INVESTIGATION OF THE ELECTROCHEMICAL FACTORS AFFECTING THE GRINDING ENVIRONMENT OF A PORPHYRY COPPER SULPHIDE ORE

Asghar Azizi¹, Seid Ziaoddin Shafaei², Mohammad Noaparast³ and Mohammad Karamoozian¹

¹Shahrood University of Technology, Department of Mining, Petroleum and Geophysics, Shahrood, Iran
²University of Tehran, School of Mining Engineering, Iran

(Received 9 May 2013; Accepted 26 August 2013)

Abstract

The objective of this study was to investigate electrochemical properties of grinding environment of the Sarcheshmeh porphyry copper sulphide ore. Influence of pH, solid content, water type, aeration condition and type of steel ball on pulp Eh, dissolved oxygen concentration (DO), open circuit potential (OCP) and EDTA extractable iron percentage and subsequently their influence on copper flotation were investigated. The results indicated that the low alloy steel balls had the lower Eh and DO values in relation to the high carbon chromium steel balls. The low alloy steel produces oxidized iron inside mill and reduces copper flotation. Gas changes from nitrogen to air and to oxygen resulted in higher Eh, DO and OCP values and consequently were caused formation of additional amount of oxidized iron species and lowered copper recovery. In addition, an increase in grinding pH and solid content and change of water type from tap water to distilled water decreased Eh and DO values and amount of EDTA extractable iron. It enhanced copper flotation.

Key words: grinding environment; pulp potential; dissolved oxygen; open circuit potential; EDTA extractable iron; copper recovery.

1. Introduction

In mineral processing, grinding is vitally important and dictates the success of downstream processes. Traditionally, grinding mills were only considered as devices to reduce particle size and liberate minerals so that value metals can be extracted economically by flotation, hydrometallurgy, pyrometallurgy or a combination of them [1].

The grinding process inevitably involves contact of the ore (minerals) with the surface of grinding device and the grinding medium. This not only causes wear, but also contamination of the ore with wear debris as well as with precipitated species on the ore surfaces, which this is often deleterious to copper flotation. Consequently, when a sulphide ore is subjected to wet grinding, corrosion of the ore and medium could be lead to complex interactions, such as galvanic effects, changes in the Eh of solution and the dissolution and precipitation of species on the ore surfaces. Galvanic interactions between the steel grinding media and sulphide ores increase steel consumption and reduce the corrosion of more noble sulphides, with commensurate higher oxygen consumption, and the possible precipitation of iron species on the ore particles [2-6]. There is some evidence that galvanic interactions between sulphide minerals and media during grinding can also affect froth stability and hence selectivity. In addition to the interactions

*Corresponding author: azizi.asghar22@yahoo.com
between the grinding media and the sulphide minerals, there are also galvanic interactions between the sulphide minerals themselves, and these galvanic interactions play an important role in the separation efficiency in subsequent flotation [7].

Flotation is an important and versatile mineral processing step used to achieve selective separation of minerals and gangue. It utilizes the hydrophobic (aerophilic) nature of mineral surfaces and their propensity to attach to rising air bubbles in a water–ore pulp as the basis for separation [9].

There are many investigations on the electrochemical behaviors in grinding system and significance of grinding environment in mineral and ore flotation [8, 10-25] but these investigations are not reported for grinding of porphyry copper sulphide ores. Therefore, this paper was aimed to study electrochemical behavior inside ball mills and influence of milling environment (pulp chemistry) on flotation process. This study was carried out on the Sarcheshmeh porphyry copper sulphide ore. The Sarcheshmeh copper ore is a major porphyry copper deposit, which is located in Kerman Province in the southeastern part of Iran.

2. Experimental section

2.1. Materials

The obtained samples from the ball mills input of the Sarcheshmeh copper mine were crushed in a jaw crusher (Fritsch 01.703). The size fraction of -2000 +250 micrometers was collected for experiments. Samples was then homogenized and sealed in polyethylene bags. Samples were chemically analyzed which their chemical compositions presented in Table 1.

| Table 1. Chemical composition of the Sarcheshmeh ore sample accompanying with size fractions (Wt %) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Element         | Cu              | Fe              | Mo              | S               | SiO₂            | Al₂O₃           |
| Weight, %       | 0.74            | 4.34            | 0.032           | 3.05            | 55.07           | 14.35           |

Samples of single crystalline pyrite and chalcopyrite were obtained to construct mineral electrodes from the Meiduck copper mine in the city of Babak, Kerman Province of Iran, and the Ghaleh Zari mine in Birjand city in south Khorasan Province of Iran, respectively.

Two type of steel ball were employed as grinding media, which their chemical compositions presented in Table 2.

| Table 2. Chemical compositions of the grinding media |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ball type       | Chemical compositions (Weight, %) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| High carbon chrome steel (HS) | C 0.039 | Si 0.698 | S 0.049 | P 0 | Mn 1 | Cr 13.25 | Mo 0.177 | Cu 0.044 |
| Low alloy steel (LS) | C 0.249 | Si 0.173 | S 0.024 | P 0.018 | Mn 0.586 | Cr 0.019 | Mo 0.002 | Cu 0.012 |

Sodium hydroxide was used as pH modifier to maintain the pH at the targeted value during grinding. Lime (CaO) was also used as modifier of pH in flotation process. Z11 (sodium isopropyl xanthate) and mercaptobenzothiazole were used as collector and MIBC (methyl isobutyl carbinol) and F742 (polypropylene glycol) were applied as frother.
Minerals and medium electrodes for electrochemical study were prepared according to the following procedure. Synthetic and natural mineral samples were cut into 0.7× 0.7 cm to fill in a Teflon tube. Copper wires were connected to the shaped medium and minerals with silver epoxy before they were encapsulated in epoxy resin. A fresh surface was generated before each experiment with 500 grit silicon carbide paper and then cleaned with acetone and double distilled water. After each experiment, the used working electrodes (minerals and medium) were repolished and then reused.

2.2. Grinding

In order to study the electrochemical behaviors of grinding environment of the Sarcheshmeh ore, a specialized grinding system was designed in R&D of the Sarcheshmeh copper mine that involved a specialized ball mill, electrochemical equipments, 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). Schematic representation of the specially designed grinding system (ball mill) is presented in Fig. 1.

2.3. EDTA extraction technique

The EDTA (ethylene diamine-tetra acetic acid disodium) extraction process was used to determine the amount of oxidized iron species from minerals and/or grinding media as a measure of the corrosion of the system. It is not an accurate measure, but it gives general information on the process. The EDTA extraction technique was carried out on the ball mill discharge [26-28]:

A 3 per cent by weight solution of ethylene diamine-tetra acetic acid disodium salt was prepared and solution pH was adjusted to 7.5 with sodium hydroxide. A 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 the pulp. The pulp was injected into the EDTA solution and then stirred for 5 minutes. At the end of the 5 minutes of extraction, 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 solids from bulk sample from which we collected 25 ml of pulp were assayed. Finally, the per cent EDTA extractable iron was determined by dividing the mass of iron in the solution by the total mass of iron in the solids.

2.4. Flotation

After grinding, the pulp was transferred to a 1.5 liter flotation cell. Flotation tests were conducted using a Denver flotation machine at the impeller speed of 1400 rpm. The pulp density was adjusted to 28% solids by volume at the beginning of each test. The slurry pH was set to be 11.8, which CaO was used for adjusting pH. Then 40 g/t collectors of Z11 (15 g/t) and mercaptobenzothiazole (25 g/t) were added to the cell and after 1 minutes, 30 g/t frothers of MIBC (15 g/t) and F742 (polypropylene glycol) (15 g/t) were added to the cell and finally after 2 minutes, air was opened and flowed inside the cell and the collecting of the froth was started. The concentrate froth samples were collected at the intervals of .5, 2, 4 and 8 min. The flotation froth was scraped every 10 s. Finally, the concentrate and tailing samples were filtered, dried and assayed.

3. Results and discussion

In order to investigate chemistry and electrochemistry inside mill, effects of five main factors (pH, solid content, water chemistry, gas purging and medium type) on the pulp potential, rest potential (open circuit potential) and dissolved oxygen concentration under different grinding conditions by measuring the Eh, OCP and DO were studied (Figs. 2-6).

Figure 2 indicates the effect of the type of the grinding media and different aeration conditions on the Eh during milling, when pulp pH, solid percentage and used water were 7-7.5, 35 and tap water, respectively. Figure 3 shows the effect of pH, solid content and water type (water chemistry) of on Eh during grinding of ore with the low alloy steel ball without aeration, when the values of all factors were constant except one which changes. All potentials were measured and reported versus the Ag/AgCl (3.0 M KCl) reference electrode (+210 mV vs. SHE).
Influence of pH, solid content and water type on pulp potential (Eh) during grinding of ore with low alloy steel ball without aeration conditions

It can be seen from Fig. 2 that steel ball type and aeration conditions are affecting pulp potential and alter the oxidation-reduction environment during grinding. Oxygenation during grinding and the use of the high carbon chromium steel ball as the grinding media increase the Eh value. This may be due to the high oxygen concentration (Fig. 4) but nitrogenization and the use of low alloy steel ball as medium result in a lower Eh value.

It is apparent from Fig. 3 that an increase in pulp pH and solid percentage decreases the Eh value and lead to a reducing environment. It is also observed that with the change of the water type from tap water to distilled water, the pulp potential is reduced.

Figures 4 and 5 indicate the effect of steel ball type and aeration conditions and effect of pH, solid content and water type on dissolved oxygen concentration, respectively. It was found that the obtained trends for dissolved oxygen concentration were similar to those attained for Eh.

As can be seen, when oxygen is added to grinding system DO value increases markedly, while grinding under nitrogen provides DO value closed to zero.
The rest potential or open circuit potential is as one of the important electrochemical properties that is not only an indication of the susceptibility of a material to corrosion, but also determines the role of grinding media and sulphide minerals in the galvanic couple when exposed to the same environment [22]. Therefore, the steady-state electrode potentials (rest potential or open circuit potential) for chalcopyrite, pyrite, low alloy steel ball under different aeration conditions during grinding of the Sarcheshmeh ore as a function of grinding time was measured, and illustrated in Fig. 6.

![Graph](image)

**Figure 6.** Influence of low alloy and high carbon chromium steel balls and different aeration conditions on open circuit potential at pH 7-7.5 and solid content equal to 35% during grinding.

This figure exhibits the effect of two types of grinding media and injecting three types of gas (oxygen, air and nitrogen) into mill on the open circuit potential at pH, 7-7.5 and solid percentage equal to 35 when tap water is used. As can be observed, the open circuits potential of both steel ball and minerals are significantly influenced by the different aeration condition and type medium in grinding of the Sarcheshmeh ore. It is seen that with increasing grinding time the rest potentials increase in the presence of oxygen. The grinding media were found to be more “noble” than the minerals. After determining the electrochemical behaviour of grinding environment of the Sarcheshmeh copper ore, EDTA and flotation experiments were carried out to study the role of factors affecting the grinding environment on the corrosion of grinding system and the flotation process. Results were presented in Figs. 7-9 and Table 3.

![Graph](image)

(a)

![Graph](image)

(b)

**Figure 7.** Influence of grinding pH (a) and solid percentage (b) on copper recovery.
Figure 8. Correlation between EDTA extractable iron percentage and copper recovery

Figure 9. Correlation between EDTA extractable iron percentage and concentrate grade (Cu %) for low alloy and high carbon chromium steel balls

According to the results of Figures 7, 8 and 9 and Table 3, several observations can be obtained. The changes of gas from nitrogen to air and to oxygen and change of medium type from high carbon chromium to low alloy steel ball influence the oxidation conditions and led to more oxidized iron (Table 3). Consequently, the increased oxidized iron amount causes a stronger galvanic couple between balls and minerals during grinding and increases corrosion rate of the balls. These trends may be caused by the fact that the considered factors significantly alter the pulp potential and dissolved oxygen concentration during grinding as shown in Figs. 2-5.

Similar trends are also observed at the lower pH and solid content and when the tap water is used. This may be due to the formation of passive ferric oxide at high pH and solid percentage.

These factors strongly affect copper recovery. When the Sarcheshmeh ore is ground with high carbon chromium steel balls in the presence of nitrogen, the highest recovery of copper is obtained in flotation, while the presence of oxygen in the mill produces an increase amount of iron species from the grinding media on copper minerals surface from ore and reduces copper recovery in flotation. As can see, the low alloy steel ball causes lower recovery of copper. These effects of grinding media on flotation have been attributed to either the metal oxidation species, derived from grinding media, which decrease the flotation recovery [13, 29-30] or sulphur rich oxidation species, derived from the mineral, which increase the mineral flotation recovery [12].

It is also observed that the increase in grinding pH and solid content raise copper flotation (Figure 7). According to Figure 7, grinding pH and solid content can be correlated with copper recovery by equations 1 and 2, respectively.

\[
y = 0.73x^2 - 11.63x + 119.18, R^2 = 0.998 \quad (1)
\]

\[
y = 18.36 \ln(x) + 6.438, R^2 = 0.954 \quad (2)
\]

In addition, it is seen that the water chemistry in the grinding stage influences copper recovery.

It can be found from the presented results (Table 3 and Figures 8 and 9) that the produced amount of oxidized iron species in
the mill significantly influences copper recovery and concentrate grade in flotation process. Copper recovery is decreased with increasing oxidized iron for both low alloy steel ball and high carbon chromium steel ball, while the grade of the concentrate is increased for one type of steel ball. As can be considered in Table 3, grinding system under nitrogen and high carbon chromium steel ball are resulted in the better recoveries and grades.

Figure 8 indicates a relationship between copper recovery and amount of oxidized iron, which recovery \( y \) is depended on the produced amount of oxidized iron \( x \) inside mill and can be expressed by the following regression equation:

\[
y = -12.7 \ln(x) + 48.72, R^2 = 0.975 \quad (3)
\]

It is apparent from Fig. 8 that a greater oxidation of iron (EDTA extractable iron percentage) results in a greater decrease of copper recovery.

Figure 9 shows that concentrate grade is correlated with EDTA extractable iron percentage for low alloy and high carbon chromium steel balls by regression equations 4 and 5, respectively.

\[
y = 1.342 \ln(x) + 12.03, R^2 = 0.976 \quad (4)
\]

\[
y = 1.577 \ln(x) + 14.89, R^2 = 0.967 \quad (5)
\]

### Table 3. EDTA extractable iron percentage and copper recovery of flotation under different grinding conditions

<table>
<thead>
<tr>
<th>Factors</th>
<th>EDTA extractable Fe (%)</th>
<th>Copper recovery (%)</th>
<th>Concentrate grade (Cu %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7-7.5</td>
<td>Solid (%)</td>
<td>Gas purging (l/min)</td>
<td>Water type</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>Non gas</td>
<td>Tap</td>
</tr>
<tr>
<td>10.10.5</td>
<td>35</td>
<td>Non gas</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>55</td>
<td>Non gas</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>Non gas</td>
<td>Distilled</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>O₂</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>N₂</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>Non gas</td>
<td>Tap</td>
</tr>
<tr>
<td>10.10.5</td>
<td>35</td>
<td>Non gas</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>55</td>
<td>Non gas</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>Non gas</td>
<td>Distilled</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>O₂</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>Air</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>N₂</td>
<td>Tap</td>
</tr>
<tr>
<td>7-7.5</td>
<td>35</td>
<td>N₂</td>
<td>Tap</td>
</tr>
</tbody>
</table>

### 4. Conclusions

Electrochemical characteristics of factors affecting grinding environment of the Sarcheshmeh porphyry copper sulphide ore and flotation were studied by measurement of the pulp potential, rest potential, dissolved oxygen concentration and amount of oxidized iron derived from steel balls and minerals. The results can be summarized as it follows.

I. Steel ball type and aeration conditions significantly influence electrochemical properties of the slurry inside the mill (i.e. pulp potential, open circuit potential and dissolved oxygen concentration) and
A. Azici et al. / JMM 49 A (1) (2013) 45 - 55

cause oxidation-reduction environment during grinding.

II. The water chemistry changes from tap water to distilled water and increases pulp pH and solid percentage, reduces the pulp potential (Eh) and dissolved oxygen (DO) leading to a reducing environment.

III. The gas changes from nitrogen to air and to oxygen due to creation of oxidation conditions (high Eh and DO value) resulted in a further amount of oxidized iron species (EDTA extractable iron value) and consequently lower copper recovery (copper floatability) while the concentrate grade was slightly increased with increasing amount of oxidized iron inside mill for one type of steel ball.

IV. Low alloy steel ball produced higher amount of EDTA-extractable-iron in the mill relatively to high carbon chromium steel ball and significantly reduced copper recovery in presence of oxygen. Also, a change of the ball type from low alloy to high carbon chromium steel ball enhanced the slurry Eh and DO value.

V. Increase in grinding pH and solid content enhanced copper recovery. This may be due to a reduced amount of oxidized iron inside the mill and formation of a passive ferric oxide film on the steel balls. In addition, regression equations were suggested for relationship between copper recovery and grinding pH ($y = 0.73x^2 - 11.63x + 119.18, R^2 = 0.998$) as well as between copper recovery and solid content ($y = 18.36\ln(x) + 6.438, R^2 = 0.954$).

VI. Water type is another factor that affects the EDTA-extractable-iron percentage and subsequently copper recovery.

VII. Copper recovery can be correlated with the amount of oxidized iron species of the mill slurry by a logarithmic regression equation ($y = -12.7\ln(x) + 48.72$).

5. Acknowledgments

This work was supported by the Sarcheshmeh copper mine (Research and Development Division) funded by National Iranian Copper Industries Company. The authors wish to thank them for supporting this research.

6. References


