COPPER(II) EXTRACTION
FROM AMMONIA LEACH SOLUTION

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Abstract: Hydrometallurgical processing of copper-bearing materials (ores, concentrates, by-products) is usually done with the use of acidic or ammonia leaching. In the case where a leaching feed material contains significant amounts of carbonate rocks and iron minerals the second method is preferential due to a higher process selectivity. However, it can also be problematic considering possible ammonia transfer during the subsequent extraction process. The paper presents results of extraction of copper(II) from ammonia leach solutions. The effect of a type of extractant, its concentration and type of diluent in organic phase on extraction efficiency and ammonia transfer was studied. A few commercial extractants were examined, namely LIX 84-I, LIX 984N, LIX 54-100. The results clearly indicate that in the case of extraction systems using hydroxyoximes the extraction efficiency is remarkably higher than for β-diketone reagent. Presented studies proved that extraction efficiency of Cu(II) is also dependent on the type of diluent and is less favourable for systems with non-aliphatic diluents. It was observed that ammonia co-extraction occurs and depends on examined parameters. Scrubbing of loaded organic phase showed that ammonia can be removed almost completely using double wash with sulfuric acid solution.

Keywords: hydrometallurgy, hydroxyoximes, LIX, copper ore, copper concentrate

Introduction

Ammonia leaching is frequently used in hydrometallurgy for processing of oxide and sulfide ores, concentrates or by-products, particularly those containing significant amounts of carbonate rocks, which during the acidic leaching contribute to increased acid consumption. Ammonia and its salts (carbonate or sulfate) are very effective and selective leaching agents. They can be a good alternative to acidic oxidative solutions, considering high stability constants of formed ammonia complexes of Ag, Au, Co, Cu, Ni and Zn. In the case of materials containing copper-iron and iron minerals (chalcopyrite, bornite, pyrite, pyrrhotite) ammonia leaching can be beneficial because of its selectivity. The selectivity means solubilization of desired metals and

precipitation of undesirable iron in one unit operation (Chmielewski et al., 2009). Iron can pose a real problem in further stages of hydrometallurgical processing, in operations such as solvent extraction.

Ammonia leaching of sulfide copper concentrates generate buffer type liquors (pH ranges from 9 to 10), because of the excess of ammonia and significant amount of ammonia sulfate as a leaching agent. Metals such as Cu, Ni, Co and Zn occur in ammonia systems as a cationic amminacomplexes. Alkalinity of the solution and free ammonia concentration affect route of extraction (Miller et al., 1981).

Solvent extraction (SX) of copper(II) from ammonia solutions proceeds similarly to that from acidic solutions, but complexation of metal (M) by ammonia ligands must be considered:

$$M^{2+} + 4NH_3 = M(NH_3)_4^{2+}. \qquad (1)$$

During extraction ammonia ligands are pushed out and a new chelate complex with hydroxyoxime is formed in organic phase. Copper(II) extraction from ammonia solution with acidic extractant HA is described as:

$$Cu(NH_3)_{4(aq)}^{2+} + 2HA_{(o)} = CuA_{2(o)} + 2NH_{4(aq)}^+ + 2NH_{3(aq)} \qquad (2)$$
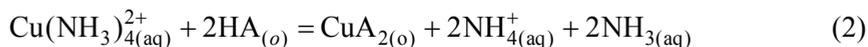
where aq and o subscripts denote the aqueous and organic phases, respectively.

Extraction of metals from ammonia solutions seems to be more complicated comparing to acidic environment. Initially, considering that extraction reaction is reversible it should be expected that the increase of ammonia or ammonium ion concentration in the aqueous phase will deteriorate extraction. Moreover, according to Jergensen (1999) the increase of pH of the aqueous phase or extractant concentration in the organic phase is not necessarily beneficial for extraction. The reason for this is that both parameters favour ammonia transfer to the organic phase. The type of hydroxyoxime extractant and diluent and content of metal in the organic phase also significantly contribute to ammonia extraction. The observed phenomenon is dangerous and should be avoided. The contact of loaded organic phase containing ammonia with a spent electrolyte can lead to formation of ammonium sulfate (carbonate or chloride) in liquors directed to electrowinning section. Crystallization of ammonium salts can be observed in tanks after few recycles of spent electrolyte to the stripping section. It is the main disadvantage of metals extraction from ammonia solutions. It complicates a technological process and negatively affects its economy. Scrubbing of the loaded organic phase before stripping with spent electrolyte significantly reduce ammonia concentration in strip liquors (Flett and Melling, 1979; Ritcey, 2006) .

In the case of multicomponent solutions, extraction of metals can be held in two ways. The first one is selective sequential extraction – stripping, while the second one is co-extraction – selective stripping. Very often it appears that the second method is

more cost-effective, because it requires less stages comparing to the first way of separation. The concept of co-extraction (selective stripping) was used for many metal couples. It was also adopted in ammonia systems for Cu-Ni separation.

The paper presents the results of extraction of copper(II) from ammonia pregnant leach solutions (PLS), coming from leaching of copper sulfide concentrates. Some commercial extractants were examined, namely LIX 84-I, LIX 984N, LIX 54-100. The extractive properties of selected reagents prepared as the organic solutions in hydrocarbon diluents were examined and compared. Moreover, the effect of extractant concentration in the organic phase on the extraction efficiency and ammonia transfer were studied.

Experimental

Reagents and solutions

Aqueous feed solutions used in solvent extraction (SX) studies were pregnant leach solutions (PLS) generated in pressure ammonia leaching of commercial flotation concentrate. Leaching with ammonia/ammonium sulfate solution resulted in leach liquors (PLS) containing 8 g/dm^3 Cu(II), 0.58 g/dm^3 Zn(II), 15 mg/dm^3 Ni(II) and 45 mg/dm^3 Co(II). The solution pH was 9.7±0.15.

The commercial extractants LIX84-I, LIX®984N and LIX 54-100, applied in SX laboratory tests, were manufactured by Cognis and supplied by Cognis Ireland Ltd. The active substance of LIX84-I is oxime of 2-hydroxy-5-nonylacetophenone. LIX®984N is a mixture of oximes: 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime. The active substance of diketone type extractant LIX 54-100 is 1-phenyldecane-1,3-dion. Escaid®100 (Exxon Mobil Chemical), Exxsol D80 (Exxon Mobil Chemical) and toluene (POCh Gliwice) were used as diluents. The chosen diluents differ in aromatic compounds content, which is equal to 19, 0.5 and 100%, respectively. No extraction modifiers were used.

Analytical methods

The aqueous solutions were analyzed for metals concentration by atomic absorption spectrometry (AAS) using a Varian SpectrAA 20Plus. The concentration of copper in the organic phase was calculated from a difference between its initial metal concentration in PLS and its concentration in raffinate at fixed organic to the aqueous (O/A) phase ratios. The measurements of pH were carried out with Elmetron CX-731 pH-meter using a Hydromet glass electrode. Ammonia concentration was determined spectrophotometrically with the Nessler reagent.

Results and discussion

The effect of type of extractant

Extraction of copper(II) was performed with the use of chosen extractants diluted in aliphatic diluent Exxsol D80. The concentration of extractants in the organic phase was equal to 10% (v/v). The pregnant leach solution from ammonia leaching was used as an aqueous phase. Extraction was performed at ambient temperature. Aqueous (A) and organic (O) phases were mixed for 5 min at different A/O ratio from 10/1 to 1/10. The McCabe-Thiele diagrams were constructed on extraction equilibrium isotherms for each system (Figs. 1-3).

The efficiency of examined systems was estimated considering few parameters, namely organic phase loading, concentration of copper(II) in the raffinates and number of theorethical stages required to reach target extraction. The McCabe-Thiele diagrams (Figs. 1-3) show that in all investigated systems it is possible to reduce copper(II) concentration to the level below 0.5 g/dm^3. It was also observed that full loading of the organic phase is possible only, when diketone reagent is used as Cu(II) extractant. However, it is quite easy to see that in the case of diketone extractant LIX 54-100 the number of extraction stages is much greater than for remaining systems. Therefore, the comparison of test data shows that extraction systems using the hydroxyoxime reagents are preferred over the one with β-diketone reagent. Therefore, LIX 54-100 was phased out from further experiments. Similar conclusions can be found in Pietek et al. (2011). The authors investigated the behavior of the same extractants during extraction of copper(II) from ammoniacal leach solutions containing around 45 g Cu/dm^3. They also chose LIX 84-I as the best extractant based on a few criteria: good stability of reagent, no propensity towards emulsion formation, low number of extraction stages and low amount of acid needed in stripping stage.
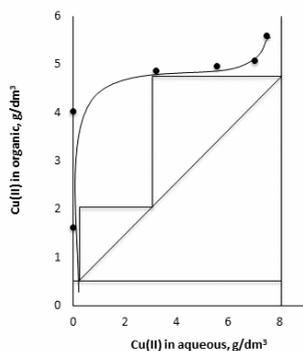

Fig. 1. Copper(II) extraction isotherm for 10% LIX 84-I in Exxsol D 80, A/O = 0.55
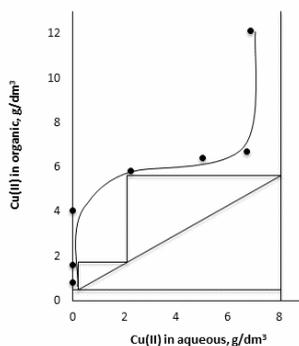
Fig. 2. Copper(II) extraction isotherm for 10% LIX 984N in Exxsol D 80, A/O = 0.65
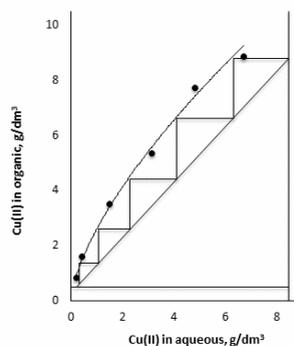
Fig. 3. Copper(II) extraction isotherm for 10% LIX 54-100 in Exxsol D 80, A/O = 1

The effect of type of diluent

Next experiments were performed in order to study the effect of type of a diluent in organic phase. LIX 84-I and LIX 984N were diluted in Escaid 100 and toluene. The concentration of extractants was equal to 10% (v/v). The obtained isotherms were compared with results from previous section for aliphatic diluent Exxsol D80 (Fig. 4). The direct evaluation of extraction curves shows that in the case of both extractants the use of aliphatic diluent (Exxsol D80) results in better extraction efficiency. The slope of isotherms indicates that extraction conditions (the number of extraction stages, organic phase loading or advance phase ratio A/O) will be less favourable for systems with non-aliphatic diluents. Moreover, the shape of generated isotherms can suggest that co-extraction of the contamination compounds (probably ammonia) takes place. It is particularly apparent in the following systems LIX 84 + Escaid 100, LIX 984 + Escaid 100 and toluene, where copper(II) loading is initially delayed and decreased at the end. Flett and Melling (1979) showed that the increase of aromatic compounds content in the hydrocarbon diluent causes greater ammonia transfer to the organic phase.

To verify this assumption the series of single extraction experiments were performed and ammonia concentration in the aqueous phase was determined. The ammonia concentration in the organic phase was calculated from a difference between its initial PLS and raffinate concentration. The obtained results are presented in Table 1. The comparison shows that the NH_3 transfer is dependent on the type of diluent and increases with the increase of aromatic compounds content. The lowest concentration of ammonia in organic phase was noted in the case of LIX 84-I diluted in Exssol D80. Therefore, this system was chosen to further investigation.
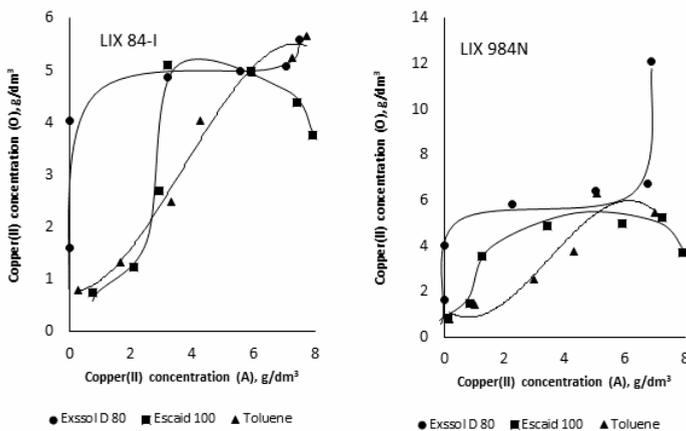

Fig. 4. The effect of diluent on extraction isotherms
for Cu(II) extraction from ammonia solutions

Table 1. Concentration of ammonia in organic phase after extraction
with hydroxyoxime extractants in different diluents

Diluent	LIX 84-I	LIX 984 N
	NH_3, mg/dm^3	
Exxsol D 80	126	258
Escaid 100	1183	921
Toluene	2237	1579

The effect of extractant concentration

To study the effect of extractant concentration the content of LIX 84-I in the organic phase was varied in the range of 5-30% (v/v). As before, extraction was performed using different A/O ratios to generate extraction isotherms. The obtained results are presented in Fig. 5. Figure 5 shows that the positive effect of LIX 84-I concentration increase in the organic phase. As expected, the copper(II) extraction efficiency was improved with increasing concentration of extractant. However, according to Fu et al. (2011) the hydroxyoxime extractants are not the most suitable reagents in the ammonia solution in spite of their high affinity towards copper(II). It is due to their high tendency to co-extract ammonia to organic phase. Considering that fact, additional tests were conducted to measure ammonia loading during copper(II) extraction. For this purpose freshly prepared organic solutions of LIX 84-I in Exssol D80 were contacted with PLS solution at the phase ratio A/O equal to 1. After given contact time the phases were separated and filtrated. The concentration of ammonia in the organic phase was calculated as before.
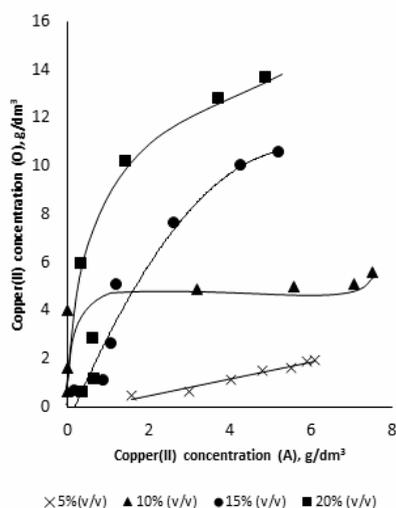

Fig. 5. The effect of LIX 84-I concentration on Cu(II)
extraction from ammonia solutions

The obtained results indicate that the amount of co-extracted ammonia decreases with the increase of extractant concentration (Table 2). However, it should be noticed that at the same time loading of the organic phase with copper(II) also increases. It means that extracted metal ions replace ammonia from the organic phase

Table 2. The effect of extractant concentration in organic phase on ammonia transfer

LIX 84 % (v/v)	Cu(II) (O) mg/dm^3	NH$_3$, mg/dm^3
5	2172	3947
10	5221	1316
15	5655	1184
30	6494	658

Washing of NH$_3$ from loaded organic phase

The problems described previously indicate that it is necessary to remove ammonia from the loaded organic phase before stripping of copper(II). For this purpose controlled washing with sulfuric acid solutions of different pH was used. First organic phase was contacted with PLS at phase ratio A/O equal to 1, to obtain the organic phase loaded with Cu(II) and NH$_3$. Then, the organic solutions were contacted with H$_2$SO$_4$ solutions at the same phase ratio. The aqueous solutions obtained after washing of the organic phase were analyzed for the concentration of copper(II) and ammonia.

The obtained results (Table 3) indicate that the increase of scrubbing solution acidity results in a greater efficiency of ammonia washing from the organic phase, although it is not complete. Only 80% of ammonia was removed in a single test after contact with pH 2 solution, with negligible losses of copper(II). Further testing was necessary to check possibilities of total washing of ammonia. The loaded organic solutions were doubly-contacted with sulfuric acid solutions of pH 2 and 3. The analysis showed that it is possible to increase the effectiveness of washing to 66 and 96%, respectively for pH 3 and pH 2 solutions. In the latter case copper losses were noticed to be at the same level as in the first scrub stage.

Removal of ammonia from loaded organic phase was also studied by Parija et al. (2000), as the scrub stage was necessary before nickel(II) stripping. They described selective stripping of Cu(II) and Ni(II) after co-extraction from PLS containing above 10 kg/m^3 of both metals. The loaded organic phase obtained in a two stage counter-current study contained Cu(II) 6.91 kg/m^3, Ni(II) 5.35 kg/m^3 and NH$_3$ 1.92 kg/m^3. The obtained in this work results showed that almost complete (99.5%) ammonia removal with irrelevant nickel(II) losses (36 g/m^3) is possible with the use of 6.75 kg/m^3 sulfuric acid.

It is known that in the case of copper(II) extraction by LIX 84 from typical ammoniacal solutions, co-extraction of Cu(II) and Ni(II) takes place. Therefore, a further step in the treatment of loaded organic solutions is selective reextraction of

nickel(II) before stripping of copper(II). Usually sulfuric acid solutions of different concentrations are used as a stripping agent.

Table 3. The effect of acidity of a scrubbing solution on ammonia washing

Initial pH	Equilibrium pH	Washing efficiency %	Cu(II) conc. mg/dm^3
6	10.66	35.4	89
4	10.65	40.4	80
3	10.49	50.4	111
2.5	10.25	55.4	321
2	9.60	80.4	54
1.5	9.01	80.4	64

Conclusions

This paper refers to copper(II) extraction from ammonia leach liquors. Special attention was paid to the problem of ammonia transfer to the organic phase. Significant differences in extraction performance were observed for examined extractants. This applies particularly to the organic phase loading, concentration of copper(II) in raffinates and number of theorethical stages required to reach target extraction. The results clearly indicate that in the case of systems using hydroxyoximes extraction efficiency is much better than for β-diketone reagent.

The results proved that extraction efficiency of Cu(II) is also dependent on the type of diluent and is less favorable for the systems with non-aliphatic diluents. Additionally it was observed that transfer of ammonia increases with the increase of aromatic compounds content in the diluent. Moreover, ammonia extraction to the organic phase was shown to be inversely proportional to extractant concentration in organic phase. This is probably related to the replacement of ammonia by copper(II) during its extraction.

The presence of ammonia in the organic phase forces the need to its elimination before stripping. The results showed that the effectiveness of washing depends on acidity of scrubbing solution. The best results were obtained when loaded organic was doubly-washed with pH 2 sulfuric acid solution.

Acknowledgments

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