

PROCESSING OF COPPER ELECTROLYTE FOR ZINC-CONTAINING PRODUCT

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Waste solutions from the electrolytic production of copper contain significant amounts of copper and nickel sulfates, sulfuric acid, arsenic and other components of the copper electrolyte. The processing of such solutions is considered in this work not only from the point of view of environmental protection, but also in terms of extracting various valuable components from the electrolyte into commercial products. A thermodynamic analysis of the interactions between barium and arsenic, as well as their compounds in the $Ba(AsO_2)_2-Ba_3(AsO_4)_2-H_2O$ system was carried out based on the E-pH diagram. The possibility of using barium compounds as a precipitant for arsenic from copper electrorefining solutions has been demonstrated. The efficiency of removing arsenic (more than 84%) from the electrolyte using barium oxide in the form of sparingly soluble barium arsenate has been established. By adding calculated amounts of zinc oxide into the working solution, it is possible to form solutions containing certain concentrations of Cu, Ni, and Zn. By further adding zinc oxide into the solution, its deep dehydration was achieved. The resulting copper-nickel-zinc and nickel-zinc solutions are the raw material for producing non-ferrous metal alloys using the electromembrane method.

Key words: copper electrolyte, E-pH diagram, arsenic, barium oxide, barium arsenate, depuration, zinc oxide, copper, nickel, zinc, membrane electrolysis, alloys

ҚҰРАМЫНДА МЫРЫШ БАР ӨНІМ ҮШІН МЫС ЭЛЕКТРОЛИТІН ӨНДЕУ

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Мыстың электролиттік өндірісінің қалдық ерітінділерінің құрамында, мыс пен никель сульфаттарының, күкірт қышқылының, мышьяқтың және мыс электролитінің басқа компоненттерінің мөлшері бар. Мұндай ерітінділерді өңдеу бұл жұмыста қоршаған ортаны қорғау тұрғысынан ғана емес, сонымен қатар электролиттен әртүрлі құнды компоненттерді тауарлық өнімге алу тұрғысынан қарастырылады. E-pH диаграммасы негізінде барий мен мышьяқтың, сондай-ақ, олардың $Ba(AsO_2)_2-Ba_3(AsO_4)_2-H_2O$ жүйесіндегі қосылыстарының өзара әрекеттесуіне термодинамикалық талдау жүргізілді. Мысты электрорафинерлеу ерітінділерінен мышьяқ үшін тұндырғыш ретінде барий қосылыстарын қолдану мүмкіндігі көрсетілді. Барий оксидін қолдану арқылы электролиттен мышьяқты (84%-дан астам) аз еритін барий арсенаты түрінде шығару тиімділігі анықталды. Жұмыс ерітіндісіне мырыш оксидінің есептелген мөлшерін енгізу арқылы, Cu, Ni және Zn белгілі концентрациялары бар ерітінділер түзуге болады. Мырыш оксидін ерітіндіге одан әрі енгізу арқылы оның терең мыссыздануына қол жеткізілді. Алынған мыс-никель-мырыш және никель-мырыш ерітінділері, электромембраналық әдіспен түсті металдар қорытпаларын алу үшін, шикізат болып табылады.

Түйін сөздер: мыс электролиті, E-pH диаграммасы, мышьяқ, барий оксиді, барий арсенаты, мыссыздандыру, мырыш оксиді, мыс, никель, мырыш, мембраналық электролиз, қорытпалар

ПЕРЕРАБОКА МЕДНОГО ЭЛЕКТРОЛИТА НА ЦИНКСОДЕРЖАЩИЙ ПРОДУКТ

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Отработанные растворы электролитического получения меди содержат значительные количества сульфатов меди и никеля, серной кислоты, мышьяка и другие компоненты медного электролита. Переработка таких растворов рассматривается в данной работе не только с точки зрения охраны окружающей среды, но и в плане извлечения из электролита различных ценных компонентов в товарную продукцию. Проведен термодинамический анализ взаимодействий бария и мышьяка, а также их соединений в системе $Ba(AsO_2)_2$ - $Ba_3(AsO_4)_2$ - H_2O на основе диаграммы E-pH. Показана возможность использования соединений бария в качестве осадителя мышьяка из растворов электролиза рафинирования меди. Установлена эффективность вывода мышьяка (более 84%) из электролита оксидом бария в форме труднорастворимого арсената бария. Введением расчетных количеств оксида цинка в рабочий раствор возможно формирование растворов, содержащих определенные концентрации Cu, Ni, Zn. Дальнейшим введением в раствор оксида цинка достигнуто его глубокое обезмеживание. Образующиеся медно-никель-цинковые и никель-цинковые растворы являются сырьем для получения сплавов цветных металлов электрохимическим способом.

Ключевые слова: медный электролит, диаграмма E-pH, мышьяк, оксид бария, арсенат бария, обезмеживание, оксид цинка, медь, никель, цинк, мембранный электролиз, сплавы.

Introduction. Processing of copper electrolytic refining solutions includes operations such as neutralization and separation of components. At the separation stage, membrane processes can be used with great efficiency. Developed by scientists of the Chemical-Metallurgical Institute (Karaganda), the electromembrane technology for processing copper electrolyte to produce Cu-Ni, Cu-Ni-Zn, Ni-Zn alloys [1] is characterized by high efficiency at electrolyte acidities in the pH range of 0,9-2,0.

However, copper-nickel solutions supplied for processing require preliminary preparation for membrane electrolysis. This is due to the content of sulfuric acid (50-110 kg/m³) and arsenic (7,0-10,0 kg/m³) in the electrolyte. Therefore, this work describes the possibility of purifying a copper electrolyte from arsenic with barium compounds and its further neutralization with zinc oxide to obtain copper-, nickel-, and zinc-containing solutions.

In works [2-4], the physicochemical patterns of the behavior of arsenic and barium in redox and exchange reactions in an aqueous environment were studied. The data obtained are of theoretical and practical interest both for the targeted synthesis of compounds and for physicochemical modeling of the processes of removing arsenic from the production cycle of non-ferrous metals.

Materials and methods. The method using E and pH as characteristic variables allows one to construct stability diagrams of minerals when describing

reactions involving solids and dissolved components [5, 6]. With its help, the thermodynamically probable behavior of chemical elements and their compounds, including minerals in contact with aqueous solutions, is assessed, the potential and pH limits within which a given element compound must be stable are established, and the chemical nature of oxidation products is revealed. To construct the E-pH diagrams of the $Ba(AsO_2)_2$ - $Ba_3(AsO_4)_2$ - H_2O system, thermodynamic data were used [7, 8].

Experiments on the deposition of arsenic from a copper electrolyte were carried out in a thermostated cell with a capacity of 150 cm³, equipped with a mechanical stirrer. A sample of barium oxide, taken in the required quantity, was added into a copper electrolyte solution at a given temperature. The experimental temperature was maintained with an accuracy of $\pm 2^\circ C$. The deposition process was carried out with continuous stirring. After a given time, the solid phase was separated by filtration, and the residual arsenic content in the filtrate was determined.

Studies on the precipitation of arsenic by barium oxide were carried out taking into account the following factors: Ba:As (x_1) (1,45:1; 2,9:1; 4,35:1; 5,8:1); temperature, °C (x_2) (25, 40, 55, 70); concentration of sulfuric acid, g/l (x_3) (80, 100, 120, 140); duration, min. (x_4) (15, 30, 45, 60) and the dosage ratio of the precipitant (x_5) (1, 2, 3, 4).

Neutralization and deep dehydration of the working solution were carried out in a thermostated cell with a

capacity of 150 cm³, equipped with a mechanical stirrer at 70°C for 1 hour by adding calculated amounts of zinc oxide.

Results and discussion. Based on the E-pH diagram (Figure 1), a thermodynamic analysis of the interactions of barium and arsenic, as well as their compounds in the Ba(AsO₂)₂-Ba₃(AsO₄)₂-H₂O system, was carried out. In accordance with Figure 1 and Table 1, the stability area of water in the diagram is limited by lines 1 and 2. The diagram also shows the stability fields of arsenic, barium and their compounds. Metal barium, arsine, Ba²⁺ ion, barium arsenite (Ba(AsO₂)₂) are stable in the reducing region, and Ba²⁺ ion and Ba(AsO₂)₂ occupy a wide range of existence and are also stable in the aqueous and oxidizing regions.

The transition of metal barium to Ba²⁺ ion occurs at a potential equal to -2,87V (line 3) and is consistent with reference data (-2,91V) [9]. In the region of the existence of hydrogen, along line 15, arsine interacts with the Ba²⁺ ion to form barium arsenite Ba(AsO₂)₂, which at higher potential values along line 11 is oxidized to arsenate Ba₃(AsO₄)₂. It should be noted that barium arsenite is stable in both acidic and alkaline

media, while the formation of barium arsenate begins at pH=8 and it is stable only in alkaline media.

At positive potential values, barium arsenate decomposes into arsenic acid derivatives: HAsO₄²⁻ (line 8), AsO₄³⁻ (line 9) and barium peroxide - BaO₂.

In the oxidation region, barium arsenite decomposes into Ba²⁺ ion, arsenic acid H₃AsO₄ (line 14) and its ionic forms H₂AsO₄⁻ (line 13), HAsO₄²⁻ (line 12).

Thus, among arsenic compounds, arsenic acid and its derivatives are stable in the oxidative region. The transition of H₃AsO₄ to H₂AsO₄⁻ occurs at pH=2,2; H₂AsO₄⁻ in HAsO₄²⁻ at pH=7,0; HAsO₄²⁻ to AsO₄³⁻ at pH=11,54. Of the barium compounds, BaO₂ and Ba²⁺ ion are stable in this region.

In the reducing region, the following are stable: AsH₃, Ba²⁺ ion and barium metal.

It should be emphasized that arsenite and barium arsenate occupy a wide range of existence: barium arsenite is stable in the reducing, aqueous and oxidizing regions, and barium arsenate in the aqueous and oxidizing regions. The data obtained became the basis for the use of barium compounds as a precipitant for arsenic from copper electrorefining solutions.

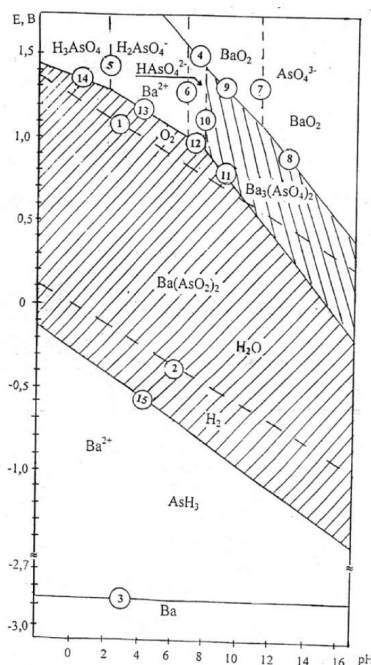


Figure 1 - E-pH diagram of the Ba(AsO₂)₂-Ba₃(AsO₄)₂-H₂O system

At the first stage, studies of the processes of arsenic deposition from a copper electrolyte were carried out using mathematical experimental design, using a five-factor design at four levels. The results of the experiments are presented in Table 2.

The data obtained made it possible to develop a method [10] for the selective purification of copper electrolyte from arsenic with barium compounds, which are added into the initial electrolyte at a mass ratio of barium to arsenic equal to 1,45:1 and deposition is carried out at a temperature of 70°C for 1 hour. The method makes it possible to reduce the duration of the deposition process and remove arsenic in the form of easily filtered and poorly soluble compounds that meet environmental safety requirements during storage or disposal.

After separation of the arsenic-containing sediment, the working solution has the following average composition (g/l): Cu - 4,4; Ni - 24,6; Zn - 20,36; H₂SO₄ - 72,8; As - 0,15. From such a solution, using known methods, it is possible to obtain various Cu-Ni-Zn alloys, which in metallurgy are called nickel silver. In their composition, metals vary within the following limits: Cu - 20-82%; Ni - 5-35%; Zn - 13-45%. The technological scheme for producing Cu-Ni-Zn is presented in Figure 2.

Then the working solution enters the processing stage. By adding calculated amounts of zinc oxide into the electrolyte, it is possible to form solutions containing certain concentrations of Cu, Ni, Zn (Table 3).

Table 1 - Reaction equations and calculated equations of interphase transitions of barium and arsenic compounds for the Ba(AsO₂)₂-Ba₃(AsO₄)₂-H₂O system

№	Chemical reaction equation	Electrode reaction equation
1	$2H_2O_{(l)} = O_{2(g)} + 4H_{(l)}^+ + 4e$	$E = 1,23 - 0,059pH$; with $P_{O_2} = 1$ atm.
2	$H_{2(g)} = 2H_{(l)}^+ + 2e$	$E = -0,059/2 \lg P_{H_2} - 0,059pH$; with $P_{H_2} = 1$ atm.
3	$Ba_{(s)} = Ba_{(l)}^{2+} + 2e$	$E = -2,84 + 0,0295 \lg[Ba^{2+}]$
4	$Ba_{(l)}^{2+} + 2H_2O_{(l)} = BaO_{2(s)} + 4H_{(l)}^+ + 2e$	$E = 2,35 - 0,0295 \lg[Ba^{2+}] - 0,118pH$
5	$H_3AsO_{4(l)} = H_2AsO_{4(l)} + H_{(l)}^+$	$\lg[H_2AsO_4^-]/\lg[H_3AsO_4] = 2,2 - pH$; $pH = 2,2$
6	$H_2AsO_{4(l)}^- = HAsO_{4(l)}^{2-} + H_{(l)}^+$	$\lg[HAsO_4^{2-}]/\lg[H_2AsO_4^-] = 7,0 - pH$; $pH = 7,0$
7	$HAsO_{4(l)}^{2-} = AsO_{4(l)}^{3-} + H_{(l)}^+$	$\lg[AsO_4^{3-}]/\lg[HAsO_4^{2-}] = 11,54 - pH$; $pH = 11,54$
8	$Ba_3(AsO_4)_{2(s)} + 6H_2O_{(l)} = 3BaO_2 + 2AsO_{4(l)}^{3-} + 12H_{(l)}^+ + 6e$	$E = 2,46 - 0,0197 \lg[AsO_4^{3-}] - 0,118pH$
9	$Ba_3(AsO_4)_{2(s)} + 6H_2O_{(l)} = 3BaO_2 + 2HAsO_{4(l)}^{2-} + 10H_{(l)}^+ + 6e$	$E = 2,24 - 0,0197 \lg[HAsO_4^{2-}] - 0,098pH$
10	$2HAsO_{4(l)}^{2-} + 3Ba_{(l)}^{2+} = Ba_3(AsO_4)_{2(s)} + 2H_{(l)}^+$	$3 \lg[Ba^{2+}] \cdot 2 \lg[HAsO_4^{2-}] = -11,15 - 2pH$; $pH = 8,1$
11	$3Ba(AsO_2)_{2(s)} + 12H_2O_{(l)} = Ba_3(AsO_4)_{2(s)} + 4AsO_{4(l)}^{3-} + 24H_{(l)}^+ + 12e$	$E = 1,93 + 0,0196 \lg[AsO_4^{3-}] - 0,118pH$
12	$Ba(AsO_2)_{2(s)} + 4H_2O_{(l)} = Ba_{(l)}^{2+} + 2HAsO_{4(l)}^{2-} + 6H_{(l)}^+ + 4e$	$E = 1,65 + 0,0295 \lg[HAsO_4^{2-}] + 0,0147 \lg[Ba^{2+}] - 0,0885pH$
13	$Ba(AsO_2)_{2(s)} + 4H_2O_{(l)} = Ba_{(l)}^{2+} + 2H_2AsO_{4(l)}^- + 4H_{(l)}^+ + 4e$	$E = 1,45 + 0,0295 \lg[HAsO_4^-] + 0,0147 \lg[Ba^{2+}] + 0,059pH$
14	$Ba(AsO_2)_{2(s)} + 4H_2O_{(l)} = Ba_{(l)}^{2+} + 2H_3AsO_{4(l)} + 2H_{(l)}^+ + 4e$	$E = 1,38 + 0,0295 \lg[H_3AsO_4] + 0,0147 \lg[Ba^{2+}] + 0,0295pH$

15	$Ba_{(l)}^{2+} + 2AsH_{3(g)} + 4H_2O_{(l)} = Ba(AsO_2)_{2(s)} + 14H_{(l)}^+ + 12e$	$E = -0,27 - 0,0049 \lg[Ba^{2+}] - 0,069pH$
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Table 2 - Partial dependences of the degree of arsenic precipitation by barium oxide in solutions on the studied factors

Function			Factor levels				Average value
			1	2	3	4	
1			2	3	4	5	6
$\alpha(x1)$	As	exp.	84,16	85,27	84,49	83,97	84,47
		teohr.	84,37	84,79	84,63	83,87	84,41
$\alpha(x2)$	As	exp.	79,36	84,61	84,04	89,88	84,47
		teohr.	79,74	82,89	86,04	89,19	84,46
$\alpha(x3)$	As	exp.	88,53	80,91	85,95	82,48	84,47
		teohr.	86,72	85,07	83,87	82,67	84,47
$\alpha(x4)$	As	exp.	82,31	85,19	84,49	85,88	84,47
		teohr.	82,76	84,26	85,15	85,79	84,49
$\alpha(x5)$	As	exp.	84,03	78,73	86,12	89,00	84,47
		teohr.	83,40	80,46	82,86	90,60	84,33

To obtain a Ni-, Zn-containing solution, the possibility of deep depuration of the electrolyte was investigated by adding calculated amounts of zinc oxide into the solution at 70°C and a time of 1 hour. Figure 3 shows the dependence of the degree of defoliation on the Cu:Zn ratio. In the process of neutralizing sulfuric acid with zinc-containing waste, copper is

displaced with an increase in zinc concentration. Copper precipitates in the form of basic copper sulfates $Cu(OH)_2 \cdot CuSO_4$. The possibility of deep decontamination of copper electrolyte using zinc oxide and obtaining a solution containing mainly Ni and Zn has been established.

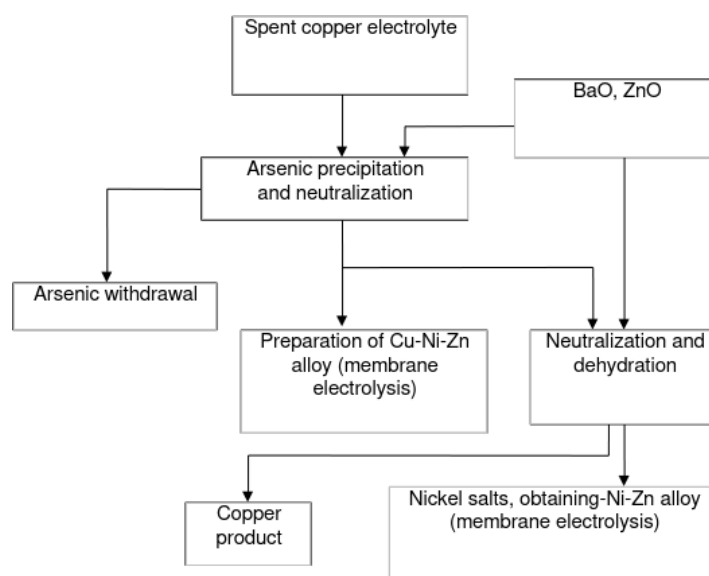


Figure 2 - Technological diagram for the production of Cu-Ni-Zn and Ni-Zn alloys during the processing of copper electrolyte

Table 3 - Composition of the electrolyte after treating it with the calculated amount of zinc oxide

№	The initial composition of the electrolyte, g/l				Amount of zinc oxide	Electrolyte composition, after treatment, g/l				
	Cu	Ni	H ₂ SO ₄	As		Cu	Ni	H ₂ SO ₄	As	Zn
1	51,7	24,8	104,7	3,5	1,8	46,5	24,7	70,5	0,15	22,8
2					3,6	24,4	24	40,1	0,09	37
3					4,4	0,7	23,6	20,4	0,05	50,1
4					5,6	0,01	23,3	-	0,01	55,2
5					6,8	0,006	18,3	-	0,01	55,7

Decontamination must be carried out to a copper concentration of 0,1 g/l, since when lower copper concentrations are reached, significant amounts of nickel and zinc are carried into the sediment. The

resulting solution containing nickel and zinc can be processed using the electromembrane method to isolate the Ni-Zn alloy (Figure 2).

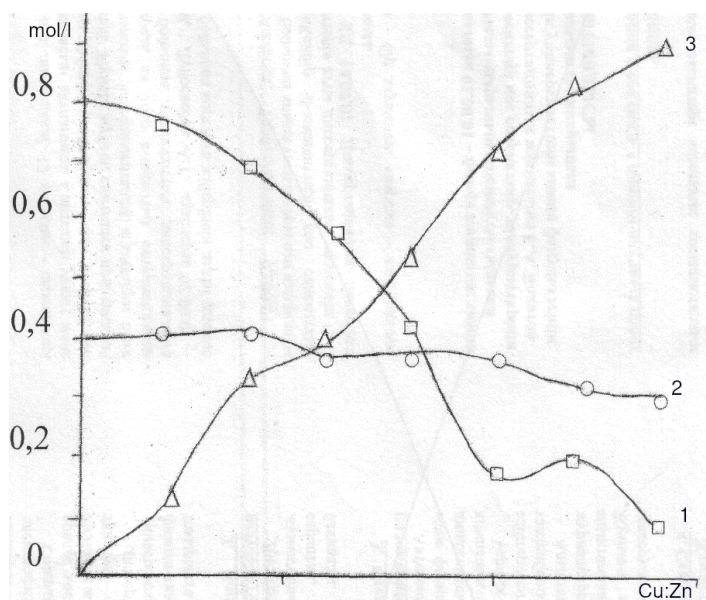


Figure 3 - Dependence of metal deposition on the Cu:Zn ratio
(1-copper, 2-nickel, 3-zinc)

Conclusions. Thus, after cleaning the copper electrolyte from arsenic with barium oxide, the possibility of using zinc oxide to neutralize it, or deep decontamination, has been established. The most optimal conditions for the formation of copper-nickel-

zinc and nickel-zinc solutions have been selected. A technological scheme has been proposed for the production of non-ferrous metal alloys of different compositions from these solutions by membrane electrolysis.

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