

Research Article

Galvanic Interaction between Chalcopyrite and Pyrite with Low Alloy and High Carbon Chromium Steel Ball

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This study was aimed to investigate the galvanic interaction between pyrite and chalcopyrite with two types of grinding media (low alloy and high carbon chromium steel ball) in grinding of a porphyry copper sulphide ore. Results indicated that injection of different gases into mill altered the oxidation-reduction environment during grinding. High carbon chromium steel ball under nitrogen gas has the lowest galvanic current, and low alloy steel ball under oxygen gas had the highest galvanic current. Also, results showed that the media is anodic relative to pyrite and chalcopyrite, and therefore pyrite or chalcopyrite with a higher rest potential acted as the cathode, whilst the grinding media with a lower rest potential acted as the anode, when they are electrochemically contacted. It was also found that low alloy steel under oxygen produced the highest amount of EDTA extractable iron in the slurry, whilst high carbon chromium steel under nitrogen atmosphere led to the lowest amount.

1. Introduction

The key to a successful separation in mineral processing is the preparation of particles with adequate liberation under the correct pulp chemical conditions [1]. Wet milling in ball mills followed by flotation is the general practice employed in the beneficiation of copper sulphide ores in which the major minerals of commercial significance typically are chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), covellite (CuS), and chalcocite (Cu_2S) [2].

It has been widely accepted that the grinding environment of sulfide minerals such as pyrite, arsenopyrite, chalcopyrite, galena, pyrrhotite, and sphalerite has a pronounced effect on the recovery and selectivity of sulphide minerals [3–10].

Galvanic interaction is one of the most important electrochemical factors, which governs the dissolution rate of sulphide minerals in hydrometallurgical systems [11]. It may occur in many minerals processing systems, flotation [12–14], leaching of sulfide [15–17], and particularly wet grinding

[18, 19]. Most sulfides are at best semiconductors. Therefore, during grinding due to sulphide mineral electrical conductivity a contact between mineral in ore and grinding media occurs which results in a galvanic couple between the media and the sulphide mineral. This increases dissolution of ferrous ions from grinding media, which are usually precipitated in the form of iron oxy-hydroxides on the surfaces of the sulphide minerals [20–22].

The extent of galvanic interaction between mineral and grinding media is dependent on the media type, minerals mineralogy, rest potential (open circuit potential) differences between sulphide minerals and grinding media, polarization behavior of the materials, comparative geometric ratio of the sulphide mineral to the medium in the couple, and grinding environment such as pH, percent solid, viscosity, Eh, gas purging (air, O_2 and N_2), temperature, rheological properties, and water chemistry (i.e., anions; Cl^- , SO_4^{2-} ; cations; Ca^{+2} , Mg^{+2} , Fe^{+2} , Fe^{+3}) [9–23].

A vast number of studies were carried out in investigating the electrochemical interactions between grinding

media and sulphide minerals [13, 14, 24, 25]. Generally, these studies indicate that most sulphide minerals are nobler than the grinding media used during grinding; therefore, a galvanic couple between the media and the sulphide mineral(s) exists, which increases the corrosion rate of the grinding media. In addition, these studies show that galvanic interaction between media and mineral not only promotes the corrosion rate of steel grinding media but also has a deleterious influence on the floatability of the ground sulphide minerals. Although extensive studies were carried out on the electrochemical interactions between grinding media and minerals in grinding of sulphide minerals and/or ores, but these investigations were not reported in grinding of porphyry copper sulphide ore. Pyrite and chalcopyrite, the most common and exploitable sulphide minerals, usually occur together and in contact with each other. Therefore, this paper was aimed to investigate the effect of galvanic interaction among chalcopyrite and pyrite with grinding media in grinding the Sarcheshmeh copper ore. In this study, influence of two factors including media type and dissolved oxygen were investigated in galvanic interaction between minerals (chalcopyrite and pyrite) and media.

The Sarcheshmeh copper ore is a major porphyry copper deposit, which is located in Kerman Province in the southeastern part of Iran. The Sarcheshmeh copper mine is the largest copper producer in Iran, and one of the major producers in the world market. In the concentrator plant, after three stages of crushing, the ore feeds to ball mills in a closed circuit with cyclones to produce 70% of the product finer than $75\ \mu\text{m}$ [26].

2. Experimental

2.1. Materials and Reagents. The Sarcheshmeh copper ore samples were obtained from the input feed to ball mills. Samples were crushed in a jaw crusher and then screened to collect the +0.25–2 mm particle size fraction. Samples were then homogenized and sealed in polyethylene bags. Representative samples were chemically analyzed which their chemical compositions listed in Table 1.

In order to construct electrodes, samples of pure pyrite and chalcopyrite were collected from the Meiduck copper mine in the Babak city in Kerman Province of Iran and the Ghaleh Zari mine in Nehbandan city in south Khorasan Province of Iran, respectively. These samples were chemically analyzed. It is specified that pure pyrite and chalcopyrite minerals have 99.3% and 97.44% pyrite and chalcopyrite, respectively.

Two types of steel ball were applied as grinding media, which their chemical compositions are presented in Table 2. In this research, samples were ground with 8 kg ball in mixing of 0.5, 0.75, and 1 inch in diameter.

For preparing minerals and medium electrodes, medium and mineral samples were cut into a size of $7 \times 7\ \text{mm}$ to fill in a Teflon tube. Then, a copper wire was connected to the back of the medium with electrically conductive silver epoxy. After that, the sample was mounted in a Teflon tube with the working surface exposed, and the central part of

TABLE 1: Chemical composition of the Sarcheshmeh ore sample (Wt %).

Particle range	Chemical compositions (Weight, %)					
	Cu	Fe	Mo	S	SiO ₂	Al ₂ O ₃
0.25 to 2 millimeters	0.74	4.34	0.032	3.05	55.07	14.35

TABLE 2: Chemical compositions of the grinding media.

Ball type	Chemical compositions (Weight, %)							
	C	Si	S	P	Mn	Cr	Mo	Cu
High carbon chrome steel	2.28	0.698	0.049	0	1	13.25	0.177	0.044
Low alloy steel	0.249	0.173	0.024	0.018	0.586	0.019	0.002	0.012

the tube was sealed with nonconductive epoxy resin. The electrodes surface was gently polished with 500 grit silicon carbide paper prior to each test and cleaned with acetone and double distilled water. After each experiment, the used medium electrodes were repolished and then reused.

2.2. Grinding. The prepared representative samples (365 g) were ground in a specialized ball mill with 8 kg balls in pH, 7–7.5, solid percentage, 35%, and rotation speed, 75 rpm for 12.5 minutes so that 70% of particles were finer than $75\ \mu\text{m}$ in diameter. This specialized grinding system was designed in R&D of the Sarcheshmeh copper Mine. Ball mill was constructed using a stainless steel pipe with diameter of 21 cm and length of 30 cm with a wall thickness of 0.7 cm. In order to study the electrochemistry of inside the mill, that is, to measure the slurry chemical conditions, polarization curves of balls, and minerals and their electrochemical interactions, an electrochemical apparatus associated with gas purging system was also linked to the mill. Schematic representation of specially designed grinding system illustrated in Figure 1.

The setup of experiments included a specialized ball mill, electrochemical tools, including, potentiostat/galvanostat coupled with a personal computer for data acquisition and potential control accompanied by a three-electrode system, the gas purging system, and meters for monitoring chemical conditions (Eh, pH, and DO).

Polarization curves of balls and minerals were determined using the computerized potentiostat/galvanostat (SAMA500 Electrochemical Analysis System, SAMA research center, Iran) and three-electrode system by Tafel extrapolation method and technique of linear sweep voltammetry (LSV).

The three-electrode system was comprised of an Ag/AgCl (3.0 M KCl) electrode as a reference electrode, Pt wire as the counter electrode, and grinding media electrode as working electrode. All potentials were measured and reported versus the Ag/AgCl (3.0 M KCl) reference electrode (+210 mV versus SHE). All polarization experiments were also carried out with a sweep rate of 50 mV/s.

Moreover, in experiments, different gases (nitrogen, air, or oxygen) were continuously injected at the rate of 6 L/min into the mill to change the oxidation conditions. The pulp was

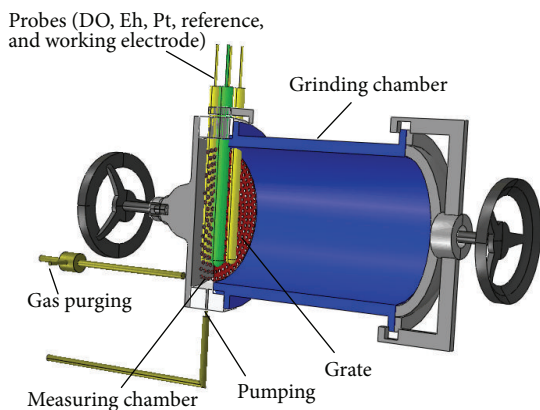


FIGURE 1: Schematic plan of specially designed ball mill.

also pumped out of the mill and mixed with the gases and then returned into the mill.

2.3. EDTA Extraction Technique. An EDTA (ethylene diamine-tetra acetic acid disodium) extraction technique has been widely used to determine the magnitude of oxidized iron species in the slurry [27]. Thus, EDTA extraction technique was carried out to determine the amount of oxidized iron species from minerals and/or grinding media on ball mill discharge as follows [27–29].

A 3 percent by weight solution of ethylene diamine-tetra acetic acid disodium salt was made up, and solution pH was adjusted to 7.5 sodium hydroxide. 250 mL of the EDTA solution was placed into a beaker and stirred using a magnetic stirrer. A 25 mL sample of the pulp was collected from mill discharge. Samples were weighted to determine the mass of pulp. The pulp was injected into the EDTA solution and then stirred for 5 minutes. At the end of the 5 minutes extraction time, the sample was filtered through a 0.22 micron Millipore filter paper using a vacuum filter. The filtrate was analyzed using atomic absorption spectroscopy (AAS). The solid from bulk sample from which have collected the 25 mL of pulp was assayed. Finally, the percent EDTA extractable iron was determined by dividing the mass of iron in the solution by the total mass of iron in the solids.

The EDTA extractable Fe percentage follows the methodology developed by Rumball and Richmond (1996) [27].

3. Results and Discussion

Potentiodynamic polarization is a direct current technique that gives fundamental information from, the corrosion rate, behavior of activity, passivity, and susceptibility to corrosion of the material. Also, polarization diagrams can be suitable to study galvanic interaction between minerals and grinding media. In the measurement, a potentiostat/galvanostat is used to control the driving force for the electrochemical reactions taking place on the working electrode (mineral or medium). Polarization curves of medium (low alloy and high carbon chromium steel balls), pyrite, and chalcocopyrite electrodes were obtained using described electrochemical

equipments. Results of potentiodynamic polarization studies for pyrite, chalcocopyrite, and low alloy and high carbon chromium steel balls under different aeration conditions at a scanning rate of 50 mV/sec are illustrated in Figures 2 and 3. According to the results of Figures 2 and 3, the following observations can be obtained.

Figure 2 indicates polarization curves of low alloy steel ball, pyrite, and chalcocopyrite under different aeration conditions and without aeration during grinding of the Sarcheshmeh copper ore with low alloy steel ball. Figure 2(a) exhibits that the cathodic polarization curves were extended from -990 mV to -585 , -377 , and -239 mV for medium, chalcocopyrite, and pyrite, respectively, whereas anodic polarization of medium, chalcocopyrite, and pyrite were extended, respectively, from -585 , -377 , and -239 mV to $+0.290$ mV.

In Figure 2(a), the activity, passivity, and transpassivity regions can be clearly distinguished both for chalcocopyrite and for pyrite. In the case of chalcocopyrite, a passivation behavior around -175 mV, and a transpassivation behavior was observed around $+180$ mV whereas for pyrite, passivation, and transpassivation behavior was seen around -63 and 199 mV, respectively. It was also observed active-passive-transpassive behavior for low alloy steel ball.

Figure 2(b) indicates that starting of passivity and transpassivity regions for low steel and chalcocopyrite are attained 49 and 125 mV and 218 and 257 mV in air purging conditions, respectively, whilst no passive phenomenon is found for pyrite.

As can be observed in Figures 2(c) and 2(d), all of the curves follow a typical form of active-passive-transpassive anodic behavior.

Figure 3 indicates polarization curves of high carbon chrome steel ball, pyrite, and chalcocopyrite under different aeration conditions and without aeration during grinding of the Sarcheshmeh copper ore. All of polarization curves for pyrite and chalcocopyrite exhibit passivation behaviour; however, they differ in nature of transition from active to passive state. The polarization plots for medium show a small passivating region, which may be due to the iron hydroxide species, which passivates the steel ball surface and prevents further oxidation. The magnitude of passivity region under nitrogen atmosphere is the greater than other conditions in all of curves.

As seen in Figure 3, the current reach a limiting value around a potential of -900 mV for pyrite and chalcocopyrite and -940 mV for high carbon chrome steel during cathodic polarization under nitrogen atmosphere (Figure 3(a)). Under air atmosphere, limiting current values attain around a potential of -910 mV for pyrite and chalcocopyrite and -860 mV for high carbon chrome steel during cathodic polarization in air purging (Figure 3(b)). Limiting current value reach to a potential of -745 and -930 mV for minerals (pyrite and chalcocopyrite) and high carbon chrome steel ball in O_2 purging, respectively, whereas is achieved value around a potential of -920 mV for both minerals and medium without aeration conditions (Figures 3(c) and 3(d)). Limiting current value is not observed for pyrite and chalcocopyrite in the anodic polarization while for the grinding media, limiting current value is attained at potentials above $+160$ mV in all of curves.

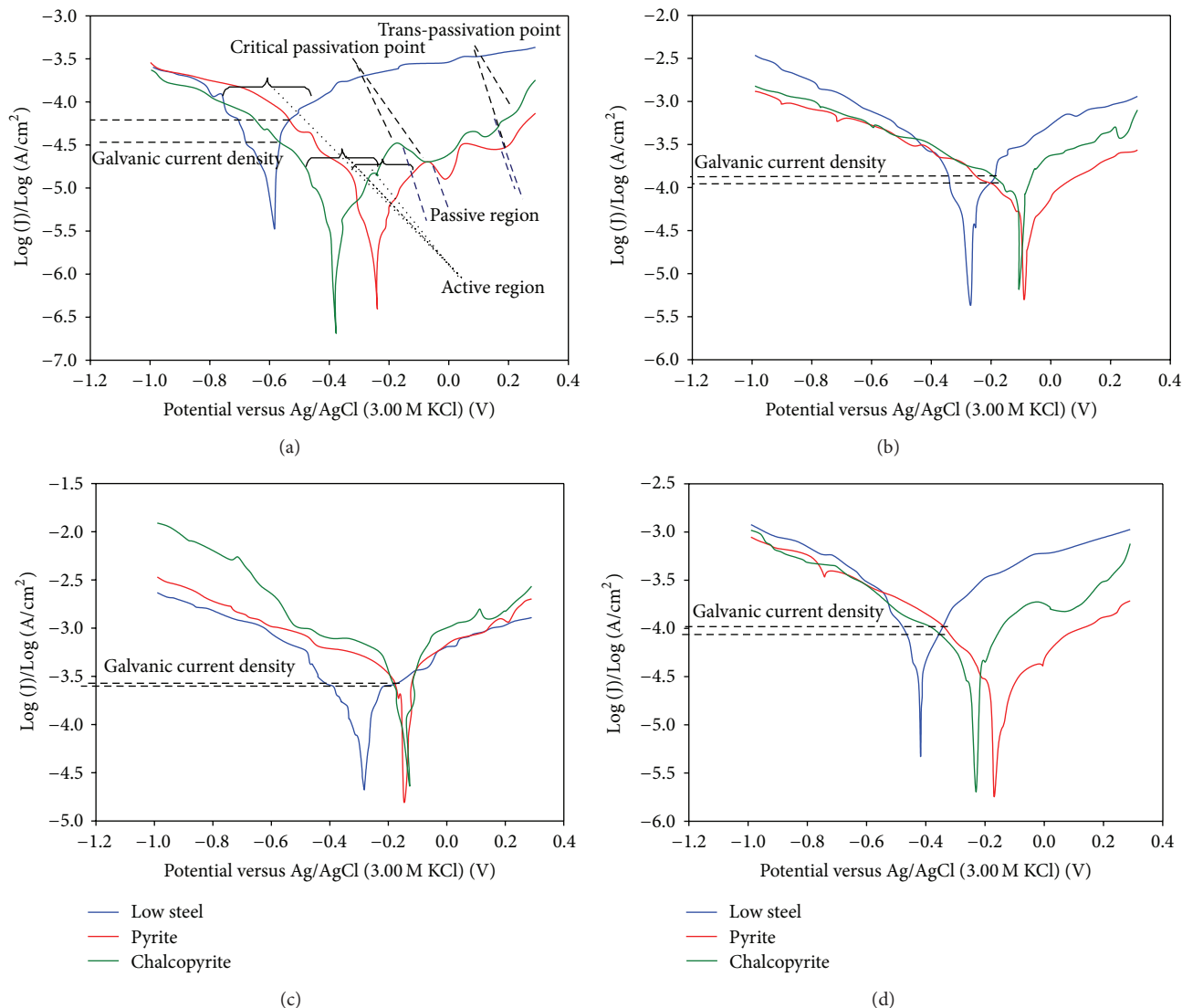


FIGURE 2: Potentiodynamic polarization sweep curves of grinding medium, pyrite, and chalcopyrite during grinding of ore with low alloy steel ball under nitrogen (a), air (b), and oxygen atmosphere (c), and without aeration (d) at a sweep rate of 50 mV/s.

In addition, Figures 2 and 3 exhibit a method of how to calculate the galvanic current from the polarization curves of the minerals and medium. Current in the polarization curves represents rate of all electrons exchange reactions at the surface of the electrodes. Table 3 presents the steady-state combination potentials and the galvanic current densities of pyrite and chalcopyrite with low alloy and high carbon chromium steel ball, measured in mill by using polarization curves, exposed to the different gases (nitrogen, air and oxygen) and at pH of 7–7.5, during grinding of the Sarcheshmeh copper sulphide ore.

As can be considered in Table 3, different aeration conditions alter the oxidation-reduction environment during grinding. Oxygen in the grinding system produces the highest galvanic current in the medium-mineral (pyrite and/or chalcopyrite) couple during grinding, whilst nitrogenation

resulted in the lowest galvanic current. As seen high carbon chromium steel ball under nitrogen gas has the lowest galvanic current for mineral-grinding media system and low alloy steel ball under oxygenation has the highest current. Therefore, the galvanic interaction between the grinding media and sulphide mineral was affected by type of media grinding and the injected gas (nitrogen, air and oxygen) type into mill during grinding.

Moreover, the derived results from Figures 2 and 3 and Table 3 show that the grinding media is anodic relative to the all sulphide minerals (pyrite and chalcopyrite), and the electrons flow from the media to the minerals. Thus, pyrite or chalcopyrite with a higher rest potential (open circuit potential, when net current is equal to zero) would act as the cathode, whilst the grinding media with a lower rest potential would act as the anode, when they are electrochemically

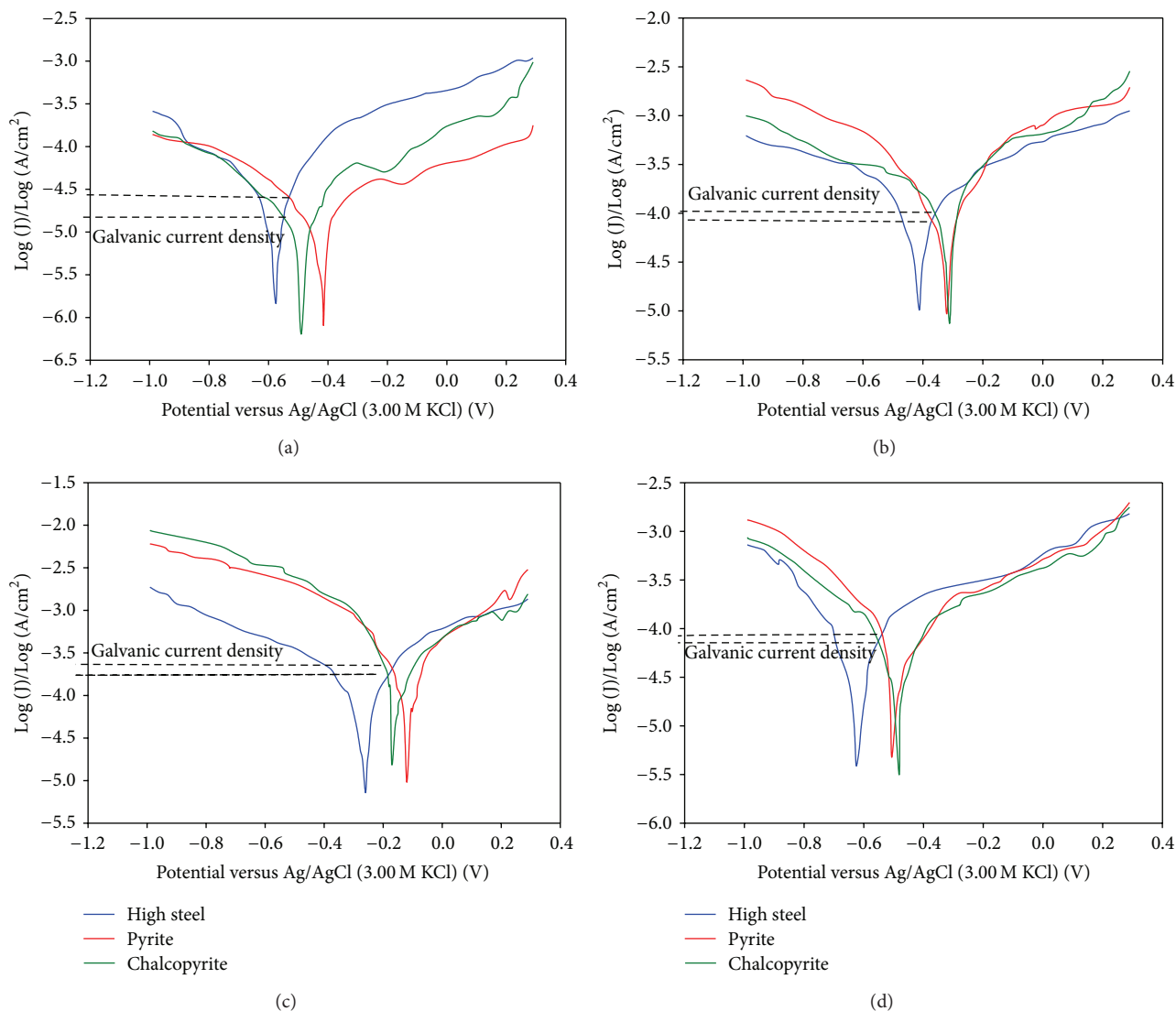
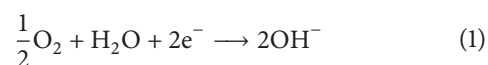


FIGURE 3: Potentiodynamic polarization sweep curves of grinding medium, pyrite, and chalcopyrite during grinding of ore with high carbon chrome steel ball under nitrogen (a), air (b), and oxygen atmosphere (c), and without aeration (d) at a sweep rate of 50 mV/s.

contacted. Model of galvanic interaction occurring between a single sulphide mineral (pyrite or chalcopyrite) and grinding media is illustrated in Figure 4(a) based on mixed potential model [30]. Pozzo et al. (1990) [31] described an electrochemical model for a two-sulphide mineral/grinding medium system as shown in Figure 4(b). According to Pozzo et al. (1990), in grinding of the Sarcheshmeh sulphide ore composed of chalcopyrite, pyrite (as two main mineral) with low alloy or high carbon chromium steel ball, the noblest electrode (the highest rest potential) in the series is pyrite (see Table 4). Therefore, pyrite will act as cathode and the grinding media always as anode. The other sulphide mineral (chalcopyrite), with lower rest potential than pyrite but higher rest potential than the grinding medium, developed an intermediate anodic (Figure 4) depending on its rest potential.

Under the above conditions, the following electrochemical reactions may be occurred on sulphide minerals and grinding media surface [22, 32–34].

Cathodic reaction on cathodic mineral surface:



Anodic reactions on medium surface:

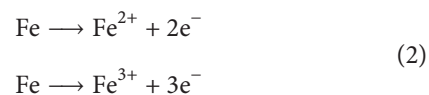


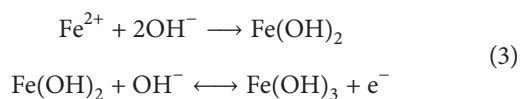
TABLE 3: The measured galvanic current densities ($\mu\text{A}/\text{cm}^2$) and combination potentials (mV) (versus Ag/AgCl (3.0 M KCl)) of pyrite, chalcopyrite with low alloy and high carbon chromium steel ball under different aeration conditions in mill.

Aeration conditions	Galvanic current density of pyrite and low alloy steel	Combination potentials (potential between pyrite and low steel ball)
Without aeration	109.63	-345
Nitrogen	63.41	-538
Air	111.97	-203
Oxygen	277.50	-179
Aeration conditions	Galvanic current density of chalcopyrite and low alloy steel ball	Combination potentials (potential between chalcopyrite and low steel ball)
Without aeration	86.54	-352
Nitrogen	33.98	-569
Air	139.23	-193
Oxygen	271.26	-189
Aeration conditions	Galvanic current density of pyrite and high carbon chromium steel ball	Combination potentials (potential between pyrite and high carbon chromium steel ball)
Without aeration	86.53	-531
Nitrogen	26.33	-535
Air	89.98	-372
Oxygen	212.18	-172
Aeration conditions	Galvanic current density of chalcopyrite and high carbon chromium steel ball	Combination potentials (potential between pyrite and high carbon chromium steel ball)
Without aeration	71.48	-552
Nitrogen	15.73	-556
Air	101.27	-362
Oxygen	170.56	-190

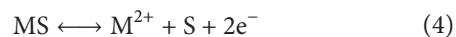
TABLE 4: Rest potential of sulphide minerals and steel media at near neutral pH [7, 32].

Mineral	Solution	Rest potential versus SHE/mV		
		N ₂	Air	O ₂
Galena	Distilled water	142	172	218
	0.5 mol/L NaCl (pH = 10.5)	45		95
Pyrite	Distilled water	405	445	485
	0.001 mol/L Na ₂ SO ₄	45		95
Pyrrhotite	Distilled water	125	262	295
Arsenopyrite	Distilled water	277	303	323
	Distilled water	190	355	371
Chalcopyrite	0.05 mol/L Na ₂ SO ₄	115		265
	0.5 mol/L NaCl (pH = 10.5)	65		115
Sphalerite	0.5 mol/L NaCl (pH = 10.5)	30		60
Mild steel	Distilled water	-515	-335	-175
	0.5 mol/L NaCl	-395		
Ferronickel steel	0.5 mol/L NaCl pH = 10.5	-255		-205

Precipitation:



Reaction on anodic mineral surface (two sulphide mineral and medium system),



As can be considered in above reactions, ferrous ions are released into the solution as a result of anodic oxidation of

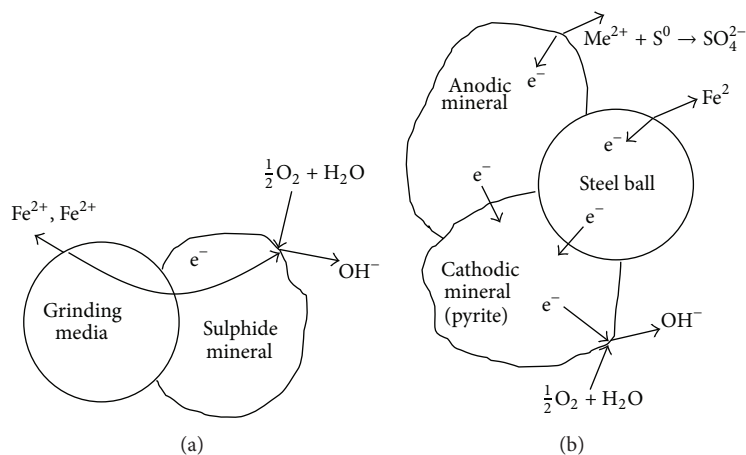


FIGURE 4: Model galvanic interactions between a single sulphide mineral (a) [31] and two sulphide minerals (b) [33] and steel ball during grinding.

grinding media simultaneously with the cathodic reduction of dissolved oxygen.

The flow of electrons from the grinding media to sulphide minerals increases the oxidation of grinding media [35], leading to more oxidized iron species in the slurry. In this work, the EDTA extraction technique was used as a measure of the corrosion of the system. It is not an accurate measure, but it gives general information on the process. The amount of oxidized iron species from minerals and/or grinding media in the mill discharge under different aeration conditions for low alloy and high carbon chrome steel balls were obtained by EDTA extraction technique as shown in Figure 5. It is observed that the grinding media, as well as the type of aeration influence the amount of EDTA extractable iron. It is seen that low alloy steel ball under oxygen atmosphere produces the highest amount of EDTA extractable iron in the slurry, whilst high carbon chromium steel ball under nitrogen atmosphere leads to the lowest amount.

4. Conclusion

The purpose of this study was to investigate the galvanic interaction between pyrite and chalcopyrite with low alloy and high carbon chromium steel balls in grinding of the Sarcheshmeh porphyry copper sulphide ore. A specialized laboratory grinding system, which linked to electrochemical equipment, was constructed to study the grinding environment electrochemistry and quantify the galvanic current between pyrite and chalcopyrite with grinding media. The major conclusions based on this research work can be summarized as follows.

- (i) High carbon chromium steel ball under nitrogen gas has the lowest galvanic current and low alloy steel ball under oxygen gas had the highest galvanic current in mineral-grinding media system.
- (ii) Grinding media was anodic relative to pyrite and chalcopyrite, and therefore the electrons flowed from the media to the minerals. Pyrite or chalcopyrite with

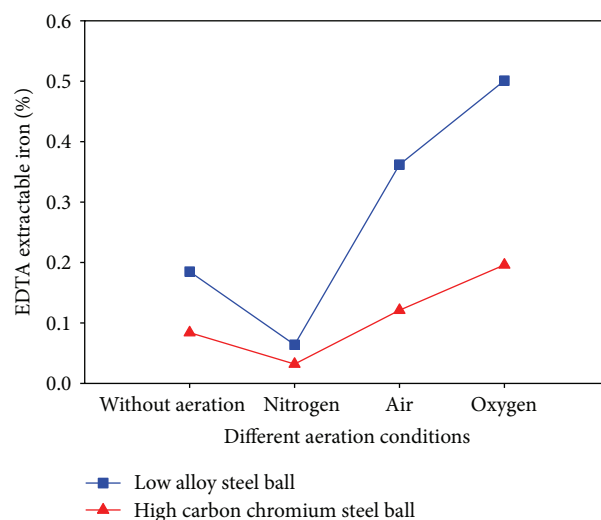


FIGURE 5: EDTA extractable iron in the mill discharge under different aeration conditions for two types of grinding media.

a higher rest potential acted as the cathode, whilst the grinding media with a lower rest potential acted as the anode, when they were electrochemically contacted in single mineral-media system.

- (iii) In two sulphide minerals-media (pyrite/chalcopyrite/media) systems, pyrite is the noblest electrode acted as cathode and the grinding media always as anode whilst chalcopyrite with lower rest potential than pyrite but higher rest potential than the medium developed an intermediate anodic depending on its rest potential.
- (iv) Low alloy steel ball under oxygen produced the highest amount of EDTA extractable iron in the slurry, whilst high carbon chromium steel ball under nitrogen atmosphere produced the lowest amount.

(v) Polarization curves for pyrite, chalcopyrite and medium (low alloy and high carbon chromium steel balls) were obtained by electrochemical equipment and using linear sweep voltammetry technique under different aeration conditions and without aeration. Approximately, in all of polarization curves of minerals and steel balls, the activity, passivity and transpassivity regions could be distinguished. The polarization plots for balls showed a small passivating region, which may be due to the iron hydroxide species, which passivates the steel ball surface and prevents further oxidation. In addition, limiting current value was also attained based on polarization plots.

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