

RATIONAL EXTRACTION OF ARSENIC FROM COPPER PRODUCTION WASTE

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Practically and theoretically important are studies aimed at creating new methods for purifying copper electrolyte with the removal of such a dangerous impurity as arsenic in a form suitable for the intended use. Using probabilistic-deterministic planning of the experiment, the course of chemical reactions in manganese- and arsenic-containing systems, the directions of reactions and the stability of their constituent phases were studied. Based on experimental data and thermodynamic analysis, the probable behavior of chemical elements and their compounds, the limits of potential and pH, within which a given compound of an element must be stable, are determined. X-ray diffraction identified the formation of manganese arsenate ($Mn_3(AsO_4)_2 \cdot 4H_2O$) in deposits formed during the extraction of arsenic from a copper electrolyte with manganese (IV) oxide.

Keywords: extraction, arsenic, copper electrolyte, manganese oxide, X-ray phase analysis

INTRODUCTION

The intensive exploitation by mankind of mineral resources, including copper-containing ores, has led to the need to involve complex, substandard raw materials, in particular “resistant” arsenic-containing ores, in the processing of non-ferrous metallurgy.

For example, it can be removed in the form of low-toxic lead arsenate [1] when extracting rare metals from industrial waste from copper production. That is, arsenic is mainly concentrated in waste temporarily stored or buried in special storage facilities, and poses a potential hazard to the environment.

According to the results of the study of the soils of the Caspian coast [2], it was found that the arsenic content is everywhere above the maximum permissible concentration. A rational solution to this environmental problem should be an increase in the volume of products based on arsenic.

The prospect of developing new methods of arsenic deposition is associated with the use of oxides of transition metals (Fe, Mn, Ni, Cu) [3–7]. Thus, it was experimentally shown in [6] that As (V) is effectively removed from the solution by resin coated with (hydro) oxides of manganese and iron in a wide pH range from 4 to 9.

The use of transition metal oxides, in particular manganese (IV) oxide, for the selective extraction of arsenic from waste solutions of copper production in the form of consumer products for agriculture is an urgent task.

The papers [8,9] present the results of thermodynamic modeling of the behavior of arsenic by construct-

ing diagrams of partial pressures and potential-pH in a manganese-containing system, as well as deposition of arsenic by manganese (IV) oxide using probabilistically determined experiment planning, using a five-factor matrix at four levels.

In this work, the targeted extraction of arsenic by manganese (IV) oxide in the form of arsenate is substantiated based on the dependence of the deposition process on changes in the pH of the working medium.

OBJECT AND RESEARCH METHODS

The object of research is the copper electrolyte of Kazakhmys Corporation LLP, of the following composition, g/l: Cu - 34.87; H_2SO_4 - 120; As - 9.86, etc. The experiments were carried out using a five-factor matrix at four levels with pH control on a laboratory И-160 МИ ionometer. The following factors were chosen as the studied factors: precipitant dosing rate (PDR); the ratio of precipitant to arsenic (Mn:As); process temperature ($t, ^\circ C$); sulfuric acid concentration (H_2SO_4 , g/l); duration of the experiment (τ /min).

Quantitative data for arsenic were determined on a microwave plasma atomic emission spectrometer (MP-AES).

The study of local elemental composition of the sample obtained during the deposition of arsenic from a copper electrolyte with manganese (IV) oxide was performed on a scanning electron microscope with a TESCAN Mira3 Schottky cathode equipped with an X-Act energy-dispersive microanalysis system (Oxford Instruments). The measurements were carried out in high vacuum at an accelerating voltage of 20 kV.

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X-ray diffraction studies of the samples were carried out on a BRUKER AXS D2 Phaser diffractometer (CuK α radiation, X-ray tube operation mode 30 kV, 15 mA, reflection geometry, high-speed energy-dispersive detector DTEX/ULTRA) with programs for EVA phase analysis, quantitative and structural analysis TOPAS and databases data of ICDD crystal structures. The survey was carried out in the range of angles 2 θ from 5 to 1000, the detector step was 0.02 $^\circ$ 2 θ , the time at the point was 0.5 s. The preparation of samples for research was carried out by firing at 500 $^\circ$ C.

RESEARCH RESULTS AND DISCUSSION

The pH analysis of the working solutions after the separation of the solid phase (Table 1) states the fact of an increase in the degree of arsenic deposition (α_s) with an increase in the acidity of the solution, which is important for organizing the selective separation of arsenic from the copper electrolyte. This also confirms our assumption that the formation of manganese arsenate occurs at low pH values of the solution and is the result of parallel reactions of the interaction of sulfate ions with manganese ions with the formation of a sulfate complex, the interaction of the manganese sulfate complex with arsenate ions with the formation of manganese hydrogen arsenate, the transition of hydroarsenate to manganese arsenate.

The obtained partial dependences of the pH of the tested solutions on the studied factors are given in Table 2 and graphically reflected in Figure 1.

Table 1 pH values of test solutions

No	PDR (x_1)	Mn:As (x_2)	t/ $^\circ$ C (x_3)	$C_{H_2SO_4}$ /g/l (x_4)	τ /min (x_5)	pH	α_s , As /%
1	1	1,0	25	120	15	0,45	47,25
2	1	1,5	40	150	30	0,23	55,80
3	1	2,0	50	175	45	0,11	50,40
4	1	2,5	60	200	60	0,09	51,95
5	2	1,0	40	175	60	0,11	46,80
6	2	1,5	25	200	45	0,01	48,70
7	2	2,0	60	120	30	0,03	66,00
8	2	2,5	50	150	15	0,06	72,40
9	3	1,0	50	200	30	0,04	46,40
10	3	1,5	60	175	15	0,03	61,30
11	3	2,0	25	150	60	0,02	27,60
12	3	2,5	40	120	45	0,13	52,00
13	4	1,0	60	150	45	0,1	45,40
14	4	1,5	50	120	60	0,13	31,50
15	4	2,0	40	200	15	0,08	52,85
16	4	2,5	25	175	30	0,07	64,40

Table 2 Selection for constructing partial dependences of the pH of the solution on the factors under consideration during the deposition of arsenic by manganese oxide

Factors		Levels of factors				Average value (geometr.)
		1	2	3	4	
x_1	α_s	0,18	0,04	0,04	0,09	0,07
x_2	α_s	0,12	0,05	0,05	0,08	0,07
x_3	α_s	0,05	0,13	0,08	0,05	0,07
x_4	α_s	0,12	0,07	0,07	0,04	0,07
x_5	α_s	0,09	0,07	0,06	0,07	0,07

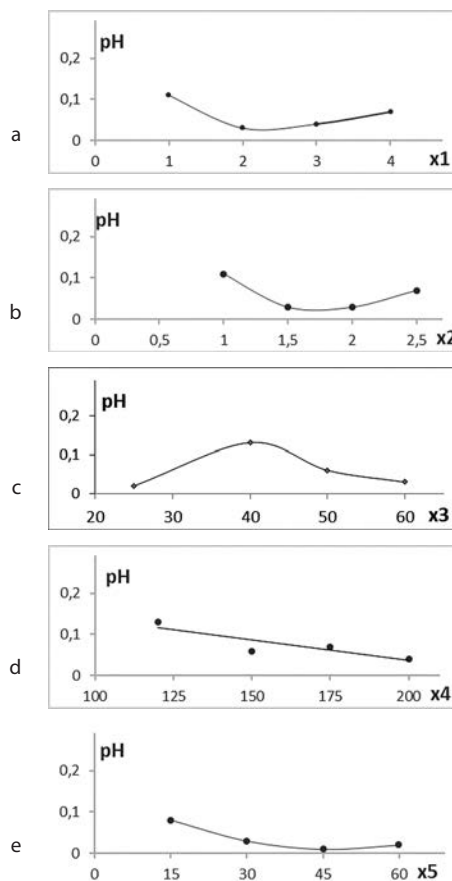


Figure 1 Partial dependences of the pH of solutions on the factors under study: x1-the multiplicity of the dosage of the precipitant (a), x2-the Mn:As ratio (b), x3-temperature, $^\circ$ C (c), x4-sulfuric acid content, g/l (d), x5-process τ /min (e)

The average values of the degree of arsenic deposition were used to search for an approximating function with the calculation of the correlation coefficient and significance (Table 3).

The generalized formula of the obtained mathematical model of dependences of solution pH on process conditions was calculated

(Protodyakonov's equation):

$$\alpha = \frac{0,0153e^{2,461X_1} X_1^{-5,8} \cdot 0,002e^{4,12X_2} X_2^{-7,17} \cdot 1,29 \cdot 10^{-11}}{2,605 \cdot 10^{-5}} \cdot \frac{e^{-0,214X_3} X_3^{8,53} (0,229 - 0,00094X_4) \cdot 1,084e^{0,08} X_5^{-1,07}}{2,605 \cdot 10^{-5}}$$

The type of average used is geometric. $R = 0,974$, $t_R = 59,779$.

In accordance with Figure 1 (a,b) the curve of dependence of the degree of extraction of arsenic on the dosing ratio, the Mn:As ratio passes through a minimum. This is due to the complexity of the formation of manganese arsenate. accompanied by the processes of adsorption and desorption of arsenic compounds in the bulk of the solid phase. Competing side reactions are the formation of manganese sulfate and the reduction of manganese (IV) oxide to manganese (III) oxide (Figure 2). The reduction of a part of Mn^{4+} to Mn^{3+} is explained by the

Table 3 **Correlation coefficients (R) and their significance (t_R) for particular dependences of the degree of arsenic deposition by manganese (IV) oxide**

Function	R	t _R	Significance
$\alpha(x_1) = 0,0153e^{2,461 \cdot X_1 - 5,801}$	1	100	Significant
$\alpha(x_2) = 0,00196e^{4,117 \cdot X_2 - 7,168}$	0,9928	97,854	Significant
$\alpha(x_3) = 1,289 \cdot 10^{-11} e^{-0,2139 \cdot X_3 + 8,527}$	0,9254	9,111	Significant
$\alpha(x_4) = 0,2287 - 0,0009414x$	0,9287	9,551	Significant
$\alpha(x_5) = 1,084e^{0,0275 \cdot X_5 - 1,07}$	0,9889	63,348	Significant

presence of trivalent arsenic up to 5 % in the copper electrolyte and its oxidation according to the reaction:

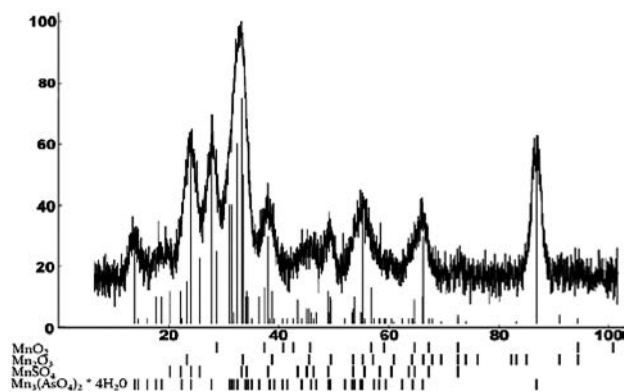
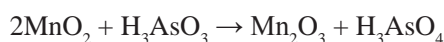


Figure 2 X-ray of solid product

The measured spectra of X-ray spectral EMF analysis are shown in Figure 3. The following elements were recorded on the energy dispersive spectra of the studied sections of the sample: Mn, O, As, S, Cu, Sb, Fe, Ca. The performed mapping (distribution of elements over the study area) shows the most dense distribution of Mn and As metals.

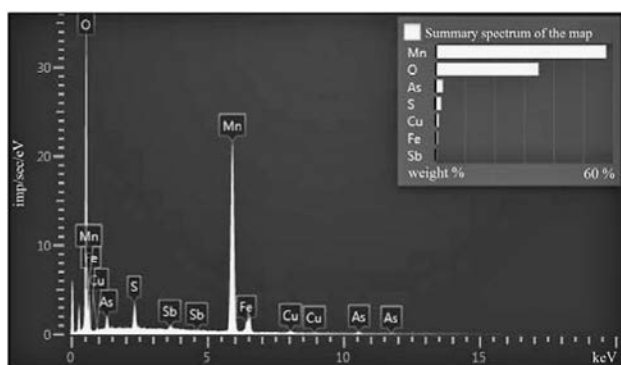


Figure 3 X-ray spectrum of an arsenic-containing sample

A comparative analysis of the X-ray diffraction patterns obtained by us (Figures 2 and 3) of a solid precipitate formed during the deposition of arsenic by manganese (IV) oxide with the data presented in [10] confirmed the presence of manganese arsenate ($\text{Mn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$) in the test sample.

CONCLUSION

The formation of manganese arsenate in an acidic medium is a complex process, where the interaction re-

actions of manganese and arsenic are accompanied by adsorption and desorption of arsenic compounds in the bulk of the solid phase.

X-ray spectral EMF analysis showed the densest distribution of Mn and As metals in the precipitates obtained.

Identification of precipitates obtained during the deposition of arsenic by manganese (IV) oxide by X-ray diffraction confirmed the formation of manganese arsenate ($\text{Mn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$) during the purification of copper electrolyte.

The possibility of selective isolation of manganese arsenate from acid waste copper solutions into a solid phase, which will become a potential raw material for the production of anthelmintic agents, has been established.

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Note: Akbota Iskakova is responsible for English language, Almeta, Kazakhstan