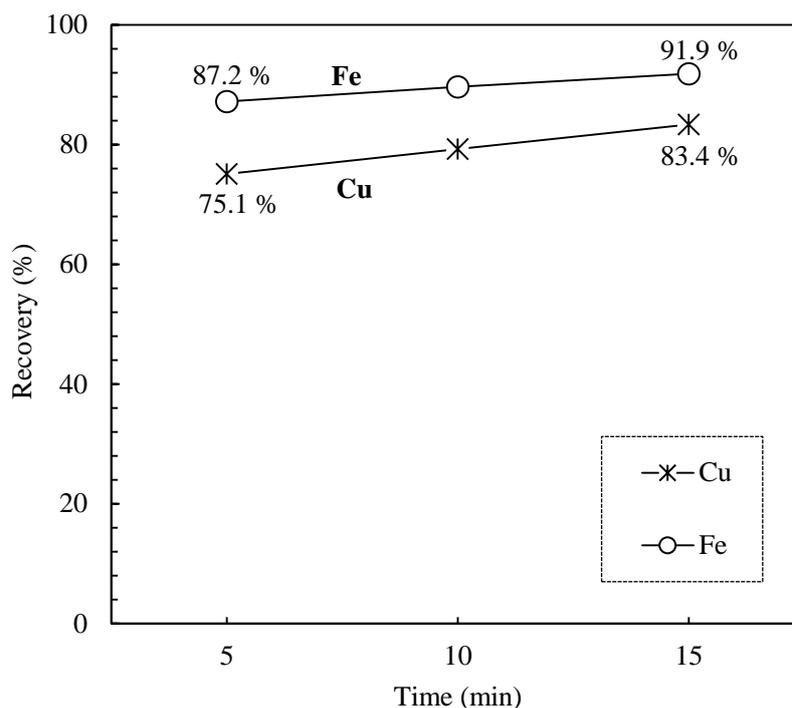


Fig. 5.11 Recovery of copper and iron as a function of flotation time.

(flotation time: 5–15 min, natural pH (4), NaHS addition: 0 g/t–ore, pulp density: 25 %, collector dosage (PAX): 100 g/t–ore, and frother dosage (MIBC): 200 g/t–ore)

5.3.1.3 Effect of sulfurizing reagent (NaHS) and its dosage

The effect of the sulfurizing reagent (NaHS) on flotation of mine tailings was performed under conditions with fixed flotation time of 15 min, natural pH (pH 4), pulp density: 25 %, PAX: 100 g/t–ore, and MIBC: 200 g/t–ore while the NaHS dosage was controlled in the range of 0–1000 g/t. The results were given in **Figs. 5.12** and **5.13**. It can be seen from the **Fig. 5.12** that both the copper and iron grade increased with the increase sulfurizing reagent dosage. When the NaHS dosage was 1000 g/t, the grade of copper and iron reached 0.6 and 40 mass%, while the recovery of them were 78 and 90 %, respectively. It can be said that the sulfurizing reagent was efficacious in the copper recovery from the mine tailing by flotation. The recovery of Cu reached about 78.43 % with the addition of sulfurizing reagent at pH of 4 (natural), when the flotation time was 5 min. The surface of chalcopyrite in mine tailings may be oxidized with rainwater naturally in the air, loading metals oxides (CuO , CuSO_4) which changed the floating characteristics. It can be considered as one reason due to copper grade in the concentrate was low under NaHS dosage of 0 g/–ore, i.e., without the

addition of sulfurizing reagent. Research on the effect of sulfurizing reagent on flotation has been widely discussed in the literature [21–24]. Generally, a sulfurizing reagent (NaHS) as a feed led to sulfurize the oxide layer of the minerals forming HS^- and S^{2-} ion on the surface. Sulphidisation enables oxide mineral of copper activation or the formation of a metal sulphide or elementary sulphur on their surfaces [25–27] for rendering them amenable to flotation using the collecting properties of thiol. Xanthates are made of heteropolar molecules that react with the activated minerals surfaces based on the chemical reactions. As the matter of fact, xanthate ions (X^-) liberated in solution by thiol collectors adsorb, via chemisorption or an electrochemical process, on the activated minerals surfaces in the form of hydrophobic species. These species enable the attachment of the mineral particles to air bubbles within the agitated pulp submitted to flotation [25, 28] and causes to improve copper flotation kinetics due to an increment of froth stability.

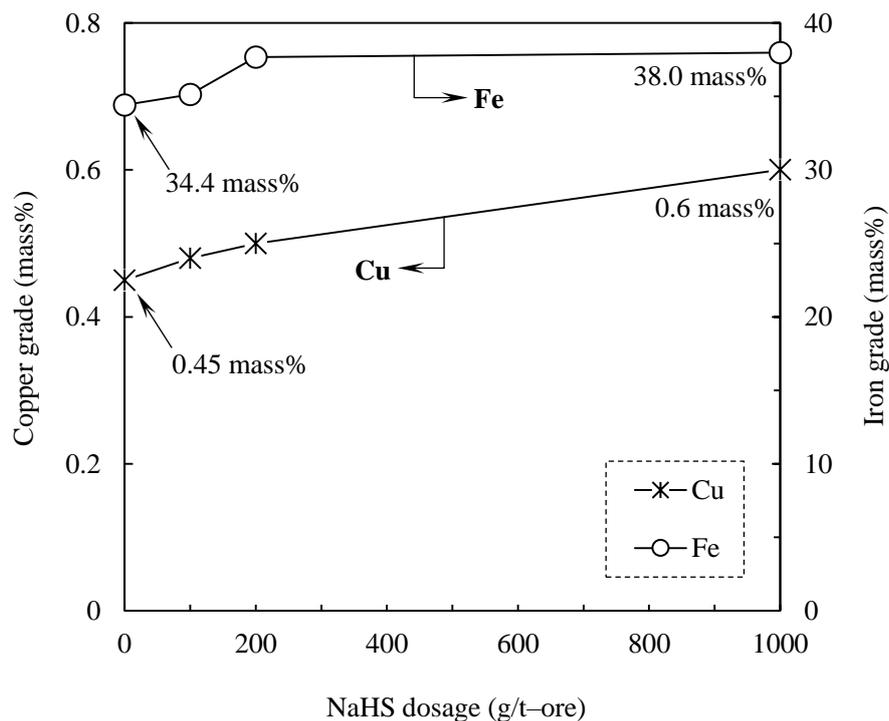


Fig. 5.12 The grade of copper and iron as a function of sulfurizing reagent dosage.

(NaHS addition: 0–1000 g/t-ore, flotation time: 15 min, natural pH (4), pulp density: 25 %, collector dosage (PAX): 100 g/t-ore, and frother dosage (MIBC): 200 g/t-ore)

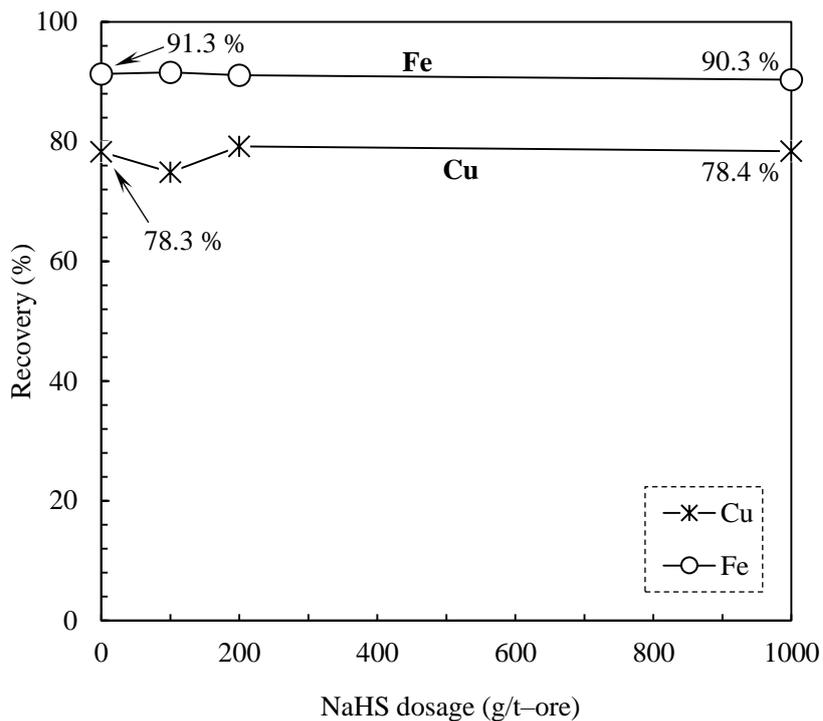


Fig. 5.13 Recovery of copper and iron as a function of sulfurizing reagent dosage.

(NaHS addition: 0–1000 g/t-ore, flotation time: 15 min, natural pH (4), pulp density: 25 %, collector dosage (PAX): 100 g/t-ore, and frother dosage (MIBC): 200 g/t-ore)

5.3.1.4 Application of the optimal flotation conditions

The optimum flotation conditions of the mine tailings are summarized in [Table 5.3](#). XRD measurement result and chemical composition of the froth are shown in [Fig. 5.14](#) and [Table 5.4](#), respectively. It was observed that a froth concentrate obtained from the flotation of mine tailings under optimal conditions consists of quartz (SiO_2), pyrite (FeS_2), and Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). As shown in [Table 5.4](#), it was revealed that copper grade in froth concentrate increased to be 0.65 mass% from the initial feed 0.34 mass%, and the enrichment ratio reached about 2 under the optimal flotation conditions. The concentrate obtained from mine tailings by flotation under the optimal conditions will be feed to the high-pressure oxidative leaching experiments for further copper extraction.

Table 5.3 The optimum flotation conditions of mine tailings.

Parameters	Conditions
pH regulator	NaOH
pH	Natural pH 4
Sulfurizing reagent	NaHS (1000 g/t-ore)
Collector	PAX (100 g/t-ore)
Frother	MIBC (200 g/t-ore)
Time	15 min
Pulp density	25 %

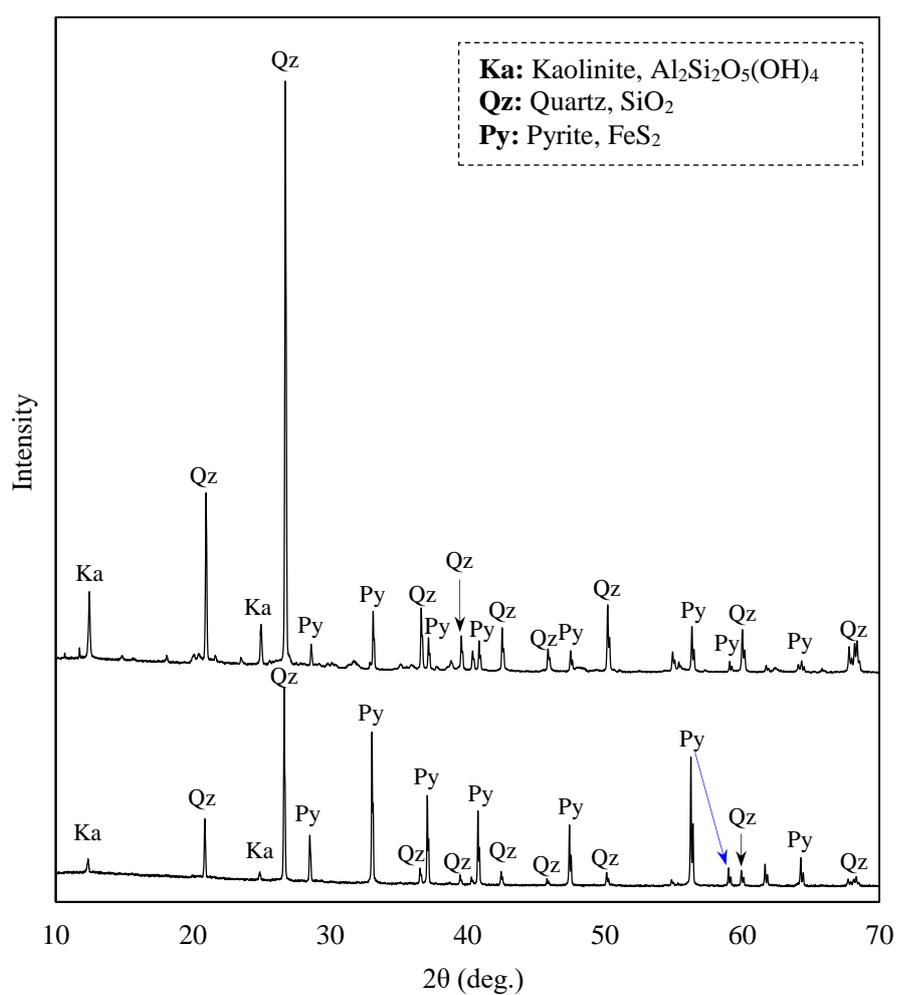
**Fig. 5.14** The XRD patterns of mine tailings and its concentrate.

Table 5.4 Chemical compositions of mine tailings and its concentrate.

Sample name	Grade (mass%)				
	Cu	Fe	Al	S	SiO ₂
Mine tailings	0.34	8.96	8.12	11.23	57.84
Concentrate of the mine tailings	0.65	33.20	2.63	32.72	23.41

5.3.2 High-pressure oxidative leaching of the concentrate of mine tailings

5.3.2.1 Effect of sulfuric acid concentration

Extraction of copper from the concentrate of mine tailings was examined using HPOL with varying H₂SO₄ concentrations from 0 (water) to 0.5 M, while the other conditions were fixed as follows: a pulp density of 100 g/L, the total pressure of 2.0 MPa, and the temperature of 180 °C for a duration of 60 min. As the results presented in [Fig. 5.15](#), the copper approximately complete dissolved (98 %) from the concentrate in PLS under an H₂SO₄ concentration of 0 M, while the iron leaching percentage reached up to 67 %. The pH of slurry before and after HPL and the free acidity (SO₄²⁻) were shown in [Table 5.5](#). The slurry pH decreased from 3.79 to 0.35 after HPOL under an H₂SO₄ concentration of 0 M, i.e., lixiviant of H₂O. It is may be due to that the concentrate contains much pyrite (FeS₂), and this FeS₂ can be the source of H₂SO₄ via [Eq. 5.6](#) [30], resulting in a decrease of slurry pH ([Table 5.5](#)) and promoting the dissolution of copper from the concentrate (chalcopyrite as the main copper mineral) according to [Eq. 5.7](#).



On the other hand, with the increasing H₂SO₄ concentration from 0 to 0.5 M, the leaching percentage of copper did not change much, whereas the iron dissolution rate increased from 67 to 80 % because of the solubility of it increased with the decreasing slurry pH and/or increasing free acidity ([Table 5.5](#)). The results obtained suggest that H₂O is the most suitable lixiviant for copper dissolution from the concentrate of mine tailings.

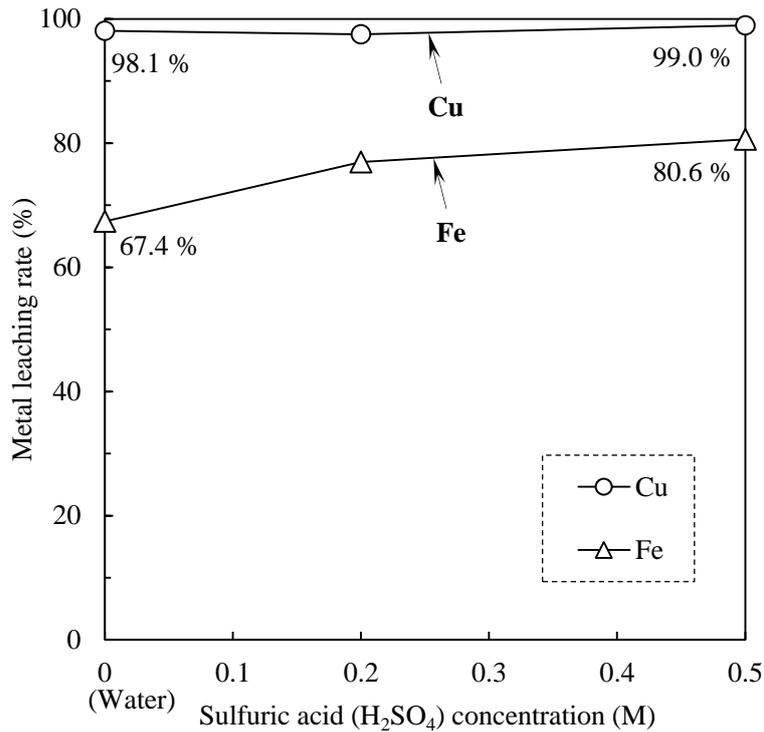


Fig. 5.15 The dissolution behavior of metals as a function of sulfuric acid concentration. (H₂SO₄ concentration: 0–0.5 M, total pressure: 2.0 MPa, temperature: 180 °C, and pulp density: 100 g/L for 60 min)

Table 5.5 The changes of slurry pH before and after high–pressure oxidative leaching and the free acidity of pregnant leach solutions.

H ₂ SO ₄ concentration (M)	Slurry pH before HPL	Slurry pH after HPL	Free acidity of PLS (g/L)
0 (Water)	3.79	0.35	24
0.2	1.21	0.14	25
0.5	1.12	0.12	36

5.3.2.2 Effect of total pressure

The effect of the total pressure ($P_{\text{Total}} = P_{\text{Vapor}} + P_{\text{Oxygen}}$) on copper dissolution from concentrate of mine tailings was evaluated with varying the P_{Total} ranges between 0.8 (with oxygen supply) and 2.0 MPa, while keeping H₂SO₄ concentration of 0 M, temperature at 180 °C, and pulp density of 100 g/L for 60 min. As shown in **Fig. 5.16**, the dissolution percentage of copper and iron were 9.6

and 1.8 %, respectively, when the P_{Total} was 0.8 MPa, i.e., without an oxygen supply. It could be concluded that some of the copper dissolved into the PLS at an early stage, and after that, the formation of passivation layers of elemental sulfur (S^0) [30] on the chalcopyrite (main copper phase of the concentrate) may impede the leaching kinetics of copper. In addition, as the slurry pH changes before and after HPOL and the free acidity of PLS shown in [Table 5.6](#), the pH of slurry did not change much (from 3.81 to 1.74), and the free acidity was 0 g/L after the HPOL under P_{Total} of 0.8 MPa. It may be due to that a little pyrite (FeS_2) dissolute in the solution, resulting in small changes in pH, and the major pyrite was still in solid due to free acidity was 0 g/L. On the other hand, the leaching percentage of copper and iron increased up to 98.1 and 67.4 %, respectively, with the increasing P_{Total} from 0.8 to 2.0 MPa. The slurry pH decreased from 3.77 to 0.23 and 3.79 to 0.35, the free acidity was 22 and 24 g/L, respectively, while the P_{Total} was 1.5 and 2.0 MPa. The reason for this could be said that oxygen gas (O_2) supply in the slurry promotes the oxidation for preventing the formation of passivation layer proceeded via [Eq. 5.8](#) [31], and dissolution of pyrite for generation of H_2SO_4 ([Eq. 5.6](#)) which can dissolve copper (see [Eqs. 5.6 and 5.7](#)) efficiently from the concentrate under HPOL conditions.



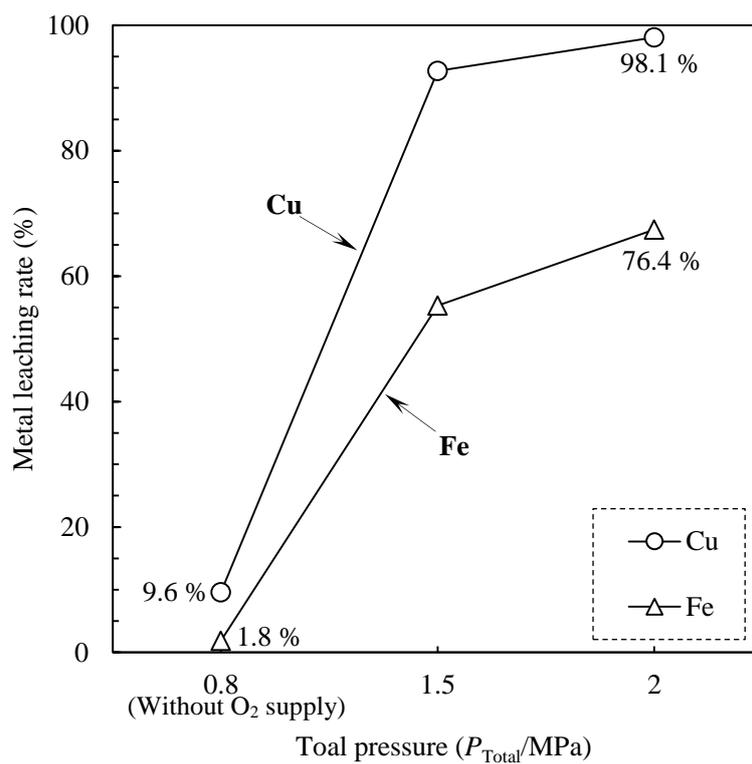


Fig. 5.16 The dissolution behavior of metals as a function of total pressure.

(total pressure: 0.8–2.0 MPa, H₂SO₄ concentration: 0 M, temperature: 180 °C, and pulp density: 100 g/L for 60 min)

Table 5.6 The changes of slurry pH before and after high–pressure oxidative leaching and the free acidity of pregnant leach solutions.

Total pressure (MPa)	Slurry pH before HPL	Slurry pH after HPL	Free acidity of PLS (g/L)
0.8 (without O ₂ supply)	3.81	1.74	0
1.5	3.77	0.23	22
2.0	3.79	0.35	24

5.3.2.3 Effect of temperature

To investigate the influence of temperature on copper dissolution from the concentrate of mine tailings, the HPOL was conducted at a temperature ranging from 160 to 180 °C, while the other conditions were fixed as H₂SO₄ concentration of 0 M, total pressure of 2.0 MPa, and pulp density of 100 g/L for 60 min. The results were shown in **Fig. 5.17**. The dissolution rate of copper and iron increased from 62.8 to 98.1 % and from 37.6 to 67.4 %, respectively, with adjusting the temperature from 140 to 160 °C. The copper and iron leaching percentage increased at an average of 17.6 and 14.9 % (**Fig. 5.17**), respectively, for every 20 °C rise in the temperature. Thus, it is clearly confirmed that the dissolution of copper from the concentrate is a temperature dependence reaction, due to the phase conversion of copper minerals may be not efficiency at low temperature. In addition, the copper and iron leaching from the concentrate was an extremely temperature dependence at the early stage (from 140 to 160 °C) with a difference of 29.0 and 26.0 % (**Fig. 5.17**), respectively. However, further increasing the temperature (160 to 180 °C) did not give significant effect on copper and iron leaching rate, which results in small rate changes of 6.3 and 3.8 % (**Fig. 5.17**), respectively. As a result, the temperature of 180 °C was selected as the optimal condition for the subsequent experiments.

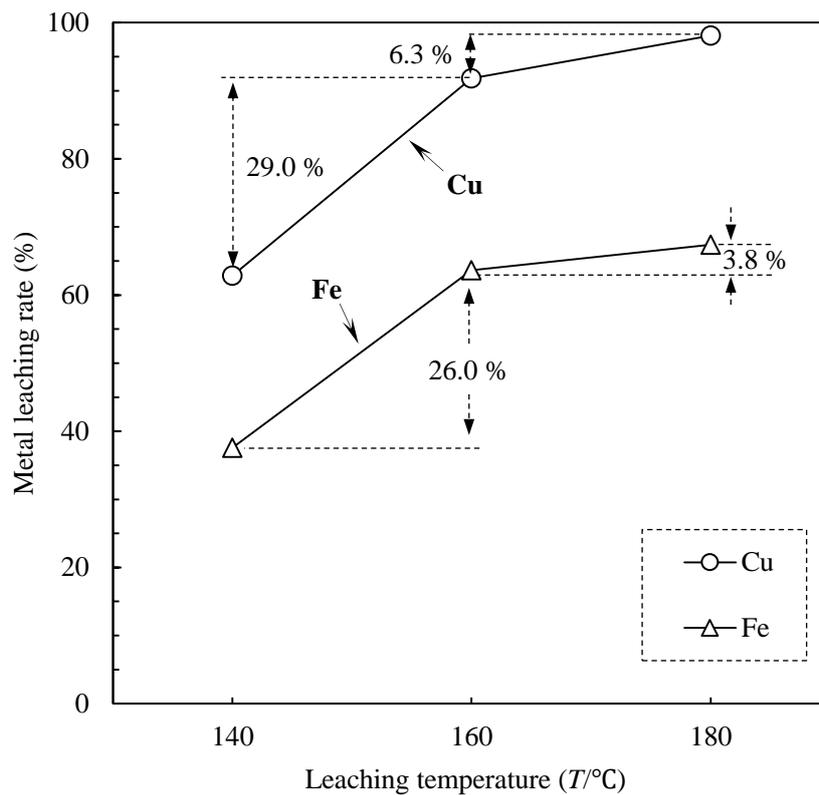


Fig. 5.17 The dissolution behavior of metals as a function of leaching temperature.

(temperature: 140–180 °C, H_2SO_4 concentration: 0 M, total pressure: 2.0 MPa, and pulp density:

100 g/L for 60 min)

5.3.2.4 Effect of pulp density

The effect of pulp density on copper HPOL from the concentrate of mine tailings was investigated under the following conditions: H_2SO_4 concentration of 0 M and a total pressure of 2.0 MPa at a temperature of 180 °C for 60 min, while varying the pulp density in a range of 100–400 g/L. As shown in **Fig. 5.18**, copper leaching percentage did not change (> 94 %) much with increasing pulp density from 100 to 400 g/L, from where it can be said that increasing the solid ratio do not give negative influence on copper dissolution rate. However, the copper concentration in PLS increased up to 2.9 from 0.7 g/L (**given in Table 5.7**) with an enrichment ratio over 4, when the pulp density varying from 100 to 400 g/L. On the other hand, the iron dissolution percentage keeps around 66 % (**Fig. 5.18**) with adjusting pulp density in the range of 100–400 g/L, whereas the iron concentration in PLS increased up from 24.9 to 102 g/L (**Table 5.7**). It suggested that the pulp density, i.e., the solid and liquid ratio of slurry, did not affect much on copper dissolution rate, for that the pulp density of 400 g/L was selected as the optimal condition.

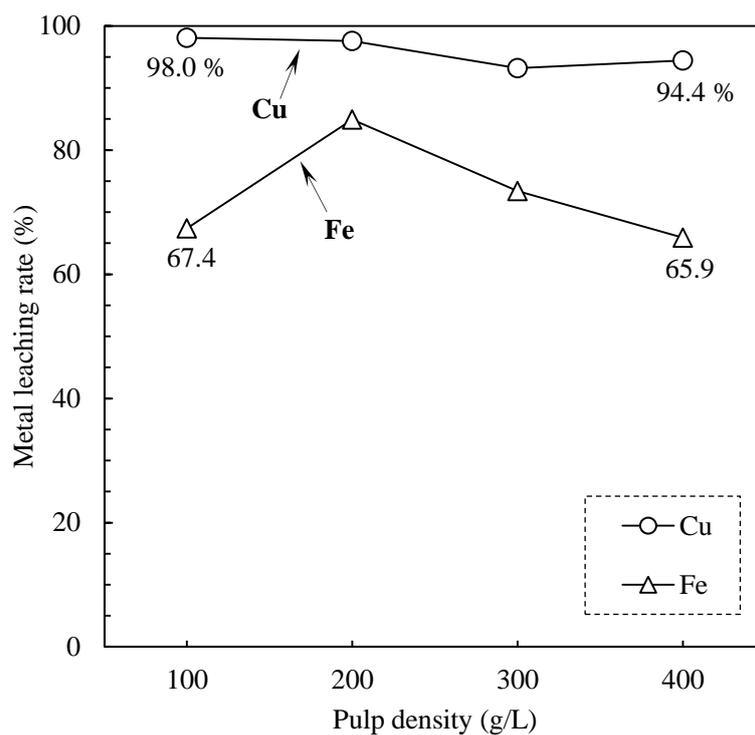


Fig. 5.18 The dissolution behavior of metals as a function of pulp density.

(pulp density: 100–400 g/L, H₂SO₄ concentration: 0 M, total pressure: 2.0 MPa, and temperature: 180 °C for 60 min)

Table 5.7 Metal concentrations in the pregnant leach solution under various pulp densities.

Pulp density (g/L)	Metal concentration in PLS (g/L)	
	Cu	Fe
100	0.71	24.93
200	1.85	82.34
300	1.99	79.82
400	2.89	102.89

5.3.2.5 Effect of free acidity

The free acidity (SO_4^{2-}) of each PLS obtained by HPOL under a variety of H_2SO_4 concentrations (0–0.5 M), total pressures (0.8–2.0 MPa), temperatures (160–180 °C), and pulp densities (100–400 g/L) were examined by titrimetric analysis. It can be seen from **Fig. 5.19**, there is an extremely strong correlation between the copper and iron dissolution percentage with a free acidity (SO_4^{2-}). The leaching percentage of copper and iron increased up to 98.1 and 76.9 % by the increasing free acidity to 24 and 25 g/L, respectively. It has been confirmed that the free acidity is one of the most important parameters for the copper dissolution process. However, both copper and iron dissolution rate did not change much, and remained constant with the further increase of free acidity over 24 g/L (**Fig. 5.19**), which suggests there is a suitable free acidity for copper leaching from the concentrate. **Fig. 5.20** shows the relationship between the concentration of copper and iron in PLS, an extremely great liner relationship with a correlation coefficient of 0.9758 was found between them, as represented in follows (**Eq. 5.10**):

$$C_{\text{Fe}} = 38.393 \times C_{\text{Cu}}, \quad (5.10)$$

Where C_{Fe} and C_{Cu} were the concentration of copper and iron in PLS, respectively.

It suggests that the separation of copper from the iron is quite difficult at the HPOL step because of the iron always co-dissolute with copper from the ore, which consists of chalcopyrite and pyrite. Accordingly, the concentration of iron in PLS about 38 times higher than that of copper under the examined HPOL conditions.

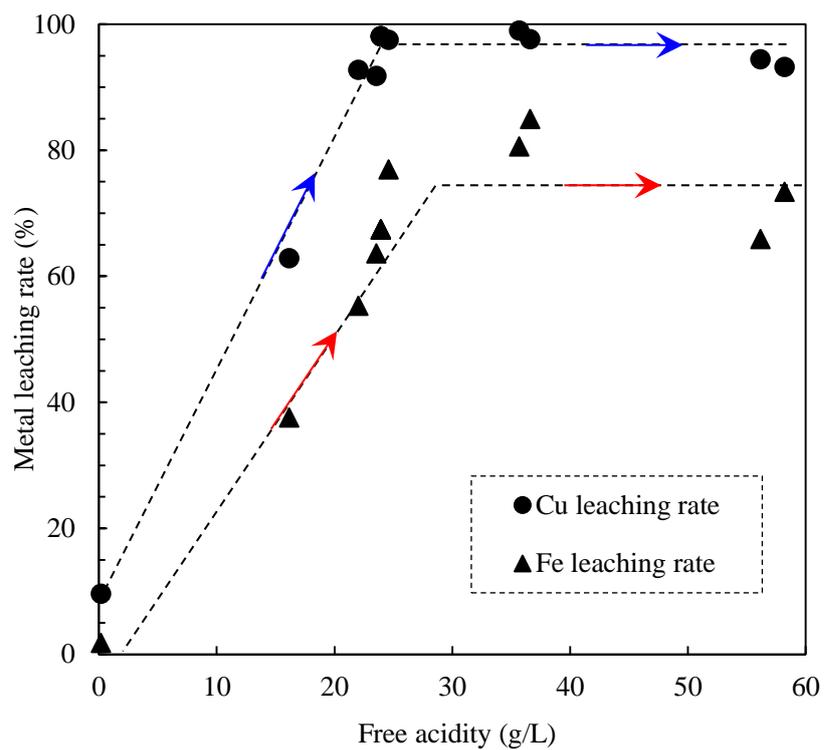


Fig. 5.19 The dissolution behavior of metals as a function of free acidity.

(H_2SO_4 concentration: 0–0.5 M, total pressure: 0.8–2.0 MPa, temperature: 140–180 °C, and pulp density: 100–400 g/L for 60 min)

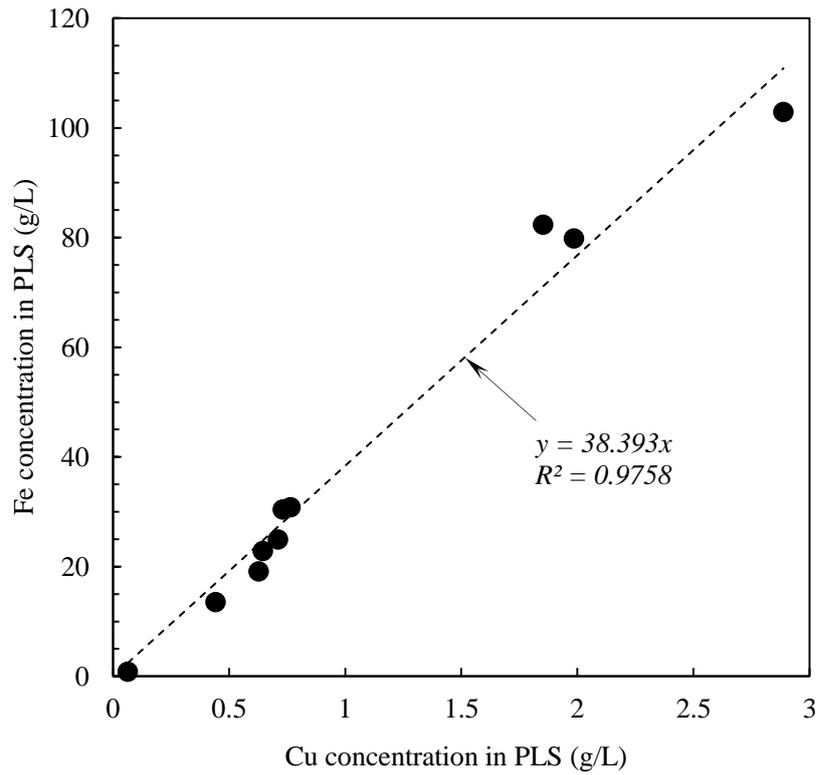


Fig. 5.20 The plot of copper concentration versus iron concentration in the pregnant leach solutions.

(H₂SO₄ concentration: 0–0.5 M, total pressure: 0.8–2.0 MPa, temperature: 140–180 °C, and pulp density: 100–400 g/L for 60 min)

5.3.2.6 The iron precipitation behavior under high–pressure oxidative leaching

In order to investigate the iron precipitation behavior under HPOL conditions with various of H_2SO_4 concentrations (0–0.5 M), total pressures (0.8–2.0 MPa), temperatures (160–180 °C), and pulp densities (100–400 g/L), the XRD analyses were conducted using the residues obtained after the experiments. As shown in **Fig. 5.21**, the major phase of iron in the residue was pyrite, hematite, and jarosite, which may be formed via **Eqs. 5.10 and 5.11** [29, 32]:

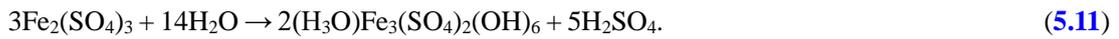
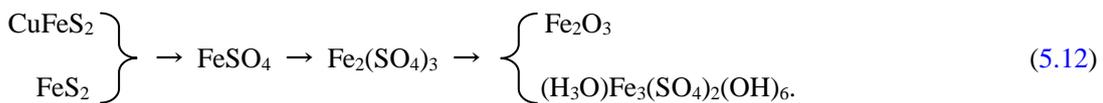


Fig. 5.22 shows the relationship of major iron phase in residues with the experimental conditions, pH, and free acidities. It is clear that the iron phase was high pH and/or free acidity dependence, in which hematite and jarosite were favoured at low acidity (pH > 1.74) and very high acidity (pH < 0.14), respectively. In addition, both hematite and jarosite present at high acidity (0.14 < pH < 1.74) under the examined HPOL conditions.

Accordingly, the oxidation of iron from the concentrate of mine tailings can be considered as a passing through process given in **Eq. 5.12**, in which the iron first released from chalcopyrite and pyrite, and then further oxidized by oxygen to Fe^{3+} followed by the hydrolysis for forming hematite and jarosite.



The hydrolysis reaction of **Eqs. 5.10 and 5.11** also can be written as **Eqs. 5.10' and 5.11'**, respectively.



Assuming the equilibrium constant of the **Eqs. 5.10' and 5.11'** were K_{He} and K_{Ja} , respectively, **Eqs. 5.12 and 5.13** were obtained.

$$K_{\text{He}} = \frac{[\text{Fe}^{3+}]^2}{[\text{H}^+]^6} \quad (5.12)$$

$$K_{\text{Ja}} = \frac{[\text{Fe}^{3+}]^6}{[\text{H}^+]^{10}} \quad (5.13)$$

If take the logarithm of both sides of [Eqs. 5.12 and 5.13](#), it becomes [Eqs. 5.14 and 5.15](#), respectively:

$$2\log [\text{Fe}^{3+}] = 6\log [\text{H}^+] - \log K_{\text{He}} \quad (5.14)$$

$$6\log [\text{Fe}^{3+}] = 10\log [\text{H}^+] - \log K_{\text{Ja}} \quad (5.15)$$

Accordingly, $\log [\text{Fe}^{3+}]$ bear a linear relationship to $\log [\text{H}^+]$. If substitute iron concentration in PLS and free acidity for $[\text{Fe}^{3+}]$ and $[\text{H}^+]$, respectively, the double logarithmic plot of that should follow a straight-line relationship too. As the plot is shown in [Fig. 5.23](#), an excellent linear relation with a correlation coefficient of 0.9855 was obtained between the $\log [\text{Fe}]$ and $\log [\text{Free acidity}]$, representing as [Eq. 5.16](#), which is in good agreement with the supposition have been made above.

$$\log[\text{Fe}] = 1.0235\log[\text{Free acidity}] - 0.0677, \quad (5.16)$$

where the $[\text{Fe}]$ and $[\text{Free acidity}]$ were iron and SO_4^{2-} concentration (g/L) in PLS, respectively.

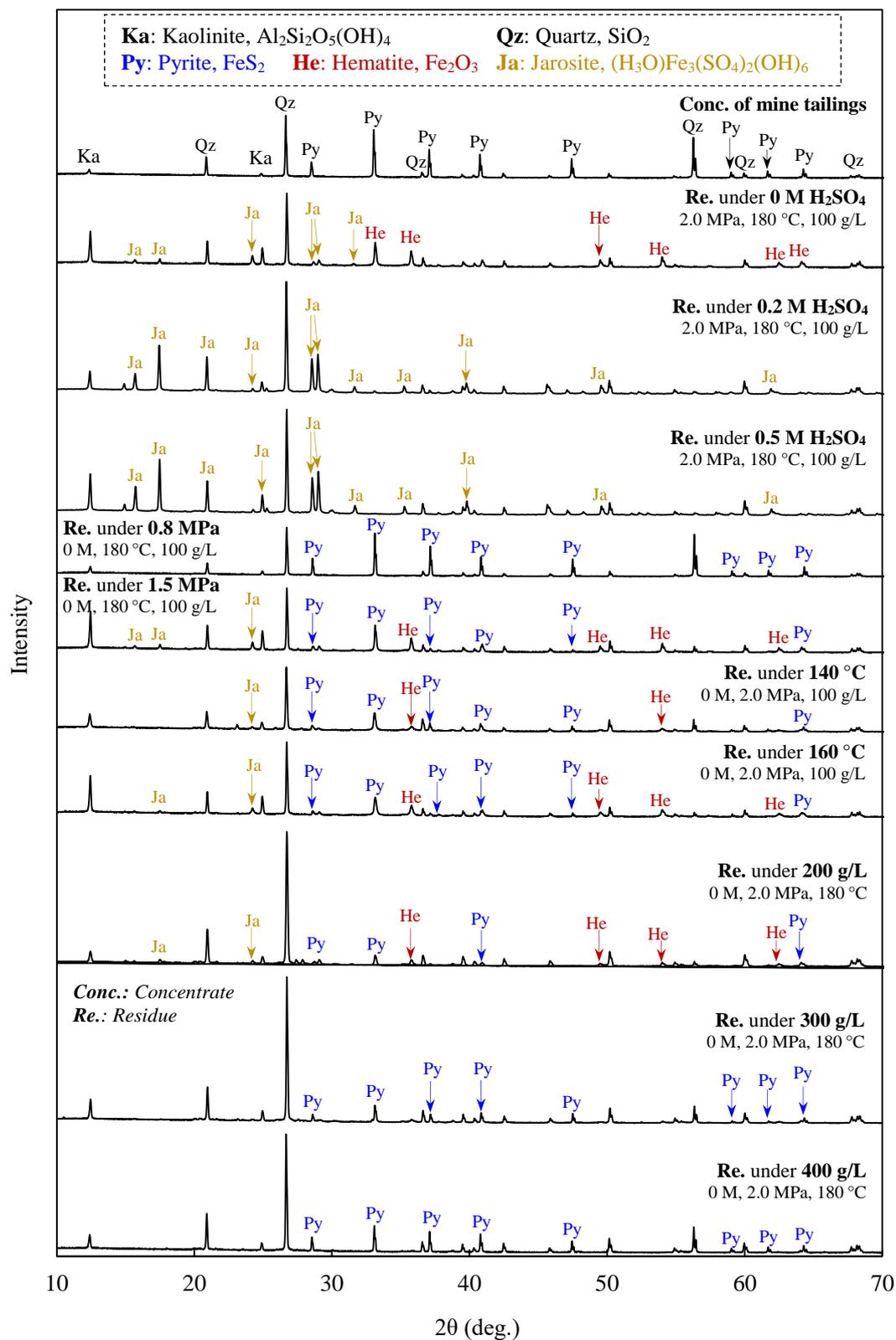


Fig. 5.21 XRD patterns of a concentrate and the residues obtained from high-pressure leaching.

(0–0.5 M, 0.8–2.0 MPa, 160–180 °C, and 100–400 g/L for 60 min)

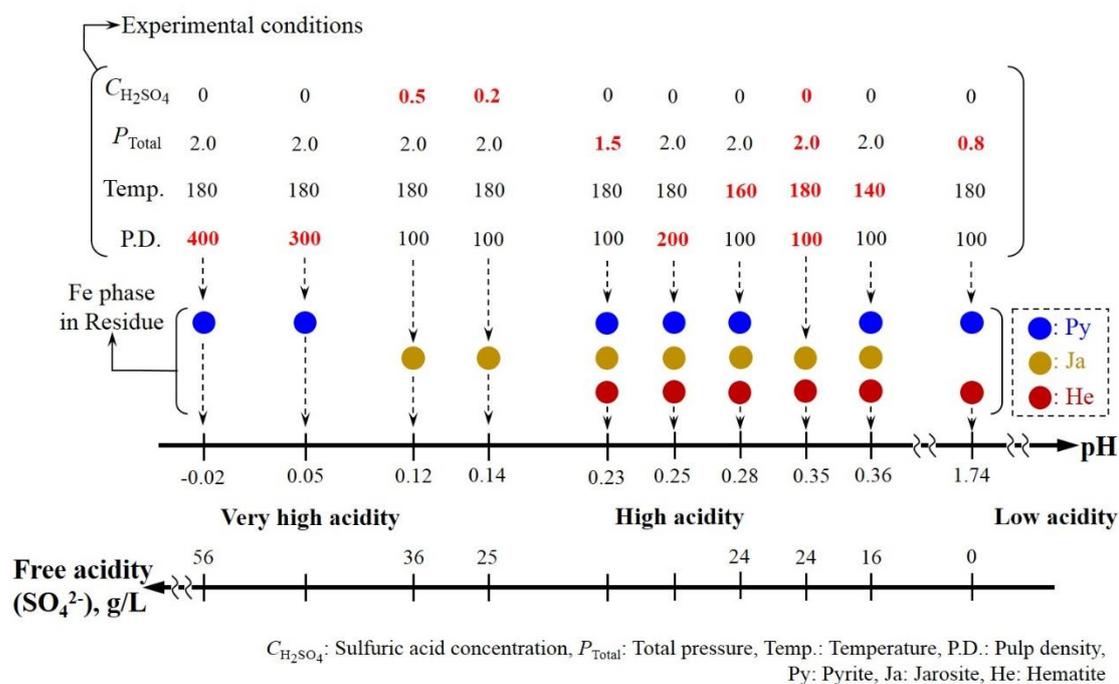


Fig. 5.22 The relationship between iron precipitation with experimental conditions, pH, and free acidities.

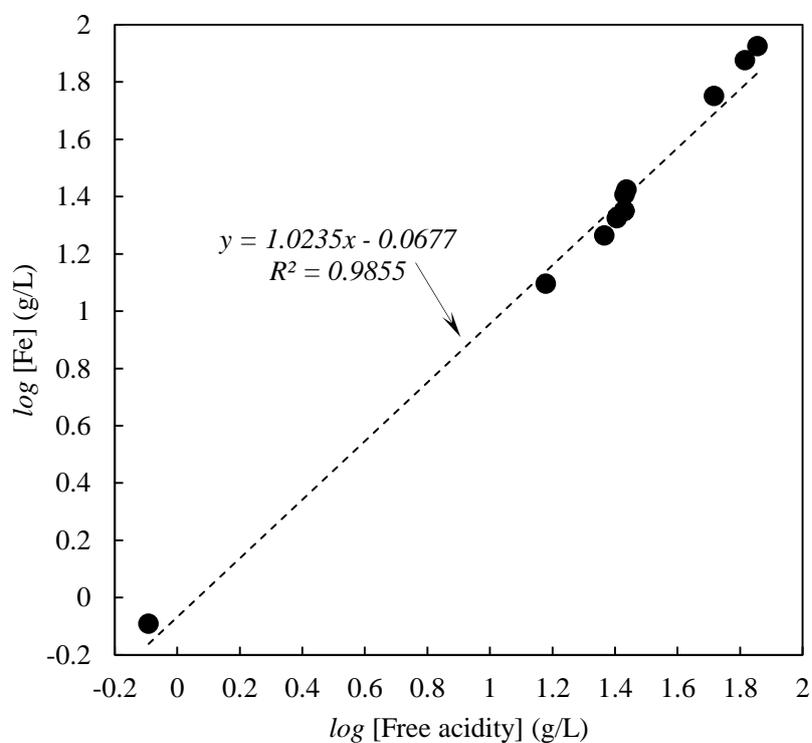


Fig. 5.23 The plot of $\log [\text{Free acidity}]$ versus $\log [Fe]$.

3.3.2.7 Application of the optimal high–pressure oxidative leaching conditions

The results of the numerical HPL experiments as described in **sections 5.3.2.1–3.3.2.6** suggested that the optimal HPOL conditions for copper extraction from the concentrate of mine tailings were found to be as shown in **Table 5.8**. Under the optimal HPOL conditions, 94.4 % of copper was dissolved with H₂O, and the obtained PLS consists of 2.9 g/L copper (**Table 5.8**). To further recovery the copper from PLS, a solvent extraction will be carried out following using the solution obtained under the optimal HPOL conditions.

Table 5.8 Metal dissolution rates and the concentrations in pregnant leach solution under the optimal high–pressure oxidative leaching conditions.

Conditions	Metal dissolution rate (%)		Metal concentration in PLS (g/L)	
	Cu	Fe	Cu	Fe
H ₂ SO ₄ concentration	0 M			
Total pressure	2.0 MPa			
Temperature	94.4	65.9	2.9	102.9
Pulp density	400 g/L			

5.3.3 Solvent extraction and stripping

5.3.3.1 Effect of pH on the copper extraction

To study the extraction of copper from the PLS obtained under the optimal HPOL conditions, the pH of the aqueous solution was adjusted from 0.1 (original pH) to 2.0 under the fixed conditions: the LIX-84I/Kerosene mixing ratio of 1, O/A ratio of 0.2 (2 mL to 10 mL), and agitating speed of 600 rpm for 15-min contacting. The results with the obtained data were shown in Fig. 5.24. It can be seen that the extraction of copper increases from 10.1 to 93.7 % with the increasing pH from 0.1 to 2.0, whereas the iron extraction rate did not change much and keeps lower than 11.3 %. From the above results, the pH of 2.0 was determined to be an optimal pH for the selective extraction of the copper from PLS.

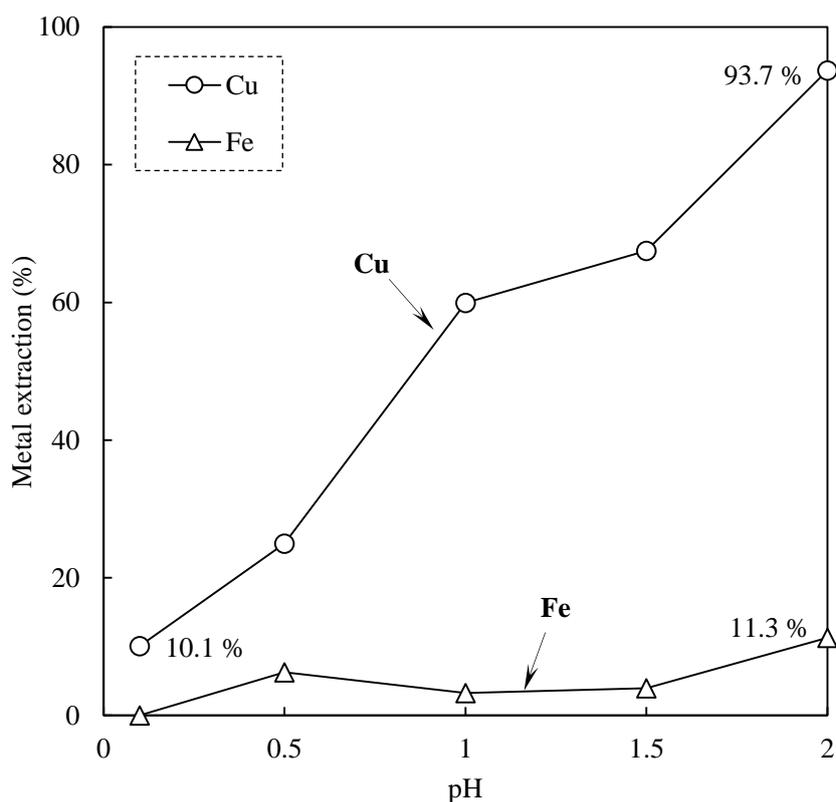


Fig. 5.24 The extraction behavior of metals as a function of initial pH.

(initial pH: 0.1–2.0, LIX-84I/Kerosene mixing ratio: 1, O/A ratio: 0.2 (2 mL to 10 mL), agitating speed: 600 rpm, and contact time: 15 min)

3.3.3.2 Effect of sulfuric acid concentration on stripping

The stripping efficiency of copper from the Cu-loaded organic phase was examined using three (3) different H_2SO_4 concentrations of 0.5, 1.0, and 1.5 M, when other parameters like O/A ratio, agitation speed, and contact time were fixed at 5, 600 rpm, and 15 min, respectively. The efficiency of copper stripping and the changes of metal concentration in the stripped solutions under different H_2SO_4 concentrations were shown in Fig. 5.25. The percentage of copper stripping from the Cu-loaded organic phase linearly increased from 24.7 to 97.4 % with an increase H_2SO_4 concentration from 0.5 to 1.5 M. As a result, a 1.5 M H_2SO_4 solution was chosen to be the suitable value for stripping of copper from the Cu-loaded organic phase. It is confirmed that the stripped copper solution contains approximately 44.8 g/L copper and 1.4 g/L iron.

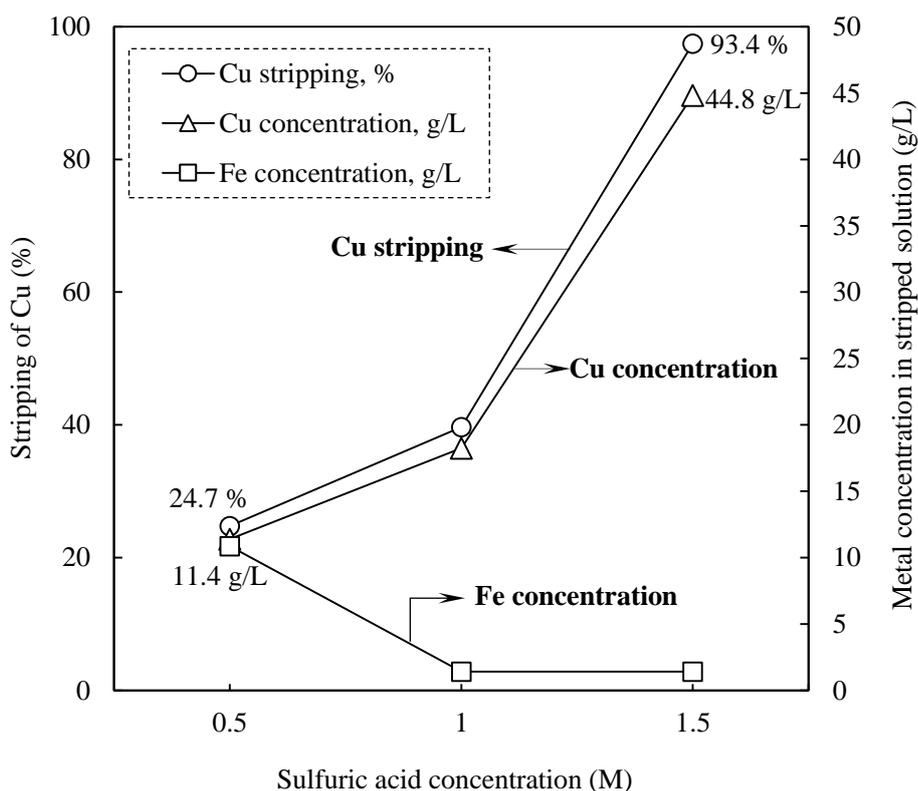


Fig. 5.25 The copper stripping behavior and the metal concentration in stripped solution as a function of sulfuric acid concentration.

(H_2SO_4 concentrations: 0.5, 1.0, and 1.5 M, O/A ratio: 5 (30 mL to 6 mL), agitation speed: 600 rpm, and contact time: 15 min)

5.3.4 A flowchart for copper recovery from mine tailings using flotation–high–pressure oxidative leaching–solvent extraction

Depending on the experiments above, a flowchart for recovery of copper from the mine tailings can be summarized as shown in [Fig. 5.26](#). The copper grade in the concentrate of mine tailings reached up to 0.65 mass% from the initial 0.34 mass%, and the copper recovery achieved to be 78.4 % by flotation under the optimal flotation conditions. Copper almost completely (94.4 %) dissolved from the concentrate of mine tailings under the optimal HPOL conditions in H₂O for 60 min, while the copper concentration of PLS reached to be 2.9 g/L. Under the optimized extraction conditions, extractant LIX–84I in kerosene was extracted over 93.7 % copper in PLS obtained from the HPOL of concentrate, while the iron extraction efficiency was lower than 11.3 %. All of the copper in Cu–loaded organic phase was stripped by 1.5 M H₂SO₄ solution, whereas the most iron (98.6 %) was left in the organic phase after stripping under the determined conditions, while the copper concentration in the stripped solution reached 44.8 g/L. Based on the above results, an effective method for the recovery of copper from the mine tailings via flotation, HPOL, and solvent extraction is proposed, and the total copper recovery achieved to be 68 %.

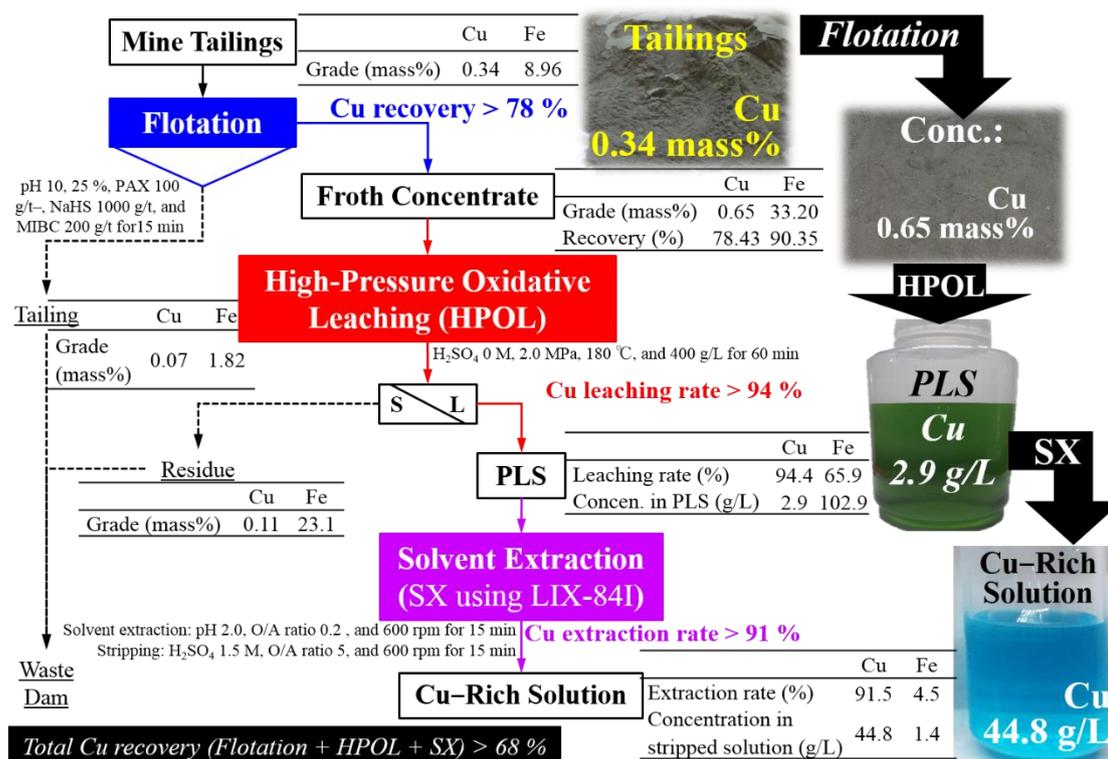


Fig. 5.26 A flowchart of the recovery of copper from the mine tailings.

5.4 Conclusion

The aim of this chapter was to develop a copper recovery process from the mine tailings for an effective utilization of secondary copper resources by a combination method of flotation–HPOL–solvent extraction. The most obvious findings to emerge from this chapter are concluded as follows:

(1) Flotation

- The grade of copper reached to be 0.65 mass% from the initial feed grade of 0.34 mass%, as enrichment ratio about 2, while copper recovery became 78.4 % under the optimal flotation conditions.
- It was revealed that both of the grade and recovery of copper increased with the addition of sulfurizing reagent which causes to improve copper flotation kinetics due to an increment of froth stability.

(2) High–pressure leaching process

- It is suggested that the presence of pyrite in the concentrate of mine tailings has a positive effect on copper dissolution under HPL conditions, because of the formed H_2SO_4 from FeS_2 could promote the leaching kinetics.
- It is confirmed that the separation of copper from iron at the HPL stage is quite difficult due to the iron always co–dissolve with copper following a linear relation of $C_{\text{Fe}} = 38.393 \times C_{\text{Cu}}$.
- The precipitation of iron was a high free acidity dependence reaction, and it can be described as $\log [\text{Fe}] = 1.0235 \times \log [\text{Free acidity}] - 0.0677$.
- Under the optimal HPOL conditions, the copper almost completed dissolved into the PLS, in which the copper concentration reached to be around 2.9 g/L.

(3) Solvent extraction and stripping

- Under the optimized extraction conditions, extractant LIX–84I in kerosene was extracted over 93.7 % copper in PLS.
- The vast majority of copper (> 97 %) in the Cu–loaded organic phase was stripped by 1.5 M H_2SO_4 solution, while the most iron (98.6 %) was left in the organic phase after stripping under the optimized conditions. As a result, the copper concentration in the stripped solution reached 44.8 g/L, and it is about 15 times higher than that of PLS obtained by HPOL of the

concentrate of mine tailings.

An efficient copper recovery process (total copper recovery of 68 %) is proposed for the utilization of mine tailings as one of the new copper resources using a combined hydrometallurgical process of flotation–HPOL–solvent extraction.

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Chapter 6: Conclusion

In this research, the flotation and high–pressure oxidative leaching were developed for recovery of copper from the low–grade copper resources. This PhD thesis is composed of six (6) chapters, each of them dealing with different aspects of development the approaches for recovery of the copper from low–grade copper resources.

Chapter 1: This chapter introduces the general overview of the low–grade copper ores and mine tailings, the conventional copper producing process and the previous research on the low–grade copper ore resources. Fundamental technologies for the recovery of copper from ores by flotation and hydrometallurgical processes are discussed throughout this dissertation.

Chapter 2: This chapter describes the direct atmospheric and high–pressure oxidative leaching (HPOL) of low–grade ores (copper grade: 0.4 mass%, CuFeS_2 as the main copper mineral) under a variety of sulfuric acid concentrations (0–1.0 M). It can be seen from the results that both copper and iron dissolution rates were low (< 20 %) under the atmospheric conditions, due to the formation of elemental sulfur onto the unreached copper particles. However, a maximum copper leaching rate of 98 % achieved under the optimal HPOL conditions, whereas the copper concentration in the pregnant leach solution (PLS) was only 0.06 g/L, that lower copper concentration causes difficulty in the subsequent process, namely solvent extraction.

Chapter 3: This chapter presents the results of the recovery of copper from the low–grade copper ore using flotation followed by HPOL. The effects of various flotation parameters, such as time, collector (PAX) dosage, slurry pH and air injection rate on beneficiation of copper from the sample were studied. The recovery of copper reached 93.1 % while a copper grade improved to 18.1 from 0.4 mass% under the collector–less optimal flotation conditions. The enrichment ratio of copper in the concentrate was 45. The concentrate obtained from the flotation of low–grade copper ore was used in HPOL study. The maximum efficiency of copper dissolution from the concentrate into

water under HPOL was 98.4 %. As a result, copper concentration in the PLS reached 15.0 g/L under the optimized HPOL conditions. A process flow for the recovery of copper from the low-grade copper ores is proposed based on this result.

Chapter 4: This chapter investigates the leaching of copper from chalcopyrite in H_2SO_4 solution at pressure oxidative conditions and kinetics of copper dissolution. Leaching variables that affect the rate of copper dissolution from chalcopyrite are particle size (-38 μm , +38–75 μm , and +75–100 μm), agitation speed (300–900 rpm), total pressure (0.8–2.0 MPa), temperature (160–180 °C) and sulfuric acid concentration (0.1–2.0 M). Under the optimal conditions, copper extraction of 94.5 % was achieved after 90-min leaching, while a dissolution of iron at 4.2 % was obtained. The kinetic study showed that the dissolution of chalcopyrite is represented by a shrinking core model with chemical reaction controlling mechanism given as $(1 - (1 - \alpha)^{1/3})$. The activation energy (E_a) for the leaching reaction was calculated to be 42.4 kJ/mol. The reaction order with respect to total pressure was about 8.0, which indicates that total pressure, i.e., oxygen partial pressure in an autoclave is the most important factor in controlling the dissolution of chalcopyrite in H_2SO_4 solution under pressure oxidative leaching conditions. The effect of Fe/Cu mole ratio (1–20 mol/mol, adjusted by addition of pyrite) on chalcopyrite leaching from a copper ore was investigated. The results show that the sulfuric acid produced during pyrite oxidation promotes the chalcopyrite dissolution.

Chapter 5: This chapter discusses the possibility of applying the developed flotation and HPOL processes for recovery of copper from mine tailings. The grade of copper reached to be 0.65 mass% and its recovery was 78.4 % under the optimal flotation conditions. It was revealed that both grade and recovery of copper increased with the addition of sulfurizing reagent (NaHS). The results of HPL using the concentrate of mine tailings obtained by flotation under the optimal conditions shown that the copper dissolution of 94.4 % was achieved in an H_2O media. The solvent extraction of pregnant leach solution obtained from the optimal HPOL indicated that 91.3 % copper was recovered in the stripped solution under the determined optimum conditions, at which the copper concentration reached to be 44.8 g/L. Finally, it was verified that the application of the combined

method consistency of flotation, HPOL, and solvent extraction is possible to recover copper from mine tailings and low-grade copper ores.

Chapter 6: This chapter provides a summary of findings from each chapter and recommendations for future research based on the obtained results and observations for recovery of copper from low-grade copper resources.

Finally, an advanced copper recovery process from the low-grade copper ores was proposed by a combination method of flotation-HPOL, which is possible and expected to apply this developed process (Flotation-high-pressure oxidative leaching process) to other materials such as Rare earth mineral and arsenic (As) rich copper mineral etc. for effective metal recovery.

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Publications in This PhD Thesis

1. Peer-Reviewed Journal Papers

- (1) **Han, B.**, et al.: “Copper Upgrading and Recovery Process from Mine Tailing of Bor Region, Serbia Using Flotation”, *International Journal of the Society of Materials Engineering for Resources*, Vol. 20, No. 2, pp. 225–229 (2014).

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- (2) **Han, B.**, et al.: “Copper Recovery from Silicate-Containing Low-Grade Copper Ore Using Flotation Followed by High-Pressure Oxidative Leaching”, *Resources Processing*, Vol. 64, No.1, pp. 3–14 (2017).

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2. International Conference Papers

- (1) **Han, B.**, et al.: “Comparison of Beaker Leaching and High-temperature and High-pressure Acid Leaching of PCBs for Valuable Metals Recovery”, *Proceedings of International Symposium on East Resources Recycling Technology (ERATH 2013, China)*, pp. 436–429 (2013).

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- (2) **Han, B.**, et al.: “Investigation of the Cu concentration process from tailings using flotation”, *Proceedings of International Conference on Materials Engineering for Resources (ICMR 2013, Japan)*, AP-4, pp. 23 (2013).

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(Chapter 3)

- (6) **Han, B.**, et al.: “COPPER RECOVERY FROM LOW–GRADE COPPER ORE USING A COMBINATION PROCESS OF FLOTATION AND HIGH–PRESSURE LEACHING”, *Proceedings of International Mineral Processing Conference 2016 (IMPC Mongolia 2016)*, pp. 75–80 (2016).

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- (7) **Han, B.**, et al.: “THE COPPER RECOVERY FROM MINE TAILINGS USING FLOTATION AND HIGH–PRESSURE LEACHING”, *Abstract Proceedings of 5th International Doctoral Symposium (Japan)*, pp. 15 (2016).

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