報告

Acid Leaching of Chalcopyrite Concentrate with Hematite Powder as an Effective Promoter*

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Leaching of chalcopyrite concentrate having specific surface area of about 3 m²/g in 0.5 mol/dm³ HCl solution was conducted at 333 K using hematite (Fe₂O₃) and ferric chloride (FeCl₃) powders, respectively. The leaching of the concentrate with Fe₂O₃ powder permits to achieve about 75 % copper extraction within 24 hours, while about 65 % copper is extracted by the leaching with FeCl₃ powder. The yield of copper in the leaching with Fe₂O₃ powder is twice or more higher than that without the promoters. High copper extraction can be achieved when much of the elemental sulfur is formed on the solid residue after the leaching. Especially, the presence of Fe₂O₃ powder gives us the elemental sulfur precipitates more than that of FeCl₃ powder. Therefore, Fe₂O₃ can be an effective promoter in the leaching of chalcopyrite concentrate using HCl solution.

KEY WORDS: Chalcopyrite, Hematite, Ferric Chloride, Acid Leaching, Elemental Sulfur, Copper Extraction

1. Introduction

It is known that high copper extraction can not be achieved in the leaching of chalcopyrite (CuFeS₂) concentrate using HCl solution without any promoters. The reaction of chalcopyrite with the solution is expressed by Eq.(1):

In this equation, when H₂S(aq) in the solution is oxidized under mild oxidation state, elemental sulfur forms a layer on the surface of chalcopyrite¹⁾. The elemental sulfur layer is considered to be a sort of barrier for the dissolution of the concentrate into the solution, resulting in low copper extraction. To overcome this difficulty, mainly three processes have been developed in the hydrometallurgical treatment of chalcopyrite: One is the ferric chloride (FeCl₃) process, the second the cupric chloride (CuCl₂) one, and the third the sulfate process using Fe(SO₄)_{1.5}²⁾. The kinetics of oxidative leaching of chalcopyrite in an acidic aqueous solution of such chlorides and sulfate media from mechanistic, electrochemical and morphological points of view have been studied since 1985³⁾⁻⁶⁾. In the meantime, these processes have several advantages related to sulfur control, metal purification and process economic⁷⁾. However, they need a lot of media, and the severe leaching conditions are required to achieve high copper yield of extraction. Under such circumstances, an alternative and novel process would be strongly expected in the field of chalcopyrite processing. The authors have introduced that hematite (Fe₂O₃) is one of the effective promoters in acid

leaching of chalcopyrite⁸⁾. However, difference in the extractive characteristics in the leaching with Fe₂O₃ and other promoters such as FeCl₃ has not been clarified yet.

The main purpose of this paper is to provide information on the difference in the yield of copper in the chalcopyrite leaching using HCl solution with Fe₂O₃ and FeCl₃, respectively.

2. Experimental

2.1 Samples

Chalcopyrite concentrate used in this experiment is supplied by Matsumine Mines, Hanaoka Mining Co. Ltd., Japan. The concentrate is composed mainly of CuFeS₂ (58 %) with impurities such as pyrite (FeS₂: 26 %), sphalerite (PbS: 8 %) and galena (ZnS). The chemical composition of the concentrate is as follows: Cu: 19.9 %, Fe: 29.8 %, S: 35.1 %, Pb: 4.5 % and Zn: 5.2 %. Apparent density of the concentrate was measured as 4.37 Mg/m³. The as-received chalcopyrite concentrate contained coarse particles so that it was ground by a ball mill. Then, sieving operation was conducted to prepare the powder passing through 74 μm as a starting sample. The specific surface area of the starting sample of the chalcopyrite concentrate was measured as about 3 m²/g. Fe₂O₃ (density: 5.26 Mg/m³, purity: 99 %) and FeCl₃ (density: 2.80 Mg/m³, purity: 98 %) powders were used as promoters in the leaching of the chalcopyrite concentrate using HCl solution. The both oxide and chloride promoters are chemical reagents and their mean diameters were about 0.1 μm.

2.2 Experimental procedure

Three kinds of leaching systems were employed in this work: One is the chalcopyrite concentrate-HCl solution system without any promoters, the second the chalcopyrite concentrate-HCl solution system with Fe₂O₃ powder and the last one the chalcopyrite concentrate-HCl solution system

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with FeCl_3 powder. In the leaching of the chalcopyrite concentrate alone, four grams of the concentrate sample were dispersed in 250 ml of 0.5 mol/dm³ HCl solution with stirring by a magnetic stirrer. In the case of the mixture of concentrate and Fe_2O_3 powders, two kinds of leaching tests were carried out: One is the leaching of the mixture containing 4.0 g chalcopyrite concentrate and 1.5 g Fe_2O_3 powders by the 250 ml HCl solution. Another test is the leaching of the both powders in the HCl solution, but the two kinds of powders were divided each other by a net in the solution so as to collect them separately after the leaching. In the leaching of the chalcopyrite concentrate with FeCl_3 powder, 4.0 g chalcopyrite concentrate and 3.0 g FeCl_3 powders were put together into the 250 ml of the HCl solution with stirring. The reason why the sample weight of Fe_2O_3 powder was set at half of the weight of FeCl_3 powder is to fit the concentration of Fe^{3+} in the solution. In all cases, the temperature of the suspension during the leaching was controlled at 333 K, and leaching time was varied from 6 hours to 3-days. After the prescribed leaching time, the mother solution was separated from the solid particles (residues) by filtration. Subsequently, the solution (filtrate) was investigated by an ICP analysis to determine the concentration of the elements dissolved in it. On the other hand, the solid particles and residues before and after the leaching were analyzed by X-ray diffraction (XRD) method to identify their constituent components and phases.

3. Results and Discussion

Fig. 1 shows the yield of copper in the leaching of the chalcopyrite concentrate with and without the promoters as a function of leaching time. The warped line (a) denotes the yield in the leaching with Fe_2O_3 powder, the line (b) the yield in the leaching with FeCl_3 and the line (c) the yield in the leaching without the promoters. From the results, the yield in the leaching without the promoters is found to reach only

Fig. 1 Yield of copper in the leaching of chalcopyrite concentrate with and without the promoters as a function of leaching time.

- (a) chalcopyrite concentrate/(HCl solution + Fe_2O_3)
- (b) chalcopyrite concentrate/(HCl solution + FeCl_3)
- (c) chalcopyrite concentrate/HCl solution

about 24 % at 24 hours leaching. Furthermore, these values are found to be always lower than the both yield values in the leaching with Fe_2O_3 and FeCl_3 , respectively. Comparing the yield values in the leaching with Fe_2O_3 powder with those with FeCl_3 powder, the former values are slightly higher than the latter ones. It is therefore found that Fe_2O_3 powder is an effective promoter in the leaching of chalcopyrite concentrate using HCl solution.

Fig. 2 shows the XRD patterns of the solids residues after the 24 hours leaching of the chalcopyrite sample with and without the promoters. That is, the pattern (a) denotes the solid residue after the leaching of the chalcopyrite sample alone, the pattern (b) the solid residue after the leaching with Fe_2O_3 powder and the pattern (c) the residue in the leaching with FeCl_3 powder. As can be seen from the figure, the peaks of chalcopyrite are found to disappear in the pattern (b), while they still exist in the patterns (a) and (c). This means that most of chalcopyrite dissolves into the HCl solution within 24 hours when Fe_2O_3 powder is present, while chalcopyrite is still remain in the sample in the cases without the promoters and with FeCl_3 powder. Moreover, it is clearly observed that the peaks intensity of sulfur in the patterns (b) and (c) is significantly higher than that in the pattern (a). In addition, the intensity of sulfur in the pattern (b) is marginally higher than that in the pattern (c). This implies that high copper extraction can be achieved when much of the elemental sulfur is formed after the leaching. Especially, the presence of Fe_2O_3 powder leads to promote the dissolution of chalcopyrite, accompanying with the elemental sulfur precipitates more than FeCl_3 powder. Majima²⁾ reported that the elemental sulfur layer formed on the surface of chalcopyrite in chloride media such as FeCl_3 -HCl solution system is porous and does not seem to be a barrier to further leaching. However, in the present study, no microscopic observation regarding the elemental sulfur layer formed on the surface of

Fig. 2 XRD patterns of the residues after 24-hours leaching of the chalcopyrite concentrate.

- (a) without the promoters
- (b) with Fe_2O_3 powder
- (c) with FeCl_3 powder

chalcopyrite was carried out. Therefore, the difference in the elemental sulfur layers when Fe_2O_3 and FeCl_3 powders were used is still in the state of uncertainty.

Fig. 3 shows the XRD patterns of the residues (a) and (b) after 3-days leaching of the chalcopyrite sample and the Fe_2O_3 powder both soaked in the HCl solution but they were divided by the net, together with that (c) after the leaching of the chalcopyrite concentrate without the promoters as a reference. The peaks of elemental sulfur can not be observed in the pattern (b) of the residue of Fe_2O_3 powder, while they are clearly observed in the pattern (a) of the residue of chalcopyrite concentrate. Taking the accuracy of XRD into account, it is not always described that no formation of elemental sulfur takes place on the surface of the Fe_2O_3 powder. In the leaching of chalcopyrite concentrate with Fe_2O_3 powder, the elemental sulfur may be formed mostly in the side of the chalcopyrite concentrate, not the Fe_2O_3 powder. No matter how the elemental sulfur layer is formed, it does not seem to be a barrier to further leaching of chalcopyrite concentrate when the Fe_2O_3 powder is present. Anyhow, Fe_2O_3 powder plays a significant role to assist the dissolution of

chalcopyrite concentrate accompanying with elemental sulfur in the vicinity of the surface of the concentrate. However, no evidence to confirm the reaction phenomena in the chalcopyrite leaching using HCl solution with Fe_2O_3 powder have been provided yet in the present experiment. Though this will be clarified in the future work, at this moment, It is only concluded that Fe_2O_3 powder is an effective promoter in the leaching of chalcopyrite concentrate using HCl solution.

4. Concluding Remarks

From the experimental results in the leaching of chalcopyrite concentrate (specific surface area: $3 \text{ m}^2/\text{g}$) conducted at 333 K using 0.5 mol/dm^3 HCl solution, the following concluding remarks could be made:

(1) Presence of Fe_2O_3 powder permits to extract about 75 % copper by the 24 hours leaching, while about 65 % copper extraction can be achieved in the leaching with FeCl_3 powder. Only about 25 % copper can be extracted by the leaching without any promoters. Therefore, Fe_2O_3 could be an effective promoter in the leaching of chalcopyrite concentrate.

(2) High copper extraction can be achieved when much of the elemental sulfur is formed after the leaching. Especially, the presence of Fe_2O_3 powder leads to promote the dissolution of chalcopyrite, accompanying with the elemental sulfur precipitates more than FeCl_3 powder.

(3) Elemental sulfur may be formed in the vicinity of the chalcopyrite concentrate, not the Fe_2O_3 powder when the powder is present. The reaction mechanism in the leaching of the chalcopyrite concentrate with Fe_2O_3 powder may be similar to that with FeCl_3 powder. However, no evidence to confirm it has been provided yet in this work. Further investigation would be needed.

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Fig. 3 XRD patterns of the residues after 3-days leaching of the individual samples, together with the residue after the leaching of chalcopyrite concentrate without the promoters as a reference.

- (a) chalcopyrite concentrate (with Fe_2O_3 powder)
 (b) Fe_2O_3 powder (with chalcopyrite concentrate)
 (c) chalcopyrite concentrate without the promoters

(和文要旨: 次ページ)

有効浸出助剤としてのヘマタイト粉を用いた黄銅鉱の酸浸出

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0.5 mol/dm³ の塩酸を用い、333 K の温度でヘマタイトならびに塩化第 2 鉄をそれぞれ浸出助剤として比表面積 3 m²/g の黄銅鉱から銅の浸出実験を行った。ヘマタイトを用いた浸出実験では、黄銅鉱を 24 時間浸出した場合、銅収率が約 75 % となるのに対して、塩化第 2 鉄では 65 % となる。ヘマタイトを用いた場合の銅収率は、浸出助剤無しの場合の約 2 倍かそれ以上となる。浸出

後の残査に硫黄が析出するとき高い銅浸出が達成される。特に、ヘマタイトを用いる方が塩化第 2 鉄を用いるよりも硫黄析出が多い。したがって、ヘマタイトは黄銅鉱の塩酸浸出において効果的助剤といえる。

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