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A Study on Copper Extraction from Ammoniac Leach Solution of Copper Oxidized Ore

FANG Jian-jun[1], LI Yi-fen[2], LIU Dian-wen[1], ZHANG Wen-bin[1]
(1. Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, China;
2. Yunnan Jinsha Mining Co. Ltd, Kunming 654100, China)

Abstract: The extractant LIX-84-I is originally produced for copper extraction from acidic leach solution of copper oxidized ores. In this study, however, it is used successfully for the extraction of copper from an ammoniac leach solution, and this technology has further been industrialized. Laboratory investigations indicate that LIX84-I is really an efficient copper extractant with a maximum extraction of as high as 99.9% under the conditions of 3 g/L Cu in leach solution, pH >4.22, phase ratio 1/1, NH_3 1.5 mol/L, and 3 min mixtures. It is found that in order to ensure a smooth plant extraction operation, it is necessary that the concentration of solid fine particles in the feed solution be kept under 120 mg/L and the CO_2 above 0.5 mol/L. The stripping can be conducted with the barren electrolyte as a stripping agent in which the sulfuric acid concentration remains about 200 g/L, and a stripping rate of 99.94% is obtained.

Key words: copper oxidized ore; ammoniac leaching; solvent extraction
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从氧化铜矿氨浸出液中萃取铜的研究

方建军[1],李艺芬[2],刘殿文[1],张文彬[1]
(1.昆明理工大学 国土资源学院,云南 昆明 650093;2.云南金沙矿业股份有限公司,云南 昆明 654100)

摘要:将原本用于从酸浸出液中萃取铜的萃取剂LIX84-I用来从氨浸出液中萃取铜,获得了成功,并实现了工业化生产.实验室研究表明,在萃取原液含铜浓度3 g/L, pH >4.22, 相比1:1,氨浓度1.5 mol/L,混合时间3 min的条件下,LIX84-I是从氨浸出液中萃取铜的有效萃取剂,萃取率可达到99.9%.在工业生产中发现,将氨浸出液中固体微粒的含量控制在不超过120 mg/L和维持二氧化碳浓度不低于0.5 mol/L,是保证生产上铜萃取作业顺利进行的必要条件.用电积残液(酸浓度约200 g/L)返回反萃作业作为反萃剂使用,可以进行铜的反萃,反萃率可达到99.94%.

关键词:氧化铜矿;氨浸;萃取

0 Introduction

In recent years the "acid leaching - solvent extraction - electrowining" technology for copper ores has been developing rapidly thanks to the development and application of a series of high - efficiency new extractants[1-3]. The acid leaching - solvent extraction - electrowining process, with its advantages of short flowsheet, less capital investment, low cost, environment - friendly and high quality product, has been widely used for treating low grad copper ores, especially oxidized ones. Up to now the copper production by this process accounts for 25% of the

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第一作者简介:方建军(1968-),男,博士,高工.主要研究方向:湿法冶金与浮选. E-mail:ruiyuanju@126.com

world's total production, and this figure is sill increasing. A limitation of the process is that it can not be used to treat the ores containing calcium – magnesium gangues because of the high acid consumption. Unfortunately, the copper oxidized ores in China are mostly of high calcium – magnesium type, so options have to be sought to deal with this kind of ores. After years of study, an innovative process has been developed by the authors of this paper, that is the "atmospheric ammoniac leaching – solvent extraction – electrowining – flotation" process (Dongchuan process). This process has found its way in a commercial application at Dongchuan copper mine in Yunnan province, south – west of China, and proved to be very successful, resulting in the settlement of long – lasting problems of the difficult – to – treat copper oxidized ores exploitations.

For the development of the Dongchuan process, one of the important breakthroughs is the success of a solvent extraction of copper from an ammoniac leach solution, using LIX84 – I as the extractant. And this technology has been commercialized for the first time at home and abroad. In this paper the results of laboratory tests and commercialization of the technology are described.

1 Experimental

1.1 Experimental materials

The LIX84 – I extractant used is produced by Cognis, it is water insoluble 2 – hydroxy – 5 – nonylacetophenoneoxime in a mixture with a high flash point hydrocarbon diluent. It forms water insoluble complexes with various metallic cations in a manner similar to that for copper which is described in the following equation:

$$Cu(NH_3)^{2+}_{4aq} + 2RH \rightarrow CuR_2 + 2NH^{+}_{4aq} \quad (1)$$

Stripping is accomplished with acid solutions such as a typical barren electrolyte from copper electrowinning, which is described in the following equation:

$$CuR_2 + 2H_{aq} + 2RH \quad + Cu^{+2}_{aq} \quad (2)$$

The diluent used was a sulfokerosene prepared in the lab; Stripping reagent was sulfuric acid solution; to adjust pH values diluted sulfuric acid or ammonia was used; the water used was from the plant water supply; the feed solution for the extraction tests was sampled from the Dongchuan process plant of 2000t/a, and its chemical analysis is shown in Table 1.

1.2 Method of experiment

The extraction experiments were carried out with a 250 mL separating funnel. First the organic phase and water phase were added into the separating funnel by a given ratio and a sulfuric solution or an ammonia solution was added to adjust pH values if needed, then mixed in a shaker for a given time; after phase separation the extraction barren solution was sent to determine Cu with a atomic absorption spectrometer for accounting the Cu extraction rate.

Tab.1 Results of chemical analysis of the feed solution for extraction tests

(Unit: g/L)

Cu	Fe	Pb	Zn	As	Sb	Bi
3.15	0.001	0.005	0.06	<0.001	<0.0001	<0.0001
Mn	CaO	MgO	SiO_2	Al_2O_3	$\sum NH_4^+$	—
0.004	0.02	0.03	0.018	0.002	18.78	

2 Results and discussion

2.1 Effect of pH on extraction

The effect of pH on Cu extraction was tested at various pH values by adjusting the ammoniac leach solution's pH which originally was 9.23, using diluted sulfuric acid or ammoniac solution as modifiers. The tests were conducted under the conditions of a phase ratio of 1/1 and a mixing time of 3 min. And the results obtained are illustrated in Fig. 1.

It is shown in Fig. 1 that Cu extraction by LIX84 – I is pH dependent. When pH <4.22, the extraction increases sharply with the increased pH. The maximum extraction appears at pH 4.22. Therefore, in general, very high extractions can be achieved in production process because the natural pH of ammoniac leach solution is usually higher than 9.

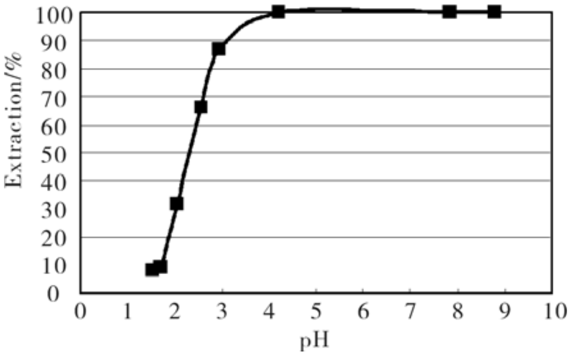

Fig. 1　Copper extraction as a function of pH values

2.2 Effect of ammonia concentration on extraction

The reaction of copper extraction from ammoniac leach solution is in fact a competitive reaction of extractant and ammoniac ions for copper (equation 1). Therefore the concentration of ammonia in the leach solution affirmatively affects the extraction. Under the conditions of a phase ratio of 1/1 and a mixing time of 3 min, the effect of ammonia concentration on the extraction is shown in Fig. 2.

It can be seen in Fig. 2 that the relationship of extraction with ammonia concentration is nearly a linear on. The higher is the ammonia concentration, the lower the extraction is. So there is a conflict that certain ammonia concentration is essential for a satisfied leach rate on one hand, and on the other hand, too high an ammonia concentration could interfere with the extraction process. Therefore a moderate ammoniac concentration must be kept to get a balance between leaching and extraction.

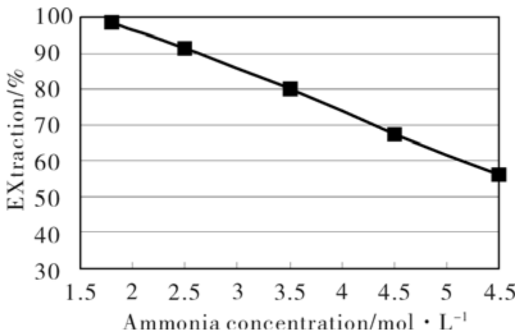

Fig. 2　Copper extraction as a function of ammonia concentration

2.3 Effect of phase ratio on extraction

Under the conditions of a Cu concentration of 3.2 g/L, an ammonia concentration of 1.8 mol/L and a mixing time of 3 min, the effect of phase ratio on the extraction is shown in Fig. 3.

As illustrated in Fig. 3 the Cu extraction increases from 30% to 99.6% as the phase ratio increases from 1/3 to 5/1, indicating that an increased phase ratio promotes the extraction. Too high a phase ratio, however, would decrease the capability of the extraction facilities. Therefore to balance the extraction and the productivity a phase ratio of 1/1 is appropriate as proved in the piratical production.

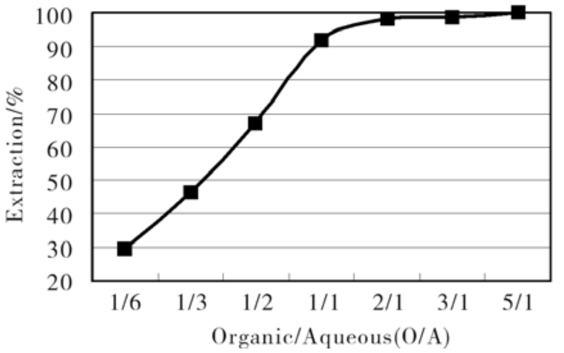

Fig. 3　Copper extraction as a function of phase ratio

2.4 Effect of acidity of stripping agent on stripping rate

As the affinity of LIX84 - I to H^+ is strong enough, the stripping can be accomplished at a relatively low acidity. Under the conditions of a phase ratio of 1/1 and a mixing time of 3 min, the effect of acidity of the striping agent on the stripping rate is illustrated in Fig. 4.

It is indicated in Fig. 4 that an increased acidity of the stripping agent is benefit for stripping. The acidity of stripping agent should be higher than 50 g/L if an over 90% stripping rate is to be achieved. A 99.94% copper striping rate is reached when the acidity of 200 g/L is provided. And this acidity is near that of the electowinig barren solution. So the later could be sent back to the stripping circuit as a stripping agent.

2.5 Effect of solid fine particles and CO_2 concentration

It has been found that there are two key factors to ensure a smooth extraction operation: one is the solid fine particles suspended in the leach solution and the other the CO_2 concentration in the solution. The extraction operation can even been stopped if the two factors failed to be carefully controlled.

It has been well known that an emulsion layer or a third phase will form in the leaching – extraction – electrwining technology for many reasons[4-6], resulting in not only a decreased extraction and phase separation speed[7], but also a lot of problems such as organic phase loss, electrolyte polluting, poor product quality and environment pollution. In the worst occasion the production has to be stopped. It has been confirmed in this study that the solid fine particles in the solution can prick up the formation of emulsion layer or the third phase. It has been testified by commercial production that the copper extraction goes down remarkably and the consumption of the extractant doubled when the concentration of solid fine particles exceeds 120 mg/L. Measures must be taken to control strictly the fine particles concentration.

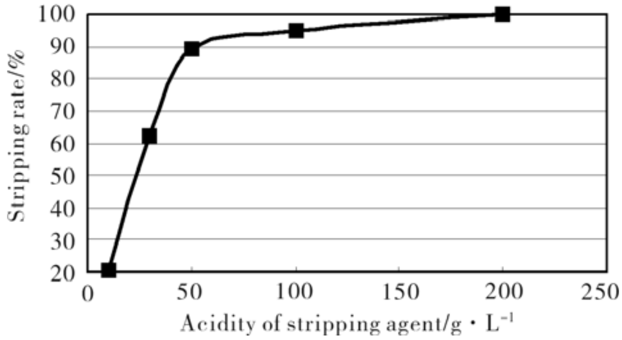

Fig. 4 Stripping rate as a function of acidity of stripping agent

Another important and interesting discovery made in the production is that the phase separation speed can be greatly improved when ammonium bicarbonate is added in the extraction system. The phase separation hardly takes place and the solvent is severely entrained into the water phase if the CO_2 concentration is $\leqslant 0.3$ mol/L. This phenomenon disappeared, however, if only $CO_2 \geqslant 0.5$ mol/L. So it is concluded that the copper extraction process with LIX84 – I is controlled to certain extent by the concentration of CO_2, and the mechanism is worthy to further investigate.

3 Conclusions

1) The extractant LIX84 – I, which was originally developed for extraction of metals from acid leach solutions, can be successfully used for Cu extraction from an ammoniac leach solution both in laboratory and commercial scale plants. In this case the extraction of copper can reach 99.95%. It is the newest application of LIX84 – I and a great breakthrough of the extraction technology.

2) The natural pH values (pH > 9) are suitable for the extraction; the effect of ammonia concentration in the leach solution on the extraction is remarkable, the higher is the concentration, the lower the extraction is, therefore it is necessary to properly control the ammonia concentration in the leaching process so that the leaching and the extraction can be balanced.

3) Copper can be stripped very well using a sulfuric acid solution of 8% ~ 12%. With nearly the same acid concentration, the barren electrolyte from the electrowinig can be sent back to the stripping circuit as a stripping agent.

4) To ensure a smooth extraction operation a concentration of solid fine particles of less than 120 mg/L and a CO_2 concentration of more than 0.5mol/L are the essential conditions.

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