Effect of externally adding pyrite and electrical current on galvanic leaching of chalcopyrite concentrate

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Abstract: Although the operating properties of Galvanox™ leaching have been widely studied in the literature, several factors concerning chalcopyrite passivation during the process remain unknown so far. The present work hence aims at investigating the significant effect of externally added pyrite features with a particular focus on its particle size (d_{80} of 0.52, 20, 45 and 2000 µm) through a series of experiments performed in a 2-L stirred-tank electro-reactor. To this end, the role of pyrite: chalcopyrite ratio (0.49:1, 2:1 and 4:1) and presence of electrical current were examined while the rest of the parameters kept constant (80 °C temperature, 400–500 mV (Ag/AgCl) redox potential, pulp density of 10% (w/v), and stirring rate of 1200 rpm). Plus, kinetic models of the leaching tests were studied based on the diffusion and chemical controlling concepts. It was found that the coarser the pyrite particles, the more favorable the copper extraction from the concentrate due to acceleration of reactions in the cathodic electrode and high mass transfers. However, this was in contradiction with the existing reports in the literature. Moreover, galvanic interactions became intensive in the presence of pyrite meaning extensive chalcopyrite dissolution with significantly reduced passivation. Ultimate copper extraction values of 24.17±1.25%, 55.79±0.91% and 57.26±1.59% were resulted at Py:Cp ratios of 0.49:1 (natural), 2:1 and 4:1, respectively. The results showed that maximum copper recovery of 67.32±2.34% was obtained at an optimum condition of pyrite grain size=2000 µm, Py:Cp=4:1, current application=500 mA, 8 h and 80 °C. Finally, detailed kinetic modeling indicated that the chemical control mechanism was dominant in the early reaction stages (t<3.5 h) concerning the availability of fresh surface for chemical agents; however, the second half of the process (8.0 h>t>3.5 h) was controlled by the diffusion control.

Keywords: copper concentrate, galvanic leaching, pyrite, electrical current, leaching kinetics

1. Introduction

Currently, around 80% of the world's copper production is conducted by conventional pyrometallurgical methods, consisting of comminution, flotation, smelting, refining, and electro-refining. Despite the high production levels, deep concerns arise about the significant emissions of sulfur dioxide caused by these operations. For example, the Peruvian copper smelters emit about 1.5×10^6 tons of SO_2 (Vakylabad et al., 2012, Carn et al., 2007). In this context, extending hydrometallurgy to sulfide minerals is presented as a promising option to reduce environmental impacts; however, the

perplexity lies in the low operation efficiencies of the processes, especially at the room temperature and atmospheric pressure (Toro et al., 2020; Torres et al., 2020).

Chalcopyrite ($CuFeS_2$) is the main source of copper, and about 70% of the world's copper produces from porphyry copper deposits (Wang, 2005) that full-scale hydrometallurgical processes are under developments so far (Petersen, 2016; Vakylabad et al., 2016). A wide variety of hydrometallurgical methods have been considered to address issues involved in the leaching of chalcopyrite-bearing ore types. For example, bioleaching (Vakylabad et al., 2016), pressure-leaching (Li et al., 2018), and Galvanox™ (Dixon et al., 2008) processes are widely reported in the literature. The first industrially commercial application was high-temperature and pressure leaching of Phelps-Dodge process (Marsden et al., 2003) developed at Bagdad, Arizona, U.S.A, in 2003. Regardless of the process, principle concern in conjunction with its leaching is a slow and incomplete dissolution of the mineral. This is mainly because of the formation of passive layers like polysulfide, metal-deficient sulfides, iron hydroxysulfate species, and elemental sulfur (S^0) on its surface (Nazari, 2012; Khoshkhoo et al., 2014; Klauber 2008; Vakylabad et al., 2016; Vakylabad et al., 2012, Hassanzadeh et al., 2021). These passive layers render electron transfers from chalcopyrite to pyrite and limite galvanic reactions. Although chalcopyrite passivation was widely investigated, researchers face contradictions concerning differences in the experimental conditions. In this regard, Debernardi and Carlesi (2013) reported a global and structured view of current confrontations. Several techniques were applied to resolve this critical issue, such as high temperature-pressure leaching, adding extra reactants, grinding chalcopyrite to finer sizes, and ultrasonic-assisted leaching (Wang et al., 2020). However, as widely reported, these approaches are time- and energy-consuming, which restrict their elaborations.

One of the effective methods for chalcopyrite leaching is Galvanox™, invented by Dixon and Tshilombo (2005) at The University of British Columbia, Canada. With this innovative atmospheric leaching process, about 98% copper recoveries were achieved at 80 °C under atmospheric conditions with a retention time of four hours. Since then, it has been taken much attention because of the low operating costs, rapid copper dissolution rate, selectivity for chalcopyrite over pyrite, low consumption of oxygen, and neutralizing agents (Dixon et al., 2008), which potentially compensated needs for high-cost pressure-leach autoclaves. This process indeed takes advantage of the galvanic interactions between minerals and substantially increases dissolution rate of the minerals forming a galvanic cell (Fuentes-Aceituno et al., 2008a; Ghahremaninezhad et al., 2010; Vakylabad et al., 2011; Sauber and Dixon, 2011; Martínez-Gómez et al., 2016). Dixon et al. (2008) pointed out that the presence of pyrite and continuous addition of ferric iron to this system is necessary to obtain high recoveries. Although different aspects of this process were broadly addressed in the literature, pyrite properties such as its grain size, its relative proportion to chalcopyrite, and the presence of external electricity were not adequately explored yet. We attempt to fill up this gap in the present work.

Pyrite is the most common mineral in sulfide ores and is typically associated with chalcopyrite (Agheli et al., 2018). Many studies reported the catalytic effect of pyrite on electrochemical leaching of the chalcopyrite concentrates. They concluded that the addition of pyrite increases chalcopyrite dissolution at a short leaching time, mainly with the galvanic interaction between the two minerals (Koleini et al., 2011; Vakylabad et al., 2011; Ruiz et al., 2015; Salehi et al., 2016; Zhao et al., 2016). In addition to that, controlling redox potential in an optimum range may eliminate the formation of passive layers on the mineral surface (Koleini et al., 2011; Ahmadi et al., 2012; Lotfalian et al., 2015; Ruiz et al., 2015; Salehi et al., 2016; Zhao et al., 2016). In this regard, Ruiz et al. (2015) assessed the galvanic effect between chalcopyrite and pyrite. Their results indicated that a very high pyrite: chalcopyrite ratio (8:1) was required to reach a fair efficiency, making it extremely difficult for being implemented in a large and industrial scale. However, Dixon et al. (2008) reported that the pyrite to chalcopyrite ratio must be in the range of two to four to achieve a reasonable recovery, and Koleini et al. (2010) indicated a mass ratio of over 4. It was reported that pyrite forms hydrogen peroxide (H_2O_2) by being drawn in water, which is a strong oxidant agent (Nooshabadi et al., 2013; Hassanzadeh et al., 2020). Interestingly, this principle fact and its effectiveness on chalcopyrite electro-leaching have been relatively overlooked in the literature, which needs to be studied in future works.

Technically, chalcopyrite leaching rate is mainly limited by an anodic half-reaction (Haque and Norgate, 2014; Li et al., 2018; Mahedi et al., 2019); while an investigation explored that it happened

because of a cathodic half-reaction (Tshilombo, 2006). As a result of galvanic interaction between chalcopyrite and pyrite, the cathodic half-cell of the dissolution reaction (reduction of the active oxidant in the system) occurs on the pyrite particle's surface, and this mineral becomes galvanically protected, decreasing its dissolution rate (Ruiz et al., 2015). In this context, by assessing the effect of various parameters (temperature, agitation speed, pyrite to chalcopyrite ratio, grain size, and potential of solution), Salehi et al. (2016) found that the maximum copper recovery was acquired after 24 hours in the optimal conditions of 4:1 pyrite to chalcopyrite ratio, 50 °C and <38 µm grains, such that the galvanic interaction between pyrite and chalcopyrite intensified the electrochemical reactions.

An alternative method for extracting copper out of chalcopyrite concentrates is bioleaching in the presence of pyrite and also other secondary sulfides. The process is taken place through the galvanic interaction between the chalcopyrite and other minerals, and also bacterial-assisted oxidation of Fe^{2+} to Fe^{3+} (Vakylabad et al. 2011; Esmailbagi et al., 2018). Meanwhile, studying the electrochemical properties on the passivating region of chalcopyrite over the potential range of 690–840 mV (SHE) at 25 °C, and 840 mV at 65 °C showed that the temperature is effective on the optimum potential for the chalcopyrite leaching process (Sandstrom et al., 2005). The steady-state sampled-current voltammetry on the chalcopyrite active-passive behavior at high temperatures (Viramontes-Gamboa, 2007 and 2010) indicated that the active-passive transition happened at ~510 mV. Sauber and Dixon (2011) investigated the pyrite-assisted leaching of chalcopyrite concentrate in an iron sulfate media. They disclosed that the pyrite had a higher electrocatalytic activity for the ferric reduction reaction than the chalcopyrite. The electrochemical method has some advantages over other methods applied by some researchers (Pinches et al., 2001; Third et al., 2002; Gericke et al., 2010). This approach improves dissolution rate of copper from chalcopyrite during the leaching process. The benefits include chalcopyrite conversion to less refractory phase, chalcocite and covellite minerals, by direct electron transfer to the mineral (Fuentes-Aceituno et al., 2008; Ahmadi et al., 2011) and the use of electrochemical control of ORP, which improves leaching rate (Harvey and Crundwell, 1997; Ahmadi et al., 2010; Martinez-Gomez et al., 2016) and promotes the chalcopyrite dissolution.

In most previous works, the use of electricity in leaching experiments was limited to electrolysis, electrowinning processes, and bioleaching tests. Furthermore, most of these works did not achieve the desired recovery over a very long period, and mostly they used microorganisms to control the oxidation-reduction potential (ORP) (Ahmadi et al., 2010; Lotfalian et al., 2015). Considering the aforementioned comments, this study investigates oxidation of chalcopyrite within a sulfate-based solution in the presence of pyrite and external current. These are critical factors in an elecrochemical leaching system that have not been sufficiently explored in the literature. In this paper, we address the role of pyrite particle size, its proportion to chalcopyrite and adding external electricity on chalcopyrite dissolution in an acidic ferric sulfate media.

2. Materials and methods

2.1. Materials, sampling, and preparations

In this work, chalcopyrite-rich flotation concentrate of the re-cleaner stage (d_{80}=45 µm) in Sarcheshmeh concentration plant was selected for sampling. The reservoir contains one billion tons of 0.70% copper and 0.03% molybdenum on average, situated in Rafsanjan (Kerman province), Iran (Hassanzadeh, 2018a). This plant is one of the largest copper concentrators worldwide, producing 50,000 copper concentrate per month with an average grade of 28-32% Cu in the final re-cleaner flotation banks. Detailed information concerning the ore body and the beneficiation plant can be found elsewhere (Hassanzadeh, 2018b). The sampling campaign was carried out in ten consecutive working days under identical operating conditions. The given samples were weighted and later dried in an oven at 60 °C overnight. The final samples were milled using a standard Bond ball mill to reach the targeted particle size of 80% passing 20 µm.

In addition to the copper concentrate, pure crystalline pyrite mineral was hand-sorted from the mine site, which was utilized in experiments with pyrite addition. The sample was washed using a 10% H_2SO_4 solution for removing acid-soluble gangues. After that, it was ground using a planetary mill (Fritsch, Pulverisette7, Germany) to reach the target d_{80}s of 0.52, 20, 45, and 2000 µm for selectively covering particle ranges. The particle size distribution (PSD) of the ground samples were measured by a dynamic

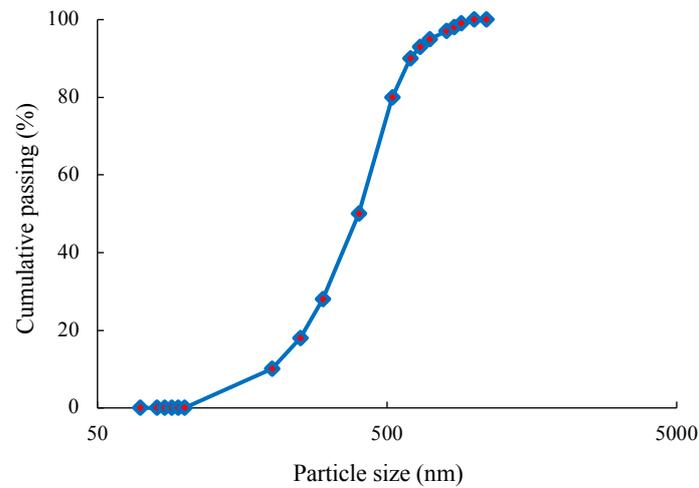light scattering and zeta meter analyzer (SZ-100, Horiba Ltd., Japan), as one is shown in Fig. 1.

Fig. 1. The particle size distribution of given pyrite (d_{80}=520 nm)

2.2. Methods

2.2.1. Chemical analyses

Semi-quantitative X-ray diffraction technique (SQ-XRD, PW17C, Philips), X-ray fluorescence (XRF, PW1480, Philips) together with Leica (DM-LP, Wetzlar, Germany) optical microscopy were applied to characterize the proportion of each mineral in the ore, elemental distributions, and mineralogical properties, respectively. According to the results of the SQ-XRD, the concentrate was composed of chalcopyrite (50.29 wt%, $CuFeS_2$) and pyrite (24.71 wt%, FeS_2) as the main minerals and covellite (1.24 wt%, CuS), chalcocite (1.20 wt%, Cu_2S), bornite (0.25 wt%, Cu_5FeS_4), cuprite (1.76 wt%, Cu_2O), sphalerite (2.53 wt%, Zns), molybdenite (0.14 wt%, MoS_2) and other non-copper bearing minerals mainly silicates as minor phases. The XRF showed that copper and iron with 21.12% and 27.00% are the dominant elements of the concentrate, and Py:Cp mass ratio equals 0.49. From mineralogical surveys and previously reported studies by authors, it is clear that the main metallic gangue mineral associated with the chalcopyrite is pyrite (Hassanzadeh and Karaks, 2017; Hassanzadeh and Hasanzadeh, 2017; Hassanzadeh et al., 2019a). In the case of the pure pyrite sample, Fig. 2 displays the X-ray diffraction analysis that dolomite (7.8 wt%, $MgCO_3.CaCO_3$) is identified as the minor non-metallic phase.
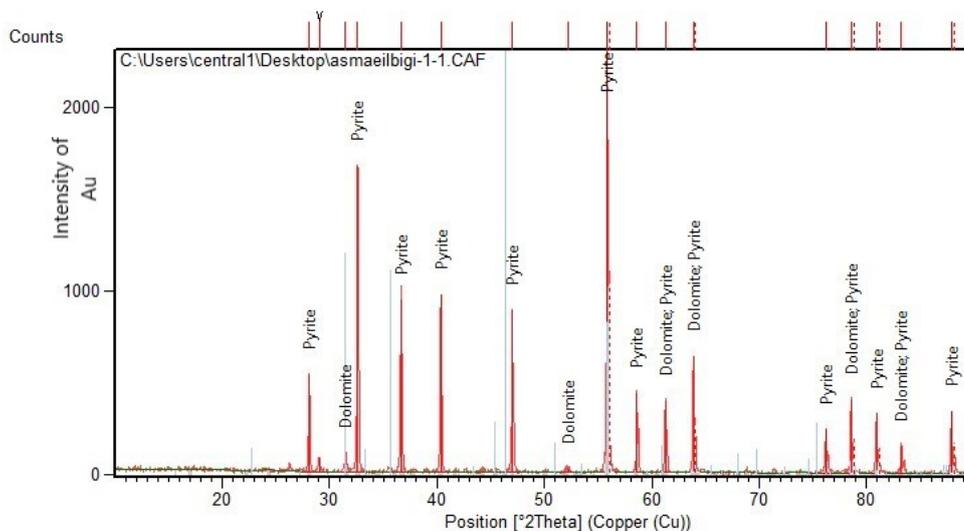

Fig. 2. XRD analysis of the pyrite

2.3. Electro-reactor and leaching experiments

The leaching experiments were performed in a 2-L glass electro-reactor containing three-electrodes shown in Fig. 3. The reactor was designed, successfully operated, and its application was verified by previous works (Ahmadi, 2010; Ahmadi et al., 2011). A titanium–platinum mesh (15 cm×9 cm×0.1 cm) as the anodic counter electrode immersed into the reactor solution, platinum foil as working electrode put into a separate small cathodic compartment (initial pH of 1.8), all of which were separated from the anode chamber with a glass frit. The reference electrode was Ag/AgCl connected to the electrolyte in the main chamber through a capillary, which ended close to the working electrode. The working electrode's potential was controlled with respect to the reference electrode using a Solartron SI 1287 potentiostat.

Leaching experiments were carried out in the electro-reactor at 10% (w/v) pulp density, an initial pH of around -0.75 (1800 g acid per 1000 g concentrate), a temperature of 80 °C, an oxidation-reduction potential (ORP) range of 400-500 mV and a stirring rate of 1200 rpm. These values were opted based on previous results (Ahmadi et al., 2011; Esmailbagi et al., 2018). To maintain the ORP in the desired range (400–500 mV) during the electrochemical leaching tests, the working electrode's potential was controlled with respect to the reference electrode. The oxidizing agent (Fe^{3+} in the form of iron sulfate) was added whenever it was necessary to control the optimum ORP at 400-500 mV. The pH and ORP values were measured with a Jenway 3540 pH meter and a Pt electrode in reference to an Ag/AgCl electrode (+207 mV vs. SHE at 25 °C), respectively. They were carefully calibrated before conducting the experiments. The overall leaching experiment lasted 8 h, and incremental samples were periodically taken every 30 min from the slurry, which were later filtered through Whatman No.41 filter paper. The remaining solids were returned to the reactor. The evaporated liquid was compensated through the reflux condenser. Eventually, samples taken from the PLS were characterized via Inductively Coupled Plasma (ICP) analysis (Plasma Quant 9100, Germany) to determine the copper concentration in the solution as a function of the operation time. Table 1 represents the experimental tests with the parameters as the addition of pyrite to the suspension (yes/no), d_{80} of pyrite (in 4 levels; 0.52, 20, 45, and 2000 μm), pyrite: chalcopyrite ratio (Py:Cp) (in 3 levels, 0.49:1, 2:1 and 4:1), and application of the electrical current (yes/no). To evaluate the impact of pyrite size on the copper leaching extraction, runs 1-4 were undertaken while the Py:Cp ratio remained constant (2:1). The effectiveness of Py:Cp at three levels was studied through running experiments 5-7. Additionally, to investigate the role of electric current in the system and its effect on copper recovery, another series of experiments was carried out. Tests 8-10 were performed by applying current to slurry at a current density of 5 mA cm^{-2} (total direct current=500 mA) and other mentioned optimum conditions (Py:Cp=2:1, d_{80} of pyrite=2000 μm). For the sake of evaluating the reproducibility of experiments, each test was amended once, and the experimental errors were calculated at 95% confidence level.
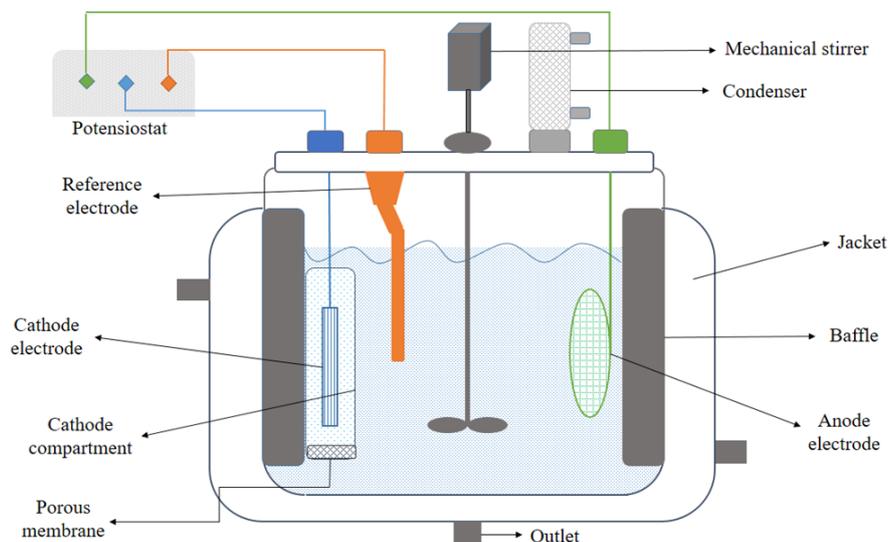

Fig. 3. A diagrammatic sketch of leaching system

Table 1. Experimental conditions of the leaching tests

Run	d_{80} of pyrite (µm)	Addition of pyrite	Current (500 mA)	Py:Cp ratio	Final copper recovery (%)
1	0.52	Yes	No	2:1	35.68±2.42
2	20	Yes	No	2:1	42.83±1.70
3	45	Yes	No	2:1	46.67±3.06
4	2000	Yes	No	2:1	55.79±0.91
5	**N/A***	**No**	**No**	**0.49:1**	**24.17±1.25**
6	2000	Yes	No	2:1	55.79±0.91
7	2000	Yes	No	4:1	57.26±1.59
8	N/A*	No	Yes	0.49:1	31.52±1.54
9	2000	Yes	Yes	2:1	62.49±2.32
10	**2000**	**Yes**	**Yes**	**4:1**	**67.32±2.34**

N/A*: not known

2.4. Modeling of leaching kinetics

Leaching kinetics rate of a metal-bearing mineral in the presence of a solution is mainly demonstrated by the shrinking core model (SCM) (Eq.1). It has been proven that the SCM model represents a realistic estimation of kinetic reactions in comparison with other models (Levenspiel, 1999; Astuti et al., 2015; Safari et al., 2009; Erdem and Yurten, 2015). Thus, the SCM kinetic modeling concept was employed for identifying the kinetic mechanism of the copper leaching process. It is worth mentioning that the SCM model presumes spherical shape and constant sizes for reactive particles. Another assumption is that the chemical reactions between particles and liquor take place on surface of the particles (Yang and Zhang 2013; Lan et al., 2015).

$$A(fluid) + bB(solid) \rightarrow Products \tag{1}$$

where A is the leaching solution, B denotes the solid particles and b represents stoichiometric coefficient of the reaction.

Two widely used SCM models including solid product layer diffusion (Eq. 2) and chemical reaction (Eq. 4) controlling models were fitted to the experimental data obtained from the leaching kinetics experiments (Levenspiel, 1999). The kinetic parameters i.e. nominal kinetic rate and coefficient of rate controlling step were estimated through the copper dissolution. Later, the kinetic diagrams were depicted in terms of pyrite particle sizes.

$$1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) = k_{pl} \times t \tag{2}$$

where:

$$k_{pl} = \frac{6bD_eC}{\rho R_0^2} \tag{3}$$

$$1 - (1 - X)^{\frac{1}{3}} = k_{cr} \times t \tag{4}$$

and:

$$k_{cr} = \frac{bK_SC}{\rho R_0} \tag{5}$$

where t (h) is leaching time and X represents the leached copper proportion at time t. k_{pl} and k_{cr} (1/min) represent the apparent kinetic rate constants of product layer diffusion and chemical reaction controlling steps, respectively. ρ (kg/m³) is the specific gravity, R_0 denotes the initial radius of particle (m), C is the concentration of the reactant (kg/m³), k_S is the reaction rate constant at the particle surface (1/min) and D_e represents the effective diffusion coefficient for porous structures (m²/min),

3. Results and discussions

3.1. Impact of pyrite grain size

The effect of pyrite grain size on the leaching behavior of chalcopyrite concentrate (d_{80}=20 µm) was investigated (Table 1, tests 1–4). The given grain sizes (d_{80} of 0.52, 20, 45, and 2000 µm) were added to the chamber at operating conditions of 400–500 mV solution potential, Py:Cp ratio of 2:1 (optimized

from the section 3.2), initial pH of -0.85, 80 °C, 10% (w/v) solid concentration and stirring rate of 1200 rpm. The summarized results of runs 1-4 are shown in Fig. 4. It can be seen that copper recovery increases by increasing d_{80} of pyrite from 0.52 µm (35.68±2.42%) to 2000 µm (55.79±0.91%) throughout 8 h of leaching period. As seen, the coarser the particles, the higher the copper extraction from the concentrate. This result is most likely contributed to the cathodic reaction (Eq. 6) occurring on the lateral surface area instead of the specific surface area, as demonstrated by Dixon et al. (2008). Besides, there could be a sharply enhanced possible attack on the pyrite with a high specific surface area. This may result in a significant reduction in the galvanic contact between pyrite and chalcopyrite.

$$4Fe^{3+} + 4e^- \rightarrow 4Fe^{2+}$$ (6)

Another possible reason for such tendency in Fig. 4 is the flowability of materials inside the system. Liu (2015) and Eskanlou et al. (2019) reported that as the particle size of a substance becomes finer, its ability to move and flow through the system decreases. In a relatively turbulent environment, interception and gravitational encountering govern the collision mechanism between pyrite and chalcopyrite particles (Hassanzadeh et al., 2018, 2019b). By increasing pyrite size, this interaction mechanism leads to exceeding mass transfer and enhancing galvanic reactions. Another study also showed that close contact between pyrite and chalcopyrite significantly increased dissolution rate of chalcopyrite compared to non-contact cases (Berry, 1978). Therefore, it can be acknowledged that as the size of particles inside the system decreases, the ability of pyrite particles to move and also the chance of their electrical contact with chalcopyrite particles diminishes, which finally reduces chalcopyrite recovery. Another possibility is related to the adhesion of fine particles. In this regard, Shi et al. (2018) showed that by dropping particle grain size, the adhesion between particles enhances, and the probability of sticking these particles to the walls of the container and/or around chalcopyrite particles increases and leads to a decrease in leaching rate. Interestingly, our result is in contradictory with the reported outcomes of Salehi et al. (2016). They showed that increasing chalcopyrite grain size (-38 µm, -55+38 µm and -74+53 µm) in the presence of Py reduces its recoverability under given operating conditions i.e. solution potential=440 mV, Py/Cp ratio=4, temperature of 50 °C, and stirring speed=800 rpm. However, the reason for such behavior was overlooked in that work. Further, Nazari et al. (2012) evaluated the effect of pyrite surface area (-75+25 µm, -125+75 µm, -150+125 µm and -354+250 µm) on the kinetics of chalcopyrite (<53 µm) leaching at Py:Cp=2 and a silver-to-pyrite ratio of 100 ppm. They manifested that the rate of reaction increases as pyrite particle size decreases because of increasing total surface area of pyrite (increasing cathodic surface area).
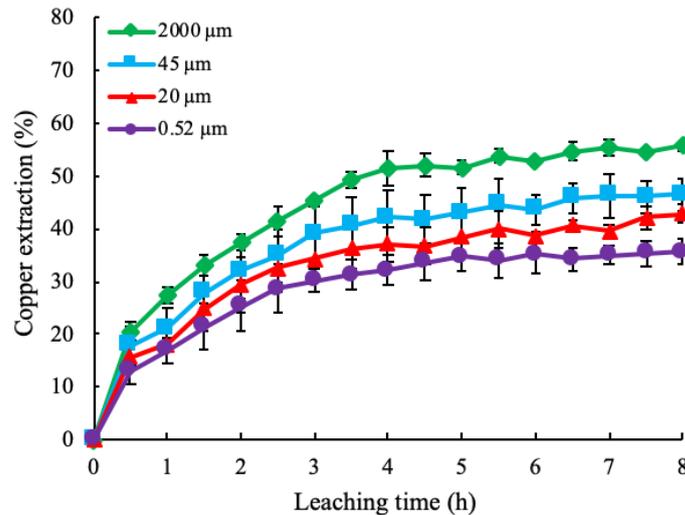

Fig. 4. Effect of pyrite particle size on copper recovery

3.2. Effect of pyrite to chalcopyrite ratio

Fig. 5 displays three different ratios of pyrite to chalcopyrite, including 0.49:1 (natural one), 2:1, and 4:1. The experiments were carried out at 80 °C, ORP potential of 470 mV, stirring rate of 1200 rpm and solid percent of 10% (w/v) (test runs 5-7). These factors were based on previous similar works (Dixon et al.,

2008; Ahmadi et al., 2011; Esmailbagi et al., 2018) that chalcopyrite passivation takes place at ORP of 440-520 mV Ag/AgCl (Dixon et al., 2008). The experimental results show that a mixture of pyrite to chalcopyrite with the ratio of 0.49:1 (natural ratio of initial chalcopyrite concentrate) after 8 hours of leaching recovers copper 24.17±1.25%, while it equals 55.79±0.91% for the corresponding ratio of 2:1. Exceeding the ratio to 4:1 improves the leaching rate in the very early stages of leaching, but it does not have a significant impact on copper extraction at the end. It can be observed that without the additive pyrite, leaching is quickly passivated after an initial fast dissolution of mainly chalcocite and covellite, as reported by Ahmadi et al. (2011). Whereas, in the presence of additional pyrite, galvanic interaction becomes intensified, leading to an extension of copper dissolution. In this regard, Dixon and Tshilombo (2005) observed that as the amount of pyrite increases up to a certain level, further pyrite addition did not improve the leaching process, which is in line with our finding in this work. This phenomenon was confirmed by other researchers (Holmes and Crundwell, 1995; Koleini et al., 2010, 2011; Nazari et al., 2011; Nazari, 2012). Koleini et al. (2010) reported a Py:Cp ratio of over 4, while Dixon et al. (2008) obtained reasonable recoveries at the corresponding value of 2:4. Also, Salehi et al. (2016) obtained maximum copper recovery of around 45% when Py:Cp=4:1 at a low temperature (50 °C) after 24 hours, under the following condition: stirring speed of 800 rpm, solution potential of 440 mV, and particle size of -38 μm. It should be noted that such discrepancy can be originated from the mineralogical properties of the materials tested. Further, Ruiz et al. (2015) examined the galvanic effect of pyrite addition on chalcopyrite leaching in H_2SO_4-$NaClO_2$ solution and Py:Cp ratios of 2:1, 4:1 and 8:1 (pyrite 9.1 μm, chalcopyrite 10.6 μm, 0.2 mol/L of H_2SO_4, 1 mol/L of NaCl, 1000 rpm, 100 °C and 0.3 L/min of O_2). They found out that galvanic interaction between chalcopyrite and pyrite led to an increase in chalcopyrite dissolution only in a short time leaching. This impact was revealed insignificant in a more extended period because of attenuation of pyrite catalytic effect.
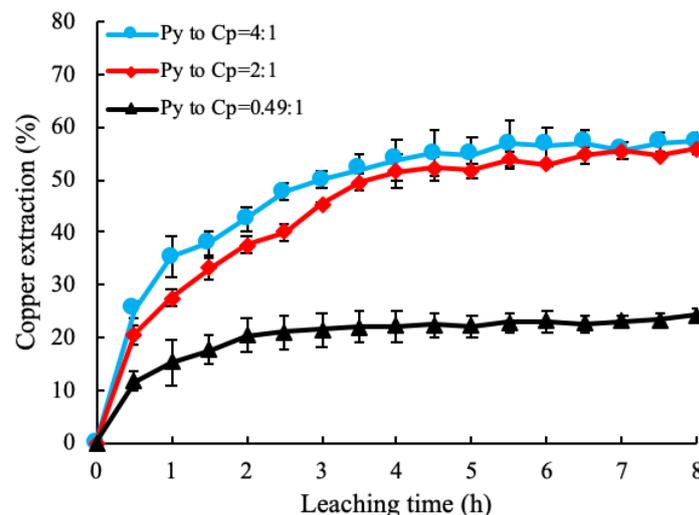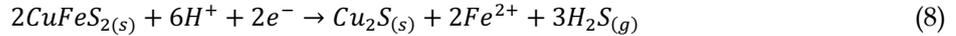

Fig. 5. Effect of Py:Cp ratio on the copper recovery as a function of leaching time

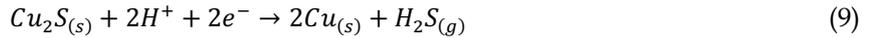### 3.3. The role of applying an external current

Results of leaching tests in the electro-reactor with the same conditions in the presence and absence of external current with different ratios of pyrite to chalcopyrite (0.49:1, 2:1 and 4:1) are shown in Fig. 6 (test runs 5-10). As seen in Fig. 6a-c, copper extraction values in the presence of electric current are always higher than those obtained without it. For instance, copper recovery of 24.17±1.25% is acquired in the absence of external current and pyrite after 8 h leaching when the Py:Cp=0.49 (test 5). However, the corresponding value is 31.52±1.54% when 500 mV current is applied to the system (test 8). By increasing Py:Cp ratio to 2:1 and 4:1, ultimate copper extraction promotes from 55.79±0.91% and 57.26±1.59% (without current) to 62.49±2.32% and 67.32±2.34% (with the current), respectively. By comparing the results of tests 5-10 (Fig. 6a-c), it can be concluded that the maximum copper extraction of 67.32±2.34% is achieved in 8 h. In this work, a low electrical current application density was chosen to minimize hydrogen evolution (Eq. 7).

$$2H^+ + 2e^- \rightarrow H_{2(g)} \tag{7}$$

By applying an electrical current across the slurry, some reactions are expected to occur. Periodic electrical contact between chalcopyrite and the working electrode electrochemically reduces chalcopyrite to more soluble minerals such as bornite (Cu_5FeS_4), chalcocite (Cu_2S), and metallic copper (Cu^0) (Fuentes-Aceituno et al., 2008; Ahmadi et al., 2011). Conner (2005) also reported that applying DC current into the leaching system significantly reduces the formation of jarosite in the solid residues. From a mechanistic viewpoint (Eq. 8), chalcopyrite can be electrolytically reduced in acid solutions to chalcocite (Biegler and Swift, 1976; Biegler, 1977; Biegler and Constable, 1977):

$$2CuFeS_{2(s)} + 6H^+ + 2e^- \rightarrow Cu_2S_{(s)} + 2Fe^{2+} + 3H_2S_{(g)} \tag{8}$$

Chalcocite can be further electro-reduced to metallic copper, according to Eq. 9 (Biegler and Constable, 1977).

$$Cu_2S_{(s)} + 2H^+ + 2e^- \rightarrow 2Cu_{(s)} + H_2S_{(g)} \tag{9}$$

In terms of galvanic interactions between different metallic sulfide minerals, Mehta and Murr (1983) observed that when pyrite, chalcopyrite, chalcocite, and covellite are in contact with each other, due to their different rest potentials, the rate of covellite dissolution is the fastest (anodic corrosion), followed by chalcocite and chalcopyrite, with the rate of pyrite dissolution as the lowest (cathodic protection). Furthermore, it was reported that chalcopyrite might be electrochemically converted to other copper sulfide phases such as talnakhite ($Cu_9Fe_8S_{16}$) (Eq. 10) and/or bornite (Cu_5FeS_4) (Eqs. 11 and 12), which might dissolve faster than the chalcopyrite (Warren et al., 1982; Lu et al., 2000).

$$9CuFeS_{2(s)} + 4H^+ + 2e^- \rightarrow Cu_9Fe_8S_{16(s)} + 4Fe^{2+} + 6H_2S_{(g)} \tag{10}$$

$$5CuFeS_{2(s)} + 12H^+ + 4e^- \rightarrow Cu_5FeS_{4(s)} + 4Fe^{2+} + 6H_2S_{(g)} \tag{11}$$

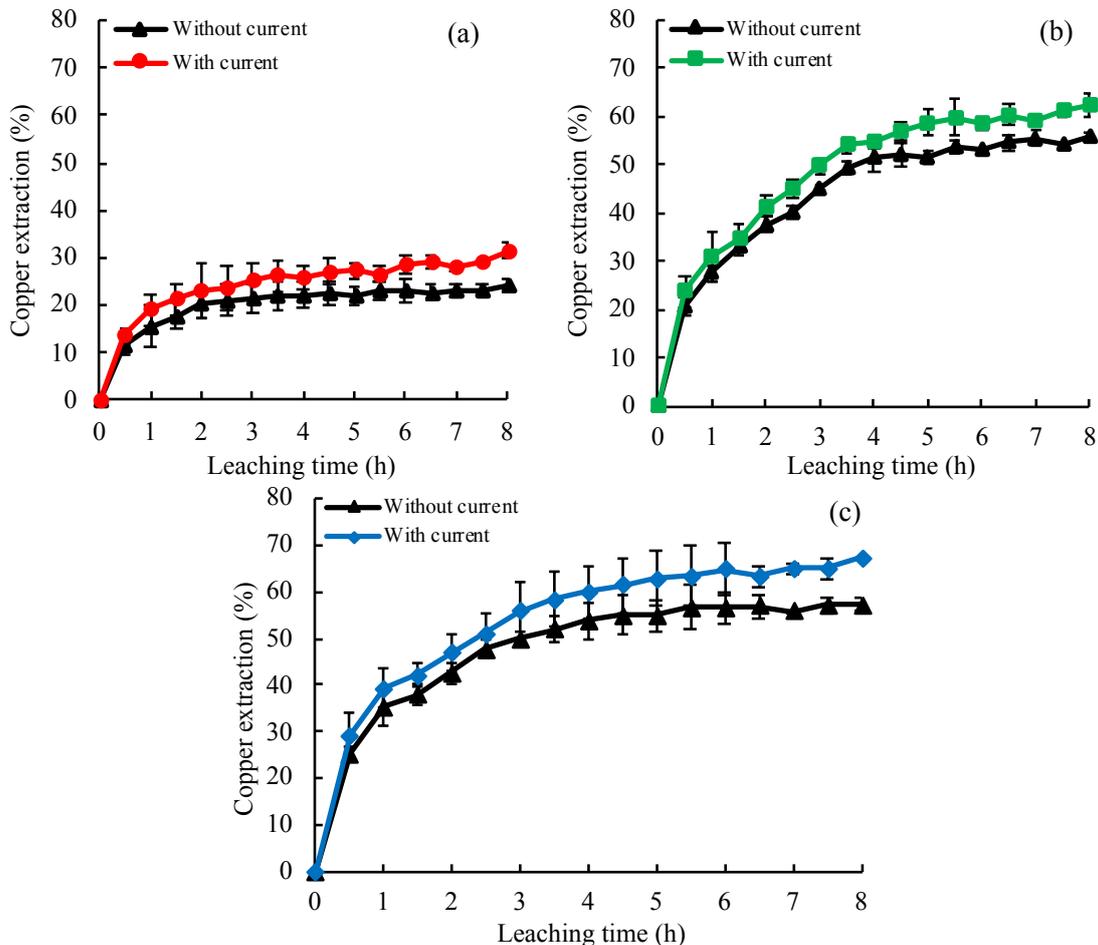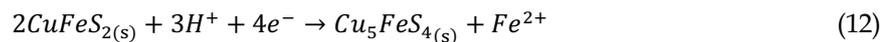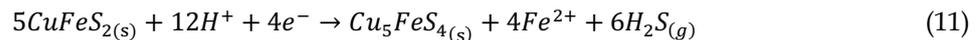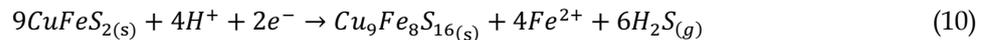$$2CuFeS_{2(s)} + 3H^+ + 4e^- \rightarrow Cu_5FeS_{4(s)} + Fe^{2+} \tag{12}$$

Fig. 6. The role of external electricity current on copper extraction at Py:Cp ratios of a) 0.49:1, b) 2:1 and c) 4:1

3.4. Kinetics modeling

Considering a single mechanism in the whole reaction period in complicated reaction environments such as chalcopyrite leaching is too simplistic. Fig. 7 exhibits copper extraction as a function of leaching time by applying commonly used two controlling mechanisms i.e. diffusion (Eq. 2, Fig. 7a) and chemical (Eq. 4, Fig. 7b) models. As qualitatively seen, there is a low goodness of fit for fitting equations (Eqs. 2 and 4). Thus, none of these controlling mechanisms can be a representative description of the entire reaction period. This led us to divide each curve into two parts i.e. t<3.5 h and t>3.5 h in order to identify the controlling kinetics steps properly where the slope of the line is the rate constant.
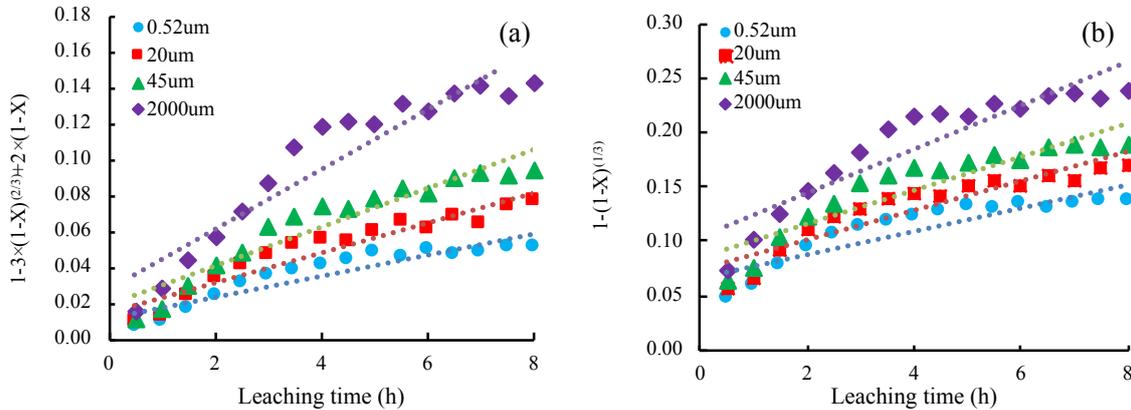

Fig. 7. Poor correlations for the main models: (a) diffusion controller and (b) chemical controller

Table 2. Nominal leaching kinetic rate values and correlation coefficients of the corresponding models

d_{80} (µm)	Diffusion through a product layer		Surface chemical reaction	
	k_{pl} (min^{-1})	R^2	k_{cr} (min^{-1})	R^2
0.52	0.002	0.74	0.025	0.97
20	0.005	0.84	0.029	0.96
45	0.006	0.90	0.033	0.98
2000	0.008	0.85	0.041	0.99

The reaction control mechanism changes completely as the leaching reaction progresses. This can be seen by dividing the leaching reaction time into different parts by studying the kinetics in detail. As shown in Fig. 8 (a-d), the reaction mechanism is chemically controlled for the first 3.5 hours (correlation coefficient above 99% (Fig. 8d)), which is independent of pyrite grain size. The leaching kinetics rate values however gradually improve by increasing pyrite's grain size (Table 2). Kinetic rate enhances from 0.025 min^{-1} (d_{80} of pyrite=0.52 µm) to 0.041 min^{-1} (d_{80}=2000 µm). The chemical control mechanism is dominant in the early stages of the reaction because of the availability of the fresh surface for chemicals. This analysis can be an essential aid to find a suitable operational solution to increase the efficiency of galvanic leaching of chalcopyrite. Appropriate chemicals should be sufficiently available at the beginning of leaching. The early hours of leaching are vital factors in process efficiency. If the leaching is not properly effective during this period (t<3.5 h), the complicated conditions of the chalcopyrite mineral leaching media may technically and economically stop the process.

In contrast, the last 4.5 hours of the leaching process shows a significant change in the reaction mechanism. Kinetic modeling directly indicates diffusion control in this period. As shown in Table 2, the kinetic rate values are 0.002, 0.005, 0.006 and 0.008 min^{-1} in the presence of pyrites grain sizes of 0.52, 20, 45 and 2000 µm. By comparing the corresponding values obtained for k_{pl} and k_{cr}, one can conclude that in all pyrite size fractions, k_{cr} is greater than k_{pl}. Utilizing additives such as chlorine or catalysts such as silver can possibly help to return the extraction curve to its initial path by removing the diffusion penetration barrier and thus increase the leaching rate. There are generally several approaches to increase the overall leaching kinetic rate. First solution is to use rapid leaching methods such as pressure leaching to reduce the reaction time. Also, increasing the specific surface area of the minerals with ultra-

grinding can increase the leaching rate. Also, under chemically controlled conditions, additives such as activated carbon can be used to increase the leaching rate, which accelerates the reaction by additional galvanic interaction (Nakazawa et al., 1998, Zhang and Gu, 2007).
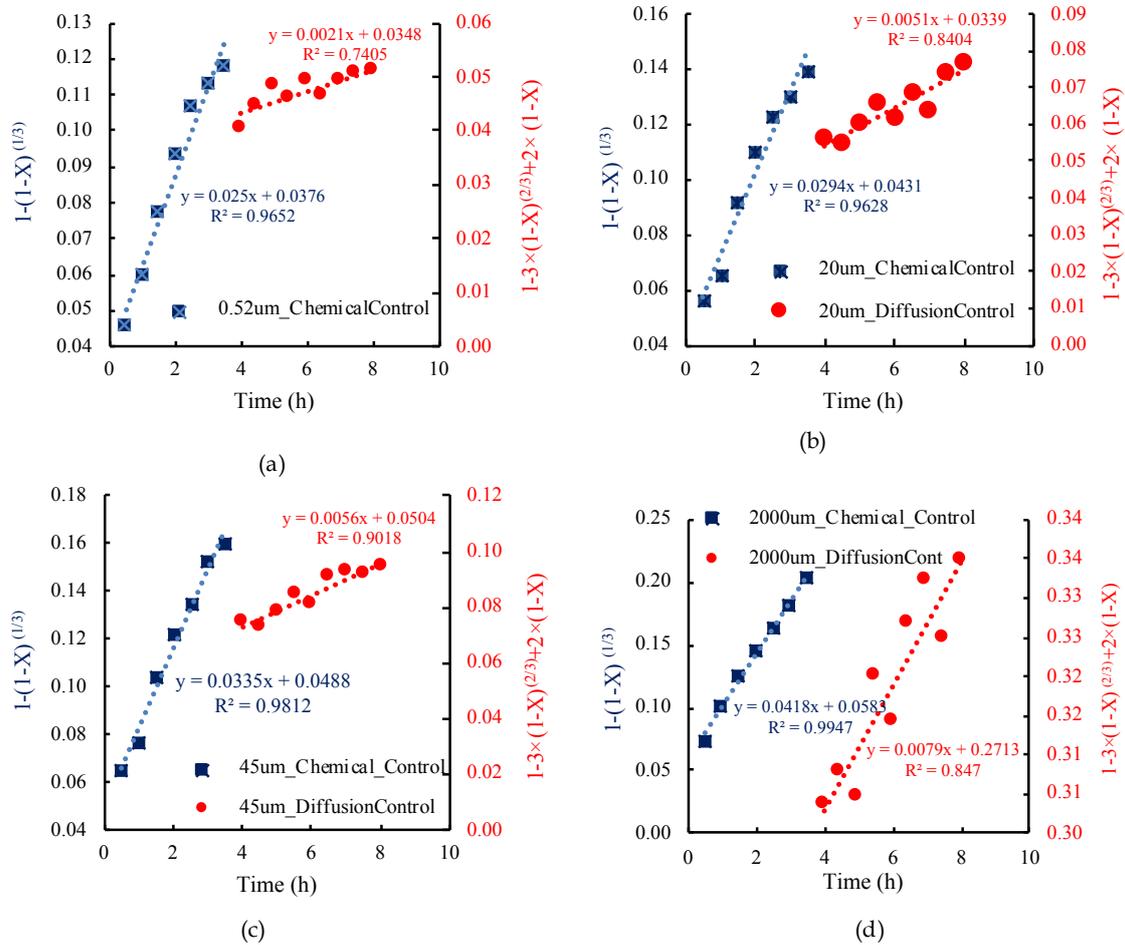

Fig. 8. Dividing the 8-hour galvanic leaching period into the t>3.5 h (dominated by the chemical controlling) and the final 4.5 hours (controlled by diffusion through a product layer): d_{80} of the pyrite is (a) 0.52 μm, (b) 20 μm, (c) 45 μm and (d) 2000 μm

4. Conclusions

Copper extraction from chalcopyrite concentrate has been a long-standing issue in hydrometalluryical processes. Among current approaches, Galvanox™ is identified as a promising and cost-effective technique. Nevertheless, its fundamental concepts need further clarifications, such as the chalcopyrite passivation phenomenon. In this study, leaching of chalcopyrite concentrate was performed using the Galvanox™ process to investigate the effect of different parameters such as pyrite to chalcopyrite ratio, applying an electrical current to the slurry, and pyrite grain size on copper extraction.

The experimental results showed that the addition of pyrite had a significant catalytic impact on the chalcopyrite concentrate leaching due to the formation of a galvanic cell between the minerals, which was caused by their difference in rest potential. Further, it was indicated that increasing pyrite particle size from 0.52 μm to 2000 μm, considerably enhanced chalcopyrite leaching rate from 35.68±2.42% (0.52 μm) to 55.79±0.9% (2000 μm) throughout 8 h of leaching period. It was related to the cathodic reaction that occurred on the lateral surface area instead of the specific surface area. However, the literature data indicated that reducing pyrite grain size improves copper extraction rate owing to the high surface area of pyrite. This contradiction was remained open for future studies. Copper extraction of 24.17±1.25% was obtained in the absence of additive pyrite in 8 h. While, in the presence of additional pyrite (Py:Cp=2:1), the copper recovery gradually increased and finally reached to 55.79±0.91%. Nevertheless,

by rising the ratio to 4:1, no significant improvement in the copper recovery was observed (57.26±1.59%). Comparing the obtained results with the existing data in the literature manifested that this ratio mainly varies between 2-4. Applying an electrical current to the slurry showed a major effect on chalcopyrite dissolution in terms of electro-reduction of chalcopyrite. Adjusting ORP potential together with applying electrical current was seemingly a promising method for leaching chalcopyrite concentrate.

Finally, we concluded that maximum copper recovery of 67.32 ± 2.34% was obtained at a stirring speed of 1200 rpm, Py:Cp ratio of 4:1, solution potential range of 400-500 mV, pulp density of 10% (w/v), pyrite particle size of 2000 µm, current density of 500 mA and temperature of 80 °C for 8 hours. Kinetic modeling approved that the early hours of leaching (t<3.5 h) is a key factor of process efficiency where the mechanism of leaching was identified as a chemically controlling mechanism. In contrast, the second half of the leaching was dominated by diffusion system.

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