Journal of Hazardous Materials 182 (2010) 55–63

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Behaviour of non-standard composition copper bearing anodes from the copper refining process

R. Marković[a], B. Friedrich[b], J. Stajić–Trošić[c], B. Jordović[d], B. Jugović[e], M. Gvozdenović[f], J. Stevanović[g,*]

[a] IRM, Mining and Metallurgy Institute Bor, 19210 Bor, Serbia
[b] IME Process Metallurgy and Metal Recycling, 52068 Aachen, Germany
[c] ICTM, Institute of Chemistry Beograd, 11000 Belgrade, Serbia
[d] Technical Faculty Čačak, 32000 Čačak, Serbia
[e] ITS-Serbian Academy of Science and Arts, 11000 Belgrade, Serbia
[f] Faculty of Technology and Metallurgy, University of Belgrade, 11000 Belgrade, Serbia
[g] ICTM, Institute of Electrochemistry, 11000 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 10 February 2010
Received in revised form 28 May 2010
Accepted 31 May 2010
Available online 4 June 2010

Keywords:
Non-standard copper bearing anodes
Electrorefining
Sulphur acidic waste solution
Alloying elements

ABSTRACT

This paper addresses on investigation the possibility of electrolytic treatment the sulphur acidic waste solution, obtained in the conventional electrolytic copper refining process. Beside the high copper concentration, the high concentration of other metals, in this case nickel, is the main characteristic of these waste solutions. Due to this fact, the copper bearing anodes with non-standard nickel, lead, tin and antimony content were specially prepared for the refining process. Nickel content of all anodes was approximately 7.5 mass%, and the content of lead, tin and antimony was varied. The preliminary results, obtained using the standard electrochemical techniques, have indicated that the copper bearing anodes could be used under the same conditions as well as in the conventional copper refining process. The measurements in constant galvanostatic pulse have pointed out that the all chemical elements from copper bearing anodes were dissolved and only copper was deposited onto the cathode. It was also pointed out that Ni concentration in the base working electrolyte (sulphur acidic waste solution), after 72 h of process, increased to 102 mass% at $T_1 = 63 \pm 2\,^{\circ}\mathrm{C}$ and up to 122 mass% at $T_1 = 73 \pm 2\,^{\circ}\mathrm{C}$, while arsenic concentration decreased to a minimum value.

1. Introduction

The commercial anodes with copper content from 98.0 to 99.5 mass%, obtained in the flame refining process and the base working solution with Cu^{2+} ion concentrations ranging from 35 to 50 g dm^{-3} and sulphuric acid concentrations ranging from 150 to 250 g dm^{-3}, are used in the conventional copper electrolytic refining process [1]. The process is developed under the force of an applied direct current such as Cu ion dissolves at the anode, enter the electrolyte and then selectively deposit onto the cathode.

Except the base metal (Cu), the anodes also contain the other ingredients that with positive effect on anode solubility as well as the quality of cathode slime, are called the alloying elements, and without those properties, are called the anode impurities.

The ingredients have impact on the structure of anode material. Thus, by changing its properties, they could be dissolved at the anode, remain dissolved into the base electrolyte, remain at the anode and become part of anode slime, forming the "floating slime" and possible deposit onto a cathode.

The aim of the present investigations was to examine the possibility of using waste sulphur acidic solutions from conventional electrolytic refining process. Waste solution, besides the high concentration of copper ion, also contains the high concentration of other metal ions, in this case Ni and As.

Therefore, the copper bearing anodes with non-standard content of alloying elements were prepared to the aim of enabling: decrease of concentration the copper ion in electrolyte by an increases the cathode deposit mass, decrease of concentration the arsenic ions, and to enable the enrichment of electrolyte with nickel ions. Chemical and electrochemical characteristics of other alloying elements were not such that significantly reduce the solubility of anode material, and all with the aim of reduction or prevention the formation of unsoluble Ni oxide, that causes the anode passivation as well as the reduction of As ion from working electrolyte [2].

Presence of Ni content up to 0.3 mass%, has no effect on solubility of copper bearing anodes, whereas in excess of that amount,

---

[*] Corresponding author. Tel.: +381 113303702.
E-mail address: jaca@tmf.bg.ac.rs (J. Stevanović).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.05.137

resulted into formation of NiO. Nickel oxide is not soluble in the sulphur acidic electrolyte, remains in the anode slime and may cause the effect known as anode passivation [2–4]. The quantity of NiO in anodes and anode slime is also the function of oxygen content such as the quantity of NiO in anode and anode slime increases with the oxygen content increase.

Sb content less than 0.01 mass%, has no significant effect on electrochemical behaviour of anodes, but it could cause Cu_2O spheroidization in the eutectic region [5,6], until Sb content higher than 0.05 mass% at presence of Ni of 0.25 mass%, leads to the formation of thin laminated inclusions at the copper grain boundaries [7]. As and Sb may form a complex of $2As_2O_5{\cdot}3Sb_2O_3$ type that easily precipitates from soluble into the fine dispersive solid state, known as the “floating slime” [6]. Pb, if is present in small amounts in anode, could be found in a form of compact solution [6], but it is the most cases in a form of oxide inclusions [7]. It was consider that high Pb content in anode, used in the conventional processes of electrorefining, decreases As, Sb and Bi ions concentration in electrolyte due to the formation of oxides [7]. It is assumed that Pb dissolved at the anode together with Cu and precipitates as $PbSO_4$.

Increase of Pb content facilitates the anode passivation, but it was established that if oxygen is present besides Pb, the anodes will not be passive [8,9]. It is well known that Sn in copper bearing anodes is almost always present as SnO_2, and rarely in the composite forms of oxides, formed at the copper grain boundaries. Only 10 mass% of total Sn is present in the solid Cu solution [10]. During the electrolysis process, Sn could be oxidized in the acidic sulphate solution to Sn^{4+} ion, which then precipitates as the stannic hydroxide and remains in the anode slime.

The Ni ion concentration in some synthetic electrolyte used in electrorefining process of unrefined anodes, was ranging between 0 and 40 g dm^{-3} [11] but no enough data can be found for behaviour of real waste sulphur acidic solutions with high concentration of the other ions, in this case As.

A degree of anode material solubility, change of real working solution composition with duration time of electrorefining process, quantity and composition of obtained anode slime and quality of cathode deposit are investigated in this paper. The subject of this work was investigation of possible use of copper bearing anodes in electrolytic treatment of the real waste sulphur acidic solutions with higher concentration of Ni and As ions, obtained in conventional copper refining process, not previously treated with some conventional technology. Respectively, the aim was to obtain the pure cathode copper from real waste electrolyte, decrease the concentration of As in the working solution by forming the unsoluble salts and increase Ni concentration in the treated waste solution.

According to the all facts, this way of treatment the real waste sulphur acidic solutions could be environmentally justified and economically payable.

2. Experimental

Copper bearing anodes, used in the process of electrorefining, were prepared from the next pure metal components: copper, nickel, lead, tin and antimony. In all anodes, nickel content was approximately 7.5 mass%, while lead, tin and antimony content was variable, where total maximum content of these elements was up to 3 mass%. Copper content in the anodes is a difference up to 100 mass%.

Induction furnace (Balzers), power of 15 kW and a graphite crucible, volume of 1.8 dm^3, were used for preparation the suitable mixture. Upon reaching the melt temperature of 1300 °C, the alloying elements were added. Graphite rods were used for oxygen reduction, and oxygen quantity in the melt was checked using device for determination the oxygen content (LECO Corp. RO-II6). Melt was casted into the suitable steel moulds at temperature of 1300 °C, only when the oxygen content was under 200 ppm. After self-cooling, the anodes were prepared for the electrolysis process by mechanical processing on the lathe removing approximately 2 mm of material from surface, polishing and degreasing the surface with ethanol.

Atomic absorption spectrophotometer (PerkinElmer 403) was used for determination of chemical composition of anodes.

During the electrolysis, values of the following parameters were measured: the direct current (A), cell voltage (V), anode potential (V) and electrolyte temperature (°C). For all experiments, the applied current density was 250 mA cm^{-2}. Direct current was supplied by an external source of direct current (HEINZINGER TNB-10-500), with characteristics of 50 A and 10 V. Starting cathode sheet was made of stainless steel with surface area of 0.0891 m^2 and reference electrode was made of pure copper (99.95 mass%).

Cell voltage was measured and recorded every 10 s for experiment duration of 72 h. Data collecting system (DA100, Yokogawa) is equipped with two multi-purpose output modules and a communication module. There were 20 channels for direct current measuring and voltage within ±20 and ±50 mV limits, with temperature-dependent resistance (up to 600 °C) and digital indicators. All inputs were independent. Scanning rate could be set to the values from 0.5 up to 60 s. MCPS 5.0 (CAD computer GmbH) software was used for data processing.

Electrochemical cell was rectangular, made of PP, with internal size ($L \times W \times H$): 140 mm × 105 mm × 470 mm. Electrolyte volume without electrodes was 6.91 dm^3, and working volume of electrolyte was maximum 6 dm^3. Distribution system of N_2, used for mixing of electrolytes during electrorefining process, consists of cylinder with N_2, washer, plastic pipes for connecting with flow meter as well as the plastic pipes, used for connecting the flow meter with glass pipe, dipped into the electrolytic cell. Thermostat “HAAKE B7 – PHOENIX 2” was used for maintenance the electrolyte temperature.

Chemical composition of electrolyte was determined by the ICP method, using simultaneous optical emission spectrometer with inductively coupled plasma (SPECTRO CIROS VISION). A part of electrolyte samples were analyzed without any previous preparation, but the occurrence of slime during solution cooling, as the result of saturated solution with metal salts, presents a significant problem for sample analyzing. Therefore, the electrolyte samples were prepared as follows: 10 ml of electrolyte from cell medium + 10 ml 37% HCl + deionised water up to 50 ml. By this way of sample preparation, the problem of precipitation was avoided.

Chemical composition of the anode slime was determined by the ICP method, and particle-size analysis was carried out using MALVERN – particle-size analyzer.

Polarization curves and cyclic voltammograms were recorded using potentiostat PAR 273A at ambient temperature of 25 ± 1 °C in aqueous sulphuric acid solution. The experiments were carried out in a standard three electrode arrangement cell (200 cm^3). The working electrode (analyzed samples of pure metals Cu and Ni as well as copper bearing anodes) had surface area of 1 cm^2. The saturated calomel electrode was used as the reference electrode, while the counter electrode was platinum foil with the same characteristics as working electrode. Prior to each experiment, the samples of working electrodes were subjected to double-stage wet polishing using 1 and 0.05 μm alumina, washed with 18 MΩ cm deionised water first and than with ethanol.

All potential values are given regarding to the saturated calomel electrode. Before the start of experiments, the samples were held in the solution at open circuit potential during 10 min in order to establish the stable corrosion potential. The samples were ana-