SOLVENT EXTRACTION OF ZINC(II) FROM AMMONIA LEACHING SOLUTION BY LIX 54-100, LIX 84 I AND TOA

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Abstract: Commercial extractants LIX 54 -100, LIX 84 I and TOA were used to recover zinc(II) from ammonia solutions. The effect of extractant and ammonia concentration, contact time and reextraction were studied. It was found that extraction of zinc depended on the ammonia, ammonium sulphate and extractant concentration but did not depend on the contact time. The McCabe-Thiele distribution isotherm for LIX 54-100 showed that 95% of zinc(II) ions can be recovered in four stages of extraction. Reextraction of Zn(II) ions from the loaded organic phase showed that the metal can be removed almost completely using sulphuric acid.

Keywords: solvent extraction, zinc(II), LIX 54-100, LIX 84 I, TOA

Introduction

Zinc is a very important metal required for various applications in hydrometallurgical, chemical and textile industries. Zinc is mainly recovered from primary sulphide concentrates and from different secondary resources such as zinc ash, zinc dross, flue dusts of electric arc furnace and brass smelting, automobile shredder scrap, rayon industry sludge etc., which contain different levels of impurities depending on their sources (Jha, 2001).

In hydrometallurgy, solvent extraction is an extremely important separation process for isolating and concentrating a valuable substance from an aqueous phase (Flett, 2005; Ritcey, 2006; Regel-Rosocka and Alguacil, 2013). Removal of metal ions from a diluted aqueous medium is generally considered as a great advantage of extraction. For zinc(II) extraction from acidic solutions the following organophosphorus acids-based extractants can be used: Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid), Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid)), Cyanex 272

(bis/2,4,4-trimethylpentyl/ phosphinic acid), D2EHPA (di-(2-ethylhexyl)phosphoric acid) and PC88A (2-ethylexyl hydrogen 2-ethylhexyl phosphonate) (Rickelton and Boyle, 1990; Caravaca and Alguacil, 1991; Nathsarmaa and Devib, 2006; Ali et al., 2006). Unfortunately, these compounds cannot be used in extraction from ammonia solutions, due to their weak solubility in the alkaline environment.

Extraction of zinc(II) from ammonia solutions is performed using β-diketone. Some authors described applying either β-diketones-based extractants or their mixtures with hydroxyoxime extractants. The β-diketone compound was used in many applications and to recover of a number of metal ions (Gotfryd and Pietek, 2013). Pawlicki et al. (2013) showed results of spectroscopic investigations related to complex compositions of 3-substituted derivatives of pentane-2,4-dione (β-diketonate) complexes with Cu(II), Co(II), Nd(III), and Ho(III). 3-allylacetylacetone and 3-benzylacetylacetone were prepared and used for the complexation study. Dziwinski and Szymanowski (1996) analysed LIX 54-100 extractant, and the results showed that the extractant contained some amounts of hydrocarbons, including C11-C14 alkanes as a solvent, six isomeric 1-phenyldecane-l,3-diones with different alkyl group structures, heptadecane-8,10-dione, l,3-diphenyl-propane-l,3-dione and an unknown compound with a carbonyl group as a fragmentation product.

Alguacil et al. (1999) demonstrated that the efficiency of Zn(II) extraction from ammonia solutions with LIX 54 increased with pH, reaching the maximum at pH = 8. The effect of pH can be caused by formation of the non-extractable ammine complex of zinc(II) at higher pH values. Reextraction was successfully obtained with sulphuric acid solutions. The reextraction efficiency increased with the acid concentration. Rao et al. (1992) investigated zinc(II) extraction with the commercial extractant Hostarex DK-16 (high molecular weight β-diketone), which has a structure similar to LIX 54. The research was carried out on solutions containing low concentrations of Zn(II) 0.01 – 0.20 g/dm^3. Chen et al. (2011) investigated the synergic effect of mixtures of β-diketone and trioctylphosphine oxide (TOPO) during Zn(II) extraction from solutions containing 15 g/dm^3 of Zn(II) and 3 mol/dm^3 of ammonia. The optimum conditions were obtained for 50% (v/v) mixture of extractants, pH 8.5 and phase ratio of 2:1. Hu et al. (2012) studied the behavior of LIX 54 with either Cyanex 923 (hydroxamic acids) or LIX 84 (2-hydroxy-5-nonylaceto- phenone oxime) mixtures. It was found that the efficiency of the first mixture was significantly higher, particularly at either ammonia concentration or higher pH of aqueous phase. It was also observed that in both cases the extraction efficiency decreased with the increase of values of these two parameters. Hu et al. (2012) investigated the extraction behavior of zinc(II) by β-diketone from the ammonia solutions into the ionic liquid and molecular organic solvent (nonane). The results showed that the extraction efficiency of Zn(II) in both extraction systems decreased with the increase of pH and total ammonia concentration, but increased with increasing of extractant concentration. Jha et al. (2001) examined solvent and synergetic effects of zinc(II) extraction in the ammonia solution used as an extractant 4-ethyl-1-phentyl-1,3-octadione (β-diketone). It was

found that extraction of zinc(II) depended on the solvent polarity and type of ligands. The synergistic effect resulted from formation of more hydrophobic and stable zinc adducts, which promoted the distribution of zinc extracts. So far, only a limited number of works has been reported on application of β-diketones for removal of zinc(II) ions from ammonia solutions. The objective of this study is to examine the process of zinc(II) ions extraction from ammonia pregnant leach solutions (PLS) from pressure leaching of the copper flotation concentrate from Polkowice Concentrator (KGHM Polska Miedź S.A.). The effect of ammonia, ammonium ions, contact time, extractant concentration and phase ratio on the recovery of zinc(II) were investigated.

Experimental

Reagents

LIX 54-100 (Henkel), LIX 84 I (Cognis) and TOA (Sigma-Aldrich) were used as organic solvents without further purification, whereas Exxsol D80 (Brenntag) was used as a diluent. The active substance in LIX 54-100 was a β-diketone which composition was based on six isomers, that is 1-phenyldecane-1,3-diones, heptane-8,10-dioneand 1,3-diphenylpropane-1,3-dione. LIX 84 I was 2-hydroxy-5-t-nonyl acetophenonoxime. TOA (trioctylamine) was a tertiary aliphatic amine usually used as an extractant for organic acids and precious metals. Exxsol D80 used as a diluent, was characterized as "de-aromatized" aliphatic hydrocarbon solvent. The major components were normal paraffins, isoparaffins and cycloparaffins. The product contained very low levels of aromatic hydrocarbons (less than 2%).

Extraction

Synthetic solutions of zinc(II) ions were prepared by dissolving a known amount of zinc sulphate ($ZnSO_4 \cdot 6H_2O$) in ammonium buffer (8.5 – 34.0 g/dm^3 of $NH_3 \cdot H_2O$, 1.8 – 18.0 g/dm^3 of $(NH_4)_2SO_4$). The initial Zn(II) concentration for the synthetic solutions was 0.5 g/dm^3. Pregnant leach solutions (PLS) were generated in pressure ammonia leaching of flotation sulphide concentrate. The solutions after ammonia/ammonium sulphate leaching contained ~0.5 g/dm^3 of Zn(II), ~0.3 g/dm^3 of Cu(II), ~0.05 g/dm^3 of Ni(II) and ~0.03 g/dm^3 of Co(II). The solution pH from pressure leaching was 9.8±0.1.

The organic phase contained one of three extractants and Exxsol D80 as the diluent. Aqueous and organic phases were shaken at 325 rpm and ambient temperature (25 ± 1°C) using a mechanical shaker type ELPAN 357. The sulphuric acid solution at a concentration of 200 g/dm^3 was used as a reextraction agent. The concentration of Zn(II) in the aqueous phase before and after extraction as well as reextraction was determined by means of flame atomic absorption spectrometry (FAAS) using a Varian SpectrAA 20 Plus instrument.

Results and discussion

Influence of ammonia concentration on zinc(II) extraction

The effect of ammonia concentration on zinc(II) extraction was investigated for selected extractants (LIX 54-100, LIX 84 I and TOA) diluted in the aliphatic diluent Exxsol D80. The concentration of extractants in the organic phase was equal to 10% (v/v). The solutions containing 0.5 g/dm^3 of Zn(II), 8.5-34 g/dm^3 of $NH_3 \cdot H_2O$, 1.8-18 g/dm^3 of $(NH_4)_2SO_4$ were used as the aqueous phase. Extraction was performed at ambient temperature. Aqueous (A) and organic phases (O) were contacted for 30 minutes at the phase ratio equal to 1. Figure 1 shows that the concentration of $(NH_4)_2SO_4$ had a significant effect on the recovery of zinc. Extraction of Zn(II) decreased sharply in the presence of $(NH_4)_2SO_4$. Similar conclusions can be found in Alguacil and Alonso (1999). The authors investigated the influence of ammonium sulphate in the aqueous phase on zinc(II) extraction using LIX 54-100. They also showed that zinc extraction decreased with increasing the ammonium sulphate concentration of the aqueous phase. This decrease was attributed to formation of metal ammine complexes in the aqueous phase, which decreased the free zinc ion concentration. Infrared studies confirmed the non-extractability of zinc ammine complexes. Higher $(NH_4)_2SO_4$ concentration led also to the increase of solution density what additionally may create some difficulties in diffusion of Zn(II) ions to extractants and led to decrease in the zinc recovery.
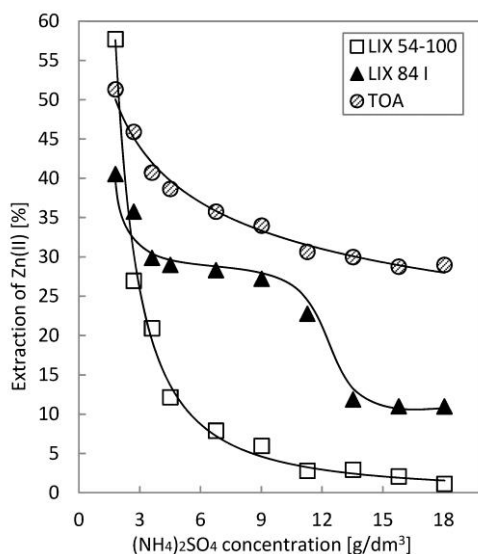

Fig. 1. Zn(II) extraction as a function of $(NH_4)_2SO_4$
concentration (extractant = 10% (v/v))

The best Zn(II) extraction results can be obtained from the solution containing 1.8 g/dm^3 of $(NH_4)_2SO_4$ and 17 g/dm^3 of $NH_3 \cdot H_2O$. For LIX 54-100 the extraction recovery was 58% for LIX 84 I 51 and 48% for TOA.

Figure 2 presents the effect of $NH_3 \cdot H_2O$ concentration on extraction of zinc. It appears that the extraction efficiency of Zn(II) decreased with increasing the ammonia solution concentration. The highest efficiency of process for LIX 54-100 (72%), LIX 84 I (66%) and TOA (47%) was obtained at $NH_3 \cdot H_2O$ concentration of 8.5 g/dm^3.

The results presented in Figs. 1 and 2 show that the best Zn(II) extraction efficiency can be observed from the solution containing 8.5 g/dm^3 of $NH_3 \cdot H_2O$, 1.8 g/dm^3 of $(NH_4)_2SO_4$ in the aqueous phase.

All subsequent experiments, including kinetic studies and extraction isotherms obtained, were carried out using the pregnant leach solutions (PLS) generated in pressure ammonia leaching of flotation sulphide concentrate. The aqueous solution contained 0.5 g/dm^3 of Zn(II), 8.5 g/dm^3 of $NH_3 \cdot H_2O$ and 1.8 g/dm^3 of $(NH_4)_2SO_4$.
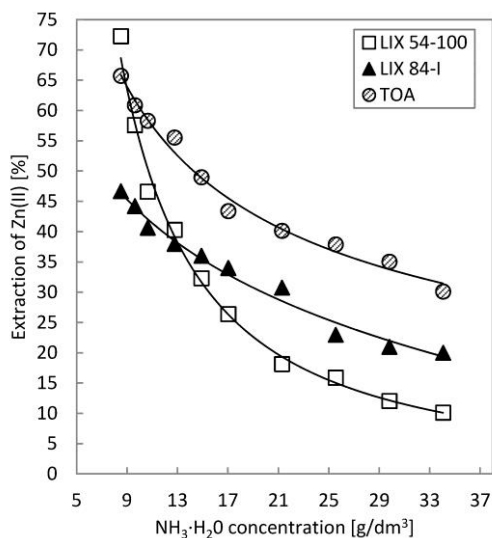

Fig. 2. Zn(II) extraction as a function of $NH_3 \cdot H_2O$ concentration
(extractant = 10% (v/v))

Effect of contact time on zinc(II) extraction

The kinetics of zinc extraction is presented in Figure 3, where the extraction efficiency was plotted vs. time. The results were obtained at ambient temperature. The contact time varied in the range of 5-60 minutes. The extractant concentration was equal to 10% (v/v). The phase ratio of aqueous-to-organic phases (A/O) was equal to 1.

It was observed that the efficiency of extraction did not depend on the contact time for LIX 54-100. For the extractants TOA and LIX 84 I, the majority of zinc(II) ions (extraction efficiency equal to 61 and 43%, respectively) were removed after 5 min of

the shaking (Fig. 3), but further increase of the extraction time up to 60 min increased extraction to 65 and 45%, respectively. It indicates that the contact time equal to 30 min was considered as the optimum time for extraction. It enables to achieve of an equilibrium of zinc extraction. It was also observed that full loading of the organic phase is possible only when β-diketone reagent (LIX 54-100) is used as the Zn(II) extractant.
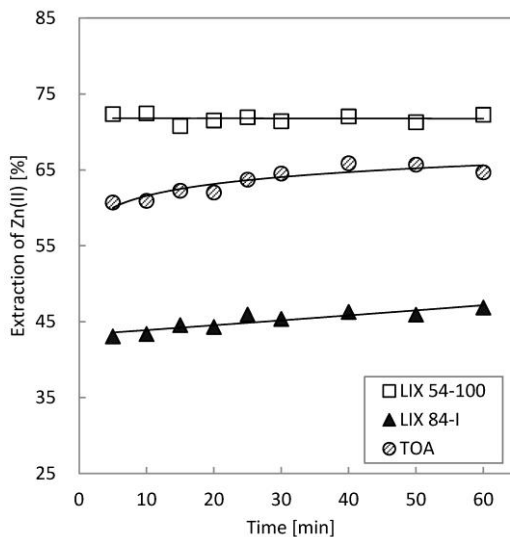

Fig. 3. Effect of contact time on zinc(II) extraction using LIX 54-100, LIX 84 I and TOA as extractants from ammonia solution (extractant = 10% (v/v))

The effect of extractant concentration

For the extractant LIX 54-100 displaying high affinity towards zinc(II) from the ammonia solution, the influence of extractant concentration was also studied. The results are presented in Table 1 and Fig. 4. The content of extractant in the organic phase varied in the range of 5-30% (v/v). The organic phase was contacted with PLS at the phase ratio equal to 1. The results showed (Fig. 4) the high extraction capacity of LIX 54-100 and increases in the recovery of zinc(II) ions with the extractant concentration. It was observed that the extraction efficiency increased from 15 to 95%, with the increase in the extractant concentration. The maximum extraction efficiency of zinc(II) equal to 95%, was obtained at higher concentration of LIX-54, 30% (v/v) (Table 1). It was done in order to increase a number of extractant molecules. However, using the concentration of extractant higher than 10% was unprofitable because of low concentration of zinc in the leach solutions. Therefore, it was assumed that optimal extractant concentration in described experiments was 10% (v/v). The similar results were observed by Hu et al. (2012). The authors investigated the effect of extractant concentration on Zn(II) extraction by usng β-diketone and its mixtures with other substances, as the extractant.

Table 1. Zinc(II) extraction using LIX 54-100 from the ammonia solutions

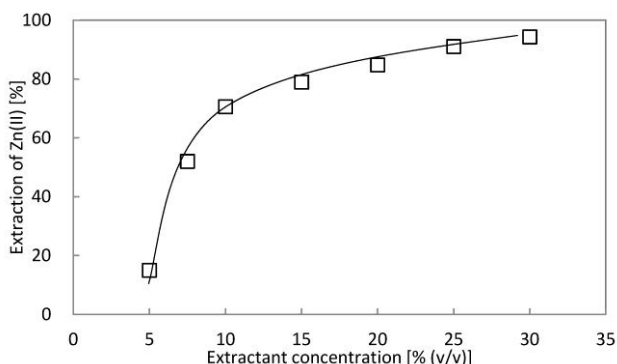| extractant concentration, % (v/v)	distribution ratio (D)	extraction Zn(II), %
5	0.18	15
7,5	1.08	52
10	2.40	71
15	3.76	79
20	5.59	85
25	10.22	91
30	16.70	94

Fig. 4. Effect of LIX 54-100 concentration on the zinc(II) extraction
from ammonia solutions

Extraction isotherm

The effect of the ratio of aqueous-to-organic phases (A/O) on the extraction efficiency of Zn(II) was also investigated (Table 2). The organic phase containing extractant LIX 54-100 (10% (v/v)) diluted in Exxsol D80 was mixed with the PLS solution (0.5 g/dm^3 of Zn(II), 8.5 g/dm^3 of $NH_3 \cdot H_2O$ and 1.8 g/dm^3 of $(NH_4)_2SO_4$) at different A/O ratio from 1/5 to 5/1. The pH value for the above ammonia leach solution was 9.7. Based on the obtained extraction isotherm corresponding the McCabe-Thiele diagram was constructed (Fig. 5). The efficiency of the examined systems was estimated considering concentrations of Zn(II) ions in the raffinate and a number of theoretical stages allow application of the extractant studied in industrial processes. The McCabe-Thiele diagram (Fig. 5) indicates that with the feed containing 0.5 g/dm^3 of Zn(II), at the phase ratio A/O equal to 1.5, four theoretical extraction stages are required to transfer almost all Zn(II) ions from the PLS solution using β-diketone, LIX 54-100. The Zn(II) concentration in the loaded organic phase after the three-stage extraction process was estimated to be 0.8 g/dm^3 showing almost complete transfer of Zn(II) to the organic phase. After the four-stage extraction process, the raffinate contained $25 \cdot 10^{-3}$ g/dm^3 of Zn(II), and the extraction efficiency was equal to 95%.

Table 2. Effect of A/O phase ratio on zinc(II) extraction from ammonia solutions for LIX 54-100

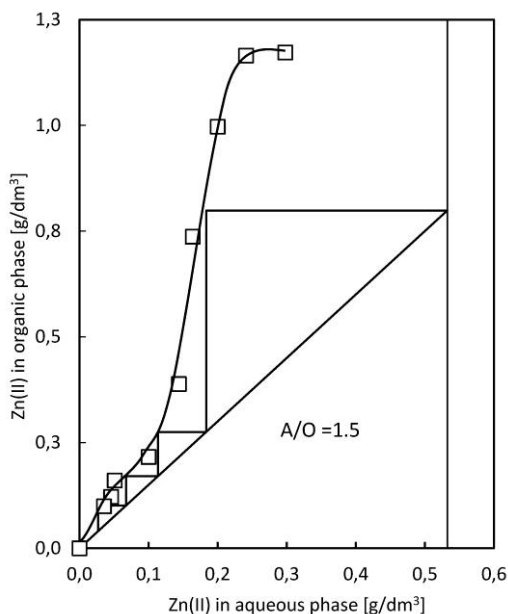| A/O phase ratio	Extraction [%]
5/1	44.0
4/1	54.7
3/1	62.4
2/1	69.2
1/1	73.0
1/2	81.2
1/3	90.4
1/4	91.4
1/5	94.6

Fig. 5. Zinc(II) extraction isotherm for LIX 54-100

Reextraction isotherm - effect of aqueous/organic ratio

A stripping test was performed using freshly loaded and pre-filtered organic phases containing 0.75 g/dm^3 of Zn(II) ions and 200 g/dm^3 of H$_2$SO$_4$ in the aqueous phase. The loaded organic and aqueous phases were shaking at different volume ratios, that is 1/5, 1/4, 1/3, 1/2, 1/1, 2/1, 3/1, 4/1 and 5/1. Based on the obtained results, the corresponding McCabe–Thiele diagram was constructed (Fig. 6). It was observed that sulphuric acid was an effective stripping agent for Zn(II) ions. The McCabe–Thiele diagram indicates that at the O/A volumetric ratio equal to 1.0 and three theoretical stripping stages required to strip almost all the extracted Zn(II) from the loaded organic phase containing LIX 54-100 as the extractant. The stripping process

efficiency was equal to 99% and concentration of Zn(II) ions in the organic phase decreased to less than $1 \cdot 10^{-3}$ g/dm^3.
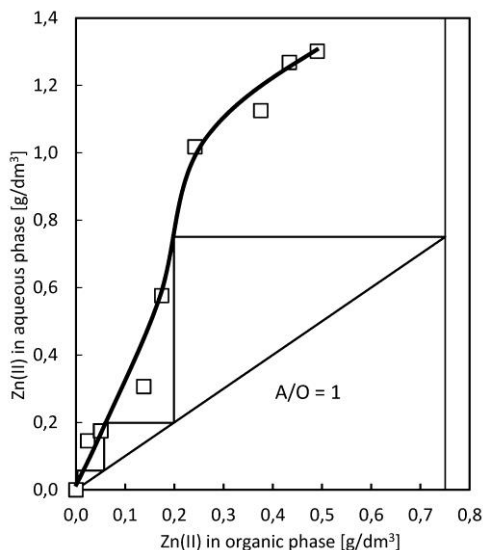

Fig. 6. Reextraction of zinc(II) for LIX 54-100

Conclusions

LIX 54-100, LIX 84 I, and TOA were used for solvent extraction of zinc(II) ions from ammonia solutions, coming from pressure leaching of the copper flotation concentrate. The experimental results showed that Zn(II) extraction was rapid and efficient, but it strongly depended on the ammonia and ammonium sulphate concentration in the aqueous phase. The most effective results were obtained for the aqueous phase containing 1.8 g/dm^3 of ammonium sulphate and 8.5 g/dm^3 of ammonia. Extraction of Zn(II) from the pregnant leach solution (PLS) did not depend on the contact time for each extractant. The extraction efficiencies of metal ions were high for LIX 54-100 and smaller for LIX 84 I and TOA. Therefore, further experiments were carried out using only extractant LIX 54-100. The increase in the extractant concentration increased the efficiency of metal ion extraction. Loading capacity of 10% (vol.) LIX 54-100 was determined to be 0.85 g/dm^3. About 95% of zinc(II) was achieved in four-process stages at the phase ratio of A/O equal to 1.5. The stripping Zn(II) ions from the loaded organic phase in the case of LIX 54-100 by using of 200 g/dm^3 of H$_2$SO$_4$ showed that the metal can be easily recovered in 99% efficiency in the three-stage process with the volumetric phase ratio of A/O equal to 1.

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