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SOLVENT EXTRACTION OF VALUABLE METALS FROM PREGNANT LEACH SOLUTIONS OF CUPRIFEROUS SHALE

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The pregnant solution after atmospheric leaching of cupriferous shale (middlings from Lubin Concentrator) with sulphuric acid and/or with sulphuric acid containing Fe(III) in the presence of oxygen were applied for solvent extraction experiments with several extractants. The solutions containing soluble sulphates of Cu(II), Zn(II), Ni(II), Co(II), Fe(II), Fe(III) and As as a contaminant. Aromatic hydroxyoximes, LIX 84, LIX 612 and LIX 984, were investigated as copper(II) extractants to evaluate their extraction and reextraction abilities. From the copper free raffinate Zn(II) was next extracted with di-(2-ethylhexyl)phosphoric acid (D2EHPA). Additionally, cobalt(II) and nickel(II) were separated from the zinc-free raffinate with di-(2,2,4-trimethylpentyl)phosphinic acid (Cyanex 272). Industrial aromatic hydroxyoximes used for copper(II) extraction were not sufficient selective and other metal ion species present in leach solutions were also transferred to the organic phase. The extractive recovery of Cu(II), Co(II) and Ni(II) was better for the solutions obtained from acidic leaching of shale in the absence of Fe(III) salts. The recovery of valuable metals was not satisfactory and further experiments are necessary to establish the optimal conditions of extraction and reextraction processes.

Key words: shale ore, atmospheric leaching, solvent extraction

INTRODUCTION

Polish copper deposits (LGOM - Legnica-Glogow Copper Basin, SW Poland) exhibit unique, sedimentary nature with three ore fractions: dolomitic, sandstone, and shale. Shale fraction indicates the highest concentrations of copper and accompanying metals (Ag, Ni, Co, Zn, Pb, V, Mo...) and simultaneously is the most troublesome in the flotation circuits, creating serious technical and ecological issues (Łuszczkiewicz, 2000, 2004).

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In the case of shale fraction observed is the dissemination of fine metal sulfides in the carbonate matter and in black shale-clay rocks that form the majority of the gangue. Such a fine dissemination of copper sulfides in carbonate matrix considerably reduces the susceptibility of the ore to the effective liberation. A relative increase of quantity of shale-clay and carbonate fractions in flotation feeds, which are known as mostly hard-to-treat in flotation circuits, is currently observed. According to the latest data (Kubacz and Skorupska, 2007) the content of shale fraction in Lubin deposit has already exceeded 25 % and is expected to increase in coming years.

Complex mineralogical structure and chemical composition of Polish copper ores mined from sedimentary deposits are the principal reasons of copper, silver and other metals losses to flotation tailings. The presence of shale creates serious technical, economical and ecological issues. The selective liberation of these fine particles would be the only way to enhance metal recovery. However, it appears to be ineffective by physical methods in the existing milling circuits. Consequently, the hydrophilic gangue-sulphide intergrowths greatly reduce both flotation selectivity and the metal grade in the concentrate.

Due to presently observed unfavourable changes in the ore mineralogical composition, the desired grade of copper concentrates can only be accomplished by lowering the copper recovery. The problem will undoubtedly increase in the next future due to forecasted increase in shale fraction content, which now reached 27 % for Lubin ore (Kubacz and Skorupska, 2007). Therefore, it can be concluded that the existing beneficiation technologies currently applied to Polish copper ores have already reached the limit of their technological efficiency. The only way to reduce significantly losses of copper, silver, and other metals to the flotation tailing is the application of an entirely innovative approach involving major change in the flotation circuits (Grotowski, 2007). This approach primarily involves the separation of the most troublesome ore fraction (shale containing middlings) and introduction of hydrometallurgical and/or biohydrometallurgical methods of their alternative, effective processing. The concept is currently analysed by BIOSHALE Consortium in the frame of comprehensive investigations conducted by several institutions (Chmielewski and Charewicz, 2005, 2006, 2006a). Atmospheric leaching in oxygenated sulphuric acid, pressure leaching and bioleaching, as an alternatives, appear to be very promising and effective.

Leaching and bioleaching in oxygenated solutions of sulphuric acid lead to solubilisation of most valuable (Cu, Fe, Ni, Co, Zn) and toxic (As) metals. Pregnant leaching solutions have to be subjected to purification and separation of metals, using solvent extractions an alternative. The preliminary studies of copper(II), cobalt(II) and nickel(II) recovery from the pregnant leach solutions by means of solvent extraction were performed in this work.

EXPERIMENTAL

The initial composition of pregnant leach solution applied for preliminary investigations of copper(II), cobalt(II) and nickel(II) recovery by means of solvent extraction is indicated in Table 1. The solution was a pregnant liquor from atmospheric leaching of Lubin shale fraction (middlings) – tailings from 1st cleaning at Lubin Concentrator (Chmielewski, 2007).

Table 1. The initial composition of pregnant leach solution

| Component | Concentration, ppm |
|-----------|--------------------|
| Copper | 4324 |
| Nickel | 4.74 |
| Cobalt | 8.65 |
| Iron | 2061 |
| Zinc | 115 |
| Arsenic | 13.50 |

The solvent extraction was used for the recovery of copper(II), cobalt(II) and nickel(II) from the pregnant solutions after leaching cupriferous shale with sulphuric acid in the absence and presence of Fe(III) salts. Aromatic hydroxyoximes, LIX 84, LIX 612 and LIX 984, were investigated as copper(II) extractants to check their extraction and reextraction abilities. From the copper free raffinate Zn(II) was extracted with di-(2-ethylhexyl)phosphoric acid (D2EHPA). Subsequently, cobalt(II) and nickel(II) were separated from the zinc free raffinate with di-(2,2,4-trimethylpentyl)phosphinic acid (Cyanex 272). All extractants were dissolved in kerosene. Sulphuric acid of different concentration (1 or 3 M) was used as a stripping solution. All experiments were performed at a room temperature. The phases were shaken at 140 r.p.m. in a shaker bath for 1 hour.

The extraction experiments were carried out varying the volume phase ratio of aqueous (A) to organic (O) phases (A/O = 1:1, 2:1, 1:2 and 1:5). The concentration of Cu, Co, Ni, Fe, Zn and As in aqueous phases were determined by spectrometric ICP-OES method. The concentrations of metals in the organic phase were determined from mass balance.

The pregnant solution obtained from leaching of shale with sulphuric acid was neutralized with Lubin middlings to pH around 2 and then was used as an initial aqueous phase for copper(II) extraction with 20 or 30 % (v/v) of aromatic hydroxyoxyme solution in kerosene. The raffinate from Cu(II) extraction was used for further extraction of Zn(II) by D2EHPA. After zinc(II) extraction, the resulting raffinate was purified from Fe(III) and compounds of arsenic by neutralization with ammonia to pH around 5.5. After phase separation, ferrous and arsenic free solution was used for extraction recovery of Co(II) and Ni(II) with Cyanex 272.

The pregnant solutions obtained from the acidic leaching of shale with Fe(III) salts were neutralized with ammonia to precipitate Fe(III). Except of Zn(II) which was

omitted in this case, the subsequent extraction of Cu(II), Co(II) and Ni(II) from purified solutions was carried out in a similar way as described above. Copper(II) was extracted with 30 % (v/v) LIX 84 or LIX 984 solutions in kerosene.

RESULTS AND DISCUSSION

PREGNANT SOLUTION FROM LEACHING WITHOUT Fe(III)

It was shown that considered copper(II) extractants were very effective and the yield of extraction above 85 % was obtained. The best extraction power exhibited LIX 984 since 99.4 % of Cu(II) was removed from initial solution at A/O 1:1. Under the same conditions LIX 84 appeared to be less effective. In each case the increase of extractant concentration in the organic phase increases yield of copper(II) extraction (Fig. 1).

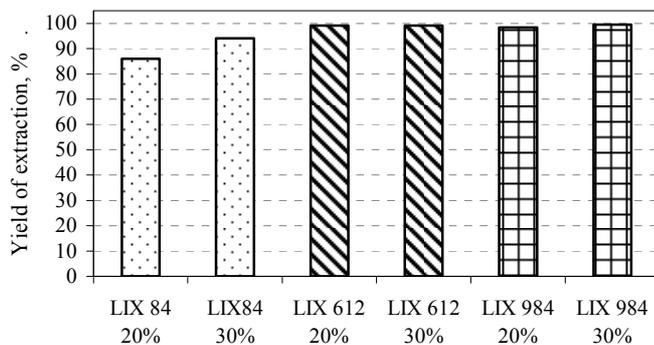


Fig. 1. Yield of Cu(II) extraction for different copper extractants at A/O = 1:1

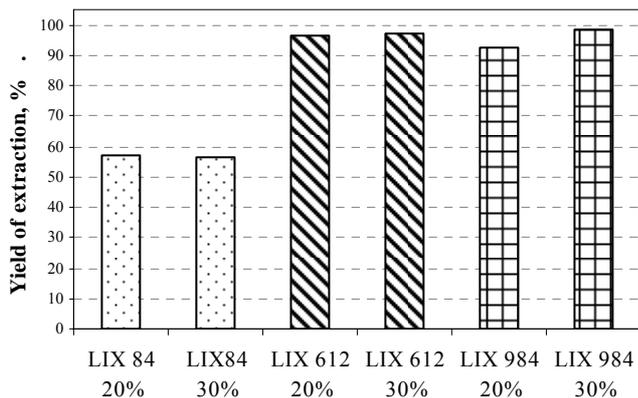


Fig. 2 Yield of Cu(II) extraction for different copper extractants at A/O = 2:1

When A/O ratio was equal to 2:1 the yield of extraction was lower for LIX 84 (around 57 %) but still high for LIX 612 and LIX 984, respectively (Fig. 2).

Moreover, it was found that examined Cu(II) extractants are not enough selective, because copper(II) was extracted together along with other metals present in the initial solution (Fig. 3).

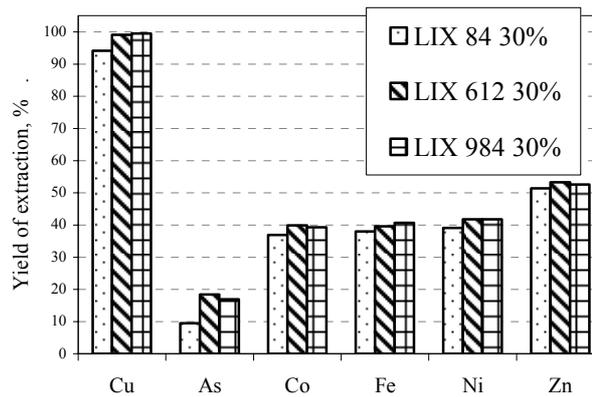


Fig. 3. Comparison of different extractants and their selectivity during copper separation from other metals present in the aqueous phase

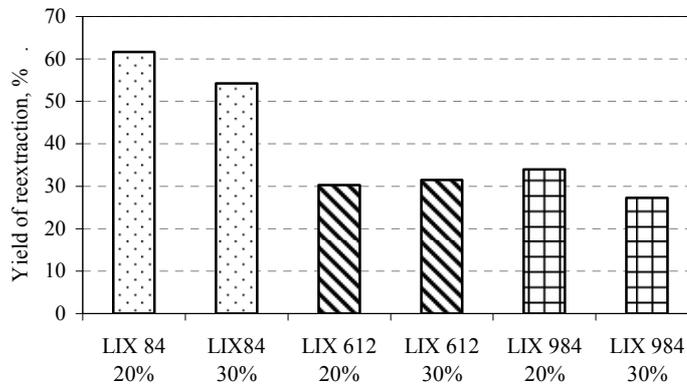


Fig. 4. Yield of Cu(II) reextraction for various copper extractants

The main purpose of this work was to investigate whether the recovery of valuable metals from pregnant leach solutions is possible or not. Therefore, the second step - reextraction of metals from the organic phase is always significant. The obtained results of copper(II) reextraction in one stage with 1 M sulphuric acid were not satisfying since the fraction of Cu(II) remaining in the organic phase was still high (Fig. 4). Probably, the higher concentration of H₂SO₄ in strip solution would affect a higher yield of metal reextraction.

The reextraction of copper(II) can be facilitated by addition to the organic phase an appropriate quantity of modifier, eg. tridecanol or nonylphenol. However, the effect of such modifiers on copper(II) extraction and reextraction from pregnant solutions of shale middlings leaching should be studied in additional experiments.

PREGNANT SOLUTION FROM LEACHING WITH Fe(III)

The pregnant solutions obtained from the atmospheric leaching of shale middlings with Fe(III) salts were neutralized with ammonia to precipitate Fe(III) as ferric hydroxide. The composition of the purified solution was found to be 0.024 ppm As, 2.91 ppm Co, 2707 ppm Cu, 0.172 ppm Fe, 1.47 ppm Ni and 15 ppm Zn.

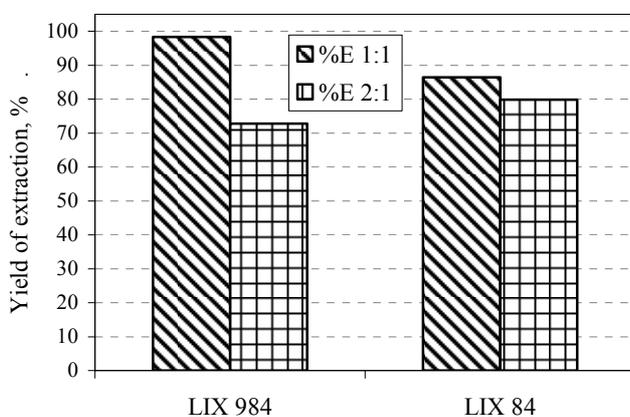


Fig. 5. Yield of Cu(II) extraction for different copper extractants at A/O = 1:1

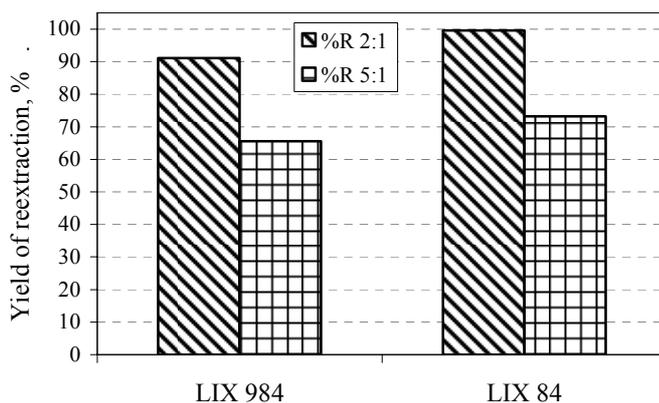


Fig. 6. Yield of Cu(II) extraction for different copper extractants at A/O = 2:1

The observed yield of Cu(II) extraction for LIX 984 and LIX 84 confirmed earlier results which indicated that the LIX 984 was evidently better for Cu(II) extraction than LIX 84 (Fig. 5). As a stripping phase 3 M H₂SO₄ was used. The comparison of reextraction abilities of both extractants exhibited that higher Cu(II) recovery was accomplished from the organic phase containing LIX 84 (Fig. 6).

Using the acidic chelating extractants for cobalt and nickel recovery can give satisfactory results. The selectivity series undergoes changes within the series phosphoric, phosphonic and phosphinic acids as shown below:

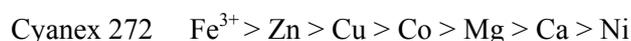
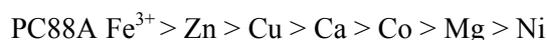
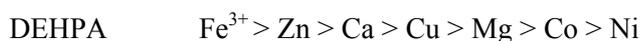


Table 2. Results of cobalt(II) and nickel(II) extraction and reextraction in the system with Cyanex 272

| Metal | Yield of extraction, % | | Yield of reextraction, % |
|-------|------------------------|---------|--------------------------|
| | A/O 1:1 | A/O 2:1 | A/O 1:1 |
| Co | 16.5 | 13.0 | 36.9 |
| Ni | 14.3 | 12.2 | 28.4 |

Unlike DEHPA, which requires concentrated HCl to strip any co-extracted ion, Cyanex 272 can be readily stripped with relatively diluted (1,5 M) H₂SO₄ (Flett, 2004). However, in our experiments the yields of Co(II) and Ni(II) extraction from pregnant acid leaching solution with Fe(III) salts with Cyanex 272 (Table 2) were not satisfying and lower than those obtained for solutions from acidic leaching of shale in the absence of Fe(III) salts.

CONCLUSIONS

The solvent extraction technique is one of the most versatile methods used for the removal, separation and concentration of metallic species from aqueous media. Our results on solvent extraction of metals from pregnant leach solutions after atmospheric leaching of shale middlings demonstrated, that application of aromatic hydroxyoximes for copper(II) extraction can give satisfying results. However, these extractants were not enough selective and other metal ion species present in leach solutions were also transferred to the organic phase. Furthermore the extractive recovery of Cu(II), Co(II) and Ni(II) was better for the solutions obtained from acidic leaching of shale in the absence of Fe(III) salts.

The recovery of valuable metals was not high and further experiments are necessary to establish the optimal conditions of extraction and reextraction processes.

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REFERENCES

- CHAREWICZ W., CHMIELEWSKI T., 2005 et al, Deliverable BIOSHALE - D 4.1., *Process variant selection options and test work programme*, Tecnicas Reunidas, March 2005.
- CHMIELEWSKI T., CHAREWICZ W., 2006, BIOSHALE, Deliverable D.4.2., *Technical aspects: Leaching tests. Results with Lubin and Talvivaara Ores*, April 2006.
- CHMIELEWSKI T., CHAREWICZ W., 2006a, Hydrometallurgical processing of shale by-products from beneficiation circuits of Lubin Concentrator, *In: Perspectives for applying bioleaching Technology to process shale-bearing copper ores*, BIOPROCOOP'06, Lubin 2006, KGHM Cuprum, Wrocław 2006, 125-145.
- CHMIELEWSKI T., 2007, *Atmospheric leaching of shale by-product from Lubin concentrator (this Journal)*.
- FLETT D.S., 2004, *Cobalt - Nickel Separation in Hydrometallurgy: a Review*, Chemistry for Sustainable Development, 12, 81-91.
- GROTOWSKI A., *Possibilities and perspectives for implementation of hydrometallurgical methods in KGHM Polska Miedz S.A.*, Proc. VIII International Conference on Non-ferrous Ore Processing, Wojcieszycze (Poland), May 21-23, KGHM Cuprum Wrocław 2007, 29-46.
- KUBACZ N., SKORUPSKA B. 2007, *Evaluation of influence of organic carbon on concentration and smelting processes*. Proc. VIII International Conference on Non-ferrous Ore Processing, Wojcieszycze (Poland), May 21-23, KGHM Cuprum Wrocław 2007, 157-166.
- ŁUSZCZKIEWICZ A. 2004, *Analysis and evaluation of beneficiation of the ore with elevated content of black shales*. Report of investigations, Archiwum Zakładu Przeróbki Kopalini i Odpadów Instytut Górnictwa Politechniki Wrocławskiej, Wrocław, October 2004.
- ŁUSZCZKIEWICZ A., 2000, *Application of copper-bearing-black shales from Lubin-Glogow region*, in: Proceedings of "Modern problems of copper ore processing in Poland", Conference. Polkowice, 16 November 2000, Komitet Górnictwa PAN / KGHM Polska Miedz S.A., 137-156.

Rotuska K., Chmielewski T. *Ekstrakcja metali użytecznych z roztworów po ługowaniu miedzionośnej rudy łupkowej*, Physicochemical Problems of Mineral Processing, 41 365-372 (2007) (w jęz. ang.).

Roztwory kwasu siarkowego po ługowaniu atmosferycznym półproduktu łupkowego (odpad I czyszczenia I ciągu ZWR Lubin) w obecności tlenu i żelaza(III) zastosowano do ekstrakcji metali przy użyciu różnych ekstrahentów. Roztwory zawierały rozpuszczalne siarczany Cu(II), Zn(II), Ni(II), Co(II), Fe(II), Fe(III) i As jako składnika niepożądanego. Aromatyczne hydroksyoksymy: LIX 84, LIX 612 i LIX 984 były stosowane jako ekstrahenty Cu(II). Z roztworu rafinatu pozbawionego Cu(II) ekstrahowano Zn(II) za pomocą kwasu di-(2-etylohexylo)fosforowego (D2EHPA). Ponadto, kobalt(II) i nikiel(II) były wydzielane z wolnego od cynku rafinatu za pomocą kwasu di-(2,2,4-trimetylopentylo)fosfonowego (Cyanex 272). Przemysłowe hydroksyoksymy aromatyczne użyte do ekstrakcji miedzi okazały się mało selektywne i obserwowano przenoszenie jonów innych metali do fazy organicznej. Odzysk ekstrakcyjny Cu(II), Ni(II) i Co(II) okazał się znacznie lepszy dla roztworów po ługowaniu pozbawionych obecności Fe(III). Odzysk metali użytecznych okazał się niezadowalający i potrzebne są dalsze systematyczne badania nad optymalizacją procesów ekstrakcji i reekstrakcji.