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Techniques of copper recovery from Mexican copper oxide ore

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Abstract: Mexican copper ore is a mixed ore containing mainly copper oxide and some copper sulfide that responds well to flotation. The joint techniques of flotation and leaching were studied. The results indicate that an ore containing 19.01% copper could be obtained at a recovery ratio of 35.02% by using sodium sulfide and butyl xanthate flotation. Over 83.33% of the copper oxide can be recovered from the tailings by leaching in suitable conditions, such as 1 h stirring at a temperature around 25 °C with a mixing speed of 500 r/min, an H_2SO_4 concentration of 1.0 mol/L and a mass ratio of the ore-slurry-liquid to solid (m_L/m_S) of 3. The overall yield of refined ore after flotation and leaching is over 89.18% of the copper, which is much better than sole flotation or leaching. A copper product containing more than 99.9% copper was obtained by using the process: flotation-agitation leaching-solvent extraction-electro-winning.
Keywords: copper oxide ore; flotation; stirring leaching; extraction

1 Introduction

Progress in science and technology and the development of the economy has increased the demand for copper products at home and abroad. Meanwhile the number of new discoveries, and the easily exploited ore, are gradually decreasing. Moreover, a rising awareness of environmental protection has lead to more and more difficulty with the smelting process[1–7].

Copper ore is mainly copper sulfide or copper-oxide ore. Flotation methods were applied to copper sulfide ore to recover a refined copper ore. Copper can be obtained after the smelting process. Flotation is now one of the main methods for dealing with copper-oxide ore. In addition, hydro-metallurgy has also been widely adopted. Since the 1960's, the simple process flow, low cost and low pollution of the agitation-leaching-solvent extraction-electro-winning process has caused it to be widely adopted. This technology now produces around 20% of the total copper worldwide[8–13].

2 Experimental

The ore used in this experiment was from Mexico. It is a mixed ore mainly containing copper-oxide that also contains some copper sulfide ore that undergoes good flotation. The acid leaching rate of copper sulfide ore is lower than that of copper oxide ore. Acid leaching can easily release harmful hydrogen sulfide gas[14]. The process flow used in this experiment was: flotation-agitation leaching-solvent extraction-electro-winning.

3 Results and discussion

3.1 Analysis of the raw ore

Emission spectrometry, chemical analysis and X-ray diffraction results showed that in the ore sample the percentage of copper was 1.19%. This consisted of copper-oxide at 0.84% and copper sulfide at 0.35%. The oxidation rate of this core sample is high.

The X-ray diffraction spectrum shown in Fig. 1 indicates that the ore is a mixed one that is mainly composed of copper-oxide. The copper-oxide ore is ramsbeckite and malachite and the gangue is mainly SiO_2. Part of the copper sulfide ore is chalcopyrite. Therefore, an acid leaching-extraction-electro-winning process is suitable for this ore.

During acid leaching the harmful gas H_2S will be released because of the existence of copper sulfide. Since the acid leaching efficiency of chalcopyrite is lower than that of copper oxide both direct acid leaching and flotation leaching will be studied in this experiment.

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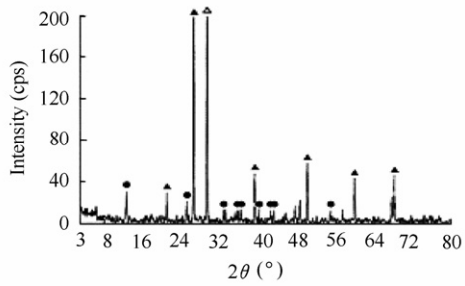

Fig. 1 X-ray diffraction spectrum of the raw ore

3.2 Direct acid leaching of the raw ore

The experimental conditions for direct acid leaching were: 20 g of raw ore, 1 h stirring at a temperature around 25 °C, a mixing speed of 500 r/min, an H_2SO_4 concentration of 1.0 mol/L, a mass ratio of the ore-slurry liquid to the solid (m_L/m_S) of 3 and a pH value of the wash filtrate of 1.5. The filter residue was washed three times and then all filtrates were collected. The result is shown in Table 1.

Table 1 Result of direct acid leaching on raw ore

Product	Lixivium	Residue	Raw ore
Recovery rate (Cu) (%)	80.94	19.06	100.00

The results in Table 1 indicate that 80.94% leachate can be obtained by direct acid leaching of raw ore. A smelly gas released from the leaching process was probably H_2S. The low leachate quantity and the release of much smelly gas caused leaching experiments on raw ore to be given up.

3.3 Techniques of flotation

There were disadvantages to the technique of direct acid leaching so flotation-acid leaching was attempted. We report the study of the selected system.

After activation by 160 g/t Na_2S and flotation by butyl xanthate, the copper oxide ore had a copper concentration of 19.10% at a recovery rate of 35.02%. The results are shown in Fig. 2 and Table 2.

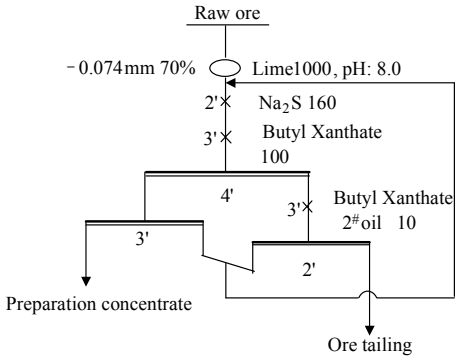

Fig. 2 Process flow of closed-circuit flotation

The concentrate from flotation was examined after the extraction. Fig. 3 is the result from an X-ray scan of the flotation concentrate. It indicates the presence of chalcopyrite, ramsbeckite and malachite. A majority of the copper sulfide ore is chalcopyrite, which was mostly floated.

Table 2 Results of closed-circuit flotation

Product	Productive rate (%)	Purity (%)	Percent recovery (%)
Preparation concentrate	2.18	19.10	35.02
Ore tailing	97.82	0.79	64.98
Raw ore	100.00	1.189	100.00

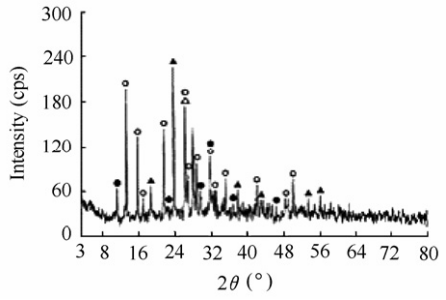

Fig. 3 X-ray result of flotation preparation concentrate

3.4 Acid leaching of the flotation tails

1) Fig. 4 is the X-ray scan of the ore tailings after flotation. The copper content is 0.79% in the tailings but chalcopyrite is not present. These results indicate that most of the chalcopyrite was floated. There were two kinds of copper ore in the tailings, malachite and chalcopyrite, that are suitable for acid leaching.

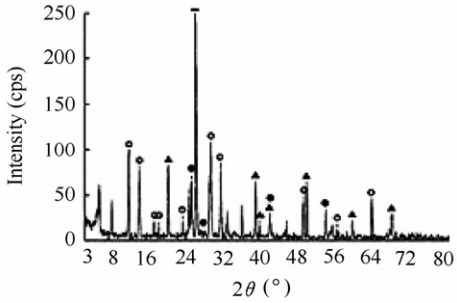

Fig. 4 X-ray results of tailings after flotation

2) Sulfuric acid was used as the leaching solution because of its high leaching capability and low price. The principal chemical reactions are:

For Malachite:

$$CuCO_3{\cdot}Cu(OH)_2+2H_2SO_4= 2CuSO_4+CO_2$$

For Chalcopyrite:

$$Cu_{15}(SO_4)_4(OH)_{22}{\cdot}6H_2O+1H_2SO_4=15CuSO_4+28H_2O$$

3) Many factors influence leaching, including the lixivium concentration, the liquid-solid ratio, the leaching time, the leaching temperature and the washing times of the filter residue. Fig. 5 shows the relationship between individual factors and the leaching of the copper.

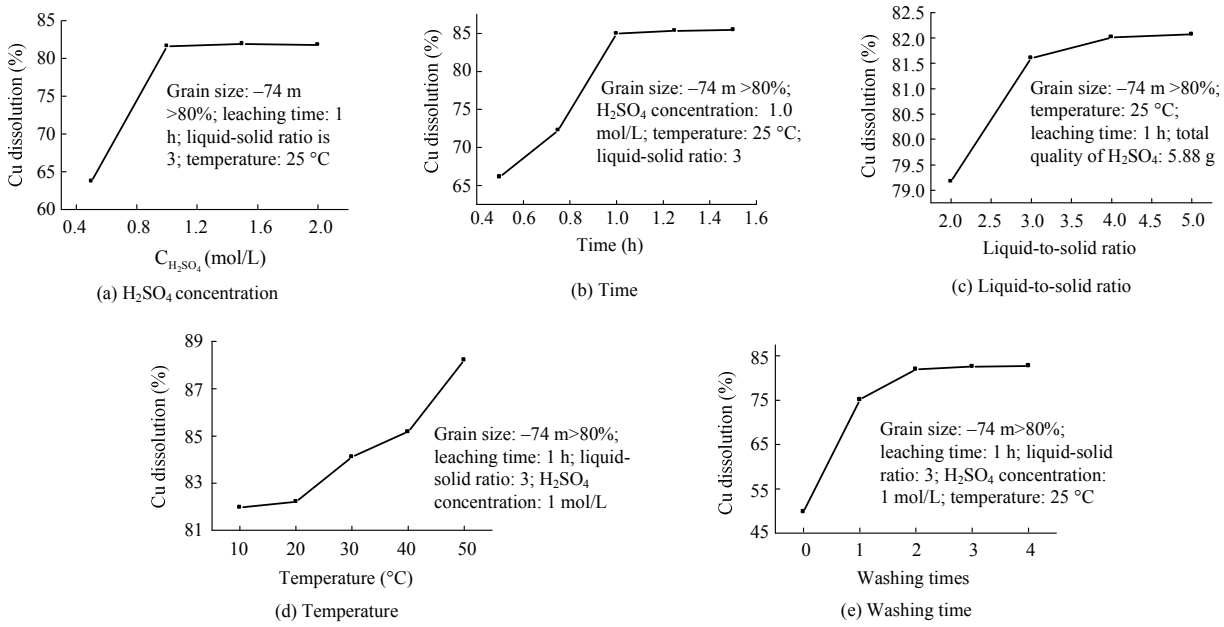

Fig. 5 Relationship between individual factors and the leaching of the copper

It can be concluded that increasing the H_2SO_4 concentration, extending the time of extraction, increasing the solid-liquid ratio and increasing the temperature will increase the amount of copper leached from the ore. Two washes of the filter residue are sufficient. Considering the economics, an optimal leaching condition would be: 1 h stirring at 25 °C with a mixing speed of 500 r/min, an H_2SO_4 concentration of 1.0 mol/L and a mass ratio of ore-slurry-liquid to solid of 3.

3.5 Solvent extraction-electro-winning process

The extraction and anti-extraction conditions are suffocated kerosene with an organic phase of 15% LIX984N, an extraction phase ratio of 1 and an anti-extraction phase ratio of 2.

The processing parameters for electro deposition were a bath voltage of 2 V and a current density of 170 A/m^2. The process flow is shown in Fig. 6. The copper content of the product was more than 99.9%.

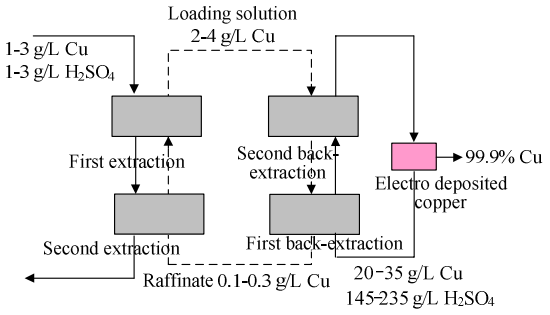

Fig. 6 Process flow of solvent extraction-electro-winning

4 Conclusions

1) The results indicate that the technology of direct leaching gives a copper recovery of 81% using Mexico copper oxide ore. However, the harmful gas H_2S was released during the process.

2) Copper ore containing 19.01% copper, at a recovery of 35.02%, was obtained by using sodium sulfide and butyl xanthate flotation.

3) The leaching of copper oxide from the ore tailings is over 83.33% under suitable conditions such as: 1 h stirring at 25 °C, a mixing speed of 500 r/min, an H_2SO_4 concentration of 1.0 mol/L and a mass ratio of ore-slurry-liquid to solid (m_L/m_S) of 3. The overall yield from the refined ore after combined flotation and leaching is over 89.18% copper. This is much better than sole flotation or leaching.

4) Copper more than 99.9% pure was obtained from the flotation-agitation leaching-solvent extraction-electro-winning process. It can be concluded that the joint technique of flotation and leaching is suitable for use on copper oxide mixed ore.

Acknowledgements

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References

[1] Cheng Q, Zhang X L. Ammonia leaching of oxidized copper ore at normal temperature and pressure. *Hydrometallurgy of China*, 2006, 25(2): 74–77. (In Chinese)

[2] Burniston T, Severs K J. Advances in copper solvent extraction by improved reagent technology. *In: Proceedings of 1st International Conference on Hydrometallurgy*. Beijing: International Academic Publishers, 1988: 231–235.

[3] Wu H S, Liu Y. Study on copper recovery from tailings by means of leaching process. *China Mining Magazine*, 2001, 10(6): 65–67. (In Chinese)

[4] Zhang J, Wu A X, Wang Y M, Chen X S. Experimental research in leaching of copper-bearing tailings enhanced by ultrasonic treatment. *Journal of China University of Mining & Technology*, 2008, 18(1): 98–102. (In Chinese)

[5] Watling H R. The bioleaching of sulphide minerals with emphasis on copper sulphides—a review. *Hydrometallurgy*, 2006(84): 81–108.

[6] Wang C Y. Exploitation of rebellious low-grade copper oxide with high-alkality gangues. *Mining & Metallurgy*, 2001, 10(4): 49–53. (In Chinese)

[7] Zhao G D, Wu H S, Liu Q, Li C. Leaching technique and its development trend of low-grade copper ores. *West-China Exploration Engineering*, 2004, 93(2): 65– 69. (In Chinese)

[8] Xie F B. Practice of agitation leaching-solvent-extraction-electrowinning process for copper oxide ores. *Mining & Metallurgy*, 2001, 10(2): 45–49. (In Chinese)

[9] Arbiter N, Aechie W. Fletcher copper hydrometallargy-evolution and milestones. *Mining Magazine*, 1994, 119 (2): 118–123.

[10] Liu G Y, Zhong H, Dai T G, Wang H, Liu J G, Luo S J, Hong J H, Xiong X H, Zhao G H, Zhou L P. Study on improving the recoveries of copper, gold and molybdenum in copper sulfide ore with high oxidation ratio in Dexing copper mine. *Mining and Metallurgical Engineering*, 2005, 25(6): 23–26. (In Chinese)

[11] Townsend B, Severs R J. The solvent extraction of copper—a perspective. *Mining Magazine*, 1990, 17(2): 25–35.

[12] Wang H Y, Zhang W. Leaching-solvent extraction-electrowininng process and extractants of copper. *Hydrometallurgy of China*, 2002, 21(1): 5–8. (In Chinese)

[13] Li X, Yang Z P, Zheng Z H. Study of water movement in unsaturated copper ore. *Journal of China University of Mining & Technology*, 2007, 17(4): 516–520. (In Chinese)

[14] Rodriguez Y, Ballester A, Blazquez M L, Gonzalez F, Munoz J A. New information on the chalcopyrite bioleaching mechanism at low and high temperature. *Hydrometallergy*, 2003(71): 47–56.