

CHALCOPYRITE LEACHING IN ACID MEDIA: A REVIEW

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Abstract

In the modern practice of copper production, more attention is increasingly being given to the possibility of treating low-percentage sulphide ores that cannot be treated with conventional procedures (crushing, grinding, flotation). In addition, the processes of obtaining copper from complex sulphide concentrates, which cannot undergo pyrometallurgical processing, are increasingly being investigated. In most cases, the extraction of copper from such raw materials is achieved by applying the leaching procedures.

Since chalcopyrite (CuFeS₂) is the most abundant copper sulphide mineral, a great part of the research is focused on studying the behaviour of chalcopyrite in the leaching process, because processes of copper extraction from increasingly poor raw materials may be created using results of these studies. In addition, the main goal of these researches is to investigate the kinetics and mechanism of oxidation of chalcopyrite under the influence of various oxidants (O₂, Fe³⁺, H₂O₂, chlorate ions, etc.) and in the same time obtaining data necessary for the development of copper production process that could satisfy increasingly technological, economic and environmental stringent criteria.

This paper presents the existing knowledge of chalcopyrite leaching and phenomena that follow chalcopyrite oxidation in acidic sulphate and chloride solutions.

Keywords: chalcopyrite; leaching; dissolution; oxidation mechanism.

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1. Introduction

Chalcopyrite is one of the most important and most abundant copper sulphide minerals [1-3]. It often occurs with other minerals in ore deposits, such as pyrite (FeS_2), galena (PbS) and sphalerite (ZnS). These minerals are mainly separated by flotation [4-6] and treated with common pyrometallurgical processes. Today, about 80-85% of the copper produced in the world is obtained by classical pyrometallurgical processes that are applied to relatively rich and less complex ores and concentrates [7].

Industrial processes related to the hydrometallurgical treatment of sulphide minerals, which include processes and operations in aqueous solutions, will be significantly more represented in the future due to the possibility of processing the increasingly poor primary raw materials [8-11] and complex sulphide concentrates [12-14]. The emission of harmful gases into the atmosphere does not accompany these processes.

The existing commercial heap leaching processes are applied to raw materials in which primary minerals are partially converted to secondary sulphide and oxide minerals. Although a great number of processes for obtaining copper from chalcopyrite ores have been studied and developed, they have yet to be successfully applied to chalcopyrite on an industrial scale [2, 10, 15, 16]. The slow leaching reaction of chalcopyrite is one of the main and limiting factors in copper production in industrial conditions [16, 17].

Unlike many other copper minerals, chalcopyrite is very inert to chemical and microbiological oxidation due to its special crystal and electronic structure [18-20]. Chalcopyrite has a crystal structure in which iron and copper ions are in tetrahedral coordination with sulphur [21]. The bond in chalcopyrite is covalent with atomic fluctuations between the two ionic conditions $\text{Cu}^+\text{Fe}^{3+}\text{S}_2^{2-}$ and $\text{Cu}^{2+}\text{Fe}^{2+}\text{S}_2^{2-}$ [22]. The reason for its refractory nature is the formation of a solid passive layer on its surface, which limits the contact of the mineral with the leaching agent and the diffusion process [23, 24] and leads to decreasing metal extraction. For this reason, finding new ways to improve the dissolution rate and the more efficient extraction of metals from chalcopyrite is still a topical issue.

Iron (III) and copper (II) ions are used as oxidants for chalcopyrite leaching in sulphate and chloride media. Many studies have shown that this mineral is very unreactive at atmospheric leaching conditions, and at moderate temperatures, around 60 °C [1, 7, 16, 25-29]. However, the corrosive nature of iron (III) chloride and the slow leaching reaction

of chalcopyrite with iron (III) sulphate have also influenced research to focus on the use of other oxidizing agents in the leaching process. In addition to the above-mentioned oxidants, research has been done, and other oxidizing agents have been used, such as hydrogen peroxide [30-33], dichromate ions [34], chlorate ions [35], silver ions [36, 37], ozone [38], nitrate ions [39, 40]. The application of microwaves [41, 42], mechanical and chemical activation [43] and organic compounds [44, 45], and the use of silver ions have also been studied in order to develop the technological processes for obtaining copper that could satisfy increasingly stringent technological, economic and environmental criteria. These studies, which are part of numerous references on the behaviour of chalcopyrite in acidic solutions, have shown that there is extensive knowledge of chalcopyrite leaching reactions. However, many ambiguities have been revealed in the behaviour of chalcopyrite, which requires that this issue has to be further studied.

This paper aims to present the results of the chemical leaching of chalcopyrite in acid sulphate and chloride media in the presence of various oxidants. Here is a brief overview of the mechanism and kinetics of chalcopyrite dissolution in different media, types of reaction products, and achieved extractions of metals under different oxidation conditions (concentration of leaching agent and oxidant concentration, temperature, agitation, the redox potential of the solution), etc.

2. Aqueous oxidation and leaching of chalcopyrite

2.1. Formation of a passive layer on the chalcopyrite surface

The slow leaching reaction of chalcopyrite is one of the main and limiting factors for obtaining copper from this mineral in the hydrometallurgical process. Most authors agree that the slow leaching kinetics of chalcopyrite is a consequence of the formation of reaction products on the mineral's surface [3, 7, 46-48]. The layers of reaction products can act as a barrier for further dissolution, i.e. they contribute to the formation of surface passivation. The nature of these layers is still the subject of numerous research and discussions, based on which different interpretations occur [24].

The nature of the passive layer and the mechanism of its formation have not been completely explained. However, it is usually assumed that elemental sulphur, metal-deficient sulphides, polysulphides, iron compounds, or jarosite, create a passive layer on the chalcopyrite surface [24, 49-58]. The differences between certain hypotheses, regarding the nature and composition of reaction products on the surface of chalcopyrite, partly occur due to different proposed kinetic expressions for explaining changes in leaching products caused by the application of different oxidants. On the other hand, different stages occur in the oxidative leaching process that are difficult to be distinguished. For this reason, the products formed at the end of the leaching process are proposed as those responsible for passivity, and spectroscopic techniques determine them.

Some researchers claim that the formation of elemental sulphur on the surface of CuFeS_2 slows down the dissolution of this mineral [51]. *Parker et al.* [52] rejected the assumption that the sulphur layer is the cause of the slow dissolution rate of chalcopyrite and suggested that metal deficient polysulphide with semiconductor properties leads to a decrease in the dissolution rate. *Klauber et al.* [49] investigated types of sulphur formed on CuFeS_2 surface during chemical leaching in an acidic medium using X-ray photoelectron spectroscopy. The results showed that sulphur is the main surface product that occurs during acid leaching with iron (III) ions. Another relevant leaching product

on CuFeS₂ surface is disulphide ion S₂²⁻. However, *Parker et al.* [59] claims that only the following forms of sulphur were detected on the surface of the leached chalcopyrite: S²⁻, S₂²⁻, S⁰, and SO₄²⁻.

Harmer et al. [54] used X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (TOF-SIMS), and scanning electron microscopy (SEM) to identify the presence of passivating layers formed during leaching of chalcopyrite in perchloric acid. These authors proposed that the formation of passivation layers during chalcopyrite leaching takes place in three stages. The first stage of oxidation involves the release of copper and iron ions into solution and polymerization of monosulphide S²⁻ to polysulphide S_n²⁻. In the next reduction step, there is no release of cations into the solution, but there is a change in the surface of the chalcopyrite. It has been observed that S_n²⁻ polysulphide, as well as other short-chain polysulphides, are reduced to the formation of elemental sulphur. The further release of the cations follows the final stage of oxidation.

Hackl et al. [58] found that elemental sulphur is sufficiently porous and not limit the diffusion of reactants/reaction products. The passive layer consists of copper sulphide.

In electrochemical studies of chalcopyrite dissolution in a mixed chloride-sulphate medium, it was found that surface passivation does not occur due to the formation of an elemental sulphur layer. It was determined that passivation layers consist of metal-deficient polysulphides (Cu_{1-x}Fe_{1-y}S_{2-z}) [50, 57]. In previous studies, *Jones and Peters* [60] identified covellite (CuS) as an intermediate product in the anodic dissolution of chalcopyrite. Later, *McMillan et al.* [61] noticed the formation of a product layer containing covellite and elemental sulphur during the anodic dissolution of chalcopyrite in chloride media. *Parker et al.* [52] noticed the formation of blue covellite on chalcopyrite surface that is anodically oxidized at a potential of 0.4 V in acid chloride solutions. The authors assumed that CuS could be a product of the reaction of CuCl₂⁻ ion with sulphur or a product of the reduction process involving the formation of H₂S in acidic HCl solutions. In electrochemical studies of chalcopyrite oxidation, *Yin et al.* [62] determined that the nature of the passive layer depends on pH value and potential. In strongly acidic solutions, a passive layer consisting of CuS₂ (at lower potentials) or elemental sulphur (at higher potentials) is formed on the chalcopyrite surface.

Extensive studies have been conducted on the chemistry of jarosite, where the formation and deposition of jarosite on chalcopyrite surface are associated with the long leaching time [51]. *Stott et al.* [63] assumed that the precipitation of jarosite, on the mineral surface during leaching, leads to a decrease in the dissolution rate. They assumed that the precipitation of Fe (III) ions in the form of iron (III) hydroxide could completely cover the chalcopyrite surface and prevent further dissolution. *Parker et al.* [59] used X-ray photoelectron spectroscopy to analyze the surface reaction intermediates and products of oxidative chalcopyrite leaching in solutions of iron (II) and iron (III) sulphate and confirmed the formation of jarosite.

Cordoba et al. (2008) associate jarosite precipitation with the passive behavior of chalcopyrite [1]. The formation of jarosite also depends on the temperature, pH, and potential of the solution. The mechanism of jarosite formation during leaching may be presented with the following equation (1) [55]:

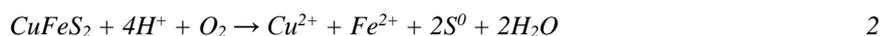


The rate of jarosite formation increases with the increase in temperature, whereas the rate is slower at temperatures below 60 °C. The pH ranges from 1 to 3, in which jarosite is mostly formed, is "ideal" for bioleaching regarding microorganism activity.

2.2. Leaching of chalcopyrite in sulphate solutions

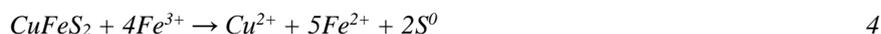
The leaching of chalcopyrite was mostly studied in the sulphate media due to the simplicity and cost of the process. However, the problem that is mainly emphasized in the largest number of papers that studied chalcopyrite oxidation refers to the slower chalcopyrite dissolution rate under atmospheric leaching conditions, resulting in inefficient copper extraction [1, 7, 16, 29]. It can be said that the chalcopyrite dissolution rate in an acidic environment depends on a large number of parameters, including the concentration and type of oxidants, agitation rate, particle size, temperature, and acid concentration.

Chalcopyrite dissolves faster in the presence of oxidants. Oxidative leaching of chalcopyrite in the sulphate medium may take place under the influence of the so-called natural oxidants (O_2 , Fe^{3+} , bacteria) and may be performed under pressure. The chemistry of chalcopyrite dissolution in the sulphuric acid/oxygen system may be represented with the following reactions (2 and 3) [53]:



2.2.1. Sulphuric acid – Fe (III) ions

The leaching of chalcopyrite in sulphuric acid solution was most studied with Fe (III) ions as an oxidant. The mechanism of chalcopyrite dissolution in the presence of Fe (III) ions is represented with the following reactions (4 and 5):



In reactions (4) and (5), sulphide sulphur is oxidized to elemental sulphur and sulphate, respectively. The reaction is initially fast and gradually slows down [49]. The reaction rate depends on the temperature and specific surface area of particles, provided that agitation is sufficient and that the pH value of the medium is such that it does not allow the hydrolysis and/or oxidation of iron ions [25].

Dutrizac [51] found that in solution of iron (III) sulphate, the leaching of chalcopyrite is incomplete and slow, and over 90% of oxidized sulphide sulphur is in the elemental form. Author leached chalcopyrite (size class -14+10 μm) in $Fe_2(SO_4)_3$ solution at 90°C and found that a time of 50 hours was required for reaching 90% of copper extraction. A layer of sulphur was detected on mineral particles, which increased with time and caused stronger passivation of chalcopyrite. *Butinelli et al.* [64] noticed that chalcopyrite still leaches slowly, even if elemental sulphur is removed during the leaching process with an organic solvent.

Reaction mechanisms of oxidation of chalcopyrite in iron (III) sulphate solution are still the subject of numerous studies, and different interpretations of kinetic data may

be found in literature [21, 24, 29, 65]. The concentration of iron (III) ions was found to affect the chalcopyrite dissolution rate, whereas oxidants have more effect on the lower concentrations of iron ions [1]. Iron (III) ions have a negligible effect on higher concentrations. *Hirato et al.* [66] found that chalcopyrite dissolution improved when iron (III) sulphate concentrations increased from 0.001 to 0.1 M. These authors found that concentrations of Fe^{3+} and FeHSO_4^{2+} ions increase when total iron concentrations increase, up to the 0.1 M. Above this concentration, iron appears in the form of FeSO_4^+ . The authors concluded that the presence of Fe^{3+} and FeHSO_4^{2+} ions is important for the dissolution of chalcopyrite in the sulphate media.

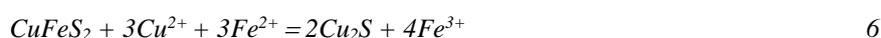
Howard and Crundwell [67] determined that the chalcopyrite dissolution rate in sulphate solution increases with increasing Fe (III) ion concentration from 0.001 to 0.05 M. Further increase in Fe (III) concentration up to 0.5 M leads to a decrease in the leaching rate. *Kaplun et al.* [68] and *Li et al.* [69] found that Fe (III) concentration of 4–8 mmol/dm³ in the sulphuric acid solution leads to an increase in dissolution rate of chalcopyrite at the initial oxidation stage and that further dissolution results in a decrease of oxidation rate.

Bogdanović et al. [70] studied the leaching of chalcopyrite ore from the Bor deposit and found that the concentration of iron (III) (1 g/dm³ to 20 g/dm³ of iron (III) ions) does not affect the chalcopyrite leaching rate, whereas there is sufficient amount of iron ions in the leaching process, which builds up in the process of decomposition of iron oxide minerals by acid. This finding is very important because it indicates that the hydrometallurgical treatment of ore from the Bor deposit does not require adding a new source of iron ions.

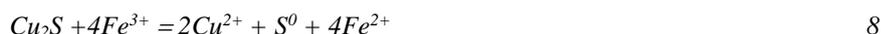
The chalcopyrite dissolution rate is also affected by the pH of the solution, whereas the acid prevents the hydrolysis reaction and precipitation of iron (III) salts. However, chalcopyrite was found to dissolve poorly at low pH values (pH < 1.0), and that a layer of iron-deficient chalcopyrite is created on the mineral surface, which results in chalcopyrite passivation [27]. At higher pH values, chalcopyrite is more easily oxidized by oxygen/iron (III) present in leaching solutions. *Cordoba et al.* [1] found that with a decrease in pH value of the solution, the chalcopyrite dissolution rate decreases, and chalcopyrite is not oxidized by iron (III) ions under these conditions, rather by FeSO_4^- ions.

Iron (II) ions are created as a reaction product in the process of chalcopyrite leaching with $\text{Fe}_2(\text{SO}_4)_3\text{--H}_2\text{SO}_4$. Therefore, it is necessary to know the influence of FeSO_4 on the chalcopyrite leaching rate. Most of the studies have shown that iron (II) ions affect the leaching of chalcopyrite only as a source of iron (III) ions and that their concentration should be reduced as much as possible to increase the leaching rate. However, *Hiroysshi et al.* [36, 71, 72] report that FeSO_4 extracts copper more efficiently than $\text{Fe}_2(\text{SO}_4)_3$. These authors showed that the oxidation of chalcopyrite with dissolved oxygen and/or iron (III) ions might be accelerated with high concentrations of iron (II) ions in sulphuric acid solutions and in the presence of high concentrations of copper (II) ions [36, 75, 76]. Based on this, the authors proposed a reaction model according to which the oxidation of chalcopyrite takes place in two reaction stages:

- Stage I represents a reduction of chalcopyrite to chalcocite (Cu_2S) in the presence of Fe(II) and Cu(II) ions (reaction 6):



- Stage II involves oxidation of chalcocite (Cu_2S) to Cu (II) ions and elemental sulphur with dissolved oxygen and/or Fe (III) ions (reactions 7 and 8):



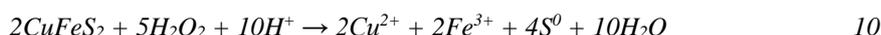
Based on the presented model, the authors explain that the redox potential of the solution controls the extraction of copper, and it is a function of the concentration of Cu (II) and Fe (II) ions in the solution.

2.2.2. Sulphuric acid - strong oxidants

The presented results of chalcopyrite leaching in sulphate solutions using Fe (III) ions and/or dissolved oxygen as oxidants indicate that the obtained extraction values are not high, especially if oxidation takes place under the atmospheric leaching conditions. Therefore, chalcopyrite oxidation was performed using stronger oxidizing agents, which, due to higher oxidation potentials, can more effectively influence the kinetics of the dissolution process. For this purpose, the following oxidizing agents were examined: hydrogen peroxide [30-33], ozone [38], dichromate ions [34], chlorate ions [35], persulphate ion [73], etc.

2.2.2.1. Sulphuric acid -hydrogen peroxide

The high oxidation-reduction potential of peroxide (1.77 V, SHE) made this reagent widely used in the oxidation of almost all sulphide minerals. The dissolution of chalcopyrite with hydrogen peroxide in the acidic medium is based on the following reactions (9 and 10) [74].



From the presented dissolution mechanism of chalcopyrite, it can be observed that part of the sulphide sulphur is transformed into sulphate (reaction 9), whereas, according to reaction (10), sulphide sulphur is oxidized to the elemental form. The oxidizing ability of hydrogen peroxide in the acidic medium is based on the following reduction reaction (11):

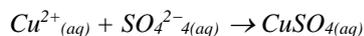


In very dilute solutions, hydrogen peroxide dissociates to reactive radicals according to the following reaction (12):



The resulting $\text{HO}^-_{2(aq)}$ peroxide radical reacts with the sulphide ion according to reaction (13), releasing elemental sulphur, whereas copper ions react with sulphur according to the following reaction (14):





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General observations concerning the achieved results of chalcopyrite oxidation in the presence of hydrogen peroxide show that with increasing hydrogen peroxide concentrations, the chalcopyrite oxidation rate in sulphuric acid solutions increases [14, 30, 77]. Based on the obtained results of the leaching of chalcopyrite with hydrogen peroxide (0.1–6 M H₂SO₄; 10–30% H₂O₂; temperature 303–353 K; stirring speed 300, 400 and 700 min⁻¹; particle size 100, 150, 200 and 300 μm) *Adebayo et al.* [30] determined that the reaction orders were 0.77 and 1.45 concerning the concentration of H₂SO₄ and H₂O₂, respectively. It was found that there is a linear relationship between the reaction rate constant and the inverse diameter of particles. The oxidation kinetics was found to follow a shrinking core model with the surface chemical reaction as the rate controlling step.

Increase of the H₂O₂ concentration (0.1–5 M) accelerates chalcopyrite oxidation in a solution of sulphuric acid (0.5–3 M H₂SO₄; 0.1–5 M H₂O₂; temperature 40 °C; size class –0.063+0.053 mm; leaching time 180 min) [31]. The reaction order with respect to the sulphuric acid concentration is 0.3. The reaction order was also determined with respect to the concentration of hydrogen peroxide, and it is approximately 1 (0.98).

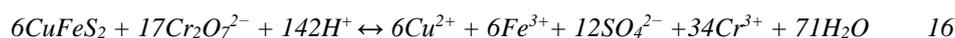
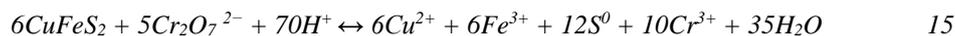
The obtained activation energy value in the system of sulphuric acid - hydrogen peroxide of 39 kJ/mol [30] indicates that the oxidation process is under chemical control. The higher activation energy of 60 kJ/mol was obtained by *Antonijević et al.* [31]. The authors indicate that the oxidation process is under chemical control.

However, a problem that most researchers point out in chalcopyrite oxidation by hydrogen peroxide is that rapid exothermic decomposition of hydrogen peroxide occurs at elevated temperatures (mostly above 60 °C). In order to avoid the rapid decomposition of hydrogen peroxide, *Mahajan et al.* [74] used ethylene glycol in leaching of chalcopyrite (1 M H₂SO₄–0.26 M H₂O₂). The addition of ethylene glycol at 65 °C increases the copper extraction from 20% to 60% during 240 min of leaching. The problem of rapid decomposition of hydrogen peroxide is also pointed out by other authors [75]. *Agacayak et al.* [75] were carried out leaching experiments (temperature in the range from 30 to 70 °C, 2 M H₂O₂) and obtained the copper extraction above 80% for a period of 90 min of leaching at 40 °C. During 90–240 min of leaching, copper extraction reaches stable values, whereas with an increase in temperature in the range of 50–70 °C, copper extraction decreases compared to the obtained values at lower temperatures [75]. These results indicate that hydrogen peroxide more easily decomposes at higher temperatures, which has been confirmed by other authors as well [31, 74].

Solis–Marcial and Lapidus studied the sulphuric acid–hydrogen peroxide–ethylene glycol system for chalcopyrite oxidation [76]. The authors performed chemical and electrochemical investigations. Chalcopyrite concentrate was used in leaching experiments under the following conditions: 0.5–2.5 M H₂SO₄; H₂O₂ concentration 0.7 M, 1.4 M, and 2.1 M; particle size ~ 165 μm). The results showed that ~ 65% of copper was leached for 60 minutes when ethylene glycol was added to the solution (1.25 M H₂SO₄–2.1 M H₂O₂).

2.2.2.2. Sulphuric acid - potassium dichromate

Oxidative dissolution of chalcopyrite by dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) in an acidic medium lead to the formation of elemental sulphur or sulphate, according to the following reactions (15 and 16) [34, 77, 78]:



Reduction of dichromate ions takes place in acidic solutions (reaction 17):



From the presented dissolution mechanism, it can be seen that sulphide sulphur oxidizes to the elemental sulphur and sulphate, whereby the authors consider that reaction (15), in which elemental sulphur is formed, is more dominant.

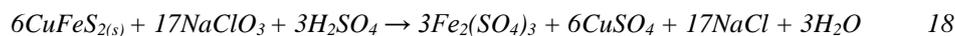
Aydogan et al. [34] investigated the kinetics of chalcopyrite leaching in the acidic solution of potassium dichromate. It was determined that the reaction rate increases with increasing sulphuric acid concentration, dichromate ion concentration, temperature, and decreasing particle size. During the leaching period of 150 minutes at 90 °C, the copper extraction of 80% was achieved (particle size below 75 µm). The diffusion model can describe the dissolution kinetics through a porous sulphur layer. The activation energy of this dissolution process was 24 kJ/mol.

However, the results of the previous studies showed that the chalcopyrite oxidation rate does not depend on the concentration of potassium dichromate. Chalcopyrite oxidation rate depends on the concentration of sulphuric acid, whereas the reaction order, concerning acid concentration, ranges from 0.8 to 0.92 [77]. Addition of chloride ions in the form of KCl (0.014, 0.028, and 0.056 M) in the solution (0.2 M $\text{K}_2\text{Cr}_2\text{O}_7$ and 0.5 M H_2SO_4 , temperature 313 K) does not increase chalcopyrite oxidation. On the other hand, with the addition of larger amounts of chloride ions (0.141, 0.197, and 0.395 M), the rate of chalcopyrite oxidation is decreased. Also, Antonijević [79] examined chalcopyrite oxidation by sodium dichromate in perchloric acid. It was found that chalcopyrite oxidizes rapidly at temperatures higher than 60 °C, whereas activation energy is 77 kJ/mol. The reaction order with respect to the perchloric acid concentration was 1.35, and the concentration of dichromate ions does not affect the chalcopyrite oxidation rate.

Based on the obtained values of activation energy in the acidic solution of potassium dichromate, it can be said that two regimes can control the chalcopyrite dissolution process: diffusion [34] and chemical [77].

2.2.2.3. Sulphuric acid - chlorate ions

The reduction potential of chlorate ion is 1.451 V, and it represents a strong oxidant that has found application in the oxidation of chalcopyrite. This oxidant was examined by Kariuki et al. [35] in the chalcopyrite leaching process in sulphuric acid solution. The experiments were carried out under the following conditions: 10 g/dm³ H_2SO_4 , up to 3 g NaClO_3 , temperature 45–200°C. The reaction of chalcopyrite dissolution in such system is presented by the following reaction (18):



Obtained results show that almost all copper from 2 g of chalcopyrite concentrate can be leached in 30 ml of solution ($70 \text{ g/dm}^3 \text{ NaClO}_3$ and $10 \text{ g/dm}^3 \text{ H}_2\text{SO}_4$) for a period of 2 h at a temperature of 165°C . In addition to the sulphuric acid solution, chlorate ions have also been used in the oxidation of chalcopyrite in the hydrochloric acid solution [28].

2.2.2.4. Sulphuric acid - persulphate ion

The advantage of using persulphate ion ($\text{S}_2\text{O}_8^{2-}$) is reflected in the possibility that it can be obtained from sulphuric acid in the electrochemical process [80]. Persulphate ion has a high oxidation-reduction potential of 2.123 V. *Dakubo et al.* [73] investigated leaching of chalcopyrite ore and concentrate in sulphuric acid at $\text{pH} = 2$ with $50 \text{ g/dm}^3 \text{ Na}_2\text{S}_2\text{O}_8$. It was determined that up to 50% of Cu could be leached from the chalcopyrite concentrate at a temperature of 40°C , and that increased particle size reduces copper extraction. With finer particles of chalcopyrite concentrate ($25 \mu\text{m}$), up to 70% of copper was extracted, whereas copper extraction of around 25% was achieved with a particle size of $125 \mu\text{m}$. Activation energy of leaching process of chalcopyrite ore in the presence of persulphate ($\text{pH} = 2$; $10 \text{ g/dm}^3 \text{ Na}_2\text{S}_2\text{O}_8$, 80% class - $75 \mu\text{m}$, temperature 23°C) was 41 kJ/mol [73].

Table 1 shows activation energy values obtained in experiments of chalcopyrite leaching in sulphate solutions in the presence of different oxidants.

Table 1. Activation energy values of chalcopyrite leaching in the sulphate medium.

Chalcopyrite sample	Solution	Temperature, $^\circ\text{C}$	Activation energy, kJ/mol	Process that determines the reaction rate	Bibliography
concentrate	H_2SO_4 - $\text{Fe}_2(\text{SO}_4)_3$	60 - 90	83.7	electrochemical control	[56]
concentrate	H_2SO_4 - $\text{Fe}_2(\text{SO}_4)_3$	45 - 100	75	diffusion control	[25]
crystal	H_2SO_4 - $\text{Fe}_2(\text{SO}_4)_3$	50 - 78	88	chemical control	[66]
	H_2SO_4 - $\text{Fe}_2(\text{SO}_4)_3$	55 - 85	in the presence of Fe(III)		[68]
			21±5 83±10 (through Cu)	mixed control	
			76±10 (through Fe)	chemical control	
			in the absence of Fe(III)		
			80±10 (through Cu) 84±10 (through Fe)	chemical control	
crystal	H_2SO_4 - $\text{Fe}_2(\text{SO}_4)_3$	50 - 90	76.5 79.5	-	[41]
ore	H_2SO_4 - $\text{Na}_2\text{S}_2\text{O}_8$	23 - 45	41		[73]
concentrate	H_2SO_4 -NaCl- O_2	85 - 100	76	-	[86]

Chalcopyrite sample	Solution	Temperature, °C	Activation energy, kJ/mol	Process that determines the reaction rate	Bibliography
concentrate	H ₂ SO ₄ -K ₂ Cr ₂ O ₇	30 - 80	48 - 54	chemical control	[77]
natural sample	H ₂ SO ₄ -K ₂ Cr ₂ O ₇	25 - 60	50	chemical control	[85]
concentrate	H ₂ SO ₄ -H ₂ O ₂	25 -50	60	chemical control	[31]
concentrate	H ₂ SO ₄ -H ₂ O ₂	30-80	39	chemical control	[30]
natural sample	H ₂ SO ₄ -H ₂ O ₂ -ethylene glycol	25-75	30	chemical control	[74]
concentrate	H ₂ SO ₄ -CuCl ₂	55 - 90	24.4 – 29.4	diffusion control	[84]
crystal	H ₂ SO ₄	35 - 68	130.70	mixed control	[82]
concentrate	H ₂ SO ₄	48 - 85	78	chemical control	[83]
concentrate	H ₂ SO ₄ -H ₂ O ₂	25 - 45	80	diffusion control	[14]

2.3. Leaching of chalcopyrite in chloride solutions

The application of chloride solutions in the hydrometallurgical processing of sulphide concentrates is very important [16]. By comparing the kinetics of the leaching process in the chloride and sulphate medium, it was determined that chalcopyrite leaches faster in the chloride medium. The leaching of chalcopyrite in the chloride medium can be carried out at atmospheric pressure and room temperature, and, at the same time, there is a possibility of reuse of the reagent in the leaching process. Significant advantages of the application of chloride systems are: a) high solubility of copper and iron; b) faster oxidation of Fe (II) ions to Fe (III) ions; c) formation of a more porous sulphur layer as a reaction product that allows the diffusion of reactants to the reaction surface, and d) faster kinetics of chalcopyrite leaching compared to sulphate systems [16, 87].

Although many processes for obtaining copper from concentrates have been studied and developed [81] not all processes have come to life at the industrial level due to the following disadvantages and limitations: a) corrosive effect of chloride, which requires the use of expensive construction materials for reactors; b) the need for fine grinding for processes conducted under atmospheric pressure; c) co-leaching of multiple elements present in concentrates which require additional treatment of the solution and e) difficult electrolysis of high-quality copper from the chloride solution.

In chloride solution, Fe (III) ions in the form of Fe (III) chloride and Cu (II) ions in the form of Cu (II) chloride are most often used as oxidants. It is considered that chalcopyrite leaching is significantly more efficient in chloride solutions where Cu (II) ions are present as an oxidant rather than in sulphate solutions where Fe (III) ions are present as an oxidant [90].

The mechanism of chalcopyrite dissolution in chloride solutions is described through the following reactions (19–21) [17]:



The redox potential of $\text{Cu}^{2+}/\text{Cu}^+$ couple is significantly higher in chloride than in sulphate solution. Also, the redox potential of $\text{Cu}^{2+}/\text{Cu}^+$ is higher than the redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in saturated chloride solution. This increase in redox potential ($\text{Cu}^{2+}/\text{Cu}^+$) is a consequence of a very strong complex of Cu (I) ions with chloride ions. The dominant chloride complexes of copper and iron that occur in a strong chloride solution are: CuCl_3^{2-} , CuCl^+ , CuCl_2 , FeCl_2 , and FeCl_2^+ [90]. Winand [91] achieved higher copper extractions by leaching chalcopyrite in the presence of chloride ions due to the formation of a complex of copper with Cl^- ions, which led to the higher solubility of copper in the Cu (I)–Cu (II)– Cl^- system.

2.3.1. Fe (III) chloride solutions

The major reaction product of chalcopyrite leaching in Fe (III) chloride solution is elemental sulphur (reactions 19–21). Habashi [92] found that the leaching rate of chalcopyrite with Fe (III) chloride shows a parabolic dependence caused by the progressive formation of an elemental sulphur layer at the solid-liquid interface, where this layer is not completely compact and can be removed by mixing the solution. In Fe (III) chloride solution, the dissolution rate is independent of temperature in the range of 45–100°C, and it is independent of acid concentration as well, but directly proportional to the surface area of chalcopyrite particles. The obtained activation energy in this chloride solution (42 kJ/mol) is lower than the energy obtained in the sulphate solution (0.1 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.3 M H_2SO_4) which is 75 kJ/mol which indicates to a faster oxidation reaction in chloride solution [25].

In the FeCl_3 –HCl solution (0–2 M FeCl_3 , 0–3 M HCl, leaching time 0–90 h), it was found that more than 95% of sulphur and less than 5% of sulphate are formed [88]. The surface of chalcopyrite particles is quickly covered with a layer of elemental sulphur during leaching. The morphology of the resulting sulphur layer does not depend on the concentration of Fe (III) chloride or hydrochloric acid. However, other authors [94, 95] determined that the dissolution rate of chalcopyrite depends on the concentration of Fe (III)–chloride, and that it is independent of the concentration of Fe (II)–chloride. The reaction order with respect to the concentration of Fe (III)–chloride was 0.5.

The results of the effect of the concentration of Fe(III) ions (0.02–0.50 M FeCl_3 in a solution of 1 M HCl and 3 M NaCl) and the effect of the concentration of NaCl (0–2 M NaCl in a solution of 0.2 M HCl and 0.2 M FeCl_3) on the kinetics of chalcopyrite dissolution indicated that electrochemical reactions on the chalcopyrite surface determine the process of chalcopyrite leaching [96]. The following anodic and cathodic reactions take place in this system (22-26):



It was found that linear kinetics occur and that the reaction rate depends on the concentration of Fe (III) ions (reaction order is 0.5). The reaction rate increases with increasing NaCl concentration to 1 M. In a solution of 1 M HCl and 3 M NaCl, the activation energy is 83 kJ/mol, while in a solution of 0.2 M HCl, the value of activation energy is 62 kJ/mol [96].

Baba et al. [97] examined the dissolution kinetics of chalcopyrite in hydrochloric acid solution. The effect of temperature (27–80°C), the effect of acid concentration (0.1–8.42 M HCl), and the effect of particle size (classes –90 + 75 µm, –112 + 90 µm and –300 + 112 µm) on chalcopyrite dissolution were investigated. The dissolution rate increase with increasing HCl concentration and temperature and with decreasing particle size. Under optimal leaching conditions (4 M HCl, 80°C, size class –90 + 75 µm, leaching time 120 minutes), about 91.33% Cu was leached. The dissolution process is under diffusion control with an activation energy of 31.6 kJ/mol. The reaction order respect to HCl concentrations is 0.42.

2.3.2. Cu (II) chloride solutions

In addition to Fe (III) chloride, the second most commonly used oxidant in chalcopyrite leaching is Cu (II) chloride [89, 90, 98, 99]. It is considered that the dissolution of chalcopyrite in acidic Cu (II) solutions take place according to reaction (27) whereby a copper complex is formed CuCl_3^{2-} :



It was determined that Cu (II) ions do not affect the dissolution rate of chalcopyrite in the concentration range 0.79–1.46 M, and Cu (I) ions in the concentration range 2.82–6.21 M (at 90°C). The ratio of Cu (II)/Cu (I) concentrations should be less than 1.9 in order for reaction (27) to be possible from a thermodynamic point of view [90]. As the concentration of copper in the solution increases, the stability of Cu (II) ions decreases, and the formation of copper complexes, $[\text{CuCl}^+]$ and $[\text{CuCl}_2^-]$, mainly occurs. The obtained complex $[\text{CuCl}_2^-]$ is more stable at 90°C than at 25°C, while the changes in the stability of the obtained complexes in the temperature range of 25–90°C are small.

High copper extraction values were achieved by oxidation of chalcopyrite in chloride solutions. For example, *Padilla et al.* [100] investigated the leaching process of chalcopyrite in a CuCl_2 –NaCl– O_2 solution at atmospheric pressure and temperature up to 105°C and obtained 93% of copper (size class –400 mesh, 2 h of leaching). As the flow of oxygen in the solution increases to 0.1 l/min, the dissolution rate also increases. Also,

it is pointed out that the rate of agitation does not have a significant effect on the dissolution rate, while the concentration of chloride up to 4 M affects the dissolution kinetics.

Skrobjan et al. [101] also found that with increasing NaCl concentration, metal extraction from chalcopyrite concentrate also increases. No presence of a solid layer of the product was observed on the chalcopyrite particles, which would affect the reduction of the dissolution rate.

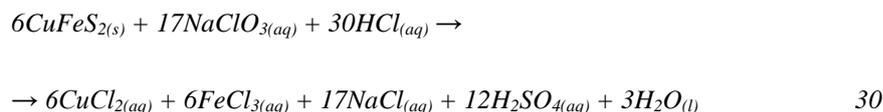
Velasquez – Yevenes et al. [98] leached four concentrates of chalcopyrite in chloride solutions with Cu (II) ions and dissolved oxygen (0.2 M HCl and 0.5 g/dm³ Cu (II), 5–15 mg/l O₂, temperature 35°C, agitation speed 800 min⁻¹) and determined that the oxidation rate of chalcopyrite increases significantly in the potential range from 550 mV to 620 mV (SHE). The authors found that the presence of dissolved oxygen in the system contributes to more efficient copper extraction. However, although dissolved oxygen has a positive effect on increasing copper extraction, excess oxygen is undesirable because it can lead to an increase in redox potential, and thus to surface passivation. At potentials above 630 mV, the dissolution rate is low. In the continuation of the research of the mentioned authors [99] in a solution of HCl (0.2 M HCl + 0.008 M Cu (II); temperature 35°C), it was shown that a low concentration of Cu (II) ions contributes to the acceleration of the dissolution kinetics of chalcopyrite, while a further increase in the concentration of Cu (II) ions does not affect the increase in the oxidation kinetics. *Nicol et al.* [102] also found that a low concentration of Cu (II) ions in a solution (0.1 g/l) leads to an increase in copper extraction but that higher concentrations of Cu (II) ions do not have a significant effect on the reaction rate. The addition of Cu (II) ions leads to the formation of an intermediate product, Cu₂S, at lower potentials (about 560 mV, SHE), which leads to an increase in the reaction rate because of the resulting Cu₂S oxidizes much faster than CuFeS₂ [103].

Recent research by *Turan et al.* [104] shows that chloride ions contribute to the oxidation of chalcopyrite in ammonium persulphate solution, which acted as an oxidizing agent. In such a leach system, the reactions (28 and 29) take place and released Fe (II) ions oxidize to Fe (III) ions, while sulphur is oxidized to sulphate.

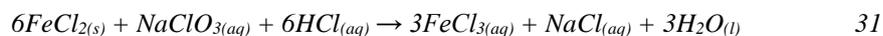


An increase in the concentration of NaCl and (NH₄)₂S₂O₈ was found to have a positive effect on metal extraction. It should be emphasized that with increasing temperature up to 60°C, an increase in metal extraction in solution was observed, while above this value, metal extraction decreases, most likely due to the decomposition of ammonium persulphate. Under optimal leaching conditions (150 g/l NaCl, 250 g/l (NH₄)₂S₂O₈, 60°C, liquid/solid = 250 ml/g, agitation rate 400 min⁻¹, leaching time 180 minutes) 75% of Cu and 80% of Fe were leached. In contrast, in the absence of chloride ions, only 14% of Cu and 21% of Fe (250 g/l (NH₄)₂S₂O₈, 60°C, liquid/solid = 10 ml/g, agitation rate 400 min⁻¹, leaching time 200 minutes) were leached. The positive influence of chloride ions on chalcopyrite leaching was also observed by other researchers [105].

Chlorate was also used for the oxidation of chalcopyrite concentrates in chloride solutions [28]. In a solution of hydrochloric acid and sodium chlorate, chalcopyrite is dissolved according to reaction (30):

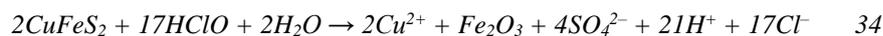
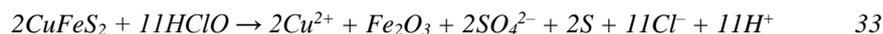


As a product of reaction (30), FeCl_3 is formed, ie the formed Fe (III) ions represent an oxidizing agent. Therefore, alternating oxidation and reduction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in solution takes place via the following reactions (31 and 32):

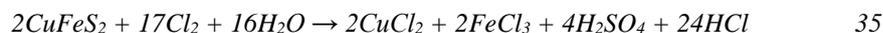


In the HCl – NaClO_3 system, about 45% of Cu (1 M HCl + 0.5 M NaClO_3) was leached after 5 h, while about 65% of Cu was leached in a solution of 1 M HCl + 1 M NaClO_3 . The dissolution rate of chalcopyrite increases with increasing concentration of HCl and NaClO_3 , whereby both, particle size (size classes: -0.1+0.074 mm, -0.074+0.043 mm and -0.043+0.038 mm) and temperature (from 25 °C to 85°C), affect the dissolution rate of chalcopyrite. X-ray diffraction analysis indicated that sulphide is oxidised to sulphate at temperatures less than or equal to 65°C, and it is oxidised to elemental sulphur at 85°C in the leaching process [28].

Shiers et al. [106] investigated the oxidation of chalcopyrite concentrate (size class -53+35 μm) and chalcopyrite ore (size class - 200 μm) in hypochlorous acid solution, sodium chlorate and potassium nitrate with and without Fe (III) ions. Leaching of chalcopyrite in hypochlorous acid solution, at pH 4-6, takes place according to the following reactions (33 and 34):



At slightly higher pH, hypochlorous acid decomposes to Cl_2 , which causes reduction of the selectivity of leaching and leads to the dissolution of both copper and iron (reaction 35)



The obtained results indicate that hypochlorous acid is the most aggressive medium for chalcopyrite leaching. The extraction of copper reached ~ 100% during the leaching of chalcopyrite concentrate (1-5 h of leaching at room temperature at a hypochlorous acid concentration of 0.3-0.4 M). Using chlorate as an oxidant, it was shown that 72% of Cu (0.4 M NaClO_3 + 0.1 M $\text{Fe}(\text{NO}_3)_3$) was extracted. In the nitrate solution after 168 h of leaching, 35-40% Cu was extracted. On the other hand, by leaching chalcopyrite ore, it was determined that the most suitable leaching medium is a nitrate

solution (0.6 M KNO_3 + 0.1 M FeCl_3) where 92% of Cu is achieved, followed by the system of $\text{ClO}_3^-/\text{Fe}(\text{NO}_3)_3$ with a 67% of Cu leached (50°C, 120 h) and finally HClO with 56% of Cu (30°C, 24 h). All examined oxidants are significantly more efficient for chalcopyrite leaching than Fe (III) sulphur - by leaching with $\text{Fe}_2(\text{SO}_4)_3$ during 168 h at a temperature of 50°C only 15% of Cu was extracted.

Ikiz et al. [107] examined the oxidation of chalcopyrite in hypochlorous acid solution. Under optimal leaching conditions (concentration of HClO = 0.2 M, pH = 5, solid/liquid ratio = 4 g/l), copper extraction from chalcopyrite ore ranges from 40% to 80% during the first 15 minutes of the reaction. The reaction rate depends on the temperature and particle size, which is in accordance with the results of other authors [28]. The Jander equation best describes the chalcopyrite leaching process. The activation energy of 19.88 kJ/mol was determined from the Arrhenius diagram, which indicates that the dissolution process was determined by diffusion through the layer of products (silicon and elemental sulphur layer) [107].

Li et al. [108] found that in perchoric acid solution chalcopyrite is completely dissolved at pH = 1 (temperature 75°C, potential 750 mV, leaching time 100 h) while with increasing pH of the solution (pH = 2) the dissolution rate decreases significantly due to low activity of Fe^{3+} ions in solution resulting from previous precipitation of iron compounds.

Based on the available literature data, it can be observed that the oxidation of chalcopyrite has not been intensively studied in the HCl – H_2O_2 system. The leaching system HCl – H_2O_2 was applied in the leaching of pyrite concentrate [109], sulphide Pb-Zn concentrate at atmospheric pressure [110], in the leaching of galena [111], and the concentrate of scheelite [112].

Petrović et al. [32] investigated the influence of agitation rate, solid to liquid ratio, acid and oxidant concentration and temperature on copper and iron extraction from chalcopyrite concentrate. It was found that in the HCl – H_2O_2 system, intense oxidation of chalcopyrite takes place in the first 60 minutes of the reaction, after which the reaction rate decreases significantly due to the rapid catalytic decomposition of hydrogen peroxide. The agitation rate and reaction temperature were found to have a negligible effect on chalcopyrite dissolution, while the solid to liquid ratio significantly affected copper and iron leaching. An increase in the concentration of hydrochloric acid (0.1–3.0 M) and hydrogen peroxide (0.5–3.0 M) in the solutions has a positive effect on the oxidative leaching of chalcopyrite. The order of the reaction was determined to be 0.30 with respect to the concentration of acid, and 0.53 with respect to the concentration of hydrogen peroxide. The dissolution kinetics of chalcopyrite in both examined systems is successfully described by the first-order kinetics equation $X=X_m(1-e^{-kt})$. The values of activation energy in chloride solutions are 19.6 kJ/mol (via Cu), and 17.1 kJ/mol (via Fe).

Table 2 shows activation energy values obtained in experiments of chalcopyrite leaching in chloride solutions in the presence of various oxidants.

Table 2. Activation energy values of the chalcopyrite leaching process in chloride solutions.

Chalcopyrite sample	Solution	Temperature, °C	Activation energy, kJ/mol	Process that determines the reaction rate	Bibliography
synthetic and natural	HCl+FeCl ₃	50 – 100	45.9	chemical reaction	[65]
natural	HCl+FeCl ₃	75 – 96	62	electrochemical control	[96]
	HCl+FeCl ₃ +NaCl	82.5 – 96	83		
crystal	HCl +FeCl ₃	52 – 85	69	electrochemical control	[94]
concentrate	HCl+FeCl ₃	65 – 110	37.4	chemical control	[113]
-	HCl+FeCl ₃	23 – 40	86.4	-	[114]
ore	HCl+FeCl ₃	30 – 90	15-28	mixed control	[26]
concentrate	HCl +FeCl ₃	3.5 – 80	55±5	chemical control	[115]
-	HCl +Fe(III)	40 – 95	48±10	chemical control	[116]
concentrate	FeCl ₃	55 – 106	40	-	[117]
concentrate	FeCl ₃	3.5 – 45	1.1	diffusion control	[118]
concentrate	FeCl ₃ +CCl ₄	45 – 80	68.9	chemical control	
concentrate	HCl+FeCl ₃ +NaCl	60 – 90	68	-	[119]
concentrate and crystal	HCl+FeCl ₃ +CuCl ₂	70 – 90	69	chemical control	[93]
ore	HClO	10 – 40	19.88	diffusion control	[107]
concentrate	HCl–Cu(II)–Cl ⁻	25 – 75	72	chemical and electrochemical control	[102]
ore	HCl	25 – 80	31.6	diffusion control	[97]
concentrate	HCl+H ₂ O ₂	30 - 60	20	diffusion control	[32]

Conclusion

Based on the obtained results of chemical dissolution of chalcopyrite in sulphate and chloride solutions, the following can be concluded:

- Chalcopyrite leached slowly in sulphate solutions. The copper extraction values are different for the same or similar experimental conditions (temperature, leaching time, particle size), and they are range up to 90%. This difference in metal extraction values can be explained by the fact that the studies were performed on different samples of chalcopyrite (different mineral composition, presence of other sulphide minerals, presence of different gangue minerals, etc.).
 - The chalcopyrite dissolution rate in sulphate solution increases when Fe (III) ion concentration increases from 0.001 to 0.05 M, while the Fe (III) concentration increasing within the range from 0.05 to 0.5 M leads to chalcopyrite leaching rate decreasing.
 - According to some studies, oxidation of chalcopyrite in Fe (II) sulphate solution is more efficient than oxidation in Fe (III) sulphate solution.

- The obtained results of chalcopyrite oxidation in the presence of strong oxidizing agents such as hydrogen peroxide indicate that with increasing oxidant concentration, the rate of chalcopyrite oxidation in sulphuric acid solutions increases, while the achieved copper extractions in the presence of hydrogen peroxide were above 80%.
 - The agitation rate can negatively affect the oxidation rate of chalcopyrite because it has been shown that peroxide decomposes more rapidly if mechanical mixing is introduced into the system. To prevent the decomposition of the oxidant, it is recommended that the temperature of the solution is kept below 60°C and/or to introduce an organic solvent into the solution.
 - Results in the solution of sulfuric acid - potassium dichromate indicate that the increase in the concentration of potassium dichromate can both positively and negatively affect the rate of oxidation of chalcopyrite, while in other studies it was found that the rate of chalcopyrite oxidation in a mentioned system depends only on the concentration of sulphuric acid.
2. Sulphuric acid - chlorate system is suitable for chalcopyrite oxidation, where copper can be quantitatively leached at elevated temperature. Based on the analysis of the kinetics of chalcopyrite leaching, it was shown that chalcopyrite dissolves chemically better in the chloride medium as compared to leaching in the sulphate medium.
- In chloride solutions, linear dissolution kinetics generally occurs, including the formation of a porous sulphur layer through which the reactants and reaction products are diffused.
 - High copper extractions were achieved by oxidation of chalcopyrite concentrate in chloride solutions.
 - The agitation can negatively affect copper extraction in the FeCl₃-HCl solution: in the conditions of solution agitation, the formed Cu (II)-chloride complexes that occur on the reaction surface in the reaction between the chalcopyrite particle and Fe (III) ions are removed. The concentration of Cu (II) ions on the reaction surface in conditions when agitation is not present in the system is high enough so that Cu (II) ions accelerate the dissolution kinetics, i.e. have a positive effect on the overall dissolution reaction.
3. The values of activation energies obtained in chloride solutions are lower than values of activation energy obtained in sulphate solutions, which indicates faster oxidation kinetics of chalcopyrite in chloride system. The obtained high values of activation energy clearly indicate the fact that chalcopyrite oxidation experiments should be carried out at elevated temperatures.
4. The slow kinetics of chalcopyrite leaching is a consequence of the formation of reaction products on the mineral surface, causing surface passivation. The nature of the passive layer and the mechanism of its formation have not been thoroughly explained. However, it is usually assumed that elemental sulphur, metal-deficient sulphides, polysulphides, iron compounds, or jarosite form a passive layer on the surface of chalcopyrite.

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