Removal of Metallic Impurities from Off-Grade Copper Concentrate in Alkaline Solution

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Abstract

The removal of metallic impurities from off-grade copper concentrate was investigated in alkaline solution with H₂O₂. The analysis results of XRD and SEM-EDS revealed the oxidative mechanisms of all sulfides. The influence of various parameters of alkaline leaching were investigated including concentrations of sodium hydroxide and hydrogen peroxide, liquid to solid ratio, leaching time and temperature. The results showed that the removal rate of Mo, As and Zn were increased with increasing leaching time and H₂O₂ concentration, and that the removal rate of Mo, As and Zn were firstly increased and then slightly decreased with increasing liquid to solid ratio, temperature and NaOH concentration, respectively. More than 95% Mo, 94% As, and 94 % Zn are removed from the off-grade concentrate under the optimum conditions, while only 1.7% Cu is dissolved. These optimum conditions were sodium hydroxide 1.5 mol/L, hydrogen peroxide 1.0 mol/L, temperature 50°C, liquid to solid ratio 5/1 mL/g and leaching time 5 h.

Keywords

Copper Concentrate, Impurities, Removal, Alkaline Leaching, Hydrogen Peroxide

1. Introduction

In China, There are many porphyry copper deposits bearing molybdenum, ar-

senic, zinc and aluminum *et al.* [1]-[7]. The copper concentrate is often obtained by conventional flotation process, but those impurities of molybdenum, arsenic, zinc and aluminum usually exist in copper concentrates. Molybdenum, aluminum and zinc are valuable metals worthy of being recovered, but arsenic lowers the economic value of the copper concentrate when the presence content of arsenic is higher than 0.5% in copper concentrate [8].

The copper concentrates with the content of arsenic less than 0.5% are generally processed by smelting/converting technology. Whilst the copper concentrates contain high amount of arsenic, the smelting/converting technology has a potential risk of environmental pollution with toxic arsenic compounds. In addition, the presence of arsenic in copper concentrates will result in the deterioration of the quality of the final copper cathodes.

There are an off-grade copper concentrate with high content of arsenic (2.17%) and low content molybdenum (2.62%), which is collected from Tibet region in China. Owing to high content of arsenic and low content of molybdenum, this copper concentrate is low economic value and is difficult to sell out. Therefore the removal impurities from this off-grade concentrate make a focus.

The removal methods of arsenic such as alkaline leaching and acid leaching have been investigated from copper concentrate, for example, enargite leaching with Na_2S - NaOH , NaHS - NaOH and NaOH - H_2O_2 media [9] [10] [11], tennantite and enargite oxidation leaching with H_2O_2 at pH 5.0 [12] and enargite leaching using atmospheric in acidic ferric sulfate media [13]. Likewise, the separation of molybdenum from sulfide ores by wet leaching has been studied including the oxygen pressure [14], sodium hypochloride [15], electro-oxidation [16] and bioleaching methods have been performed [17].

Although there many reports on dealing with molybdenite and As-sulfides, respectively, there is little information concerning the treatment of copper concentrate associated with arsenic, molybdenum and zinc. To upgrade the copper concentrate, a new method is investigated to remove the impurities in the copper concentrate in alkaline solution using H_2O_2 as an oxidant.

2. Materials and Experiments

2.1. Copper Concentrate and Reagents

An off-grade copper concentrate with chalcopyrite, tennantite and molybdenum was selected as the raw material in this work to better understand the leaching behavior of metals in the alkaline leaching process. The concentrate was from Huatailong Mining Development Co. Ltd, Mozhuogongka region in Tibet province, P.R. China. It was first dried overnight in an oven to remove moisture, and then sieve to collect particles of less than 0.075 mm. All chemicals like sodium hydroxide and hydrogen peroxide were of analytical grade, supplied by Shanghai Sinopharm Chemical Co. Ltd, Republic of China.

2.2. Leaching Tests

All leaching experiments were conducted in a conical flask using a shaking ma-

chine. The copper concentrate sample was used in 20 to 100 g scale. The liquid to solid ratio varied from 2/1 to 10/1 mL/g. The temperature variation studies were performed from 20°C to elevated temperature 70°C. The concentrations of NaOH and H₂O₂ were changed from 0.5 to 2.5 mol/L and 0.4 to 1.4 mol/L, respectively. The leaching time also was ranged from 1 h to 7 h. After a certain leaching treatment, the slurry was withdrawn from the reactor and vacuum filtered was washed twice with 400 mL distilled water. The volume of the filtered pregnant solution was measured by a measuring cylinder and 5 mL of liquor sample was collected to assay molybdenum, copper, arsenic and zinc by an inductive coupled plasma-atomic emission spectrometer (ICP-AES), and then the residues were dried for 8 h at 105°C. The dried residues were used to be analyzed.

2.3. Analysis and Methods

S content in solid samples was determined using a high frequency IR carbon and sulfur analyzer (CS-3000, Beijing Nake Analysis Instrument Co. Ltd). The other elements in solid samples were all analyzed using acid or alkaline digestion and atomic absorption spectrometer (PE-AA700, PerkinElmer Company, USA). Element concentrations in solution were all measured by an inductive coupled plasma-atomic emission spectrometer (Optima 2100DV, PerkinElmer Company, USA). Mineral compositions of solid samples were performed by an X-ray diffractometer (D/Max 2500, Rigaku). The constituents and morphology of the copper concentrates before and after leaching were examined by Scanning Electron Microscope-Energy Dispersive X-Ray spectroscopy analyses (SEM-EDS, Jeol JSM 6010LA) at 10-20 KeV and high vacuum conditions.

3. Results and Discussion

3.1. Analyses and Characterization

Table 1 shows in the chemical composition of a copper concentrate sample, indicating that besides copper and iron, silicon, sulfur, arsenic, calcium and zinc are the main associated with elements. Mineralogical analysis of the copper concentrate given in **Figure 1** indicates the sample consists of chalcopyrite (CuFeS₂), tennantite (Cu₁₂As₄S₁₃), molybdenite (MoS₂), calcite (CaCO₃) and quartz (SiO₂). The phase of zinc exists as zinc sulfide by chemical phase analysis [18].

3.2. Theoretical Leaching Behaviors of Cu, As, Mo and Zn Phase and Chemistry of Solution

The removal of metallic impurities from the copper concentrate is related to the oxidation and dissolution of sulfides including Cu-, As-, Mo- and Zn- sulfides in the copper concentrate. The leaching behaviors of metal phases in the copper concentrate under alkaline leaching conditions can be predicted from thermodynamic diagrams.

Figure 2 indicates the thermodynamically stable regions of the form of Cu, Fe and sulfur in aqueous solution. In the Cu-Fe-S-H₂O system [19], soluble Cu²⁺,

Table 1. Chemical composition of copper concentrate sample (% wt).

Constituent	Cu	Fe	S	Ca	Mo	As	SiO ₂	Zn
Wt (%)	11.40	10.51	13.70	5.98	2.62	2.17	39.36	0.42

Figure 1. X-ray patterns of copper concentrate and the residues.

Figure 2. Eh-pH diagram for the Cu-Fe-S-H₂O system with the preponderant copper and iron species shown in each domain [19].

Fe²⁺ exist only in acid solution (pH < 6) and Fe³⁺ exist only in acid solution (pH < 3). A potential increase leads to the sequential alternation CuFeS₂→Fe₂O₃ and CuS→Cu₂S→ Cu²⁺ or Cu⁺. In alkaline solution, as potential increases CuFeS₂→CuS→ Cu₂S is possible and its further increase leads to the formation

of insoluble CuO and Fe₂O₃.

At the same time the oxidation of CuFeS₂ during oxidative alkaline leaching is difficult and complicated owing to the multilevel translation (CuFeS₂→CuS→Cu₂S). From thermodynamic considering, the oxidative reaction of chalcopyrite may be written as follows:

Copper oxide is expected to solubilize in alkaline solution via the following reaction by Wagman *et al.* [20].

where n refers to the ionic state of hydrolysis and may present 0, 1, 2, 3 or 4. As shown in Equation (2), the species of CuO dissolved in alkaline solution may be Cu(OH)₂, Cu(OH)₃⁻ or Cu(OH)₄²⁻. But Cu(OH)₂ is a dominant aqueous species and is easily transformed into CuO in high alkaline solution.

The Eh-pH diagram for the behavior of Cu-As-S-H₂O system is presented in Figure 3 [21] [22]. As shown in Figure 3, the transformation of Cu₁₂As₄S₁₃→As (V) takes place in the whole pH range from 0 to 14 under oxidizing atmosphere. In alkaline solution, the soluble states of As (V) exist as H₂AsO₄⁻, HAsO₄²⁻ and AsO₄²⁻ under oxidizing atmosphere. As pH increases above 12, the most of As (V) occurs as AsO₄²⁻. At the same time the transformation of copper in the tennantite will turn into CuO in alkaline solution under oxidizing atmosphere.

The Eh-pH diagram for the behavior of Mo-S-H₂O system [23] is shown in Figure 4. It is indicated that the transformation of MoS₂→Mo (VI) takes place in the whole pH range from 0 to 14. Reaction of Mo (VI) in aqueous solution can be deemed as a complex formation of between MoO₄²⁻ and H⁺. In alkaline solution, the concentrate of hydrogen ion is so low that most of Mo (VI) occurs as monomeric MoO₄²⁻ [24].

The Eh-pH diagram for the behavior of Zn-S-H₂O [25] system is also given in Figure 5. It shows the thermodynamically states of the forms of zinc in aqueous. In the Zn-S-H₂O system, the soluble states of zinc exist as Zn²⁺ and ZnO₂²⁻ in solution. As pH of the solution is above 13, the most of soluble state of zinc exists ZnO₂²⁻, which means that ZnS can be oxidized in alkaline leaching under oxygen.

3.3. Removal Behaviors of Metallic Impurities of Off-Grade Copper Concentrate

3.3.1. Effect of Temperature on the Removal of Metallic Impurities

H₂O₂ is thermolabile, and higher temperatures are generally favorable for leaching from the perspective of leaching kinetics, therefore, the temperature was researched in the range of 20°C to 70°C under the other constant conditions of NaOH 1.5 mol/L, H₂O₂ 1.0 mol/L, leaching time 5 h, and liquid to solid ratio 5/1 mL/g. The experimental results are presented in Figure 6.

The extractions of Mo, As and Zn increase from 49.2% to 95.6%, 38.9% to 93.4%, 45.3% to 94.4%, respectively, when the temperature increases from

Figure 3. Eh-pH diagram for the Cu-As-S-H₂O system with [Cu] = 0.075 M, [As] = 0.025 M, [S] = 0.1 M. Sulfur oxidation includes all sulfoxy species [21] [22].

Figure 4. Eh-pH diagram for the Mo-S-H₂O system at 25°C with [Mo] = 1 mol/kg and [S] = 1 mol/kg drawn using HSC chemistry software [23].

20°C to 50°C. The extractions of Mo, As and Zn plateau 95.6%, 93.4%, and 94.4%, respectively, at 60°C, and then decrease to 86.9%, 84.9% and 88.2%, respectively, when the temperature was increased to 70°C. These results indicate the optimum effect of H₂O₂ for the oxidation of CuFeS₂, MoS₂ and ZnS is

Figure 5. Eh-pH diagram for the Zn-S-H₂O system at 25°C standard condition [25].

Figure 6. Effect of temperature on the leaching of metals.

obtained at 50°C, whereas at temperatures higher than 60°C and peculiarly at 70°C, H₂O₂ was resolved too early due to the high temperature and did not act a role in the oxidation [26], with a large amount of tiny bubbles produce immediately after the addition of H₂O₂, which means that the concentration of H₂O₂ will decrease rapidly in the solution and this will lower the kinetics of the leaching process. The dissolution of copper increase in the temperature range of 20°C to 70°C, but it only reaches a maximum of 1.95% at 70°C. Thus 50°C with a ex-

traction of Cu 1.75% was selected as the optimum temperature for the subsequent experiments.

3.3.2. Effect of Leaching Time on the Removal of Metallic Impurities

The influence of the leaching time on Cu, Mo, As and Zn extraction was investigated at NaOH 1.5 mol/L, H₂O₂ 1.0 mol/L temperature 50°C, and liquid to solid ratio 5/1 mL/g. The result is given in **Figure 7**. About 96 % Mo, 93% As and 94% Zn were leached after 5 h. Further prolonging leaching duration give no significant increase in As and Zn extraction, which means that 5 h is enough to leach Mo, As and Zn from copper concentrate. In spite that the copper extraction increases with the extension of leaching time, the overall is also less than 2.07% within 7 h.

3.3.3. Effect of Sodium Hydroxide Concentration on the Removal of Metallic Impurities

In order to study the effects of NaOH concentration on the extraction of Mo, As and Zn, and the dissolution of copper. NaOH concentration was varied from 0.5 to 2.5 mol/L, while liquid to solid ratio 5/1 mL/g, H₂O₂ 1.0 mol/L, leaching time 5 h and temperature 50°C. The results are shown in **Figure 8**. The extractions of Mo, As and Zn increase from 72.2% to 95.8%, 66.5% to 93.4%, 58.4% to 94.3%, respectively, when the NaOH concentration rises from 0.5 mol/L to 1.5 mol/L. Even when NaOH concentration further increases, the extractions of As and Zn show no significant difference. On the other hand, it is also observed in Fig. 8 that the Mo extraction decreases slightly with the rise of NaOH concentration, which was is good agreed with the results obtained by several researchers [27] [28]. It can be explained that Mo (VI) in the solution can be absorbed by Fe₂O₃ produced much in situ precipitation. In spite that the Cu extraction increases with increasing the NaOH concentration from 0.5 to 2.5 mol/L, the maximum extraction of Cu is only 2.05% at NaOH 2.5 mol/L. Therefore, sodium hydroxide concentration 1.5 mol/L was chosen as for the subsequent experiments.

3.3.4. Effect of Hydrogen Peroxide Concentration on the Removal of Metallic Impurities

The influence of H₂O₂ concentration on the removal of metallic impurities was investigated at NaOH 1.5 mol/L, liquid/solid ratio 5/1 mL/g, leaching time 5 h and temperature 50°C. As presented in **Figure 9**, the extraction of Mo, As and Zn is higher than that of Cu in these experiments, which can be explained by the Eh-pH diagrams of Cu-Fe-S-H₂O, Cu-As-S-H₂O, Mo-S-H₂O and Zn-S-H₂O systems, respectively, for the oxidative leaching behaviors of metals in the copper concentrate.

The standard reduction potential of H₂O₂ ($E_{\text{H}_2\text{O}_2/\text{OH}^-}^0 = 0.87 \text{ V}$) is higher than that of O₂ ($E_{\text{O}_2/\text{OH}^-}^0 = 0.401 \text{ V}$), therefore using H₂O₂ as an oxidant instead of oxygen, the oxidation reactions of CuFeS₂, Cu₁₂As₄S₁₃, MoS₂ and ZnS can take place as follows:

Figure 7. Effect of leaching time on the leaching of metals.

Figure 8. Effect of sodium hydroxide on the leaching of metals.

Figure 9. Effect of hydrogen peroxide on the leaching of metals.

The extraction of Mo, As and Zn increase from 30.8% to 95.7%, 48.4% to 93.4% and 51.3% to 94.4%, respectively, when hydrogen peroxide concentration increases from 0.4 mol/L to 1.0 mol/L. However there is no significant change on the extraction of Mo, As and Zn when the hydrogen peroxide concentration is above 1.0 mol/L. Although the Cu extraction increases with the rise of H₂O₂ concentration, the maximum Cu extraction is only 2.0% at H₂O₂ 1.3 mol/L. Considering the economic factor, the optimum H₂O₂ concentration is fixed at 1.0 mol/L for the subsequent experiments.

3.3.5. Effect of Liquid to Solid Ratio on the Removal of Metallic Impurities

The effect of liquid to solid ratio on the removal of Mo, As, Zn and Cu was investigated under the conditions of sodium hydroxide 1.5 mol/L, hydrogen peroxide 1.0 mol/L, leaching time 5 h and temperature 50°C. The results are given in **Figure 10**. The extractions of Mo, As and Zn increase along with increasing the liquid to solid ratio from 2 to 5 mL/g, maximize to 95.8%, 93.4% and 94.4%, respectively, at the ratio of 5 mL/g and then decrease slightly. Cu extraction also decreases distinctly with the rise of liquid to solid ratio. The lower dissolved fractions of Mo, As, Zn and Cu can be explained by the fact that at higher liquid to solid ratio, more quartz reacts with NaOH to form the thick slurry, which can postpone the mass diffusion in the liquid-solid phase system. This similarly result is reported in the oxidative alkaline leaching of Ni-Mo ore by Wang *et al.* [23]. At the same time, it is found that Si extraction increases from 10.34% to 26.23% during the leaching when the liquid to solid ratio rise from 5 to 9 mL/g. considering this fact, the liquid to solid ratio 5 mL/g was selected.

Figure 10. Effect of sodium hydroxide on the leaching of metals.

3.4. Morphology of the Leach Residues

According to the above results, the optimum conditions for selective extraction of Mo, As and Zn from off-grade copper concentrate are listed as follows: NaOH concentration of 1.5 mol/L, H_2O_2 concentration of 1.0 mol/L, temperature 50°C, liquid to solid ratio of 5/1 mL/g, leaching time 5 h. Under these conditions, the Mo, As and Zn extractions are up to about 95.8%, 93.4% and 94.4%, respectively, and only 1.74 % Cu was dissolved into the solution.

Figure 1 shows the XRD results of the residues leaching for 3 h and 5 h at the optimum other conditions. Compared with the XRD pattern of original concentrate (**Figure 1**), the peaks of molybdenite and tennantite in the residues have disappeared, which indicate that tennantite and molybdenite can be oxidized completely. There occur as new phases including tenorite (CuO) and delafissite ($CuFeO_2$) in the residues. According to the reaction Equations (6) and (7), tenorite could produced from the oxidation of chalcopyrite and tennantite. If Equation (6) could takes place, there exist CuO and F_2O_3 in the residues, however F_2O_3 formed could not detected in the residues by X-ray diffraction method. This may be attributed to a fact that F_2O_3 is amorphous. However there occurs as a new delafissite in the residues, it is thought to originate from the oxidation of chalcopyrite. A chalcopyrite electrode was studied by Electrochemical Impedance Spectroscopy in an alkaline solution for different oxidation potentials by Velásquez *et al.* [29]. This result shows that the $CuFeO_2$ on the surface of chalcopyrite can be formed by an oxidation process (+0.8 V vs. SCE). The standard reduction potential of H_2O_2 ($E^0 H_2O_2/OH^- = 0.87$ V) exceeds 0.8 V, it is possible that chalcopyrite was oxidized to form $CuFeO_2$ during alkaline leaching process. And the oxidation of chalcopyrite could be taken place as follows:

Figure 11. The SEM-EDS results determined on the cross-section of the residue: (a) CuFeO_2 , (b) Fe_2O_3 and (c) CuFeS_2 .

In order to further understand the oxidation mechanism of chalcopyrite, the microscopic structure of the residue and the chemical compositions of the points analyzed by SEM coupled with EDS, are presented in **Figure 11**. The SEM result indicates that the surface structures of primary particles have a porous and rough surface morphology. As can be seen from **Figure 11**. EDS-A, B, C, The EDS analysis results show that the elements distributed at the points A, B and C are close to the theoretical elemental contents of CuFeO_2 (w.t. 36.9% Fe, w.t. 41.2% Cu, 21.1% O), Fe_2O_3 (w.t. 69.8% Fe, w.t. 30.2% O) and CuFeS_2 (w.t. 30.4% Fe, w.t. 34.6% Cu, w.t. 35.0% O), respectively, namely, it indicates that the phases of micro-area A, B and C occur as delafossite, Fe_2O_3 and chalcopyrite, respectively. These results show that chalcopyrite can oxidize simultaneously as

the Equations (6) and (10) in alkaline solution containing H_2O_2 .

4. Conclusions

The studies have been carried out to up-grade the copper concentrate. These impurities of Mo, As and Zn were leached mainly in alkaline solution containing hydrogen peroxide.

The oxidative mechanisms of chalcopyrite, tennantite and molybdenite in the copper concentrate were demonstrated by methods of XRD and SEM-EDS analysis, especially the chalcopyrite oxidation simultaneously takes place as Equations (6) and (10):

About 95.80% Mo, 93.4% As, and 94.4% Zn can be removed under the optional conditions: sodium hydroxide 1.5 mol/L, hydrogen peroxide 1.0 mol/L, temperature 50°C, liquid to solid ratio 5/1 mL/g and leaching time 5 h.

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