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Hydrometallurgical recovery of copper from leach liquor of polymetallic nodules in solvent extraction process

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ABSTRACT

Purpose: Purpose of this paper is to present the possibilities of copper(II) recovery from the synthetic sulphate leach liquor containing cobalt(II), nickel(II) and manganese(II).
Design/methodology/approach: The investigations have been undertaken in order to determine the influence of major parameters on the extraction process of copper(II) from the leach liquor of polymetallic manganese nodules. Copper(II) ions were extracted with Kelex 100 and LIX 70 in kerosene. The effect of different parameters such as pH of aqueous phase, extractants concentration in the organic phase, concentration of sulphuric acid as the stripping reagent were investigated.
Findings: The optimal conditions of metal ions selectivity extraction have been determined. Over 99% of Cu(II) can be effectively extracted with 5% Kelex 100 and 10% LIX 70 at pH of 2.0 from model leach liquor in the presence of Co(II), Ni(II) and Mn(II), while less than 10% of the other metals is transported to the organic phase. The selectivity of Cu(II) extraction over Co(II), Ni(II) and Mn(II) with Kelex 100 depended upon the acidity of aqueous solution and the selectivity increased with decreasing of pH in the feed solution. Separation of Cu(II) from these metal ions is very effective. Cu(II) can be recovered successfully from the loaded organic phase with Kelex 100 through stripping with 2.0 M H_2SO_4.
Practical implications: The results can be used during the hydrometallurgical recovery of metals from nodules on the industrial scale.
Originality/value: The study on the solvent extraction of Cu(II) using LIX 70 and Kelex 100 from leach liquor of polymetallic manganese nodules has not been reported yet. Conducting this research is therefore the most reasonable and necessary.
Keywords: Copper; Solvent extraction; lIX 70; Kelex 100

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1. Introduction

Solvent extraction, also called liquid-liquid extraction is one of the most important, economical and practical process in hydrometallurgical industry for separation and purification of several metals - nonferrous, rare earths, the platinum group metals (PGMs). This method have a number of advantages like: high selectivity and metal purity [1-3]. Manganese nodules, which are located at the bottom of the world's oceans, have been recognized as the potential source of copper, cobalt and nickel [4-6]. The chemical composition of the ferro-manganese concretions is showed in Table 1 [7].

Table 1.
The average contents of selected metals in manganese nodules [7]

Metal	Content, %		
	Pacific	Indian Ocean	Atlantic
Mn	19.63	17.23	13.17
Fe	12.20	13.52	13.39
Ni	0.65	0.53	0.41
Cu	0.47	0.34	0.19
Co	0.28	0.21	0.22

Manganese and iron oxides are the major components of the mineral phases, while copper, cobalt and nickel are disseminated in the oxide matrix. The most stable species of these elements are MnO_2, Fe_2O_3, CuO, Ni_3O_4 and Co_2O_3 [8]. These metals are not present in separate mineral phases and therefore they can not be liberated by means of conventional physical methods. Dissemination of copper, cobalt and nickel in Fe/Mn oxide phase require the application of chemical reductants to decompose the oxide matrix and to liberate metallic compounds during leaching. High moisture content (30-40%), high porosity (about 60%) and inability for common physical beneficiation eliminate the application of simple and economically feasible smelting processes for manganese nodules [9]. Numerous metallurgical and hydrometallurgical processes for recovering of important metals from manganese nodules have been studied in recent forty years. The extraction processes developed so far mainly belong to two categories: pyrometallurgical treatment (smelting, reductive roasting, sulphatizing, chloridizing, etc.) and hydrometallurgiacal procesing (leaching in hydrochloric acid, sulphuric acid, ammonia, etc.) [10,11]. Investigations on acid leaching of manganese nodules have been reported by numerous investigators [12-17]. Zhang et al. [4,5] presented an extensive review concerning pyrometallurgical pre-treatment followed by hydrometallurgical processing for recovery of manganese from these manganese sources. Solution after leaching of nodules usually contains Cu(II), Co(II), Ni(II), Mn(II) and Fe(III). Selective recovery of Cu(II), Ni(II) and Co(II) is often difficult from solutions containing soluble Fe(III) and Mn(II). Fe(III) ions present in the solution may precipitation as jarosite in the presence of ammonium sulphate according to following equation [4]:

$$3Fe(SO_4)_3 + 12H_2O + (NH_4)_2SO_4 \rightarrow 2NH_4Fe_2(SO_4)_3(OH)_6 \quad (1)$$

Though the iron removal is mainly achieved by precipitation techniques, the use of solvent extraction also allows the iron(III) removal from acidic aqueous solutions. Organophosphorus acid derivatives such as di(2-ethylhexyl)phosphoric acid (D2EHPA) and tri-n-buthyl phosphate (TBP) have been used for iron(III) removal from acidic solutions [2,3].

Copper, cobalt and nickel also can be selectively leached from nodules with ammonia-SO_2 solutions or H_2SO_4 under high temperature and high pressure. Both manganese and iron remain in the solid residue [9]. Copper could be selectively extracted from aqueous solutions (nitrate, sulphate or chloride media) with commercial extractants such as primary/tertiary/quaternary amine [18], di(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and di(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) [19,20], hydroxyoximes [21-25]. Copper is strongly complexed by these extractants at low pH. For example, Cu(II) has been successfully recovered from HCl solutions with the mixed extractant: Alamine 336 and LIX 54. Unfortunately, this process can't be applied for Cu(II) extraction in the presence of other metals, as the amines react with a number of metal chloride complexes [18]. Cu(II) cations can be extracted from aqueous acid media using LIX-reagents, representatives of different extractant classes: LIX 984N-I, LIX 860N, LIX84-I and LIX 65N. Cu(II) extraction with these extractants can be successfully done at low pH values [19].

In this work the selectivity extraction of copper(II) from synthetic leach liquor of polymetallic manganese nodules containing cobalt(II), nickel(II) and manganese(II) ions has been studied. Based on the literature survey the composition of solution after leaching of nodules with sulphuric acid has been determined. Copper(II) ions were extracted with Kelex 100 and LIX 70 in kerosene from sulphate solutions.

2. Experimental

2.1. Reagents

Inorganic chemicals, i.e. copper(II), manganese(II), nickel(II), cobalt(II) sulphates, sulphuric acid were of analytical grade and were purchased from POCh (Gliwice, Poland).

The synthetic leach liquor of polymetallic nodules containing 0.03 M Cu(II), 0.03 M Ni(II), 0.003 M Co(II) and 0.3 M Mn(II) were used for the solvent extraction. Aqueous solutions were prepared with deionized water.

Organic reagents, i.e. LIX 70 is a chelating organic extractant and was obtained from General Chemicals, INC., Kelex 100 (7-(4-ethyl-1-methylocty)-8-hydroxyquinoline) from Ashland Chemical. Distilled kerosene was used as the diluent in solvent extraction.

2.2. Procedure

Solvent extraction was carried out using equal volumes of both phases (10 cm^3 each), which were mechanically shaken (200 min^{-1}) for 20 minutes at the constant temperature (25 ± 2°C). The metal ions content in the aqueous phase has been determinated by means of AAS Solaar 939 (Unicam) spectrophotometer, while

the pH value has been measured with CX-731 (Elmetron) pH-meter. The concentration of metals in the organic phase was calculated from the mass balance. The distribution ratio (D) and extraction percent (%E) were determined as equal to:

$$D = \frac{[Me]_{org}}{[Me]_{aq}} \quad (2)$$

$$\%E = \frac{D}{D+1} \cdot 100\% \quad (3)$$

where $[Me]_{org}$ and $[Me]_{aq}$ are concentrations of the metal ions in the organic and aqueous phases after extraction, respectively.

3. Description of achieved results of own researches

3.1. The influence of pH

The metal ions were extracted from synthetic leach liquor containing Cu(II), Co(II), Ni(II), Mn(II) with 5% Kelex 100 and 10% LIX 70 in kerosene. The extraction of metal ions as a function of pH was investigated in the pH range 0.5-3.0. Efficiency of Cu(II) extraction with both extractants increased with increase of the equilibrium pH of the aqueous phase. It was observed from Fig. 1 that the percentage of extraction of Cu(II) with 5% Kelex 100 and 10% LIX 70 is the highest at pH 2.0 and 3.0. The separation of Cu(II) over Co(II), Ni(II) and Mn(II) with 10% LIX 70 was very effective. Percentage of extraction of Cu(II) amounted to 99,9% at pH 2.0 and 3.0, while other metal ions did not extracted in these conditions into organic phase (Fig. 2). As can be seen from Fig. 3, the selectivity of Cu(II) extraction with 5% Kelex 100 was less effective as about at pH 3.0 of aqueous phase 30% of Co(II) and 10% of Ni(II) were transported with Cu(II) to the organic phase.

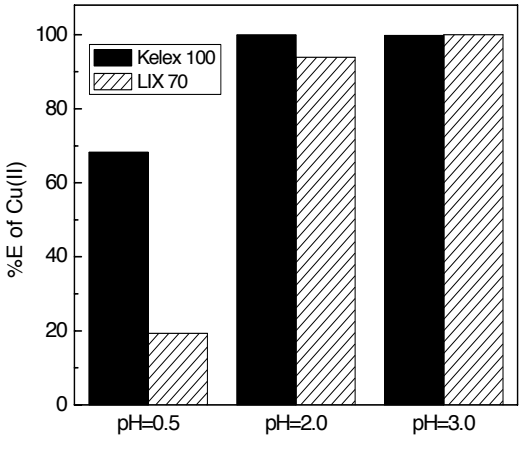

Fig. 1. The extraction of Cu(II) (% E) from synthetic leach liquor containing Co(II),Ni(II) and Mn(II) with 5% Kelex and 10% LIX 70 in kerosene

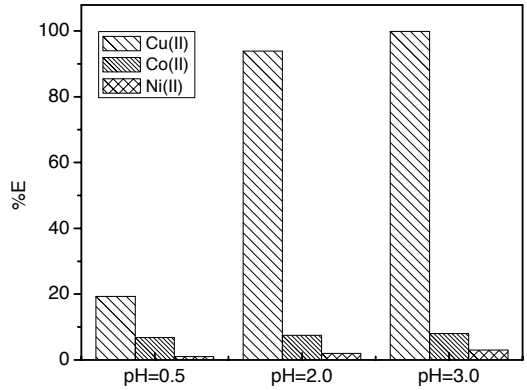

Fig. 2. The efficiency of Cu(II) extraction (% E) from synthetic leach liquor with 10% LIX 70 in kerosene

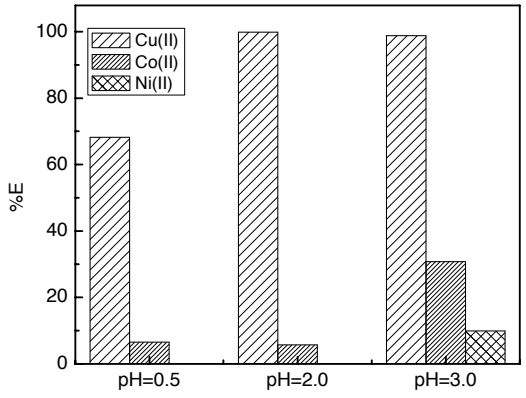

Fig. 3. The extraction (%E) of Cu(II), Co(II),Ni(II) and Mn(II) with 5% Kelex

3.2. The effect of extractants concentration

The effect of extractants concentration on the extraction of Cu(II) from the synthetic leach liquor of polymetallic nodules has been studied. In order to find the optimum concentration of LIX 70 and Kelex 100 in kerosene, the concentration of extractants varied between 2.0-10.0%. It was observed that extraction and the distribution ratio (D) depends strongly on the concentration of extractant. The distribution ratio (D) of Cu(II) increased with increase of Kelex 100 and LIX 70 concentration (Fig. 4).

3.3. The effect of stripping agent

The effect of the concentration of stripping agent, H_2SO_4, on the percentage Cu(II) stripped, extracted in an organic phase has been studied. Fig. 5 shows the dependency of the stripping of Cu(II) from organic phase with Kelex 100 on the concentration of H_2SO_4. The concentration of H_2SO_4 varied beteen 0.1-2.0 M. The percentage of Cu(II) stripped from the organic phase increased with increasing H_2SO_4 concentration. The highest efficiency of

stripping was for 2.0 M H_2SO_4 and was equal to 99.8%. Unfortunately, the stripping of Cu(II) from organic phase with LIX 70 was no possibility by using H_2SO_4 solutions. The results suggest that stripping of Cu(II) from this organic solution is a very difficult and requires the use of highly concentrated acids.

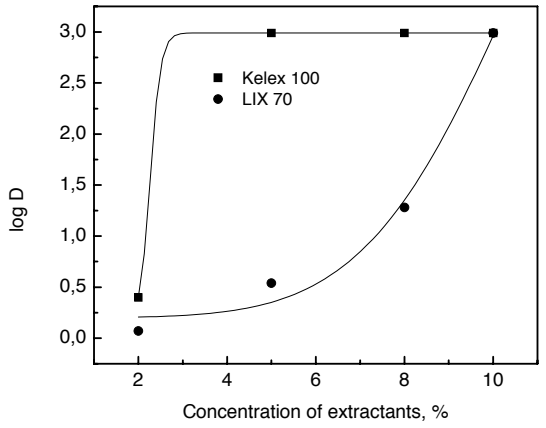

Fig. 4. Effect of extractants concentration on Cu(II) distribution coefficient. Aqueous phase: synthetic leach liquor, pH=3.0; organic phase: Kelex 100 in kerosene; LIX 70 in kerosene

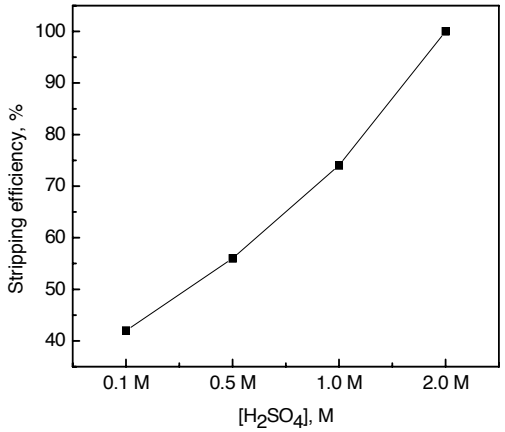

Fig. 5. Effect of H_2SO_4 concentration on the stripping (%) of Cu(II) from 5% Kelex 100 loaded organic phase

4. Conclusions

The results presented have been provided evidence for high selectivity of copper (II) extraction over cobalt(II), nickel(II) and manganese(II) from synthetic leach liquor of polymetallic nodules using chelating extractants such as Kelelx 100 and LIX 70 in kerosene. With increasing concentration of these extractants (2.0-10%) and pH of aqueous phase in range 0.5-3.0, the efficiency of Cu(II) extraction increases. The best selectivity for Cu(II) extraction over other metal ions containing in synthetic leach liquor of polymetallic nodules was obtained with 10% LIX 70. Efficiency of Cu(II) extraction with 10% LIX 70 was very high (99.9%) and other metal ions didn't extracted to organic phase. The selectivity of Cu(II) extraction was slightly lower for 5% Kelex 100 at pH 3.0. Percentage of extraction of Cu(II) was equal to 98.8%, but it was observed co-extraction of 30% Co(II) and 10%Ni(II). The selectivity of Cu(II) over the other metal ions is a very important process parameter. The investigation of the stripping of Cu(II) from loaded organic phase showed that 2.0 M H_2SO_4 can be used to the stripping of Cu(II) only from Kelex 100 loaded organic phase.

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