Influence of hydroxyethylated-2-butylene-1,4-diol on copper electrodeposition from sulphate electrolytes containing large amounts of zinc

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The influence of an organic additive hydroxyethylated-2-butylene-1, 4-diol (Ferasine) on the electroextraction of copper from sulphate electrolytes was studied through of potentiodynamic and galvanostatic methods. It was found that Ferasine decreases the cathodic currents reached at different vertex potentials and quantities of deposited copper which shows that it inhibits the cathodic reaction of copper deposition. The influence of Ferasine is stronger expressed in electrolytes containing 130 g/L H$_2$SO$_4$ than in neutral electrolytes. The inhibiting effect of additive increases with increase in cathodic potential. Dense and smooth copper coatings on Cu cathodes with current efficiency higher than 90% are deposited when Cu$^{2+}$ concentration is higher than 5 g/L and current densities are in the range 0.5 $\pm$ 2 A/dm$^2$. More fine-grained are observed in the presence of H$_2$SO$_4$ and hydroxyethylated-2-butylene-1,4-diol (Ferasine). Non-adherent, dark-red Cu slime is obtained when the concentration of Cu$^{2+}$ ions is lower than 5 g/L. Ferasine changes the preferred crystallographic orientation (hkl) of Cu coatings from (220) to (111) only during deposition in electrolytes containing H$_2$SO$_4$. In the absence of acid the preferred orientation, both in the absence or presence of Ferasine remains (111).

**Key words:** copper; cyclic voltammograms; deposition; electroextraction; zinc.

**INTRODUCTION**

The main part of the wastes containing Zn or Cu is generated from hydrometallurgy, metal galvanizing, plating industry and smelting processes. For example, the waste product known as “blue powder” that results by condensing furnace gases during the thermometallurgical processing of non-ferrous ores contains: Zn (25-41 wt.%), Pb (20-25 wt.%), Fe (3-5 wt.%), Cu (0.5-1 wt.%), etc. [1, 2]. The purification of the electrolyte for Zn electrowinning after cementation is another process that produces wastes containing large amount of different metals such as: copper cake, containing 36-54 wt.% Cu and 5-10 wt.% Zn; copper-cadmium cake, containing 10 wt.% Cu, 30 wt.% Zn, 12 wt.% Cd; collective cake, containing 5.8 wt.% Cu, 35.9 wt.% Zn, 7.2 wt.% Cd; cobalt-nickel cake, containing 25 wt.% Cu, 20 wt.% Zn and 3 wt.% Cd. [3]. Cementates obtained during the hydrometallurgical zinc winning process, where the sulphate leach liquor is treated with arsenic trioxide and zinc powder for the removal of Cu, Ni, Co, Cd and other impurities contain: Cu (28.6 wt.%), Zn (22.4 wt.%) and Cd (6.7 wt.%) [4]. Flue dusts at a secondary copper smelter treated in the electrowinning zinc plant contain: Zn (40-65 wt.%) and Cu (1-6%). [5]. These industrial wastes are a source of different valuable metals like copper, zinc, cadmium, etc.

There are numerous investigation concerning the influence of organic additives on the process of Cu electrodeposition from sulphate electrolytes, containing only Cu$^{2+}$ ions but their influence on the Cu electroextraction from electrolytes, containing large amounts of Zn$^{2+}$ is not studied.

Muresan et al. [1, 2], studied the effect of horse-chestnut extract (HCE) and IT-85, representing a mixture of triethylbenzyl-ammonium chloride (TEBA) and hydroxyethylated-2-butylene-1, 4-diol (Ferasine) upon the morphology and structure of Cu deposits, as well as upon the cathodic polarization and compared to the effect exerted by thiourea and animal glue. Varvara et al. [6-9] studied the influence of TEBEA, Ferasine and IT-85 on the kinetics of Cu electrodeposition from such electrolytes and on the morphology and structure of Cu deposits. Maher Alodan and William Smyrl [10] established that at concentrations of thiourea $>$1 mM strong effects on copper in solutions of sulfuric acid is observed. Moo Seong Kang et al. [11] observed that even in the presence of very low concentrations of thiourea in sulphate electrolyte extremely smooth and bright copper deposits. M. Quinet, et al. [12] investigated the effects of thiourea and saccharin, on copper electrodeposition from acid sulphate solutions using different
electrochemical methods: cyclic voltammetry, chronopotentiometry, and electrochemical quartz crystal microbalance as well as using different observation techniques: scanning electron microscopy (SEM) and atomic force microscopy (AFM). A. L. Portela et al. studied copper electrodeposition on platinum electrodes from slightly acidic solutions of copper sulphate containing nicotinic acid (NA) [13]. Run-lan YU et al. [14] studied the inhibition behavior of some new mixed additives such as gelatin + hexadecylpyridinium bromide (HDPBr), gelatin + polyethylene glycol (PEG), gelatin + polyacrylamide (PAM), gelatin + PEG + cetyl-tri-methyl ammonium bromide (CTABr) and gelatin + PAM + CTABr using cyclic voltammetry as well as cathodic polarization in order to improve the quality of cathodic copper [14]. DC and pulse plating of copper in acidic sulphate solutions containing benzotriazole (BTA) has been studied by N. Tantavichet and M. Pritzker [15]. Using electrochemical and spectrophotometric techniques B. Bozzini et al. investigate the effects of PEG during Cu electrodeposition from an acidic sulphate solution [16]. B. Bozzini et al. report in situ visible electroreflectance measurements carried out during potentiostatic electrodeposition of Cu from acidic sulphate solutions in the absence and presence of PEG [17]. The behaviour of 3-diethylamino-7-(4-dimethylaminophenylazo)-5-phenylphenazinium chloride (Janus Green B, JGB) during Cu electrodeposition from an acidic sulphate solution was studied by B. Bozzini et al. [18]. The effect of a new ionic liquid additive 1-butyl-3-methylimidazolium hydrogen sulfate-[BMIM]HSO₄ on the kinetics of copper electro-deposition from acidic sulphate solution was investigated by cyclic voltammetry, polarization and electrochemical impedance measurements and compared with those exerted by the conventional additive, thiourea (Q.B. Zhang et al. [19]. Copper electrodeposition on to a platinum substrate from an acid sulphate plating bath was investigated with and without the additive benzotriazole (BTAH) by A. C. M. de Moraes et al. [20]. Copper electrodeposition in the presence of various types of aromatic and aliphatic amines was studied by H.H. Abdel-Rahman et al. [21]. M. Gu and Q. Zhong investigated copper electrodeposition and nucleation on a glassy carbon electrode from acid sulfate electrolytes in the presence of 3-mercaptop-1-propanesulfonate sodium salt (MPS) and its combinations with chloride ions (Cl) or/and polyethylene glycol (PEG) by utilizing cyclic voltammetry (CV), chronopotentiometry (CA) and scanning electron microscopy (SEM) [22]. To improve the quality requirements for copper deposits, the influence of some inhibition agents added to the acidic copper bath has been studied by C. C. Vaduva et al. [23].

The aim of this paper is to study the influence of hydroxyethylated-butyne-2-diol-1,4 (Ferasine) and some experimental conditions on the process of Cu electroextraction from sulphuric acid electrolytes containing large concentrations of Zn²⁺ - ions. This study is an attempt, using electrolytes modelling wastes produced in zinc hydrometallurgy, to obtain conditions for separately electrowinning of these metals.

EXPERIMENTAL

The experiments were carried out in a thermostated (37 ± 1°C), three-electrode glass cell without stirring of the electrolyte. The cathode (2.0 cm²) and both anodes (4.0 cm² total area) were Pt plates. The reference electrode was a mercury/mercurous sulphate electrode in 0.5 M H₂SO₄ (SSE), its potential vs. NHE being +0.720 V. The studies were carried out using a cyclic potentiodynamic technique. Potential scanning at a rate of 30 mV/sec in the potential range from +1.000 to -1.800 V vs SSE was performed by means of a computerized PAR 263A potentiostat / galvanostat using Soft Corr II software. Amount of deposited metals was obtained by integration of the respective anodic peaks on cyclic voltammograms (CVAGs).

Galvanostatic deposition was carried out on copper cathodes (4.0 cm²) at current densities in the range 0.5 ± 2 A/dm² using two Pb-Ag (1%) anodes. Pt and Cu electrodes were degreased in ultrasound bath and than only Cu cathode was etched in HNO₃ (1:1).

Cu²⁺ ions (1, 5 or 10 g/L) were added to the base electrolytes: BE-1, containing 220 g/L ZnSO₄·7H₂O (50 g/L Zn²⁺) and BE-2, containing 220 g/L ZnSO₄·7H₂O (50 g/L Zn²⁺) and 130 g/L H₂SO₄. The organic additive in both electrolytes was 30% solution of hydroxyethylated-butyne-2-diol-1,4 (Ferasine).

X-ray powder diffraction patterns for phase identification of copper cathode and deposits were recorded in the angle interval 20-1100 (2θ) on a Philips PW 1050 diffractometer, equipped with Cu Kα tube and scintillation detector. The surface morphology of the deposits was examined and EDX Analysis was made by scanning electron microscopy (SEM) using a JEOL JSM 6390 microscope.
RESULTS AND DISCUSSION

Potentiodynamic studies

Figure 1 shows CVAGs obtained in electrolytes, containing 1 g/L Cu\(^{2+}\) and 50 g/L Zn\(^{2+}\) without Ferasine (curve 1), and with 1 mL/Ferasine (curve 2) and 1 g/L Cu\(^{2+}\), 50 g/L Zn\(^{2+}\) and 130 g/L H\(_2\)SO\(_4\) without Ferasine (curve 3) and with 1 mL/Ferasine (curve 4). The scan direction is changed at cathodic potential (vertex potential) -1.6 V.

![Figure 1. Cyclic voltammograms obtained on Pt cathode in electrolytes, containing: 1) Cu\(^{2+}\) - 1 g/L and Zn\(^{2+}\) - 50 g/L, 2) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L and Ferasine 1 mL/L, 3) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L and H\(_2\)SO\(_4\) - 130 g/L, 4) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L, H\(_2\)SO\(_4\) - 130 g/L and Ferasine 1 mL/L. E\(_{\text{vertex}}\) = -1.6 V vs SSE.](Image)

It is observed that at potentials between -0.4 V and -0.2 V anodic peaks, obviously due to the Cu dissolution, appear. It is seen that only on the curves obtained in electrolytes without H\(_2\)SO\(_4\) (curves 1 and 2) more negative (at ~1.250 V) anodic peaks, due to the Zn dissolution, appear. The anodic peaks obtained in the electrolytes containing Ferasine (curves 2 and 4) are lower than those obtained in electrolytes without additive (curves 1 and 3) which means that Ferasine inhibit the metal deposition.

Figure 2 shows CVAGs obtained in electrolytes, containing 10 g/L Cu\(^{2+}\) and 50 g/L Zn\(^{2+}\) (curve 1), 10 g/L Cu\(^{2+}\), 50 g/L Zn\(^{2+}\) and 1 mL/L Ferasine (curve 2), 10 g/L Cu\(^{2+}\), 50 g/L Zn\(^{2+}\) and 130 g/L H\(_2\)SO\(_4\) (curve 3) and 10 g/L Cu\(^{2+}\), 50 g/L Zn\(^{2+}\), 130 g/L H\(_2\)SO\(_4\) and 1 mL/L Ferasine (curve 4). The scan direction is changed at cathodic potential (vertex potential) -1.6 V. The cyclic voltammograms are similar to those obtained in the case with the lower Cu\(^{2+}\) concentration (1 g/L). In this case (10 g/L) at all (even at more negative than -1.6 V) vertex potentials only Cu deposition takes place.

![Figure 2. Cyclic voltammograms obtained on Pt cathode in electrolytes, containing: 1) Cu\(^{2+}\) - 10 g/L and Zn\(^{2+}\) - 50 g/L, 2) Cu\(^{2+}\) - 10 g/L, Zn\(^{2+}\) - 50 g/L and Ferasine 1 mL/L, 3) Cu\(^{2+}\) - 10 g/L, Zn\(^{2+}\) - 50 g/L and H\(_2\)SO\(_4\) - 130 g/L, 4) Cu\(^{2+}\) - 10 g/L, Zn\(^{2+}\) - 50 g/L, H\(_2\)SO\(_4\) - 130 g/L and Ferasine 1 mL/L. E\(_{\text{vertex}}\) = -1.6 V vs SSE.](Image)

The influence of Ferasine on the cathodic currents reached at different vertex potentials and on the amount of deposited Cu during scanning to different vertex potentials is shown in Figures 3, 4, 5 and 6. It is seen that Ferasine decreases significantly the current values and the amounts of deposited Cu or Zn only in electrolytes containing H\(_2\)SO\(_4\). The polarizing effect of additive is more strongly expressed at more negative vertex potentials which, perhaps, is due to the increased Ferasine adsorption on the cathodic surface at more negative potentials.

![Figure 3. Current densities reached at different vertex potentials on Pt cathode in electrolytes, containing: 1) Cu\(^{2+}\) - 1 g/L and Zn\(^{2+}\) - 50 g/L, 2) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L and Ferasine 1 mL/L, 3) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L and H\(_2\)SO\(_4\) - 130 g/L, 4) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L, H\(_2\)SO\(_4\) - 130 g/L and Ferasine - 1 mL/L.](Image)
Fig. 4. Amounts of copper or zinc deposited during scanning to different vertex potentials in electrolytes, containing: 1) Cu\(^{2+}\) - 1 g/L and Zn\(^{2+}\) - 50 g/L, 2) Cu\(^{2+}\) - 1 g/L and Zn\(^{2+}\) - 50 g/L, 3) Cu\(^{2+}\) - 1 g/L and Zn\(^{2+}\) - 50 g/L – Zinc, 4) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L and Ferasine 1 mL/L. 5) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L and H\(_2\)SO\(_4\) – 130 g/L - Copper, 6) Cu\(^{2+}\) - 1 g/L, Zn\(^{2+}\) - 50 g/L, H\(_2\)SO\(_4\) – 130 g/L and Ferasine 1 mL/L.

Fig. 5. Current densities reached at different vertex potentials on Pt cathode in electrolytes, containing: 1) Cu\(^{2+}\) - 10 g/L and Zn\(^{2+}\) - 50 g/L, 2) Cu\(^{2+}\) - 10 g/L, Zn\(^{2+}\) - 50 g/L and Ferasine 1 mL/L, 3) Cu\(^{2+}\) - 10 g/L, Zn\(^{2+}\) - 50 g/L and H\(_2\)SO\(_4\) – 130 g/L, 4) Cu\(^{2+}\) - 10 g/L, Zn\(^{2+}\) - 50 g/L, H\(_2\)SO\(_4\) – 130 g/L and Ferasine – 1 mL/L.

Galvanostatic studies

The effect of Ferasine on the preferred crystallographic orientations, surface morphology and composition of galvanostatically deposited coatings on Cu substrates was also studied. In all cases only copper is detected by EDX Analysis.

Ferasine changes preferred crystallographic orientations (hkl) of Cu coatings from (220) to (111) during deposition in electrolytes containing H\(_2\)SO\(_4\) (Figures 7 and 8). In the case of deposition from electrolytes without acid proffered orientation is (111) both in the presence or absence of Ferasine.
The grain size of all coatings is presented in Table 1. It is observed that in all cases the coatings deposited in electrolytes containing Ferasine are more fine-grained.

**Table 1. Grain size (μm) of Cu coatings obtained in different electrolytes**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 g/L Cu$^{2+}$ + Zn$^{2+}$ 50 g/L</td>
<td>25-30</td>
</tr>
<tr>
<td>10 g/L Cu$^{2+}$ + 50 g/L Zn$^{2+}$ + 1 mL/L Ferasine</td>
<td>15-18</td>
</tr>
<tr>
<td>10 g/L Cu$^{2+}$ + 50 g/L Zn$^{2+}$ + 130 g/L H$_2$SO$_4$</td>
<td>12-18</td>
</tr>
<tr>
<td>10 g/L Cu$^{2+}$ + 50 g/L Zn$^{2+}$ + 130 g/L H$_2$SO$_4$ + 1 mL/L Ferasine</td>
<td>10-12</td>
</tr>
<tr>
<td>10 g/L Cu$^{2+}$ + 50 g/L Zn$^{2+}$ + 130 g/L H$_2$SO$_4$ + 5 mL/L Ferasine</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>20 g/L Cu$^{2+}$ + 50 g/L Zn$^{2+}$ + 130 g/L H$_2$SO$_4$ + 5 mL/L Ferasine</td>
<td>9-12</td>
</tr>
<tr>
<td>20 g/L Cu$^{2+}$ + 100 g/L Zn$^{2+}$ + 130 g/L H$_2$SO$_4$ + 5 mL/L Ferasine</td>
<td>15-20</td>
</tr>
<tr>
<td>5 g/L Cu$^{2+}$ + 50 g/L Zn$^{2+}$ + 130 g/L H$_2$SO$_4$ + 5 mL/L Ferasine</td>
<td>&lt; 6</td>
</tr>
<tr>
<td>1.25 g/L Cu$^{2+}$ + 14 g/L Zn$^{2+}$ + 16.5 g/L H$_2$SO$_4$ + 0.6 mL/L Ferasine</td>
<td>&lt; 1-2</td>
</tr>
</tbody>
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**Figure 9.** SEM micrograph of Cu coating obtained after 30 min. deposition at 1 A/dm$^2$ in an electrolyte, containing 10 g/L Cu$^{2+}$, 50 g/L Zn$^{2+}$ and 130 g/L H$_2$SO$_4$. Magnification x 1000.

**Figure 10.** SEM micrograph of Cu coating obtained after 30 min. deposition at 1 A/dm$^2$ in an electrolyte, containing 50 g/L Zn$^{2+}$, 10 g/L Cu$^{2+}$, 130 g/L H$_2$SO$_4$ and 5 mL/L Ferasine. Magnification x 1000.

**CONCLUSION**

1. Organic additive Ferasine decreases the cathodic currents reached at different vertex potentials and quantities of deposited copper which shows that it inhibits the cathodic reaction of copper deposition. The influence of Ferasine is stronger expressed in electrolytes containing 130 g/L H$_2$SO$_4$. The inhibiting effect of additive increases with increase in cathodic potential.

2. Dense and smooth copper coatings on Cu cathode with current efficiency higher than 90% are deposited when Cu$^{2+}$ concentration is higher than 5 g/L and current densities are in the range of 0.5÷2 A/dm$^2$. At 1 A/dm$^2$ the deposition potential is -0.500÷-0.600 V. In all cases the current efficiency of Cu deposition is higher than 90%. Non-adherent, dark-red Cu slime is obtained when the concentration of Cu$^{2+}$-ions is lower than 5 g/L. In the case of low Cu$^{2+}$ concentration the deposition potential is more negative (between -1.000 and -1.100 V) due to the concentration polarization. In this case the current efficiency is less than 75% because of increased hydrogen evolution.

3. Ferasine changes the preferred crystallographic orientation (hkl) of Cu coating from (220) to (111) during deposition in electrolytes containing H$_2$SO$_4$. In the absence of acid the preferred crystallographic orientation both in the absence or presence of Ferasine.
ВЛИЯНИЕ НА ХИДРОКСИСЕТИЛИРАНИЯ-2-БУТИН-1,4-ДИОЛ ВЪРХУ ЕЛЕКТРООТЛАГАНЕТО НА МЕД ОТ СУЛФАТНИ ЕЛЕКТРОЛИТИ СЪДЪРЖАЩИ ГОЛЕМИ КОЛИЧЕСТВА ЦИНК

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(Резюме)

Посредством потенциодинамични и галваностатични методи беше изследвано влиянието на органичната добавка хидроксисетилран-2-бутин-1,4-диол (ферасин) върху електроелектролизата на мед от сулфатни електролити съдържащи големи количества Zn²⁺ - йони. Беше установено, че ферасинът намалява колиностото на медта отложен върху медния катод, с добив по ток по-висок от 90%, отлагат, като концентрацията на Cu²⁺ е по-висока от 5 г/л и плътността на тока е 30 г/л. Влиянието на ферасин е по-сило върху медния катод, като концентрацията на Cu²⁺ е по-висока от 5 г/л и плътността на тока е 30 г/л. Влиянието на ферасин е по-сило върху медния катод, като концентрацията на Cu²⁺ е по-висока от 5 г/л и плътността на тока е 30 г/л. Влиянието на ферасин е по-сило върху медния катод, като концентрацията на Cu²⁺ е по-висока от 5 г/л и плътността на тока е 30 г/л. Влиянието на ферасин е по-сило върху медния катод, като концентрацията на Cu²⁺ е по-висока от 5 г/л и плътността на тока е 30 г/л. Влиянието на ферасин е по-сило върху медния катод, като концентрацията на Cu²⁺ е по-висока от 5 г/л и плътността на тока е 30 г/л.