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TREATMENT OF WASTE SULFURIC ACID COPPER ELECTROLYTE[*****]

Abstract

The aim of this paper was to investigate the possibility of using the copper anodes with high nickel content for electrolytic treatment of waste sulfuric acid copper electrolyte. Nickel content in each anode was about 10 wt. %. Lead, antimony, and tin content was within the limits ranged from 0.1 to 1.4 wt. %. Copper mass content in anodes was in the range from 86 to 90 wt. %, and was mathematical deference to 100 wt. %. Electrolytic processing was done in galvanostatic conditions at the current density of 250 A/m^2, electrolyte temperature of 63 ± 2 ° C, duration of each test of 72 h. The mass of each anode was about 7 kg. The waste sulfuric acid electrolyte with concentration of 30 g dm^3 Cu^{2+} ions and 225 g/dm^3 SO$_4^{2-}$ ions was used as the working solution. Changing the anode mass, changing the content of copper and nickel ions in the working solution and the mass of obtained cathode deposit were the subject of discussion in this paper. The difference in weight of anode at the beginning and end of the process confirmed that the anodes are dissolved during the process. A significant reduction of Cu^{2+} ions concentration was achieved as well as an increase in concentration of Ni^{2+} ions in the working solution. Mass of cathode deposit, obtained during electrolytic refining of anode with the smallest impurity content, was greater than the mass of dissolved correspondent anode for about 2%. Mass of cathode deposit, obtained by refining the anode with the content of Pb + Sn + Sb from 1.5 to 3.5 wt. %, was less than the mass of dissolved correspondent anode by about 2 %.

Keywords: *anode, electrolyte refining, waste electrolyte, copper, nickel*

INTRODUCTION

High purity copper production in the industrial conditions is carried out by two independent processes: electrolytic refining and elecrowining. Electrolytic refining process is used for purifying the flame refined copper obtained by pyrometallurgical processing of copper ore or copper waste. Electrowining is used to extract the copper from the copper solution obtained after hydrometallurgical treatment [1, 2].

Under the influence of direct current, copper is deposited directly on cathode from the copper solution during the electrowining process. Lead alloyed with Sb, Ag, Sn and

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Ca is commonly used as an insoluble anode where the oxygen appears according to the following reaction, [1]:

$$H_2O \rightarrow H^+ + (OH)^- \rightarrow 1/2O_2 + 2H^+ + 2e\ ;$$

$$E^o = +1.23\ V.$$

The commercial copper anode with copper content from 98.0 to 99.5 wt. % and working solution with copper concentration from 35 to 50 g/dm^3 and free sulfuric acid concentration from 150 to 250 g/dm^3, are used in the commercial copper electrolytic refining process [3,4].

In addition to copper as the base metal, the other impurities are present in copper anode. These impurities have the impact on structure characteristics of anode material, and could change its properties. During the constant galvanostatic pulse, the impurities could be dissolved on anode with the possibility to: remain dissolved into the base electrolyte, to become a part of the anode slime forming the "floating slime" and eventually to precipitate onto the cathode. The impurities could cause the anode passivation, contamination of cathode deposit and electrolyte contamination. In the industrial environments, the control of impurities in the electrolyte is achieved by continuous discharging a part of electrolyte from circulation system with the aim to control the content of copper and other elements. The choice of treatment methods depends on type and contamination level. The chemical methods, solvent extraction, membrane processes, ion exchange, electrochemical methods are commonly used [5,6].

Large quantities of solid wastes, generated in the copper smelting process, are needed to be recycled with the goal of recovering the useful components. The recycling process is cheaper than the copper production process from raw materials, and the mineral resources could be kept. The anodes, produced from secondary materials, are generally rich in nickel, lead, antimony and tin, and have a low content of selenium, tellurium and silver [7]. The aim of this paper was to examine the possibility of application the copper anode with high copper content to recover the copper from waste sulfuric acid copper electrolytes. The anode chemical composition has to provide the reduction of copper content to minimum and to significantly increase the nickel content. By the proposed process, copper from electrolyte and anode could be valorized in the form of copper cathodes, and nickel from anode would be converted into the working solution, what would create the conditions for further treatment with the aim of nickel valorization as the final product.

EXPERIMENTAL PROCEDURE

Induction furnace, power up to 15 kW, was used for preparation the suitable mixture for obtaining the anode materials with nickel content of 10 wt.% and different contents of lead, tin and antimony, wherein total maximum content of these elements was up to 3.5 wt.%. The mixture was prepared by melting the anode copper (99.2 wt. % Cu) and pure metal components of nickel, lead, antimony and tin. The detailed procedure of preparing the mixture and melting process of copper anodes with Ni content of 7.5 wt. % is shown in an earlier paper by the same author [8]. When the oxygen content was less than 200 ppm, the melt was cast into suitable steel moulds at temperature of 1300 °C. After natural cooling, the anodes are prepared for the electrolysis process by mechanical finishing on the lathe, Figure 1, removing about 2 mm of material from the surface and by drilling the holes for connection with the electrode holder and electrical contacts. Final preparation of anode consisted of polishing the surface with abrasive paper from 600 to 1200, marking, measuring, hanging on the electrode holder, and rinse with distilled water just before immersing in the electrolytic cell and degreasing with ethanol. The mass of each anode was about 7 kg. The final anode shape is shown in Figure 2, which shows three holes with threaded for anode connection with electrode holder and current supplier.

Figure 1 *Copper anode mechanical finishing*

Figure 2 *Final copper anode*

Current density for all experiments was 250 A/m^2. Direct current is provided from an external DC power source, Heinzinger TNB-10-500, feature 50 A and 10 V. The starting cathode is made of stainless steel, and the reference electrode was copper.

Anode samples for chemical analysis were taken from the bottom, middle and top of the anode in order to determine the distribution of characteristic elements. RFA method (PANalytical Axios) was used for chemical analysis. The chemical composition of electrolyte is determined by method of simultaneous optical emission spectrometry with inductively coupled plasma (ICP-OES), SPECTRO Ciros VISION.

RESULTS AND DISSCUTION

Each of the anodes was analyzed on 26 elements, in accordance with the existing software. The results of chemical analysis of samples taken from the bottom, middle and top of anode A1 are shown in Table 1. The average values of the elements content were obtained by mathematical calculation. Copper content was the difference up to 100 wt. %.

Table 1 *Chemical composition of anode A1*

Element	**Content, wt. %**			
	Sampling position			**Average content**
	Bottom	**Middle**	**Top**	
Ni	10.02	9.78	9.79	9.86
Pb	0.143	0.143	0.138	0.14
Sn	0.09	0.093	0.091	0.092
Sb	0.071	0.074	0.073	0.073
Zn	< 0.0015	< 0.0015	< 0.0015	< 0.0015
P	0.0055	0.0054	0.0056	0.0055
Mn	< 0.0005	< 0.0005	< 0.0005	< 0.0005

Fe	0.016	0.016	0.014	0.015
Si	0.022	0.027	0.020	0.024
Mg	< 0.0002	< 0.0002	< 0.0002	< 0.0002
Cr	0.0003	0.0003	0.0004	0.0003
Te	0.012	0.012	0.010	0.012
As	0.021	0.021	0.021	0.021
Cd	0.0014	0.0014	0.0013	0.0014
Bi	0.0035	0.0034	0.0033	0.0034
Ag	0.061	0.062	0.063	0.062
Co	< 0.0015	< 0.0015	< 0.0015	< 0.0015
Al	< 0.0010	< 0.0010	< 0.0010	< 0.0010
S	0.0045	0.0047	0.0046	0.0046
Be	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Zr	< 0.0003	< 0.0003	< 0.0003	< 0.0003
Au	0.0018	0.0018	0.0019	0.0018
B	< 0.0005	0.0005	< 0.0005	< 0.0005
C	0.0016	0.011	0.0016	0.0047
Ti	0.002	0.0019	0.002	0.002
Se	0.0055	0.0055	0.0054	0.0055

There is no major difference of Ni, Pb, Sn, Sb content and content of other impurities, compared to the anode sampling position (table 1). These results confirmed the homogeneous distribution of impurities within the anode. The same conclusion is applied to anodes A2 and A3. Therefore, complete tables for these two anodes will not be shown, but only the average content values for characteristic elements will be shown: Ni, Pb, Sn, Sb and Cu (Table 2). Content of oxygen in all anodes was less than 100 ppm.

Table 2 *The average content of characteristic elements in anodes A1-A3*

Anode	Content, wt. %				
	Ni	Pb	Sn	Sb	Cu
A1	9.86	0.14	0.092	0.073	89.7
A2	10.04	0.385	0.41	0.382	88.6
A3	10.41	1.38	1.2	0.92	85.9

By measuring the anode mass at the beginning and end of experiment (after 72 h), the values of dissolved anode mass are obtained, 1,752 g for anode A1, 1,367 g for anode A2 and 1,785 g for anode A3.

Starting electrolyte was the waste sulfuric acid copper electrolyte with the following chemical composition (g/dm^3): Cu - 30; Ni - 20.5; As - 4; Pb - 0004; Sn - 0:01; Sb - 0.3 and SO_4^{2-} - 225.

Concentration of copper and nickel ions was controlled every 24 hours during the each test duration of 72 h. The values of Cu^{2+} and Ni^{2+} concentration changes in comparison to the starting values, expressed in percentages, are shown in Table 3.

Table 3 *Cu^{2+} i Ni^{2+} ions concentration changes*

Time	Anode					
	A1	A2	A3	A1	A2	A3
	Concentration changes of Cu^{2+} ion, %			Concentration changes of Ni^{2+} ion, %		
start	100	100	100	100	100	100
24 h	69.43	64.62	58.77	151.53	139.02	143.41
48 h	48.41	32.00	26.15	207.14	163.41	206.83
72 h	13.38	20.92	4.31	235.71	212.68	236.10

Observing the data for the working electrolyte composition changing, it could be seen that the concentration of Cu^{2+} ions in the electrolyte during the process is decreased. The largest decreasing, in the amount of 95.7 % was observed for the anode with the lowest copper content (85.9% wt.) and maximal content of impurities Pb + Sn + Sb (3.5 wt.%). Decreasing the concentration of Cu^{2+} ion is accompanied by Ni^{2+} ion concentration increasing in electrolyte to the value of about 140%. These results are in agreement with the results obtained by an electrolytic refining of copper anodes with 7.5 wt. % Ni and total sum of Pb + Sn + Sb up to 3 wt. % [8.9].

Decreasing the concentration of copper ions in the electrolyte has confirmed that copper is deposited on cathode and by electrowining process from solution. The ratio of obtained cathode deposits and dissolved masses of corresponding anode demonstrates that these values are very close (Figure 3).

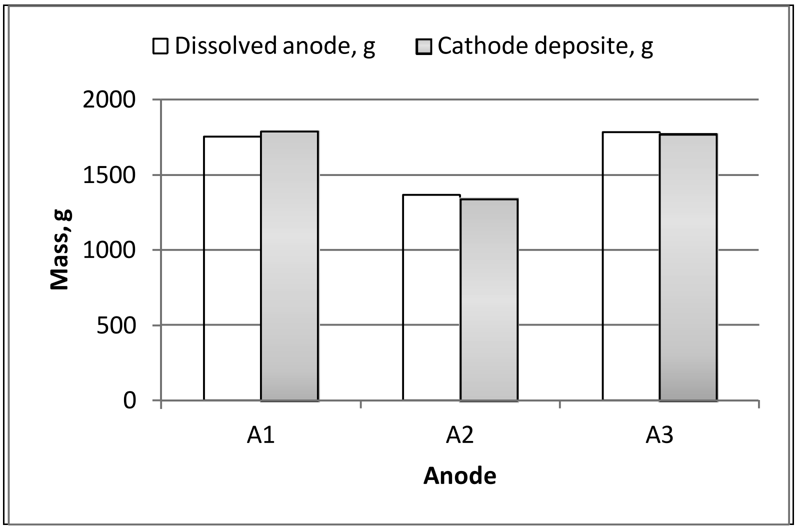

Figure 3 *The mass ratio of disolved anode and cathode deposite*

Mass of the obtained cathode deposit was about 2 wt. % greater than the mass of dissolved anode with lowest total impurity content and the highest copper content (anode A1). Mass of cathode deposits, obtained by electrolytic refining of anodes with total content of Pb, Sn and Sb content in the range from 1.5 to 3.5 wt. % was less than the mass of dissolved anode by about 2%.

CONCLUSION

By the process of electrolytic refining of copper anode with nickel content of 10 wt. % in the waste sulfuric acid copper electrolyte, the copper concentration was decreased, increased the concentrations of nickel ions and produced cathode copper. Compared to the chemical composition of copper anode from commercial copper production, chemical composition of this anode is significantly different. Very high content of nickel and increased content of lead, antimony and tin is also specific characteristic of these anodes (total value of Pb, Sn And Sb was up to 3.5 wt. %). During the anode electrolytic refining, in the working solution with copper content of 30 g/dm^3, concentration of Cu^{2+} ion is significantly decreased (more than 95%) and concentration of Ni^{2+} ion is increased up to 140%.

Reduction of copper contents in the solution is confirmed by weight of the obtained cathode deposits, which is very close to the weight of the soluble anode. Thus, the weight of cathode deposit was about 2 wt. % greater than the weight of dissolved anode with the highest copper content (anode A1). Masses of cathode deposits, obtained by refining the anodes with total content of Pb, Sn, and Sb from 1.5 to 3.5 wt. % (anodes A2 and A3), were slightly less than the weight of dissolved anode (approximately 2 wt.%).

Considering the fact that recycling process is cheaper than copper production from the primary raw materials, in addition to saving the mineral resources, it is reasonable to expect the positive economic effects.

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TRETMAN OTPADNOG SUMPORNO-KISELOG ELEKTROLITA BAKRA*****

Izvod

Cilj ovog rada bio je da se ispita mogućnost korišćenja bakarnih anoda sa visokim sadržajem nikla za elektrolitičku preradu otpadnog sumporno-kiselog elektrolita bakra. Sadržaj nikla u anodama bio je oko 10 mas. %, a sadržaj olova, antimona i kalaja kretao se u granicama od 0.1 do 1.4 mas. %. Maseno učešće bakra u anodama bilo je u opsegu od 86 do 90 mas. % i predstavljalo je razliku do 100 mas. %. Elektrolitička prerada je rađena u uslovima galvanostatskog režima rada, pri gustini struje od 250 A/m^2, temperaturi elektrolita od 63±2^{o}C, u trajanju od 72 h. Masa svake anode bila je oko 7 kg. Otpadni sumporno-kiseli elektrolit sa sadržajem Cu^{2+} jona od 30 g/dm^3 i sadržajem SO_4^{2-} jona od 225 g/dm^3 korišćen je kao radni rastvor. Promena mase anoda, promena sadržaja jona bakra i nikla u radnom rastvoru i masa dobijenog katodnog taloga bili su predmet diskusije u ovom radu. Razlika u masi anoda na početku i kraju procesa potvrdila je da su se anode tokom procesa rastvarale. Postignuto je značajno smanjenje koncentracije Cu^{2+} jona i povećanje koncentracije Ni^{2+} jona u radnom rastvoru. Masa katodnog taloga dobijenog elektrilitičkom rafinacijom anode sa najmanjim sadržajem nečistoća bila je veća od mase rastvorene korespodentne anode za oko 2 % dok su mase katodnih taloga dobijenih rafinacijom anoda sa sadržajem Pb+Sn+Sb od 1.5 - 3.5 mas. % bile manje od masa rastvorenih anoda za oko 2 %.

Ključne reči: *anoda, elekrolitička rafinacija, otpadni elektrolit, bakar, nikl*

UVOD

Dobijanje bakra visoke čistoće u industrijskim uslovima odvija se kroz dva nezavisna procesa: elektrolitičkom rafinacijom i elektroekstrakcijom. Proces elektrolitičke rafinacije koristi se za prečišćavanje plameno rafinisanog bakra dobijenog pirometalurškom preradom rude bakra ili bakarnog otpada, a proces elektroekstrakcije bakra za izdvajanje bakra iz rastvora dobijenog nakon hidrometalurškog tretmana [1, 2].

Procesom elektroekstrakcije, pod dejstvom jednosmerne struje bakar se iz rastvora taloži direktno na katodi. Olovo legirano sa Sb, Ag, Sn i Ca najčešće se koristi kao nerastvorna anoda na kojoj se

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tokom procesa izdvaja kiseonik prema sledećoj reakciji [1]:

$H_2O \rightarrow H^+ + (OH)^- \rightarrow 1/2O_2 + 2H^+ + 2e;$

$E^o = +1,23$ V.

U standardnom procesu elektrolitičke rafinacije bakra koriste se komercijalne anode sa sadržajem bakra od 98.0 do 99.5 mass % i osnovni radni rastvor koncentracije Cu od 35 -50 g/dm^3 i H_2SO_4 od 150 - 250 g/dm^3 [3,4]. U anodama su, pored bakra kao osnovnog metala, prisutne i druge nečistoće koje utiču na strukturu anodnog materijala i samim tim menjaju njena svojstva. Za vreme trajanja konstantnog galvanostatskog pulsa, primese mogu da se rastvore iz anode uz mogućnost da: ostanu rastvorene u osnovnom elektrolitu, pređu u nerastvoran talog, formiraju "lebdeći mulj" i eventualno se istalože na katodi, čime mogu da izazovu pasivaciju anode, zaprljanje katodnog taloga i elektrolita. U industrijskim uslovima, kontrola sadržaja nečistoća u elektrolitu postiže se kontinualnim izvođenjem dela elektrolita iz cirkulacionog sistema radi izdvajanja bakra i drugih nečistoća, a izbor metode za njegovo prečišćavanje zavisi od vrste i stepena onečišćenja. Najčešće se koriste različite hemijske metode, solventna ekstrakcija, membranski procesi, jonska izmena, elektrohemijske metode [5,6].

Velike količine čvrstih otpadnih materijala koje nastaju u procesu topljenja bakra potrebno je reciklirati u cilju izdvajanja korisnih komponenti. Proces reciklaže jeftiniji je od procesa proizvodnje bakra iz primarnih sirovina, a postiže se i očuvanje mineralnih resursa. Anode dobijene iz sekundarnih sirovina generalno su bogate niklom, olovom, antimonom i kalajem, a zabeležen je nizak sadržaj selena, telura i srebra [7]. Cilj ovog rada bio je da se bakarne anode sa visokim sadržajem nikla (10 mas. %) primene za izdvajanje bakra iz otpadnog elektrolita bakra. Hemijski sastav anoda trebao je da omogući da se u otpadnom rastvoru sadržaj bakra svede na minimum i da se značajno poveća koncentracija nikla. Predloženim postupkom bakar iz rastvora i anode bio bi valorizovan u formi katodnog bakra, a nikl iz anode bio bi preveden u radni rastvor čime bi se stvorili uslovi za dalji tretman u cilju valorizacije nikla do krajnjeg proizvoda.

EKSPERIMENTALNA PROCEDURA

Indukciona peć snage do 15 kW, korišćena je za pripremu odgovarajuće smeše za dobijanje bakarnih anoda sa sadržajem nikla od 10 mas.% i različitim sadržajem olova, kalaja i antimona, pri čemu je ukupan maksimalan sadržaj ovih elemenata iznosio do 3,5 mas. %. Smeša je pripremana topljenjem anodnog bakra i čistih metalnih komponenti nikla, olova, antimona i kalaja. Detaljna procedura pripreme smeše i procesa topljenja za bakarne anode sa sadržajem Ni od 7,5 mas. % prikazana je u ranijem radu istog autora [8]. Rastop je izlivan u odgovarajuće čelične kalupe na temperaturi od 1300°C, tek kada je sadržaj kiseonika bio ispod 200 ppm. Nakon prirodnog hlađenja, anode su pripremane za proces elektrolize mehaničkom obradom na strugu, slika 1., skidanjem oko 2 mm materijala sa površine i bušenjem otvora za elektrodni nosač i električne kontakte. Finalna priprema anoda sastojala se od poliranja površina abrazivnim papirima krupnoće od 600 do 1200, obeležavanja, merenja, kačenja na elektrodni nosač, ispiranja destilovanom vodom a neposredno pre ulaganja u ćeliju i odmašćivanja etanolom. Masa svake anode bila je oko 7 kg. Finalni izgled anode prikazan je na slici 2. na kojoj se vide tri otvora sa navojem za kačenje anode na elektrodni nosač i povezivanje sa strujnim snabdevačem.

Sl. 1. *Priprema bakarnih anoda*

Sl. 2. *Bakarne anode*

Gustina struje taloženja za sve eksperimente iznosila je 250 A/m^2. Jednosmerna struja obezbeđena je sa spoljnjeg izvora jednosmerne struje, HEINZINGER TNB-10-500, karakteristika 50 A i 10 V. Polazna katoda je od nerđajućeg čelika, a referentna elektroda od bakra.

Uzorci za hemijsku analizu anode uzimani su sa dna, sredine i vrha anode u cilju utvrđivanja raspodele karakterističnih elemenata. RFA metoda (PANalytical-Axios) korišćena je za hemijsku analizu. Hemijski sastav elektrolita određen je metodom simultano optičke emisione spektrometrije sa indukovano kuplovanom plazmom (ICP-OES), SPECTRO CIROS VISION.

REZULTATI I DISKUSIJA

Svaka anoda analizirana je, saglasno postojećem softveru, na 26 elemenata. Rezultati hemijskih analiza za uzorke uzete sa dna, sredine i vrha anode A1 prikazani su u tabeli 1. Srednje vrednosti sadržaja elemenata, dobijene su matematičkim putem. Sadržaj bakra predstavlja razliku do 100 mas. %.

Tabela 1. *Hemijski sastav bakarne anode A1*

Element	**Sadržaj, mas. %**			
	Pozicija uzorkovanja anoda			**Srednja vrednost**
	Dno	**Sredina**	**Vrh**	
Ni	10,02	9,78	9,79	9,86
Pb	0,143	0,143	0,138	0,14
Sn	0,09	0,093	0,091	0,092
Sb	0,071	0,074	0,073	0,073
Zn	< 0,0015	< 0,0015	< 0,0015	< 0,0015
P	0,0055	0,0054	0,0056	0,0055
Mn	< 0,0005	< 0,0005	< 0,0005	< 0,0005

Fe	0,016	0,016	0,014	0,015
Si	0,022	0,027	0,020	0,024
Mg	< 0,0002	< 0,0002	< 0,0002	< 0,0002
Cr	0,0003	0,0003	0,0004	0,0003
Te	0,012	0,012	0,010	0,012
As	0,021	0,021	0,021	0,021
Cd	0,0014	0,0014	0,0013	0,0014
Bi	0,0035	0,0034	0,0033	0,0034
Ag	0,061	0,062	0,063	0,062
Co	< 0,0015	< 0,0015	< 0,0015	< 0,0015
Al	< 0,0010	< 0,0010	< 0,0010	< 0,0010
S	0,0045	0,0047	0,0046	0,0046
Be	< 0,0001	< 0,0001	< 0,0001	< 0,0001
Zr	< 0,0003	< 0,0003	< 0,0003	< 0,0003
Au	0,0018	0,0018	0,0019	0,0018
B	< 0,0005	0,0005	< 0,0005	< 0,0005
C	0,0016	0,011	0,0016	0,0047
Ti	0,002	0,0019	0,002	0,002
Se	0,0055	0,0055	0,0054	0,0055

Iz tabela se vidi da nema velikih odstupanja u sadržaju Ni, Pb, Sn i Sb, kao ni u sadržaju ostalih primesa, posmatrano u odnosu na pozicije uzorkovanja anoda, čime je potvrđena homogena raspodela nečistoća unutar anode. Isti zaključak važi i za anode A2 i A3 tako da neće biti prikazane kompletne tabele za ove dve anode već samo vrednosti srednjih sadržaja za karakteristične elemente: Ni, Pb, Sn, Sb i Cu (tabela 2). Sadržaj kiseonika u svim anodama bio je manji od 100 ppm.

Tabela 2. *Srednje vrednosti sadržaja karakterističnih elemenata u anodama A1-A3*

Anoda	**Hemijski sadržaj, mas %**				
	Ni	**Pb**	**Sn**	**Sb**	**Cu**
A1	9,86	0,14	0,092	0,073	89,7
A2	10,04	0,385	0,41	0,382	88,6
A3	10,41	1,38	1,2	0,92	85,9

Merenjem masa anoda na početku i kraju eksperimenta dobijena je vrednost rastvorene mase anoda koja iznosi: 1752 g za anodu A1, 1.367 g za anodu A2 i 1.785 g za anodu A3.

Polazni elektrolit predstavljao je otpadni sumporno-kiseli elektrolit bakra sledećeg hemijskog sastava (g/dm^3): Cu – 30; Ni – 20.5; As – 4; Pb – 0.004; Sn – 0.01; Sb – 0.3 i SO_4^{2-} – 225.

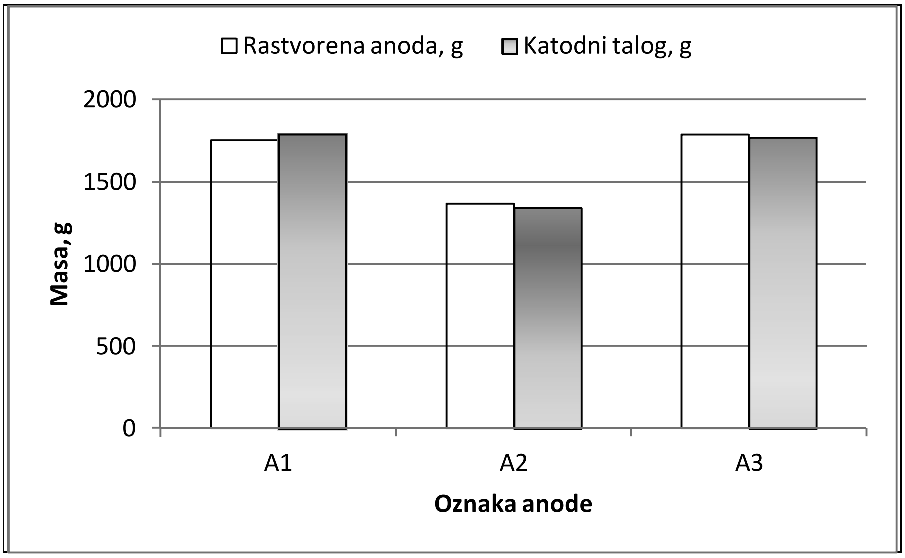
Koncentracija jona bakra i nikla kontrolisana je tokom svakog eksperimenta, na svakih 24 h za ukupno vreme trajanja od 72 h. Vrednosti promene koncentracije Cu^{2+} i Ni^{2+} jona u odnosu na polazne vrednosti, izražene u procentima, prikazane su u tabeli 3.

Tabela 3. *Promena koncentracije* Cu^{2+} *i* Ni^{2+} *jona u elektrolitu*

Vreme	**Oznaka anoda**					
	A1	**A2**	**A3**	**A1**	**A2**	**A3**
	Promena koncentracije Cu^{2+} jona, %			**Promena koncentracije Ni^{2+} jona, %**		
Start	100	100	100	100	100	100
24 h	69,43	64,62	58,77	151,53	139,02	143,41
48 h	48,41	32,00	26,15	207,14	163,41	206,83
72 h	13,38	20,92	4,31	235,71	212,68	236,10

Posmatrajući podatke za promenu sastava radnog elektrolita, vidi se da se koncentracija Cu^{2+} jona u elektrolitu tokom procesa smanjuje. Najveće smanjenje, u vrednosti od 95.7 %, registrovano je kod anode koju karakteriše najniži sadržaj bakra (85,9 mas. %) i najviši sadržaj nečistoća Pb+Sn+Sb (3.5 mas. %). Smanjenje sadržaja Cu^{2+} jona praćeno je povećanjem sadržaja Ni^{2+} jona u elektrolitu do vrednosti od oko 140 %. Dobijeni rezultati su u saglasnosti sa rezultatima dobijenim elektrolitičkom rafinacijom bakarnih anoda sa 7,5 mas. % Ni i sadržajem Pb+Sn+Sb do vrednosti od 3 mas. % [8,9].

Smanjenje koncentracije bakarnih jona u elektrolitu potvrđuje da se bakar taloži na katodi i procesom elektroekstrakcije iz rastvora. Odnos dobijene mase katodnog taloga i rastvorene mase odgovarajuće anode pokazuje da su ove vrednosti veoma bliske (sl. 3).



Sl. 3. *Odnos masa rastvorenih anoda i masa katodnih taloga*

Kod anode sa najnižim sadržajem ukupnih nečistoća i najvišim sadržajem bakra (anoda A1) masa dobijenog katodnog taloga bila je za oko 2 mas. % veća od mase rastvorene anode. Mase katodnih taloga dobijenih rafinacijom anoda sa sadržajem Pb+Sn+Sb od 1,5 - 3,5 mas. % bile su manje od masa rastvorenih anoda za oko 2 %.

ZAKLJUČAK

Elektrolitičkom rafinacijom bakarnih anoda sa sadržajem nikla od 10 mas. %, u otpadnom sumporno - kiselom elektrolitu bakra, smanjena je koncentracija jona bakra, povećana koncentracija jona nikla i dobijen katodni bakar. U poređenju sa hemijskim sastavom bakarnih anoda koje se koriste u komercijalnom procesu dobijanja katodnog bakra, hemijski sastav ovih anoda je bitno različit. Osim jako visokog sadržaja nikla, za ove anode je karakterističan i povećani sadržaj olova, antimona i kalaja (zbirna vrednost do 3,5 mas. %). Tokom procesa elektrolitičke rafinacije ovih anoda, u radnom rastvoru sa sadržajem bakra od 30 g/dm^3, značajno je smanjena koncentracija Cu^{2+} jona (više od 95 %) i povećana koncentracija Ni^{2+} jona (oko 140 %), posmatrano u odnosu na polazne vrednosti.

Smanjenje sadržaja bakra u rastvoru potvrđeno je dobijenom masom katodnog taloga koja je veoma bliska masi rastvorene anode. Tako je masa katodnog taloga bila za oko 2 mas. % veća od mase anode sa najvećim sadržajem bakra (anoda A1) koja je rastvorena tokom procesa. Mase katodnih taloga dobijenih rafinacijom anoda sa ukupnim sadržajem Pb, Sn i Sb od 1,5 do 3,5 mas. % (anode A2 i A3) bile su neznatno manje od masa rastvorenih anoda (oko 2 mas. %).

Imajući u vidu činjenicu da je proces reciklaže jeftiniji od procesa proizvodnje bakra iz primarnih sirovina, pored očuvanja mineralnih resursa realno je očekivati i pozitivne ekonomske efekte.

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