

Pressure leaching of chalcopyrite with oxalic acid and hydrogen peroxide

M. Deniz Turan^{a,*}, Zeynel Abidin Sari^b, Hasan Nizamoglu^a

^a Firat University, Department of Metallurgical and Materials Engineering, Elazığ 23119, Turkey

^b Department of Metallurgy Iskenderun Vocational School of Higher Education, Iskenderun Technical University, Hatay 31200, Turkey

ARTICLE INFO

Article History:

Received 27 July 2020

Revised 2 October 2020

Accepted 21 October 2020

Available online 5 November 2020

Keywords:

Chalcopyrite

Pressure leaching

Copper

Oxalic acid

Hydrogen peroxide

Autoclave

ABSTRACT

This study investigated the dissolution behavior of metals from chalcopyrite concentrate in a pressure reactor system in the presence of hydrogen peroxide by oxalic acid leaching. The fact that the compounds formed by copper and iron with oxalic acid had different dissolution coefficients showed that metals could be selectively extracted based on the leaching temperature. The effects of various leaching parameters on metal extraction in the autoclave system were investigated at different H₂O₂ concentrations (1–5 M), H₂C₂O₄ concentrations (25–125 g/L), leaching temperatures (318–443 K) and leaching times (15–180 min). While iron and copper extraction as a result of 180 min of leaching with 5 M H₂O₂, 318 K and 100 g/L H₂C₂O₄ was respectively 90.6% and 1.73%, 88.5% of copper and 2.11% of iron could be extracted as a result of 180 min of leaching with 3 M H₂O₂, 443 K and 100 g/L H₂C₂O₄. The reversal of the copper and iron extraction dissolution behavior started after the leaching temperature of 378 K. In the XRD analysis of leach residues obtained at low leaching temperatures, Cu₂O₄ peaks were dominant, while at high temperature conditions, Fe₂O₃ peaks were dominant.

© 2020 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Chalcopyrite (CuFeS₂) is the most important commercial copper sulphide mineral and is the principal source of commercially produced copper. Metal extraction from chalcopyrite and its concentrate is carried out by pyrometallurgical and hydrometallurgical methods [1]. Pyrometallurgical methods include melting–converting–refining–electrolyzing methods, which are classical and widely used methods. Concentrate treatment using furnaces is characterized by a number of environmental and technogenic problems, such as large emission of SO_x (SO₂ and/or SO₃) gases and as a consequence, overproduction of sulfuric acid, storage and transportation problems. These gas emissions may also include toxic compounds of heavy metals [2].

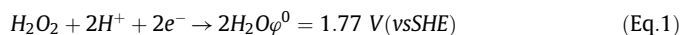
Hydrometallurgical methods were developed as opposed to classic pyrometallurgical routes. To overcome these environmental problems and obtain some economic advantages, the use of hydrometallurgical processes for copper production seems appropriate as an alternative method because it has many advantages such as being eco-friendly and having easy operation, low energy depletion and low cost [3].

Chalcopyrite is the most abundant copper mineral and the most refractory and compact for aqueous extraction processing and difficult to leach. In this sense, there are different options such as pressure leaching, strong various oxidants (hydrogen peroxide, ozone and Cr(VI) ions) in acidic media and bioleaching to achieve high metal extraction efficiency from chalcopyrite [4]. The most attractive one of these options is

pressure oxidative leaching, because it has high kinetic parameters and high specific productivity [5]. During leaching of copper sulfide concentrates, the most significant problems that are encountered are low extraction yields and high iron contents of pregnant solutions. To reduce the iron concentration in leaching solutions, iron can be converted to insoluble forms such as jarosite, hematite and goethite. All of these conditions may be supplied by the use of high temperature and the presence of oxidants in the leaching medium [6]. This oxidative leaching medium is usually provided by addition of oxygen gas into a reactor system [7], but this route, feeding of gas into a pressurized system, may be difficult, unsafe and expensive [8].

Hydrogen peroxide is a strong and environmentally safe oxidizing agent. This fact, along with the high value of its oxidation–reduction potential (1.77 V, vs SHE), has made this reagent extensively investigated in the oxidation processes of almost all sulphide minerals.

The oxidative action of hydrogen peroxide in acidic solutions is based on Eq. (1) [9]:



Furthermore, hydrogen peroxide can also behave as a reducing agent:



On the other hand, hydrogen peroxide is a highly unstable compound which decomposes in mineral dissolution processes. Its decomposition can be accelerated by the presence of catalytic metals,

* Corresponding author.

E-mail address: mdturan@firat.edu.tr (M.D. Turan).

mineral particles, as well as impurities. In order to avoid rapid decomposition of hydrogen peroxide, some stabilizers, such as phosphoric acid, acetic acid, citric acid, oxalic acid and polar organic solvents, have been recently used in leaching processes [10,11]. To obtain the maximum benefit from the decomposition product of hydrogen peroxide, the leaching process can be put into practice in a closed system.

Usage of hydrogen peroxide in enclosed containers leads to formation of active oxygen as a decomposition product in relation to temperature increase. This formed oxygen provides an oxidizing leaching environment, while also playing a significant role in providing the pressure necessary for the reactor.

Oxalic acid is a good leaching agent, because its decomposition mechanism can be described as complex formation and reduction. Oxalic acid and oxalate ions are reducing agents, and they are thermodynamically unstable in specific media. Oxalate ions ($C_2O_4^{2-}$) have four oxygen atoms, these oxygen atoms have the ability to bond with metallic ions and form a ring. Oxalate ions have the ability to produce five-membered rings and complex ions in the presence of ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron [12]. Due to the chelating feature of oxalic acid, it hinders iron precipitation by composing soluble complex anions in a wide range of pH. In the meantime, there are many studies on iron removal using oxalic acid, and many experimental studies have been publishing on the basic mechanisms that are involved [13–19]. In these studies, iron is removed from ores by using oxalate ions which have a tendency to compose in the form of aqueous ferric oxalate ($Fe(C_2O_4)_3^{3-}$) and ferrous oxalate ($Fe(C_2O_4)_2^{2-}$). The reaction of aqueous oxalic acid with copper ion results in formation of copper oxalate (CuC_2O_4) precipitates. Many studies have been carried out by researchers related to formation of copper oxalate precipitation [20,21]. The leaching process of copper-containing samples with an aqueous solution of oxalic acid results in low copper dissolution, because the complex is scarcely soluble in water [22].

In this study, leaching of chalcopyrite concentrate with oxalic acid in a pressure reactor in the presence of hydrogen peroxide was investigated. By examining the effects of various parameters, it was aimed to explain the dissolution mechanism of chalcopyrite under certain conditions.

There are some studies in the literature on autoclave leaching of chalcopyrite. It is seen that, in general, these studies have used hydrogen peroxide, oxygen gas, ozone, various organic and inorganic acids. However, no finding has been encountered on leaching of chalcopyrite with oxalic acid in an autoclave system.

2. Material and methods

The chalcopyrite concentrate that was used in the leaching experiments was obtained from a copper flotation facility (Elazığ-Turkey). This concentrate was classified by passing through a 200-mesh sieve, and this grain size was used in all experiments. The specimens were dried in a stove at a temperature of 333 K for 12 h, and then, kept in closed containers to be used later. Following taking all specimens into the solution with the help of a microwave digestion unit to conduct the chemical analyses of the dried specimens, analysis in terms of metals was carried out by ICP-OES (Perkin-Elmer, Optima 2000DV). The sulfur contents of the concentrate were determined gravimetrically by the $BaSO_4$ method [23] and the XRF method. The results obtained from the chemical analysis are shown in Table 1. From the metallic composition for the mineral sample

(Table 1), mineralogical composition assumption as 81.7% $CuFeS_2$, 0.43% PbS , 7.7% FeS_2 , 2.4% SiO_2 and others.

Mineralogical analyses of the concentrates and leach residues obtained under some conditions were carried out by XRD (Shimadzu XRD-6000). The morphological structure of the final residue obtained as a result of the leaching experiments was characterized by a scanning electron microscope (JEOL JSM 7001F FE-SEM). Before characterization, the powder specimens were coated with gold. Electron microscope image of the residue that was obtained under the optimum leaching conditions was taken under 15000X magnification. According to the particle size distribution results (Malvern Instruments MasterSizer X), it was determined that the particle sizes of the chalcopyrite concentrate were as $d(0.10)=2.90 \mu m$, $d(0.50)=15.65 \mu m$, $d(0.90)=56.03 \mu m$, while the BET surface area (Micromeritics ASAP 2020) value was $0.532 m^2 g^{-1}$.

The pressure leaching experiments were carried out in an autoclave made out of titanium with a capacity of 0.1 L (Amar Equipment, Model No: 3680). Temperature control was achieved with a thermocouple in the reactor. Stirring of the leaching solution was provided by a four-blade fan made out of titanium. System parameters as temperature, stirring speed and pressure were controlled by a PID control system with a computer connected to the reactor (Fig. 1).

The leaching experiments were carried out in the form of quickly heating the prepared solutions and the solid placed into the reactor container and starting the stirring process when the desired temperature was reached. Stirring was stopped at the end of the leaching experiments, the autoclave was quickly cooled, and the undissolved solid was separated by filter paper. The loaded leaching solutions were analyzed in terms of copper and iron by AAS (Perkin Elmer, AAnalyst 400).

The Eh-pH diagram for the $Fe-H_2O_2-H_2C_2O_4$ system was formed by using the HSC diagram module. From the thermodynamic data of the reactions that could be given by multiple metals in the aqueous medium, the Eh-pH diagram was formed by combining the solubility values of oxides and hydroxides and the equilibrium constants of the reactions.

In the leaching experiments, oxalic acid dihydrate salt (Merck No 100,492) and hydrogen peroxide (35% Merck No 108,600) were used. All chemicals were used as received and without any further purification. Double-distilled water was used in all experiments.

The effects of various parameters on extraction of metals from chalcopyrite were investigated. The stirring speed of 400 rpm and solid/liquid ratio of 1:25 g/mL were kept as the constant parameters. The variable leaching parameters were as leaching temperatures of 318–443 K, H_2O_2 concentrations of 1–5 M, leaching times of 15–180 min and oxalic acid concentrations of 25–125 g/L.

3. Results and discussion

3.1. Dissolution in presence of oxalic acid and hydrogen peroxide

It was described that dissolution of iron oxide compounds in oxalic acid solutions takes place via a reduction mechanism. In addition to this, it was stated that oxalic acid has a reduction ability with its high acidity and complex-forming power [18]. It was reported that iron oxide dissolves in a solution with oxalic acid by forming a complex by two mechanisms as either Fe (III) oxalate or Fe (II) oxalate, and this situation could occur as a result of the following reactions [24].

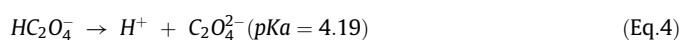
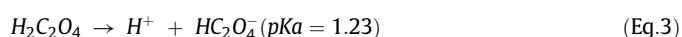


Table 1

The chemical composition of the chalcopyrite concentrate.

Component	%						mg/kg		
	Cu	Fe	S	Pb	SiO_2	LOI*	Co	Zn	Ni
Content	28.31	28.52	29.36	0.37	2.40	13.36	947	802	490

* LOI: Loss on ignition at 1073 K.

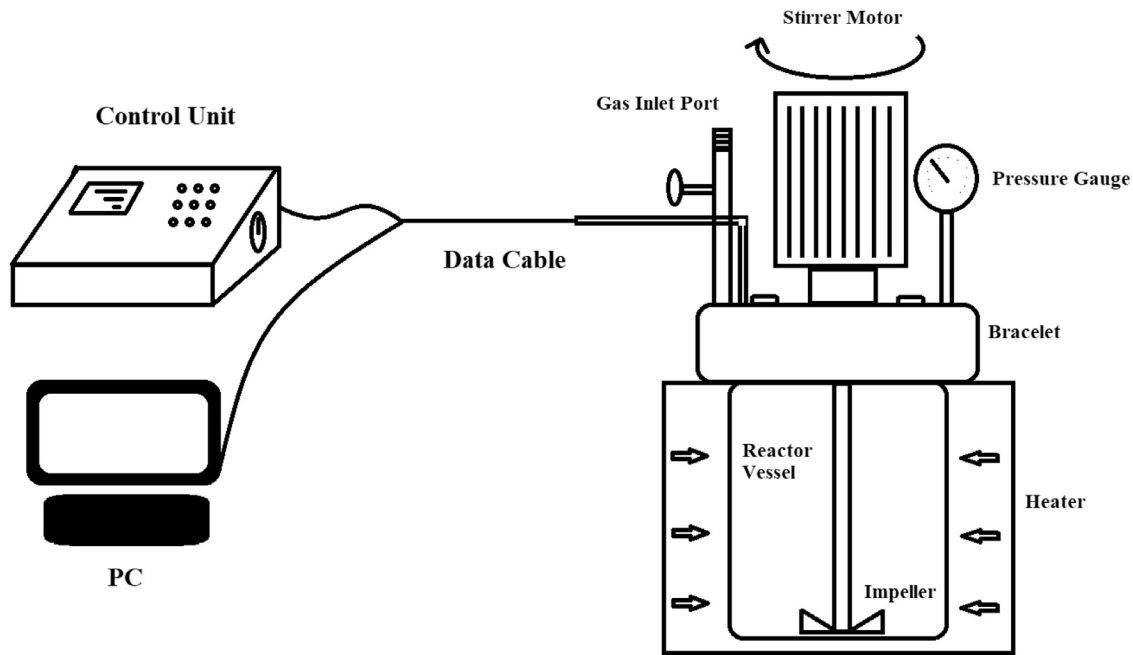


Fig. 1. Autoclave leaching system.

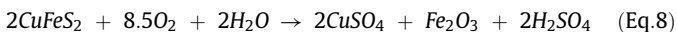
The solution pH controls the distribution of various oxalate ions in the leaching system. Moreover, the Fe (III) oxalate and Fe (II) oxalate species vary by the pH and the total oxalate concentration. In the presence of ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions, oxalate ions have the ability to generate five-membered rings and form complex ions. "Paniyas et al. 1996, studied the effect of pH and oxalic acid concentration on the speciation of various Fe(III)-oxalate complexes. Assuming that oxalic acid is in large excess in the solution, which is a valid assumption for the systems under study, the speciation of oxalic acid is not affected by the presence of ferric ion. Thus, the concentration of Fe(III)-oxalate complexes is negligible in proportion to the concentrations of oxalic acid dissociation products.

The reaction of aqueous oxalic acid with copper ions results in formation of aqueous copper oxalate ($\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$). The aqueous copper oxalate structure with a very low solubility precipitates in the form of the copper oxalate (CuC_2O_4) complex. This is expressed by the following equation [25]:

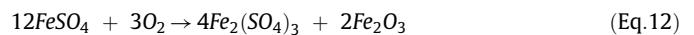
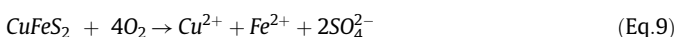


In systematic experiments involving leaching of chalcopyrite concentrate in a high-pressure reactor, for reactions among iron, copper and oxalate ions to occur, the concentrate needs to be decomposed in the presence of an oxidizing agent such as hydrogen peroxide.

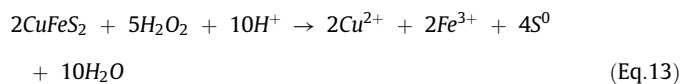
Hydrogen peroxide and chalcopyrite dissolution in an acidic solution in the autoclave medium may be revealed by high- and low-temperature process pressure leaching experiments. The total chemical reaction of the high-temperature process is expressed as follows:



The mineral iron that is oxidized is decomposed into copper and sulfate ions (Eq. (9)) In this case, copper, iron sulfate and sulfuric acid form in the autoclave system (Eqs. (10)–(12) [26]. Iron (II) sulfate is then oxidized into iron (III) sulfate, and the final component is hydrolyzed at high temperature. As in Eq. 12, it precipitates in the form of hematite (Fe_2O_3).



High-temperature oxidizing pressure leaching has a similar chemical mechanism to that of chalcopyrite oxidation. However, specific temperature conditions promote elemental sulfur formation and acid consumption (Eq. (13)) [26].



The chemical mechanism of chalcopyrite leaching is based on the oxidation of sulfur by oxygen. In addition to this, metal cations (Cu^{2+} , Fe^{2+}) react with the oxalic acid in the solution and form copper and iron oxalate complexes.

Various scientific articles have been proposed for leaching of chalcopyrite in sulfate solution with dissolved oxygen as the oxidant.

Yu et al. [27] studied the rate of chalcopyrite leaching in the sulfuric acid solution at the temperature range of 125–175 °C and the oxygen pressure range of 0.52 to 2.76 MPa. They have noticed that slightly elemental sulfur is produced under these conditions. Vizsolanyi et al. [28] dissolved chalcopyrite in a dilute sulfuric acid under conditions of 110 °C and 3.4 MPa. They found that the elemental sulfur and hydrolyzed iron are produced during the leaching steps. Sanchez et al. [29] studied two-stage leaching of chalcopyrite using a fixed H_2O_2 , H_2SO_4 , ethylene glycol in an autoclave environment. The proposed process consists of two consecutive stages, the first of which uses a H_2SO_4 – H_2O_2 –EG–oxalic acid leaching solution for the selective dissolution of iron and the formation of solid copper oxalate; the second stage employs a H_2SO_4 – H_2O_2 –EG–EDTA leach solution to dissolve the copper oxalate and react with the remaining chalcopyrite from the first stage. Antonijevic et al. [2] studied kinetics of chalcopyrite dissolution by hydrogen peroxide in sulphuric acid. The leaching with oxygen overpressures is another alternative to accelerate the

dissolution of metals from sulfides in sulfate media. Padilla et al. [30] studied the leaching of sulfidized chalcopyrite also at ambient pressures in $\text{H}_2\text{SO}_4\text{--NaCl--O}_2$. These investigators found that the copper dissolution in that media was rapid and reported copper extractions over 90% in less than 90 min at about 100 °C. Padilla et al. [31] studied of the pressure leaching of the sulfidized chalcopyrite concentrate in $\text{H}_2\text{SO}_4\text{--O}_2$ media. These investigators reported that selective copper dissolution from sulfidized chalcopyrite can be obtained at 100 °C and oxygen overpressures of about 304 kPa in less than 3 h of residence time. However, for longer times, iron extraction increases rapidly and selectivity decreases. Turan and Altundogan. [4] studied of leaching of chalcopyrite concentrate with hydrogen peroxide in the presence of sulfuric acid in an autoclave system using an experimental design method. They said that the decomposition product of hydrogen peroxide, oxygen, is sufficient to provide either oxidation or high pressure condition for leaching of chalcopyrite concentrate.

3.2. Leaching experiments

In the autoclave system, extraction of metals from the chalcopyrite concentrate was carried out by oxalic acid leaching in the presence of hydrogen peroxide. In the experiments carried out in the autoclave system, instead of a gas system fed from outside to the pressure leaching medium conditions, the oxygen arising as a result of decomposition of hydrogen peroxide used as a leaching agent in the medium and the pressure values provided by it were utilized. Hydrogen peroxide used in pressure leaching studies not only increases the pressure of the medium by providing oxygen especially as a result of decomposition by temperature increase, but it also provides the leaching environment that is required for oxidative leaching conditions. Additionally, the presence of Cu-Fe in the leaching environment serves as a significant catalyst in the decomposition of hydrogen peroxide. Furthermore, it is understood that the gas products and water vapor forming as a result of decomposition of oxalic acid also contribute to the total pressure of the medium.

First of all, the effects of leaching temperature and leaching time on iron and copper dissolution in the autoclave conditions were examined at a constant H_2O_2 concentration of 1 M. As seen in Fig. 2, the dissolvability of iron increased by leaching temperatures increasing up to 423 K and increasing leaching times, while on the other hand, copper almost did not dissolve at all. This situation suggests that, under these conditions, copper precipitates in the form of its oxalates. It was determined that, in the leaching process carried out in the autoclave, with the increasing leaching temperature, the

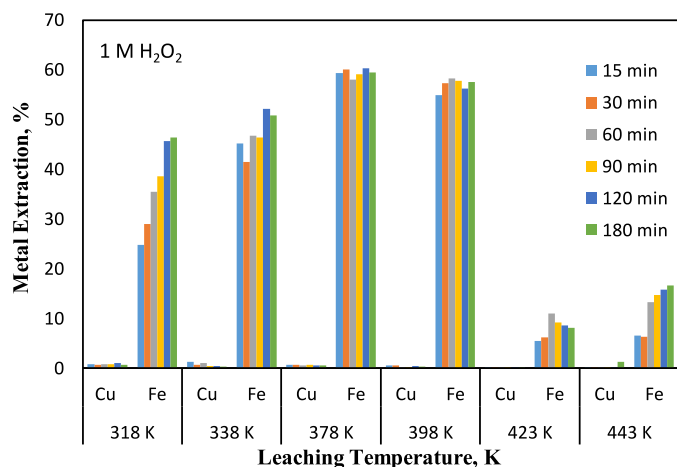


Fig. 2. Effect of leaching time and temperature at 1 M H_2O_2 concentration ($\text{H}_2\text{C}_2\text{O}_4$ concentration: 100 g/L; liquid-solid ratio: 25 mL/g; stirring speed: 400 rpm).

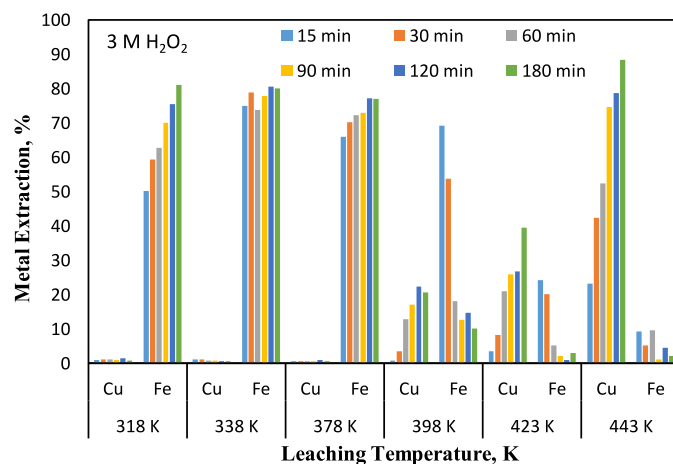


Fig. 3. Effect of leaching time and temperature at 3 M H_2O_2 concentration ($\text{H}_2\text{C}_2\text{O}_4$ concentration: 100 g/L; liquid-solid ratio: 25 mL/g; stirring speed: 400 rpm).

pressure constantly increased in connection to the decomposition of the leaching solution (hydrogen peroxide, water and oxalic acid) (Fig 5). Iron and copper dissolved most by 61% and 1%, respectively. On the other hand, with a further increase in the leaching temperature, it was seen that copper still did not enter the solution, but the amount of dissolved iron was significantly reduced. This situation reveals that the iron oxalate structure that forms is affected by the increased pressure in the medium.

Fig. 3 shows the effects of leaching time and leaching temperature on metal extraction at the 3 M constant concentration of H_2O_2 . As seen in the Figure, with the leaching temperature increasing up to 398 K, it was seen that high iron dissolvability was achieved in a shorter leaching time. At the lowest leaching temperature of 318 K and in 180 min of leaching time, the dissolutions of iron and copper were respectively 81% and 0.8%. At 318 K and under the conditions of 1 M and 3 M H_2O_2 , the autoclave gauge pressure values were respectively 3.6 and 11.3 bar. Here, it may be stated that the pressure value is significantly effective on the iron passing into the solution based on the increasing peroxide concentration. However, despite the same leaching conditions, it was determined that the dissolution behaviors of copper and iron interestingly changed with increased leaching temperature. While almost no copper entered the solution up to then, with the increasing temperature, there was a fast increase in the dissolvability of copper and a fast reduction in the dissolvability of iron. Especially after the leaching temperature of 378 K (28.9 bar),

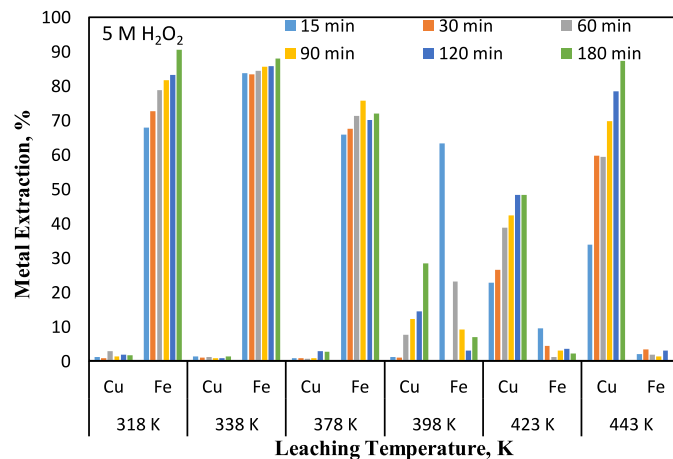


Fig. 4. Effect of leaching time and temperature at 5 M H_2O_2 concentration ($\text{H}_2\text{C}_2\text{O}_4$ concentration: 100 g/L; liquid-solid ratio: 25 mL/g; stirring speed: 400 rpm).

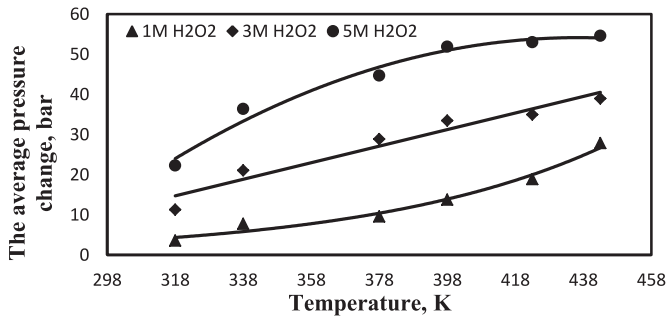


Fig. 5. Average pressure values vs leaching temperature ($\text{H}_2\text{C}_2\text{O}_4$ concentration: 100 g/L; Leaching time: 180 min; liquid-solid ratio: 25 mL/g; stirring speed: 400 rpm).

the amount of copper entering the solution increased by a highly substantial amount, and 88% Cu extraction was obtained at 443 K (39 bar). It was observed that the iron entering the solution in these conditions was limited to 2%, and there was perhaps a selective leaching under these conditions.

The results of the experiments where 5 M H_2O_2 was used are shown in Fig. 4. Here, it is also seen that the change in the dissolvability of the metals started at 378 K. In the plot, it is seen that, at the lowest temperature value (318 K and 22.3 bar), the highest amount of iron entering the solution was by 90%, while the maximum copper dissolution was by 3%. On the other hand, as a result of 180 min of leaching at a temperature of 443 K (54.6 bar), the extraction of copper and iron was respectively 88% and 2%. According to the dissolved iron concentration calculations under leaching conditions at low temperatures, it can be said that some of the pyrite in the concentrate did not leach. In studies conducted with similar concentrates, the situation that pyrite is not dissolved has been revealed by other researchers [29].

According to the obtained results, the extraction behavior of the metals from chalcopyrite significantly changed in connection to the increased temperature and hydrogen peroxide and the changing pressure. Especially in low temperature and low hydrogen peroxide concentration conditions, it was observed that iron dissolved at high ratios from chalcopyrite, but as opposed to this, copper almost did

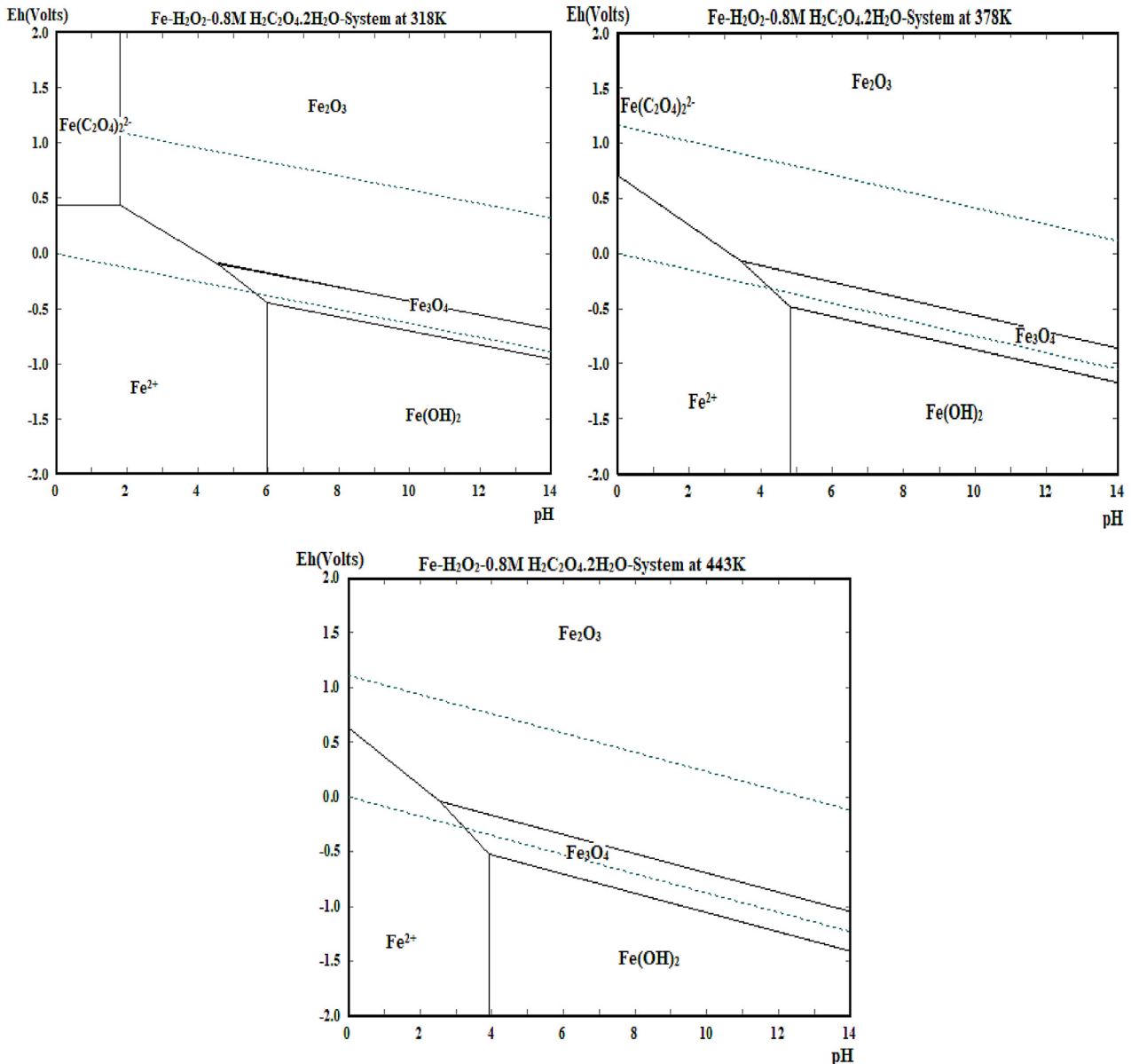


Fig. 6. Eh-pH diagram for Fe-H₂O₂-0.8 M H₂C₂O₄•2H₂O system at 318, 378, and 443 K.

Table 2

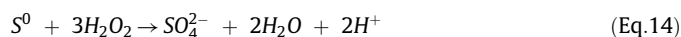
Calculation of the thermodynamic constants parameters at different temperatures for iron species in the iron dissolution system.

Species	logK		
	318K	378K	443K
$\text{Fe}^{2+} + 2\text{C}_2\text{O}_4^{2-} \rightarrow \text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$	12.73	10.71	9.14
$\text{Fe}^{3+} + 3\text{C}_2\text{O}_4^{2-} \rightarrow \text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$	19.23	16.18	13.81

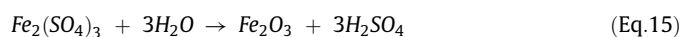
not enter the solution at all. On the other hand, with the increased leaching temperature and hydrogen peroxide concentration, the dissolution behavior was completely reversed, and copper entered the solution to a high degree. This showed that selective copper leaching could be performed in the specified leaching conditions. Accordingly, it may be stated that selective copper extraction could be obtained by a single-step leaching process at high temperatures, while copper could be selectively gained from the solid residue obtained at low temperature with a second-stage leaching process, or copper oxalate salt could be obtained. Fig. 5 demonstrates the autoclave gauge pressure changes based on leaching temperature and hydrogen peroxide concentration.

Especially in experiments conducted at high temperatures where iron did not enter the solution, it is believed that medium conditions stated in iron removal processes from leaching solutions by the hematite method were provided. In these conditions, it is considered that the increase in the copper extraction values occurred as a result of decomposition of the formed oxalated structure as a result of the possibility of sulfur found in the structure of chalcopyrite to be oxidized up to sulfate in high oxidative leaching conditions Eqs. (9), (14) and/or in high temperature and pressure settings [32].

Moreover, considering the oxidative potential of the medium, the fact that sulfur may be oxidized up to sulfate species.



Hematite precipitation is in fact a prevalent method that is used to remove iron from loaded leaching solutions [33]. At temperatures of 423 K and higher and under oxygen pressures of 15–18 bar, iron is precipitated in the form of fine-grain Fe_2O_3 crystals in the autoclave based on the following reaction:



In this case, it is understood that the experimental conditions met the required and sufficient conditions for hematite formation, and as the gauge temperature read at the aforementioned leaching temperature was high, the precipitation process could be facilitated under the temperature of hematite formation stated in the literature.

Moreover, to understand the dissolution behavior of iron from chalcopyrite concentrate under autoclave conditions and different temperatures with representative parameters, Eh-pH diagrams were created (Fig. 6). As it could be understood from these diagrams, by the increase in the temperature of the medium, the presence of iron oxalate shifts to a narrow region and is replaced by hematite at high Eh values and all pH values. This shows that the highly oxidative property of the hydrogen peroxide used for the experimental studies and increased temperature corresponded to the Eh-pH scale of the medium in terms of hematite formation. At the same time, calculation of the thermodynamic constants parameters at different temperatures for iron species in the iron dissolution system is seen in table 2.

In leaching conditions at high temperatures, the effects of oxalic acid concentration were investigated in the range of 25–125 g/L (Fig. 7). According to the obtained results, the extraction of copper and iron was constant at all oxalic acid concentrations. This result shows that, in fact, the control of copper extraction at high

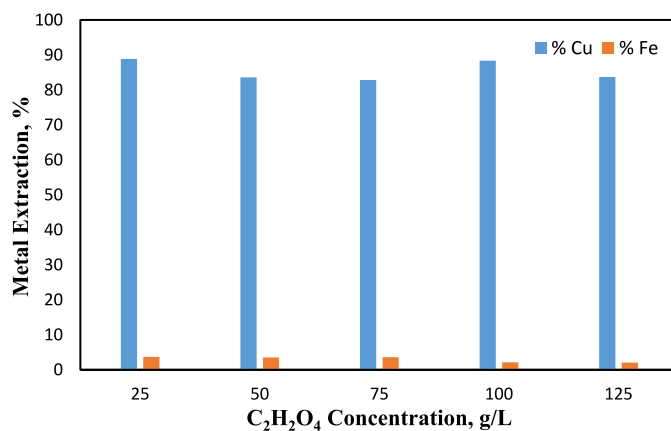


Fig. 7. Effect of $\text{C}_2\text{H}_2\text{O}_4$ concentration (H_2O_2 concentration: 3 M; leaching time: 180 min; leaching temperature: 443 K; liquid-solid ratio: 25 mL/g; stirring speed: 400 rpm).

temperatures is mostly independent of oxalic acid. To confirm this situation, experiments were designed to conduct leaching processes in solutions without oxalic acid. However, before the mixture was fed into the reactor, excessive bubbling occurred, and it was observed that the isothermal conditions were no longer present. It is also

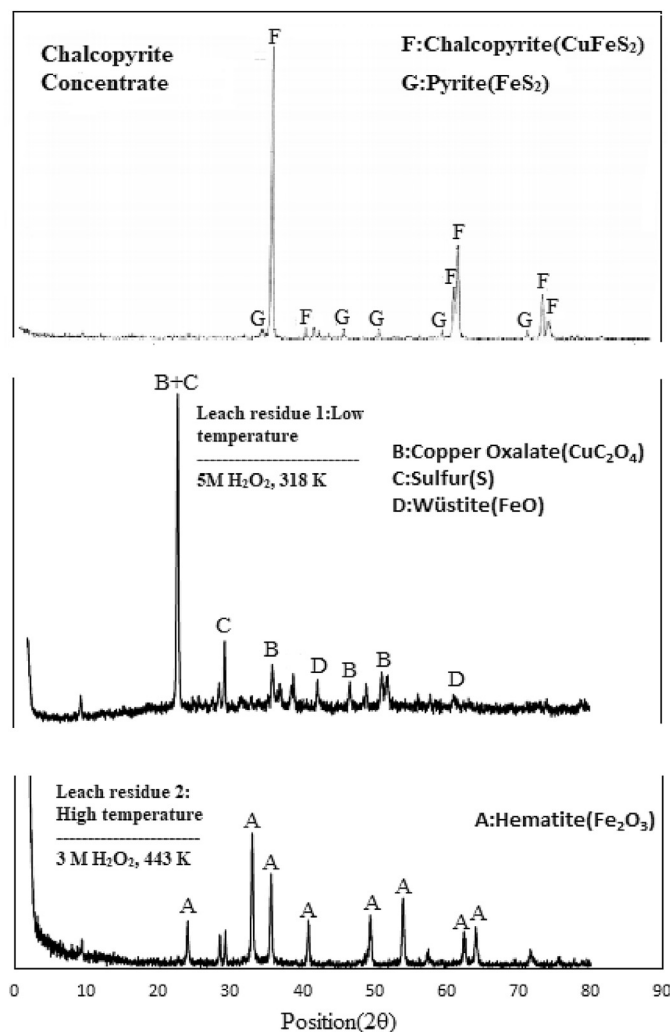


Fig. 8. XRD patterns of chalcopyrite concentrate and leach residues ($\text{C}_2\text{H}_2\text{O}_4$ concentration: 100 g/L; leaching time: 180 min).

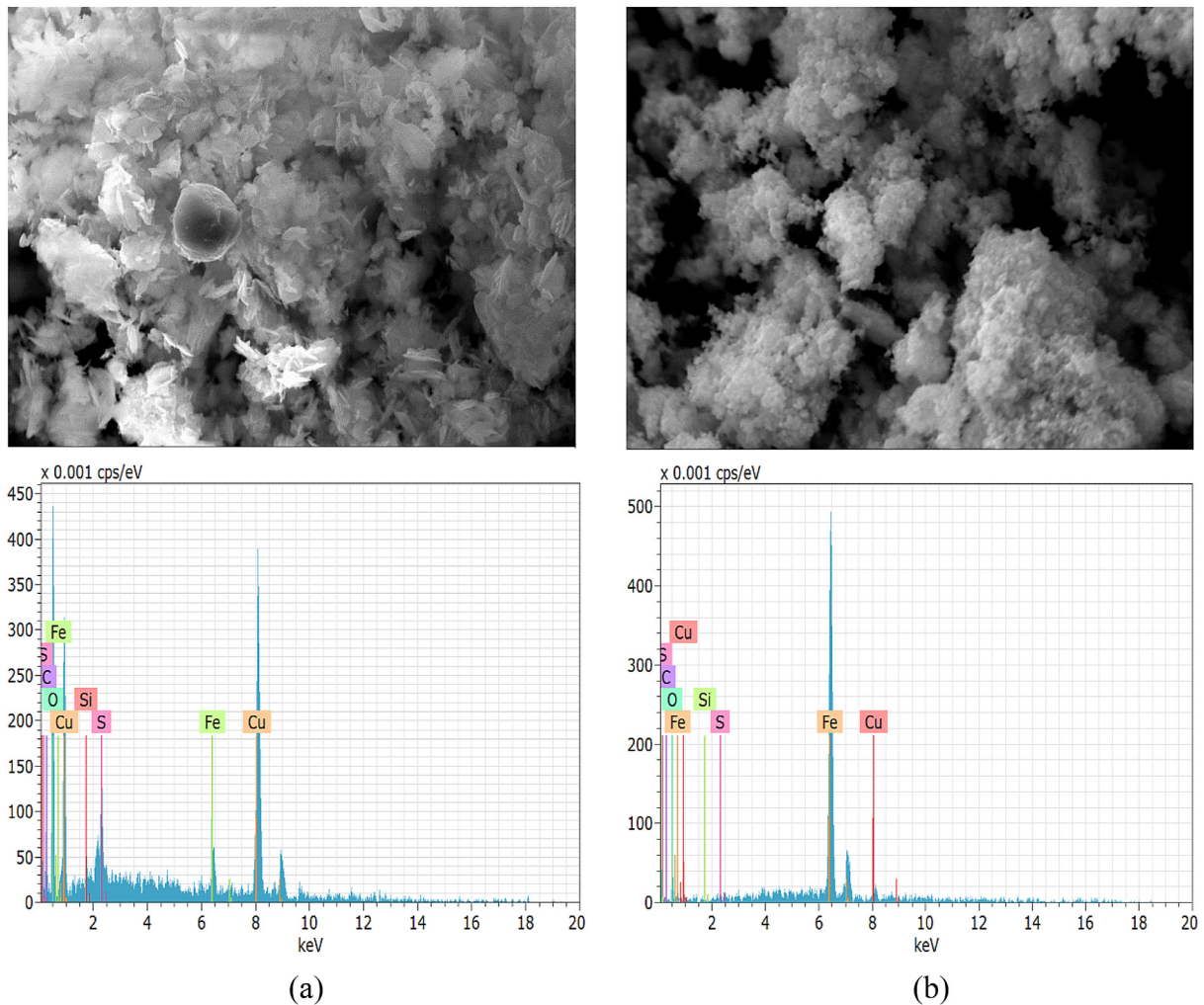


Fig. 9. SEM (15000X) microphotograph and EDX analysis of leaching residues (a) at low temperature (318 K), (b) at high temperature (443 K).

known that oxalic acid actually has a stabilizing effect that delays decomposition of peroxide. While this behavior causes iron to pass into the solution in the oxalate form and copper to stay solid in the same form at low temperatures, it is understood that, at high temperatures, it is an important leaching agent only for gradual decomposition of peroxide.

3.3. Characterization of leaching residues

The solid waste obtained after filtering the loaded solution in the experiments carried out under the optimum conditions in the autoclave system was characterized based on its mineralogical and morphological properties (Figs. 8 and 9). Fig. 8 shows that the most dominant peak in the residue obtained as a result of the leaching process conducted in low-temperature conditions was mostly in the form of copper oxalate and elemental sulfur. Accordingly, it is thought that, based on the temperature and concentration values of the leaching environment, copper precipitated in the form of the copper oxalate ($\text{CuC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$) complex which has a low dissolvability coefficient. On the other hand, it may be stated that iron was dissolved in the form of the iron oxalate ($\text{Fe}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$) complex which has a high dissolvability coefficient. This selective leaching behavior may be attributed to differences in dissolvability at low temperatures. This is because, while the dissolvability of iron (II)

oxalate is 293 K 0.008 g/100 g water, that of copper (II) oxalate is 293 K 2.16×10^{-10} g/100 g water [34].

Additionally, not encountering the chalcopyrite mineral phase in the waste showed that the structure of the chalcopyrite was decomposed under these conditions. On the other hand, the sulfur-containing copper form was transformed into chalcosine, and this showed itself in the form of small peaks. Moreover, as the iron in the form of chalcopyrite (CuFeS_2) and pyrite (FeS_2) was taken into the solution in the form of high-dissolvability iron oxalate complexes, dominant peaks belonging to iron ions were not encountered in the leaching residue. In addition to this, the wustite form was encountered in a few small peaks belonging to iron ions. Fig. 8 shows that, according to the X-ray analysis peaks of the leaching residue obtained in high-temperature conditions, the iron mostly got enriched as a solid in the form of hematite.

Fig. 9(a) shows the SEM-EDX analyses of the leaching waste obtained in the conditions where the leaching temperature was 318 K. Here, it is possible to state the presence of oxalate salts. According to the EDX analysis, it is understood that the dominant peaks belonged to copper and oxygen. Fig. 9(b) demonstrates that the hematite obtained in the optimum conditions where the leaching temperature was 443 K precipitated in the form of grains that were partly fascicle-like. Moreover, the dominant one among the elements determined in the EDX analysis was the Fe peak.

The process flow schema projected for this study is seen in Fig. 10.

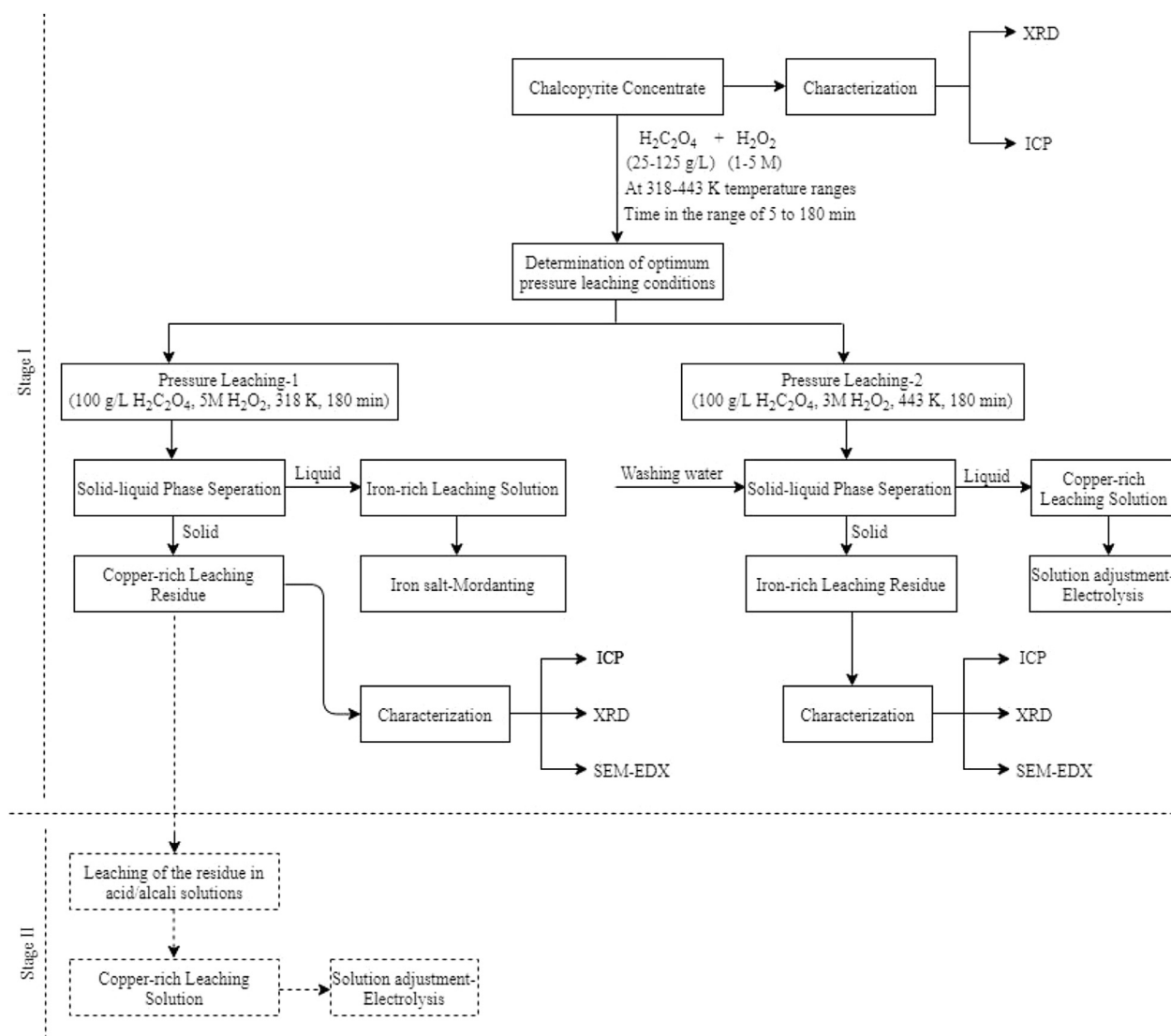


Fig. 10. Proposed flow sheet for pressure leaching of chalcopyrite.

Conclusions

The important findings obtained in the study are listed below:

- It was determined that the necessary pressure values and required oxidizing environment could be provided in an autoclave system without feeding gas from outside by using H₂O₂.
- It is possible to have selective leaching with increased temperature depending on the dissolvability differences of copper and iron oxalate in the presence of oxalic acid.
- It was determined that the dissolution behaviors of copper and iron changed in autoclave leaching of chalcopyrite concentrate in the presence of oxalic acid and hydrogen peroxide, and they were reversed after a certain temperature. In the experiments at low temperatures, while the copper stayed a solid in the oxalate form, the iron passed into the solution as its oxalate. At high temperatures, while the iron stayed in the solid residue in the hematite form, the copper passed into the solution as its sulfate.
- In the conditions of 5 M H₂O₂, 318 K, 100 g/L H₂C₂O₄ and 180 min of leaching time, the iron and copper extractions were obtained respectively as 90.6% and 1.73%.

- The dissolvability behavior in favor of the copper started after the leaching temperature of 378 K. Accordingly, at a leaching temperature of 443 K and under the conditions of 100 g/L oxalic acid, 3 M H₂O₂ and 180 min of leaching time, the extraction levels of copper and iron were respectively 88.5% and 2.11%.
- Eh-pH diagrams of the copper and iron in the chalcopyrite concentrate were created under the existing conditions, and the dissolution mechanism was explained.
- According to the results of the XRD analyses, the leaching residue obtained under low-temperature conditions was in the form of copper oxalate (CuC₂O₄), while that obtained under high-temperature conditions was completely in the form of hematite (Fe₂O₃).
- According to the results that were obtained, while copper oxalate salt could be obtained at low temperatures in autoclave leaching of chalcopyrite in the aforementioned conditions, it seems possible for the copper to pass into the solution and to produce copper from the loaded solution in processes carried out at high temperatures. In the aforementioned leaching conditions, at high temperature, the amount of hematite precipitate was determined as 15.72 g/L, while the copper concentration in the solution was determined as 10.02 g Cu²⁺/L.

Declaration of Competing Interest

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

Acknowledgments

The authors would like to acknowledge the TÜBİTAK (The Scientific and Technological Research Council of Turkey) under project No. 315M006, and Research Foundation of Firat University under project No. FUBAP-MF.15.25 for supporting the study.

References

- [1] Wang S. Copper leaching from chalcopyrite concentrates. *J Miner Metals Mater Soc* 2005;57:48–51.
- [2] Antonijević MM, Janković ZD, Dimitrijević MD. Kinetics of chalcopyrite dissolution by hydrogen peroxide in sulphuric acid. *Hydrometallurgy* 2004;7:329–34.
- [3] Nadirov RK, Syzdykova LI, Zhussupova AK, Ussebaev MT. Recovery of value metals from copper smelter slag by ammonium chloride treatment. *Int J Miner Process* 2013;124:145.
- [4] Turan MD, Altundoğan HS. Leaching of chalcopyrite concentrate with hydrogen peroxide and sulfuric acid in an autoclave system. *Metall Mater Trans B* 2013;44B:809–19.
- [5] Dalton RF, Raymond P, Enrique H, Barry H. Cuprex—new chloride-based hydrometallurgy to recover copper from sulfide ores. *Min Eng* 1988;40(1):24–8.
- [6] Dreisinger DB, Lu J. Pressure oxidation of ferrous ions by oxygen and hematite precipitation from concentrated solution of calcium, copper and iron chlorides. *Hydrometallurgy* 2013;140:59–65.
- [7] Padilla R, Pavez P, Ruiz MC. Kinetics of copper dissolution from sulfidized chalcopyrite at high pressures in H₂SO₄-O₂. *Hydrometallurgy* 2008;91:113–20.
- [8] Turan MD, Altundoğan HS. Leaching of a copper flotation concentrate with ammonium persulfate in an autoclave system. *Int J Miner Metall Mater* 2014;21:862–70.
- [9] Petrović SJ, Bogdanović GD, Antonijević MM. Leaching of chalcopyrite with hydrogen peroxide in hydrochloric acid solution. *Trans Nonferrous Metals Soc China* 2017;28:1444–55.
- [10] Turan MD, Sari ZA, Miller JD. Leaching of blended copper slag in microwave oven. *Trans Nonferrous Metals Soc China* 2017;27:1404–10.
- [11] Pecina T, Franco T, Castillo P, Orrantia E. Leaching of a zinc concentrate in H₂SO₄ solutions containing H₂O₂ and complexing agents. *Miner Eng* 2008;21:23–30.
- [12] Pariyan K, Hosseini MR, Ahmadi A, Zahiri A. Optimization and kinetics of oxalic acid treatment of feldspar for removing the iron oxide impurities. *Sep Sci Technol* 2020;55:1871–82.
- [13] Sari ZA, Turan MD, Nizamoglu H, Demiraslan A, Depci T. Selective copper recovery with HCl leaching from copper oxalate material. *Min Metall Explor* 2020;37:887–97.
- [14] Panias D, Taxiarchou M, Paspaliaris I, Kontopoulos A. Mechanisms of dissolution of iron oxides in aqueous oxalic acid solutions. *Hydrometallurgy* 1996;42:257–65.
- [15] Mandal SK, Banerjee PC. Iron leaching from China clay with oxalic acid: effect of different physico chemical parameters. *Int J Min Process* 2004;74:263–70.
- [16] Veglio F, Passariello B, Abbruzzese C. Iron removal process for high-purity silica sands production by oxalic acid leaching. *Ind Eng Chem Res* 1999;38:4443–8.
- [17] Lee SO, Tran T, Jung BH, Kim SJ, Kim MJ. Dissolution of iron oxide using oxalic acid. *Hydrometallurgy* 2007;87:91–9.
- [18] Martínez-Luévanos A, Rodríguez-Delgado MG, Uribe-Salas A, Carrillo-Pedroza FR, Osuna-Alarcón JG. Leaching kinetics of iron from low grade kaolin by oxalic acid solutions. *App Clay Sci* 2011;51:473–7.
- [19] Yang Y, Wang X, Wang M, Wang H. Recovery of iron from red mud by selective leach with oxalic acid. *Hydrometallurgy* 2015;157:239–45.
- [20] Krishnamurthy KV, Harris GM. The chemistry of the metal oxalato complexes. *Chem Rev* 1960;61:213–46.
- [21] Sarada K, Vijisha KR, Muraleedharan K. Exploration of the thermal decomposition of oxalates of copper and silver by experimental and computational methods. *J Anal Appl Pyrolysis* 2016;120:207–14.
- [22] Humar M, Pohleven F, Sentjerc M. Effect of oxalic, acetic and ammonia on leaching of Cr and Cu from preserved wood. *Wood Sci Technol* 2004;37:463–73.
- [23] Jeffery GH, Basset J, Mendham J, Denny RC. Vogel's textbook of quantitative chemical analysis. 5th Ed. New York: John Wiley & Sons Inc.; 1989. p. 374.
- [24] Lopez CO, Carmona MER. Thermodynamic analysis of stability in iron removal from kaolin by using oxalic acid. *Cerámica* 2013;59(2):326–30.
- [25] Pourmortazavi SM, Hajimirsadeghi SS, Nasrabedi MR, Kohsari I. Electrosynthesis and characterization of copper oxalate nanoparticles. *Synth React Inorgan Metal-Organ Nano-Metal Chem* 2012;42:746–51.
- [26] Aleksei K, Kirill K, Stanislav N. Pressure leaching of chalcopyrite concentrate. *Proceed Int Seminar Metall Mater* 2017;1964:020048.
- [27] Yu PH, Hansen CK, Wadsworth ME. A kinetic study of the leaching of chalcopyrite at elevated temperatures. *Metall Trans* 1973;4:2137–44.
- [28] Vizsolyi HV, Warren IH, Mackiw VN. Copper and elemental sulphur from chalcopyrite by pressure leaching. *J Metals* 1967:52–9.
- [29] Sanchez AR, Lazaro I, Lapidus GT. Improvement effect of organic ligands on chalcopyrite leaching in the aqueous medium of sulfuric acid-hydrogen peroxide-ethylene glycol. *Hydrometallurgy* 2020;193:105293.
- [30] Padilla R, Zambrano P, Ruiz MC. Leaching of sulfidized chalcopyrite with H₂SO₄-NaCl-O₂. *Metall Mater Trans B* 2003;34B:153–9 c.
- [31] Padilla R, Vega D, Ruiz MC. Pressure leaching of sulfidized chalcopyrite in sulfuric acid-oxygen media. *Hydrometallurgy* 2007;86:80–8.
- [32] Marsden JO, Wilmet JC. Medium-temperature pressure leaching of copper concentrates - part I: chemistry and initial process development. *Miner Metall Process* 2007;24(4):193–204.
- [33] Sanchez AR, Lapidus GT. Study of chalcopyrite leaching from a copper concentrate with hydrogen peroxide in aqueous ethylene glycol media. *Hydrometallurgy* 2017;169:192–200.
- [34] Turan MD, Sari ZA, Erdemoğlu M. Copper enrichment in solid with selective reverse leaching with oxalic acid. *J Sustain Metall* 2020;6:428–36.