Solvent extraction of copper and zinc from bioleaching solutions with LIX984 and D2EHPA[①]

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Abstract: The solvent extraction of copper and zinc from the bioleaching solutions of low-grade sulfide ores with LIX984 and D2EHPA was investigated. The influences of extractant content, aqueous pH value, phase ratio and equilibration time on metals extraction were studied. The results show that LIX984 has a higher selectivity for copper than for iron, zinc and other metals, and has the copper extraction rate above 97%, while the zinc and iron extraction rate is less than 1.6% respectively. Zinc extraction is carried out following the copper extraction from the raffinate. The zinc extraction with di(2-ethylhexyl) phosphoric acid(D2EHPA) is low due to its poor cation exchange. A sodium salt of D2EHPA is used and the zinc extraction rate is enhanced to above 98%. Though iron (Ⅲ) is strongly extracted before the extraction of zinc by D2EHPA, it is difficult to strip iron from the organic phase by sulfuric acid. The zinc stripping rate is above 99% with 100 g/L sulfuric acid, while that of iron is 0.16%. Hence, the separation of zinc from iron can be achieved by the selective stripping.

Key words: solvent extraction; bioleaching; copper; zinc; LIX984; D2EHPA

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1 INTRODUCTION

Copper extraction has been successfully commercialized for decades due to the availability of copper-selective extractants[1,2]. Most of the commercially available copper-specific extractants are oxime types. Among them the LIX series from Henkel Corporation have been extensively used. LIX984, a mixture of LIX860 and LIX84 with a volume ratio of 1 : 1, shows a high selectivity for copper over other metals. However, the commercialization of zinc extraction is hardly available in literature. The reasons are the lower price of zinc than that of copper, and the most important of all, the absence of efficient extractant for zinc. There are many reports on zinc extraction, discussing the removal trace of zinc impurity from the solutions[3-7]. However, the extractants used for the zinc extraction show a weaker selectivity on zinc than on the other metals such as iron, copper, calcium and manganese etc. Although the phosphate-type extractants are believed as the most common one for zinc extraction, the major disadvantage of these reagents is that the strong extraction of iron(Ⅲ). D2EHPA (di (2-ethylhexyl) phosphoric acid) has been usually used for the separation of the cobalt from nickel or impurities removal from solutions[4], and is considered to be a competent candidate for zinc extractant[7-9]. The solvent extraction and separation of copper and zinc from different mediums with various extractants have been reported[10-13]. In China, LIX984 has been used in several plants to produce copper from sulfide ores by bioleaching. In the present work, a bioleaching solution of complex sulfide ores was obtained, which contained copper, zinc and iron etc. The extraction and separation of copper and zinc from the solution were investigated by using LIX984 and D2EHPA as the extractant for copper and zinc, respectively.

2 EXPERIMENTAL

2.1 Materials and reagents

LIX984 was obtained from Dexing Copper Mine. The active components of LIX984 are 2-hydroxy-5-nonyl-acetonphenoneoxime and 2-hydroxy-5-dodecylsalicylaldoxime. D2EHPA was obtained from Shanghai. No. 260 kerosene, obtained from Suzhou Refinery, was used as diluent. Other reagents were analytically pure.

The bioleaching solution was obtained from an experimental plant of heap leaching, which contained 0.54 g/L copper, 3.70 g/L zinc, 3.26 g/L iron and 0.40 g/L calcium. The solution pH value was 2.27. For the oxidizing activities of bacteria (*Thiobacillus ferrooxidans*), most of the iron in the solution existed as ferric ions.

2.2 Methods

Copper extraction was carried out in a separa-

tory funnel with a mechanical shaking, followed by zinc extraction from the raffinate. The aqueous phase and the organic phase were mixed in a predetermined ratio and shaken for a predetermined time. After phase disengagement, the aqueous phase was separated, in which the metal concentrations were analyzed by a atomic absorption spectrophotometer. The metal concentrations in the organic phase were calculated according to mass balance. The pH value of the aqueous phase was adjusted to the desired value by adding diluent sulfuric acid or sodium hydroxide solution. All experiments were conducted at (25 ± 1) °C.

3 RESULTS AND DISCUSSION

3.1 Copper extraction

Firstly copper was extracted from the solution by LIX984. The influences of extractant content and equilibration time on the copper extraction were investigated.

3.1.1 Influence of extractant content

The influence of extractant content on the copper extraction was studied in the range of 1%-5% (volume fraction), using a phase ratio of 1 : 1 and an equilibration time of 5 min. The experimental results are shown in Fig. 1. It can be seen that at the extractant content of 1%, the copper extraction rate is 96.94%. When the extractant content is increased to 2%, the copper extraction rate is 98.68%, while the extraction rate of zinc and iron is 1.60% and 1.41% respectively. The separation factor $(\beta = D_{Me1} / D_{Me2}$, where D means the distribution coefficient) of Cu to Zn, and that of Cu to Fe is more than 4 500 and 5 200, respectively. In the given extractant content range, the copper extraction keeps in a high level, and the extraction of zinc and iron keeps in a very low level. It indicates that LIX984 shows a remarkable selectivity for copper over zinc and iron.
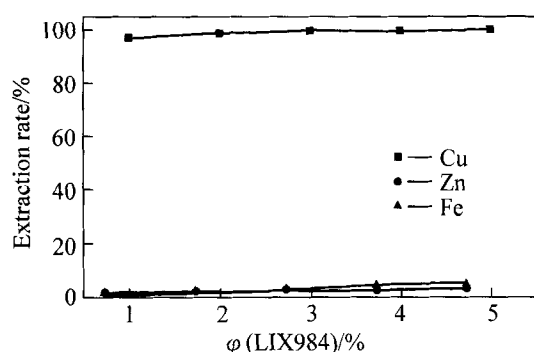

Fig. 1 Influence of LIX 984 content on copper extraction

3.1.2 Influence of equilibration time

The influence of time on the copper extraction

was studied by using LIX984 with a volume fraction of 2% and a phase ratio of 1 : 1. The results are shown in Fig. 2. It can be seen that when the time is increased from 1 min to 2 min, the copper extraction rate increases from 69.62% to 96.26%. The equilibrium of copper extraction is reached after 2 min. However, the extraction of zinc and iron is independent of the equilibration time and keeps in a very low level. It further demonstrates the high selectivity of LIX984 on copper over zinc and iron.
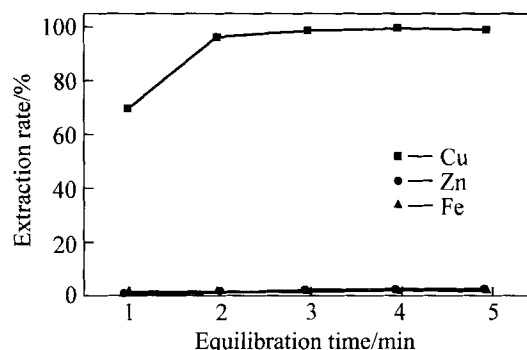

Fig. 2 Influence of equilibration time on copper extraction

3.2 Zinc extraction

From the above results it follows that copper is easily extracted and separated from the solution, while zinc and iron remains in the raffinate. In order to efficiently recover zinc, D2EHPA was used as the extractant for zinc. Zinc extraction experiments were carried out with varying extractant content, equilibration time, phase ratio and aqueous pH value. If not the variable, the extractant content, the equilibration time and the phase ratio (O/A) was 30% (volume fraction), 5 min and 1 : 1, respectively. The raffinate obtained from the previous copper extraction contained 0.01g/L copper, 3.64 g/L zinc, 3.21 g/L iron and 0.40 g/L calcium. The pH value of the raffinate was 2.04.

3.2.1 Influence of extractant content

Fig. 3 shows the influence of D2EHPA content on the zinc extraction. It can be seen that at the extractant content of 5%, the iron extraction rate is above 43%, while the extraction of zinc and calcium is both in a low level less than 5%. When the extractant content is increased to 30%, the zinc extraction rate increases to 43.20%, and the extraction rate of iron and calcium increases to 61.38% and 16.85%, respectively. It demonstrates that with the increase of D2EHPA content, although the zinc extraction is increased, the extraction of iron and calcium is also increased. Iron(Ⅲ) is strongly extracted by D2EHPA before zinc, and portion of calcium is co-extracted.

The zinc extraction rate is low due to the poor cation exchange of the extractant. The phosphate
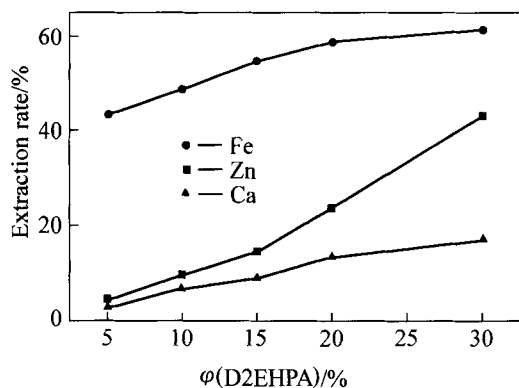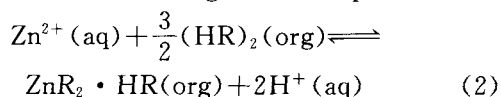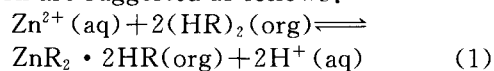
Fig. 3 Influence of D2EHPA content on zinc extraction

type extractant exists as dimers or polymers in the nonpolar organic solvent, which affects the extraction of metals[9]. It has been reported[9,14] that the extracted species of phosphate type extractant in the organic phase is $ZnR_2 \cdot 2HR$ or $ZnR_2 \cdot HR$. Hence, the equilibrium equations of zinc extraction in this work are suggested as follows:

$$Zn^{2+}(aq)+2(HR)_2(org) \Longleftrightarrow$$
$$ZnR_2 \cdot 2HR(org)+2H^+(aq) \tag{1}$$

$$Zn^{2+}(aq)+\frac{3}{2}(HR)_2(org) \Longleftrightarrow$$
$$ZnR_2 \cdot HR(org)+2H^+(aq) \tag{2}$$

Where   HR represents the extractant molecule.

The released hydrogen ion from cation exchange enhances the acidity of solution, which also affects the equilibrium of metal extraction.

3. 2. 2   Influence of equilibration time

The influence of equilibration time on the zinc extraction is shown in Fig. 4. When the time is increased from 1 min to 7 min, the zinc extraction rate increases from 37. 13% to 43. 20%, while that of iron increases from 40. 46% to 70. 92%. The equilibrium of zinc extraction is reached in a short time, while that of iron is reached in a longer time. Therefore, according to the difference between the equilibrium time of zinc and iron extraction, it is helpful to run the extraction in a shorter time to reduce the extraction of iron, which is called "nonequilibrium extraction", although the selectivity is still not evident in this condition.
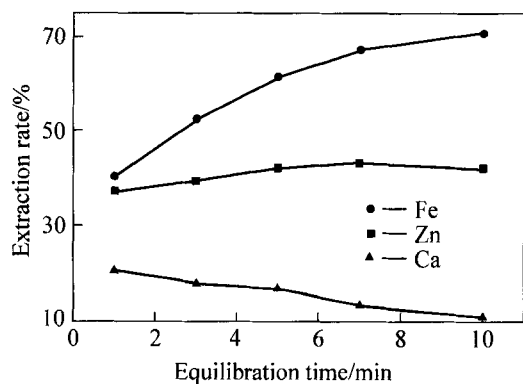

Fig. 4   Influence of equilibration time on zinc extraction

It is interesting that the calcium extraction decreases with the increase of time. The calcium extraction rate is 20. 56% after 1 min, however it decreases to 11. 15% after 10 min. This maybe caused by the extraction competition of zinc and iron over calcium with increasing time. When the equilibration time is increased, more zinc and iron are extracted and displaced the already extracted calcium in the organic phase, which causes the decrease of the calcium extraction.

3. 2. 3   Influence of phase ratio

The influence of phase ratio (O/A) on the zinc extraction is shown in Fig. 5. With the increase of O/A ratio, the zinc extraction is increased. When the O/A ratio is increased from 0. 5 to 1. 5, the zinc extraction rate increases from 21. 10% to 53. 57% due to more extractants involved in the extraction of metals. However, the iron extraction increases slightly and nearly reaches equilibrium even in the low O/A ratio. The calcium extraction is moderately increased with the increase of phase ratio.
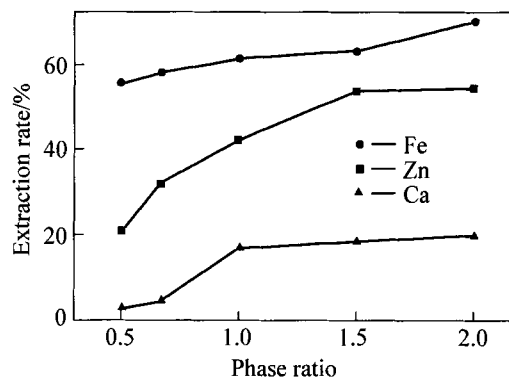

Fig. 5   Influence of phase ratio on zinc extraction

3. 2. 4   Influence of aqueous pH value

The extraction of zinc, iron and calcium is increased when the aqueous pH value is increased (Fig. 6). It can be seen from Eqns. 1 and 2, that increasing the pH value of aqueous can move the equilibrium towards the right, which accelerates the metal extraction. At the aqueous pH value of 1. 5, the extraction rate of zinc, iron and calcium is 27. 76%, 53. 67% and 1. 80%, respectively. When the aqueous pH value is increased to 3. 0, the extraction rate of zinc, iron and calcium increases to 61. 80%, 83. 26% and 15. 41%, respectively. At a low pH value, the co-extracted calcium is negligible.

3. 2. 5   Extraction of zinc with the sodium salt of D2EHPA

From the above results it can be seen that the increase of the D2EHPA content, the phase ratio (O/A) and the aqueous pH value can elevate the zinc extraction. However, due to the poor cation exchange of D2EHPA, the increase of zinc extraction is limited. To enhance the extraction of zinc, a sodium salt of D2EHPA is used. The extractant is
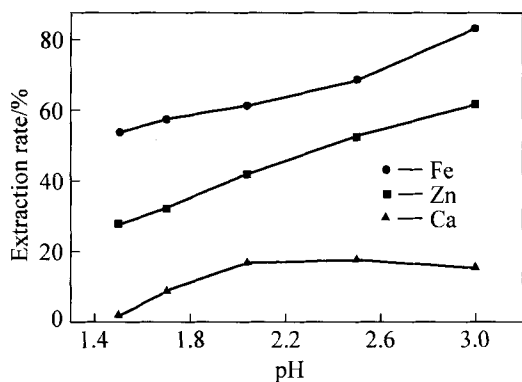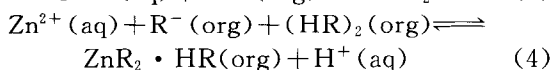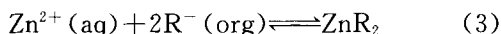
Fig. 6 Influence of aqueous pH value
on zinc extraction

neutralized by adding a stoichiometric quantity of 6. 25 mol/L NaOH solution into the organic phase and stirring quickly to form a single phase.

The influence of percentage neutralization of D2EHPA on the zinc extraction is shown in Fig. 7. It can be seen that using the sodium salt of D2EHPA can enhance the metal extraction remarkably. The metal extraction is increased with the increase of the percentage neutralization. When 70% of the extractant was neutralized, the extraction rate of zinc, iron and calcium is 98. 09%, 95. 25% and 30. 08%, respectively. With the increase of the percentage neutralization, the zinc extraction is increased to the same level as that of iron. According to Ref. [13], it is assumed that the sodium salt of extractant exists as monomers in the kerosene, and the extractant that is not neutralized still exists as dimers. So, the extraction equation of zinc with the neutralized organic phase may be suggested as:

$$Zn^{2+}(aq) + 2R^-(org) \rightleftharpoons ZnR_2 \qquad (3)$$
$$Zn^{2+}(aq) + R^-(org) + (HR)_2(org) \rightleftharpoons$$
$$ZnR_2 \cdot HR(org) + H^+(aq) \qquad (4)$$

Obviously, in the course of zinc extraction with the sodium salt of D2EHPA, the released H^+ from the cation exchange is decreased steeply due to the neutralization effect of NaOH. Hence, the equilibrium pH value is kept in a high level and the zinc extraction is accelerated.
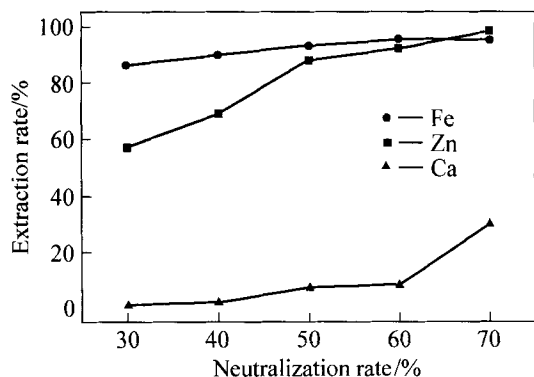

Fig. 7 Influence of neutralization rate
on zinc extraction

3. 3 Selective stripping

Though using the sodium salt of D2EHPA can increase the zinc extraction, the problem is that iron is more strongly extracted before zinc. Iron is a very sensitive impurity and has detrimental effect on the zinc electrowinning. Therefore, iron is usually required to remove from the zinc solution before entrance into electrowinning by cementation in the conventional hydrometallurgical process. In this case, the separation of zinc from iron in the organic by selective stripping was investigated. The stripping experiments were carried out with varying the concentration of sulfuric acid and equilibration time. The loaded organic phase came from the solvent extraction of zinc contained 3. 58 g/L zinc, 3. 01 g/L iron and 0. 10 g/L calcium.

The results of stripping experiment are shown in Fig. 8. In the tested range of sulfuric acid concentration, zinc is easily stripped by sulfuric acid and iron is hardly stripped even in the high concentration of sulfuric acid. Zinc stripping rate is above 99%, while iron stripping rate is 0. 16% with respect to sulfuric acid concentration of 100 g/L. The influence of equilibration time on the zinc stripping rate is shown in Fig. 9. After 4 min, the zinc stripping rate is above 99%, while the iron stripping rate is 0. 14%. The iron stripping increases slightly with the increase of equilibration time but the total amount is negligible.
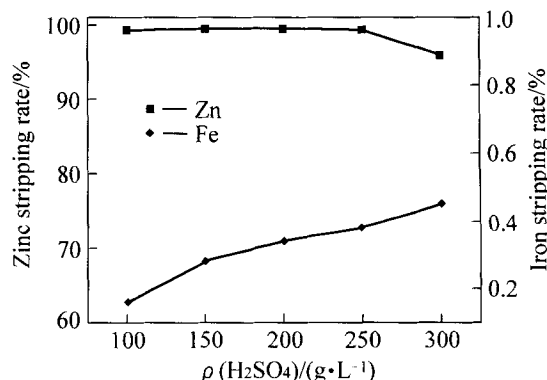

Fig. 8 Influence of sulfuric acid concentration
on zinc stripping

Therefore, though iron is strongly extracted into the organic phase and made it difficult to separate zinc from iron, it is feasible to separate zinc from iron in the following process by selective stripping with sulfuric acid. The extracted iron is hardly stripped by sulfuric acid and remained in the organic phase. The build-up of iron in the organic phase will depress the extraction ability of D2EHPA in the next recycle extraction. Hence, it is necessary to strip iron from the organic phase following the zinc stripping. The iron in the organic phase can be stripped by concentrated hydrochloric acid or by galvanic stripping[15], but the latter
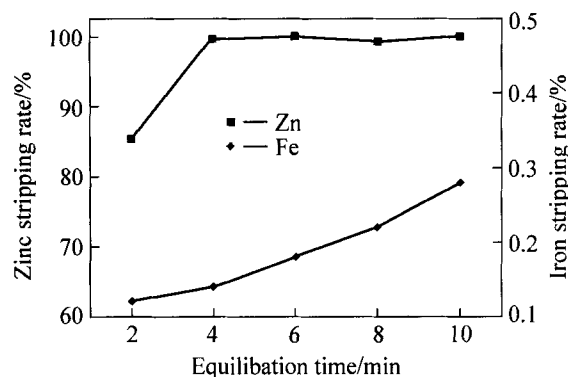
Fig. 9 Influence of equilibration time on zinc stripping

is more complex in operation. The influence of the concentration of hydrochloric acid on the iron stripping is shown in Fig. 10. The experiments are carried out by using an O/A ratio of 1 : 1 and an equilibration time of 5 min. The iron stripping is increased with the increase of the concentration of hydrochloric acid. With 6 mol/L HCl, the iron stripping rate is above 90%.
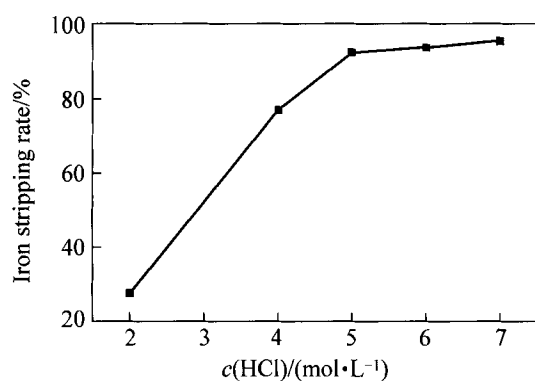

Fig. 10 Influence of hydrochloric acid concetration on iron stripping

4 CONCLUSIONS

1) Copper and zinc in the bioleaching solutions of low-grade sulfide ores can be separated and recovered by solvent extraction. Copper extraction is carried out with LIX984, followed by zinc extraction with D2EHPA.

2) LIX984 shows a higher selectivity for copper than for zinc and other metals, which gives the copper extraction rate above 97%, while the extraction rate of zinc and iron is less than 1.6%, respectively. The zinc extraction is increased with the increase of the D2EHPA content, the phase ratio (O/A) and the aqueous pH value.

3) The increase of zinc extraction is limited due to the poor cation exchange of D2EHPA. Using a sodium salt of D2EHPA enhances the zinc extraction rate above 98%. Though iron (Ⅲ) is

strongly extracted before zinc by D2EHPA.

4) It is difficult to strip iron from the organic phase by sulfuric acid. The zinc stripping is above 99% with 100 g/L sulfuric acid, while that of iron is 0.16%. Hence, the separation of zinc from iron can be achieved by selective stripping. Iron can be stripped by concentrated hydrochloric acid to avoid its buildup in the organic phase.

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