

RESEARCHES REGARDING RECYCLING OF PROCESS WATERS FROM A ROMANIAN METALLURGICAL PLANT

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This study investigates the feasibility of implementation of the waste waters management in the copper electro refining process of RBG Phoenix Baia Mare, Romania, which is a plant well known for heavily polluting the local environment. This consists in the purification and recycling of spent electrolyte solutions from copper refining containing large amounts of copper and significant quantities of As, Sb and Bi as impurities. To achieve this goal, liquid - liquid extraction for the removal of As, Sb and Bi was used. From a literature survey two commercial solvent extraction reagents, namely LIX 1104[®] by Henkel Corporation (now Cognis) and SBX 50[®] produced by AVICIA were selected for screening. This paper describes the comparative results of the screening tests for the two extractants.

INTRODUCTION

The objective of this research is the technical, economic and environmental assessment of existing technologies for waste water treatment for a metallurgical plant from Romania.

During the copper electro refining process a volume of electrolyte is periodically removed off, in order to maintain the impurities levels within the optimum ranges. The plant of Allied Deals Phoenix – Baia Mare uses as raw material a complex copper ore with quite high concentrations of As, Sb and Bi, impurities to be found in the electrolyte bleed.

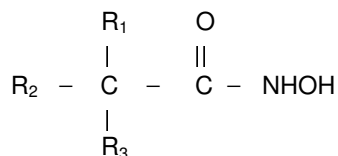
These impurities are distributed both in the waste waters coming from the electrolysis cells and in the final useful products. Moreover, the overall process ends with a stage of common neutralization of the waste waters, leading to products highly contaminated with As, Sb and Bi, which must be ecologically deposited.

This paper aims to design and establish a flow sheet of a process which removes the contaminants and recycles the mother electrolyte. Solvent extraction has been shown by several authors to be a promising technique for As, Sb and Bi removal from copper tank house electrolytes and was chosen in this study for application to the problem of impurity control at Baia Mare.

The application of solvent extraction for impurity control in copper electro refining has been demonstrated in numerous studies and also in plant practice.

The use of hydroxamic acid extractants for extraction of arsenic, antimony and bismuth has been described by Schwab and Kroke (1).

The general structural formula of the extractant is:



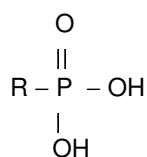
were R₁, R₂, R₃, is an mixture of C₁₀ – C₁₉ branched chains, the commercial name of one of them being LIX 1104 SM (1), (2).

Dreisingher and Leong (3) reported a comparison of arsenic, antimony and bismuth extraction with DBBP, DPPP, TBP and LIX 1104 SM. The reagent LIX 1104 SM was reported to be superior to the other reagents in extracting As, and free acid co extraction.

A joint project between ASARCO and ZENECA (4) led to a new efficient process for the selective removal and recovery of only antimony and bismuth by solvent extraction. The process has been

reported by Cupertino et al. (4), as well as by Flett (5) and the solvent used was a new organo-phosphorus extractant DS 5834, being similar to M₂EHPA but with much lower water solubility.

The active group of the extractants is:



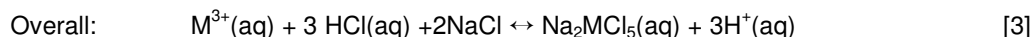
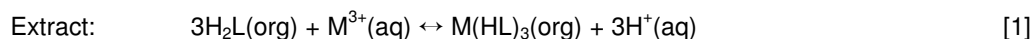
where R = 2 ethyl-hexyl, for M₂EHPA, and
R = iso-C₁₈H₃₇, for DS 5834

The reported extractant is completely selective over copper, nickel, arsenic and iron (III), has fast extraction kinetics, rapid phase separation characteristics and is completely stable in contact with fresh, hot electrolyte solutions.

Later San Manuel Refinery together with Zeneca Specialities reviewed the currently available technologies for the control of antimony and bismuth and the solvent extraction technology has been chosen as most suitable. Zeneca developed and included on the list of commercially extractants a similar reagent more suitable for antimony and bismuth recovery than the previous DS 5834, under the name of SBX-50.

The successful results have been reported by Kim and coworkers (6).

The following are the generic equations for the reagent, where the extractant is denoted by H₂L and M denoted Sb / Bi (6):



Based on the above literature survey it was decided to screen LIX 1104 SM for the removal of As, Sb and Bi and SBX – 50 for the removal of Sb and Bi, from the Baia Mare copper refinery electrolyte.

EXPERIMENTAL

The extractants LIX 1104 SM and SBX-50 were kindly supplied by HENKEL Mining Chemicals and Zeneca (now Avecia) respectively.

The diluent used were kerosene from FCN Pitesti, Romania. Synthetic solutions of As, Sb and Bi were prepared from analytical grade arsenic acid, bismuth chloride and antimony oxide by dissolution in H₂SO₄. Distilled water has been used for dilution.

An actual liquor from Baia Mare assaying 1.3 g/l As; 0.12 g/l Sb; 0.063 g/l Bi; 0.073 g/l Cl⁻; 0.33 g/l Fe; 38.5 g/l Cu and 172 g/l H₂SO₄ was also used in the test work. On start-up the maximum levels of impurities expected in the tank house will be 5-6 g/l As; 0.2 g/l Sb and 0.6 g/l Bi. An operating level of 2 g/l As; 0.08-0.1 g/l Sb and 0.005 g/l Bi has been chosen as the goal for this study.

Metal ion analyses were carried out in UK using a Perkin Elmer ICP spectrophotometer. For the analyses at IMNR Romania an OES-DCP Beckman (SUA) Spectaspan V was used. SO₄²⁻ was determined gravimetrically.

RESULTES AND DISCUSSIONS

Extraction isotherms

For the extraction with LIX 1104 SM 20 % in kerosene, extraction isotherms (fig. 1-3) have been obtained using synthetic solutions with following composition: 9.6 g/l As, 0.875 g/l Sb, 1.025 g/l Bi and 150 g/l H₂SO₄. Time contact phase was 15 min.

The figure 1 shows that extraction temperature for As must be under 40°C for a good extraction. The Sb isotherms in fig. 2 show that temperature influences very little the extraction yield and that for Bi (see fig. 3), the optimum temperature is ambient temperature.

Although the previous experiments lead to the general conclusion that 20 – 40°C is the optimum temperature for simultaneous extraction of all impurities, the extraction tests with LIX 1104 SM for the

real solution were performed at 60°C, from economic reasons, as this is the temperature at which the electrolyte leaves the electro refining tank.

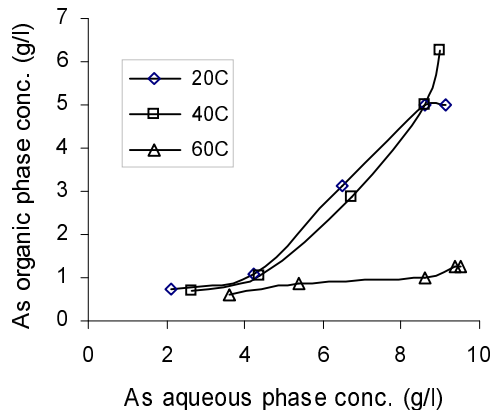


Fig. 1 As Extraction isotherms with 20% LIX in kerosene from synthetic solution

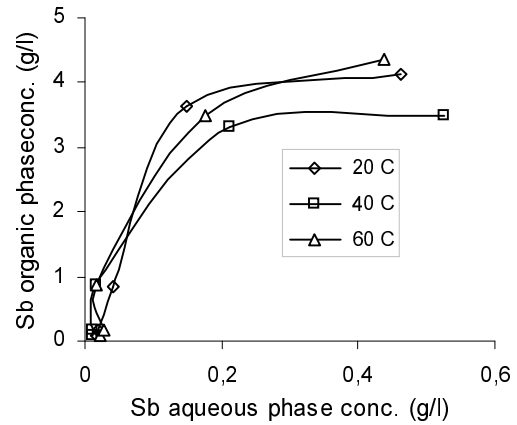


Fig. 2 Sb Extraction isotherms with 20% LIX in kerosene from synthetic solution

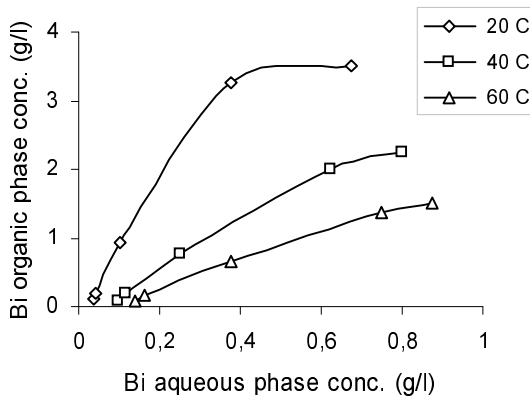


Fig. 3 Bi Extraction isotherms with 20% LIX in kerosene from synthetic solution

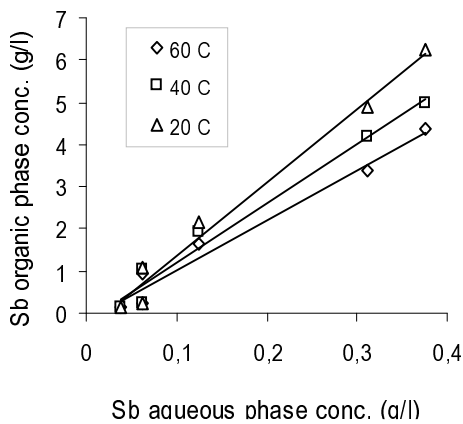


Fig. 4 Sb Extraction isotherms with 10% SBX in kerosene from synthetic solution

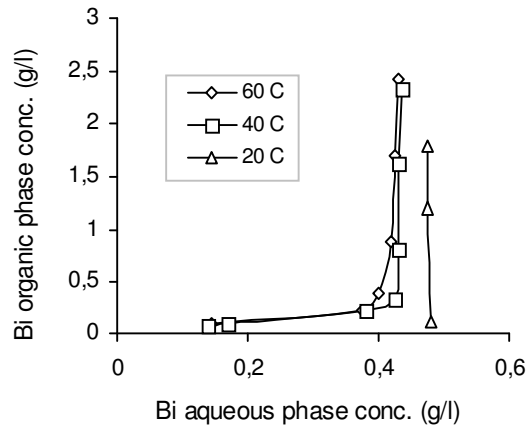


Fig. 5 Bi Extraction isotherms with 10% SBX in kerosene from synthetic solution

For SBX 50, extraction isotherms by synthetic solutions (fig. 4, 5) have been obtained for Sb and Bi at different temperatures (20,40 and 60°C) by contacting individual feed solutions (Sb 1.25 g/l in 165 g/l H₂SO₄ and 0.6 g/l Bi in H₂SO₄ 150 g/l) with SBX solution 10 % in kerosene. Time contact phase was 10 min. The Sb isotherms show that Sb extraction decreases with increasing temperature, but this decrease is not very strong and Bi extraction decreases with increasing temperature too.

The 10% solution of SBX 50 in kerosene proves to be a very good extractant for antimony and bismuth. No third phase or unbreakable emulsions were observed. Phase disengagement was fast (<10 min).

McCabe-Thiele diagrams

The tests for drawing the McCabe-Thiele diagrams were performed using refinery electrolyte, enriched in impurities by addition As, Sb and Bi.

For the extraction with LIX 1104 SM, the electrolyte solution used in tests had the following composition: 6.375 g/l As, 0.175 g/l Sb and 0.675 g/l Bi. Working temperature was 60°C and time contact phase 15 min.

Figure 6 show that LIX 1104 SM is a good extractant for all the electrolyte contaminants, especially for Sb and Bi which need only one extraction stage in order to be fully eliminated. Arsenic however, determines the number of extraction steps, and for a ratio O:A = 10:1 it requires two extraction steps to achieve the value of 2 g/l As in the electrolyte, the industrial operating level.

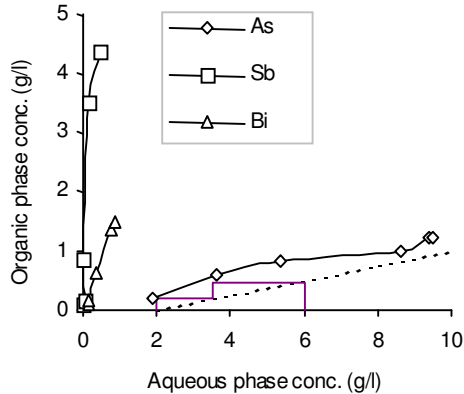


Fig. 6 McCabe-Thiele diagram for impurities extraction with 20% LIX in kerosene from real electrolyte solution

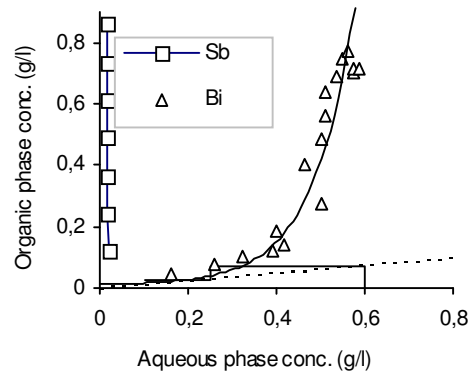


Fig. 7 McCabe-Thiele diagram for impurities extraction with 10% SBX in kerosene from real electrolyte solution

For obtaining McCabe-Thiele diagram in the case of SBX there were used electrolyte solutions with following composition: 0.14 g/l Sb and 0.587 g/l Bi. Working temperature was 60°C and time contact phase 10 min.

Fig. 8 shows that Sb extraction with SBX 50 is as good as the extraction with LIX from spent electrolyte solution, needing only one extraction stage for complete removal. Bismuth is extracted in 3 extraction stages at O:A ratio 8:1, for a ratio O:A = 10:1 two extraction steps being needed, much more than in case of LIX.

Stripping isotherms

Stripping isotherms for LIX 1104 SM and SBX 50 are shown in fig. 8 and 9 respectively. Stripping experiments have been performed using an organic phase loaded by contacting with tank house electrolyte solution.

The LIX composition for stripping tests was: 2.5 g/l As, 0.807 g/l Sb and 0.286 g/l Bi. Stripping was carried out by contacting 35 ml of the loaded organic with 40 ml of water for 20 minute at 60°C. Phase disengagement was very good (< 5 min), but the stripping with water doesn't work for any of the impurities.

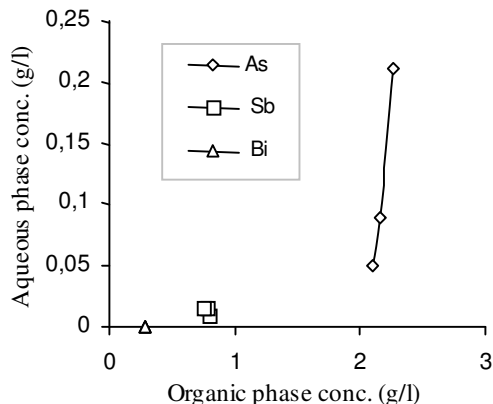


Fig. 8 Stripping isotherms with water for a 20 % LIX organic phase

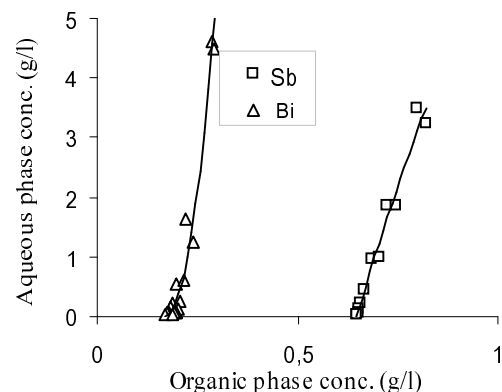


Fig. 9 Stripping isotherms with CaCl₂ and HCl for a 10 % SBX organic phase

For SBX 50 stripping was carried out by contacting 250 ml of the loaded organic (with 1 g/l Sb and 0.47g/l Bi) with 10 ml of stripping solution (2.5 mol/l CaCl_2 and 1 mol/l HCl) for 10 minute at 60°C. The aqueous solutions were then diluted in 1 mol/l HCl to prevent hydrolysis and analyzed. The organic phase was then further contacted with 10 ml of fresh stripping solution and the process repeated.

Fig. 9 show that it is not possible to fully strip Sb and Bi from the loaded organic phase with this stripping solution. A residual concentration of ≈ 0.65 g/l Sb and ≈ 0.2 g/l Bi is the limit at 60°C. Both Sb and Bi are not completely stripped using a solution with a $[\text{Cl}^-]$ concentration < 6 mol/l, but for stripping solutions with a higher concentration of $[\text{Cl}^-]$ at O:A = 1:1 ratio one strip stage is sufficiently.

CONCLUSIONS

LIX 1104 SM is a good extractant for all the electrolyte contaminants, but stripping with water doesn't work for any of the impurities. Arsenic determines the number of extraction steps, and for a ratio O:A = 10:1 it requires 2 extraction steps, at 60°C and 15 min time contact phase, to achieve the value of 2g/l in the electrolyte. In this conditions Sb and Bi need only one extraction stage in order to be fully eliminated.

SBX 50 is a good extractant for Sb and Bi. Bismuth is extracted in 3 extraction stages at O:A ratio 8:1 at 60°C working temperature and 10 min time contact phase. In this conditions antimony is better extracted with SBX from the spent electrolyte solutions in only one extraction step. Both Sb and Bi are not completely stripped using a solution (CaCl_2 and HCl) with a $[\text{Cl}^-]$ concentration < 6 mol/l, but for stripping solutions with a higher concentration of $[\text{Cl}^-]$ at O:A = 1:1 ratio one strip stage is sufficiently.

ACKNOWLEDGMENTS

HENKEL Mining Chemicals for the supply of LIX 1104 SM reagent;
ZENECA (now AVECIA) the supply of SBX 50 reagent;
FCN Pitesti Romania for diluent;
ALLIED DEALS PHOENIX Baia Mare Romania for help and the supply of electrolyte solution.

THIS WORK WAS SUPPORTED BY EU UNDER INCO COPERNICUS PROGRAM

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