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Co-extraction and selective stripping of copper (II) and molybdenum (VI) using LIX 622

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Abstract

LIX 622 diluted with kerosene was used to co-extract copper (II) and molybdenum (VI) from acidic sulphate solutions. The influence of equilibrium pH and extractant concentration on metal co-extraction has been studied. The extraction of both metals is sensitive to equilibrium pH; however, molybdenum is extracted preferably to copper at acidic pH values. For aqueous phases containing both metals, conditions were established for the co-extraction, selective stripping of copper and molybdenum and NH_3 removal from the stripped organic solution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Co-extraction; Selective stripping; Copper (II); Molybdenum (VI); LIX 622

1. Introduction

The process of solvent extraction is one of the most versatile procedures used for the removal, separation and concentration of metallic species, broadening its applications in the recycling of resources in the field of metallurgy and wastewater treatment as demand increases for the development of new approaches to resolve the various problems presented.

In solvent extraction processing there are two basic process approaches for metal separation in a multi-elemental system: selective extraction and selective stripping. Sometimes, selective stripping is more economical and operationally advantageous, because, for example, it requires fewer stages than selective extraction.

The selective stripping approach has been used in a series of metal combinations and using various extractants (e.g. zinc from nickel, nickel from cobalt, lead from copper, nickel from copper, LIX 64N, LIX 87QN) [1–8]. Copper and molybdenum are often presented together in a number of raw materials, secondary resources and liquid effluents; thus their recovery/separation seems to be attractive from various points of view.

Both metals can be extracted by oximes [9–11]. The extraction of metals, especially copper, by oximes can be explained by a cation exchange reaction, e.g.:

$$\mathrm{Cu_{aq}}^{2+} + 2\mathrm{HR_{org}} \rightleftarrows \mathrm{CuR_{2_{org}}} + 2\mathrm{H_{aq}}^{+} \qquad (1)$$

where HR represents the extractant and the subscripts 'aq' and 'org' to the aqueous and organic phases, respectively. Therefore, the extracted complex had a 2:1 extractant/metal stoichiometry; in addition, oximes formed chelated complexes with a number of metals, which in the case of copper (II) leads to the formation of defined six-membered ring complexes. The formation of 2:1 (oxime:metal) compounds was also reported for molybdenum (VI) [12,13]. However, the overall extraction mechanism of Mo (VI) by LIX 622 seems to be more complicated than that represented by a simple 2:1 (oxime:metal) stoichiometry and it should even include a solvation reaction (Table 1) [14].

There is not much information available on the use of these extractants for copper and molybdenum co-extraction coupling with the selective stripping approach [15]; thus the present works deals with studies carried out with LIX 622 for co-extracting copper and molybdenum from sulphate media and selective stripping for their separation.

2. Experimental

LIX 622 extractant, a reagent based in the mixture of 5-dodecylsalicylaldoxime and tridecanol in a high flash-point hydro-carbon diluent [16], supplied by Henkel,

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Table 1
Species formed in the extraction of molybdenum (VI) by LIX 622 (R: LIX 622)

Species	log K_{ext}
MoO_4H_2HR	9.4, max: 9.9
$MoO_4H_3HR^+ \cdot HSO_4^-$	13.8 ± 0.1
MoO_2R_2	9.7, max: 10.7

was used as received by diluting it to the adequate concentration with kerosene (Fluka): boiling range, 200–250°C; flash point, 70°C; density (20°C), 0.80 g/l; aromatics, 10%.

Molybdenum and copper solutions were prepared by dissolving weighted amounts of the analytical reagent grade, sodium molybdate and copper sulphate, in distilled water and adjusting the desired pH value with sulphuric acid solutions. The concentration of the metals in the initial solutions was determined by ICP. All other chemicals and reagents used were of analytical grade. Methrom 691 pH-meter with combined electrode was used for pH measurements.

Extraction and stripping equilibrium experiments were carried out by shaking of the appropriate aqueous and organic phases in thermostatted separatory funnels, provided with water jackets, at 20°C and for the time required. After phase disengagement the aqueous phase as analysed by ICP, and the content of the metals in the equilibrated organic phases was calculated by mass balance.

Ammonia aqueous solutions were mainly used to study molybdenum stripping from loaded organic phases. The ammonia content of the organic/aqueous phases was estimated by the Indo-phenol method [17] and by using a selective ammonia electrode, respectively.

3. Results and discussion

3.1. Extraction

The influence of equilibrium pH on the co-extraction of copper and molybdenum was studied using an aqueous solution of 0.1 g/l (each) copper and molybdenum and an organic solution of 2.5% (v/v) LIX 622 in kerosene. The two phases were equilibrated for 20 min at O/A phase ratio of 1. Previous experiments showed that this contact time ensures complete extraction equilibrium for both metals.

These results, shown in Fig. 1, indicate the marked influence of pH on metal extraction, especially in the case of copper. The copper extraction falls off substantially from the equilibrium pH of near 1. However, molybdenum extraction remained almost constant in the range 1.6–1.0. At most acidic pH values Mo (VI) is extracted preferably to copper (II).

The influence of aqueous pH on the extraction of both metals can be explained by taking into account the extraction reaction between the acidic/chelating reagent (LIX 622) and the metal ions (e.g. as represented in Eq. (1)). Thus, at less acidic pH values the corresponding equilibrium shifts to the right, increasing the extent of metal extraction (Fig. 1).

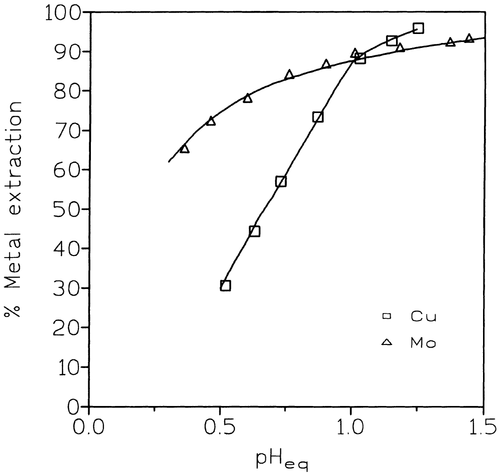

Fig. 1. The influence of pH on copper and molybdenum co-extraction.

As can be seen from Fig. 1, copper extraction was near 50% at pH_{eq} 0.65 when a 2.5% (v/v) LIX 622 was used as the organic solution. In order to fix a suitable extractant concentration for achieving higher copper extraction, the extractant concentration in the organic phase was varied between 2.5 and 10% (v/v) in kerosene.

Results of single-stage extraction experiments carried out at different reagent concentrations are shown in Table 2. Extraction of both copper and molybdenum increases with increasing extractant concentration; however, molybdenum is more strongly extracted than copper.

Once the possibility of the co-extraction of both metals by LIX 622 had been established, further studies were carried out to optimise conditions for the extraction and separation of copper and molybdenum.

To determine the number of stages required at different volume phase ratio, an extraction isotherm was obtained with 5% (v/v) LIX 622 (Fig. 2). The single extraction at O/A phase ratio of 1 gave a raffinate containing 1.7 mg/l Cu and 3 mg/l Mo. A three-stage counter-current batch simulation test was conducted at an O/A phase ratio of 4.5. The raffinate obtained showed the presence of 0.8 mg/l copper and molybdenum. The extraction of both metals is thus in excess of 99%.

Table 2
Influence of LIX 622 concentration on metal extraction[a]

Extractant concentration (% v/v)	Extraction (%)	
	Mo	Cu
2.5	80.5	50.0
5	91.5	79.5
7.5	95.5	90.1
10	97.2	96.0

[a] Aqueous feed: 0.1 g/l Cu and 0.1 g/l Mo (pH_{eq}: 0.65±0.01). Organic feed, LIX 622 in kerosene; O/A phase ratio, 1.

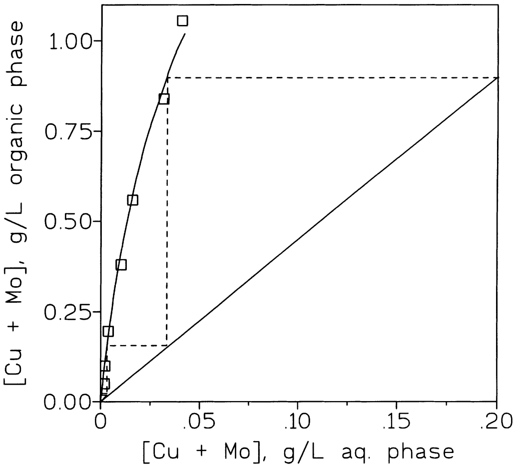

Fig. 2. McCabe–Thiele diagram for copper–molybdenum co-extraction.

3.2. Stripping

A loaded organic phase (1% (v/v) LIX 622 in kerosene), containing 0.1 g/l (each) copper and molybdenum, was used to carry out selective copper stripping. Aqueous feed containing various sulphuric acid concentrations (typical of copper electrowinning operations) was used in the experiments.

Preliminary tests have shown that 2.5 min was enough to reach maximum copper stripping. Results of these experiments are shown in Table 3. There is marginal molybdenum co-stripping with copper as the sulphuric acid concentration increases. The optimum sulphuric acid concentration to achieve efficient copper stripping is estimated to be of 170 g/l.

Using this acid concentration a two-stage counter-current simulation was carried out at an O:A phase ratio of 1. After stripping, the organic phase was found to contain up to 5 mg/l corresponding to >95% copper stripping. The copper-rich pregnant aqueous solution was found to contain up to 5 mg/l molybdenum.

As demonstrated above, sulphuric acid solutions could not strip molybdenum from loaded organic phases. Preliminary tests showed the possibility of molybdenum stripping using ammonia aqueous media; thus, the copper-free organic phase was used for carrying out molybdenum stripping experiments using these alkaline solutions. Single-stage stripping studies carried out at O:A phase ratios of 1 using various ammonia aqueous concentrations are shown in Table 4. It can be seen that the increase of the initial NH_3 concentration increases the extent of molybdenum stripping.

Table 3
Copper stripping at various H_2SO_4 concentrations (O/A phase ratio: 1)

Initial H_2SO_4 concentration (g/l)	Stripping (%)	
	Cu	Mo
80	78.0	3.7
120	84.5	3.9
160	89.9	4.0
200	94.5	4.2
240	94.5	4.2

Table 4
Molybdenum stripping at different NH_4OH concentrations (equilibration time: 60 min)

Initial NH_3 aqueous concentration (mol/l)	Stripping Mo (%)
0.5	86.7
1.0	95.7

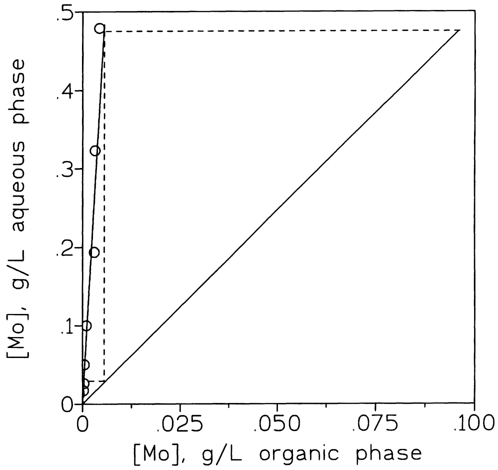

Fig. 3. McCabe–Thiele diagram for molybdenum stripping.

The stripping of molybdenum can be represented by the general equilibrium:

$$(\mathrm{Mo(VI)} + \mathrm{R})_{\mathrm{org}} + \mathrm{NH_4OH_{aq}} \rightleftarrows (\mathrm{NH_4})_2\mathrm{MoO_4}_{\mathrm{aq}} + \mathrm{HR_{org}} \quad (2)$$

where $(\mathrm{Mo(VI)}+\mathrm{R})_{\mathrm{org}}$ represents the various species present in the loaded organic solutions (Table 1) and ammonium molybdate is the species formed in the aqueous phase as a consequence of the stripping reaction.

A stripping isotherm was obtained using 1 mol/l ammonia aqueous solution and the organic phase was loaded with 0.096 g/l molybdenum (Fig. 3). Based on this, a two-stage counter-current simulation was carried out at an O:A phase ratio of 5. The spent organic solution was found to contain up to 1 mg/l molybdenum. The percentage of stripping was in excess of 99%. On the other hand, Table 5 shows the per-

Table 5
Percentage of molybdenum stripped (batch experiments)

A:O phase ratio	Mo stripped (%)
1:1	98.6
2:1	99.5
3:1	99.6
5:1	99.7
1:2	96.9
1:3	96.7
1:5	95.5

Table 6
NH_3 washing of the stripped organic solution (equilibration time: 10 min)

Initial pH	NH_3 removed (%)
3.4	90
3.2	97
3.0	100
2.8	100

centage of molybdenum stripped at various A:O phase ratios and using the aqueous and organic phases mentioned above.

It is known that oxime extractants when used in ammoniacal medium usually pick up some ammonia [18]. It was estimated that after molybdenum stripping the ammonia present in the organic solution is 0.08 g/l. Preferably this ammonia should be removed before attempting the recirculation of the organic solution.

The ammonia from the organic solution was therefore removed by a pH-controlled washing operation. Single-stage washing experiments were carried out at an O:A phase ratio of 1 with washing phases of various initial pH values. The results of these experiments are shown in Table 6. It can be observed that with an initial pH of 3.2 most of the ammonia is removed in a single stage.

4. Conclusions

LIX 622 extracts both copper and molybdenum from aqueous sulphate media. The extraction of both metals is pH-dependent; however, molybdenum is extracted preferably to copper as the equilibrium pH shifts to more acidic values. From a solution of pH 1.4 containing 0.2 g/l copper and molybdenum, both metals are almost quantitatively extracted in three stages using a 5% (v/v) LIX 622 solution in kerosene.

Selective copper stripping from loaded organic solutions can be achieved using sulphuric acid solutions. Using a 170 g/l H_2SO_4 aqueous solution the copper-pregnant solution carried only up to 5 mg/l molybdenum and the spent organic solution retained also up to 5 mg/l copper, thus resulting in the separation of the two metals through co-extraction and selective stripping.

The copper-free organic phase was treated for molybdenum stripping using ammonia aqueous solutions. After two stages with 1 mol/l NH_3 aqueous solution the extent of molybdenum stripping is >99%. The entrained ammonia is removed in a single-stage pH-controlled step, allowing the recirculation of the unloaded organic solution to the extraction stage.

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