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Investigation of the process of precipitation of arsenic from copper electrolyte with manganese oxide (IV)

The work is aimed at researching the process of depositing arsenic from copper electrolyte with manganese oxide (IV) using the method of stochastic determined design of experiments on four levels. The chosen factors are: the frequency of dispensing of the precipitant; the ratio of precipitant to arsenic; the temperature of process; concentration of sulfuric acid; duration of experiment. Analysis of the partial dependencies of arsenic deposition showed that the increase in the amount of precipitant and the duration of the experiment had a significant influence on the course of the process. IR spectroscopy of precipitation showed the presence of arsenate ions AsO_4^{3-} in them. The kinetic curve of the differential-thermal analysis of the solid sediment characterizes the process of its destruction as a step-wise process — the removal of crystallized water (from 250 °C to 350 °C), the decomposition of manganese hydroarsenate (from 470 °C to 630 °C) and manganese arsenate (from 690 °C to 900 °C). It is established that the process of formation of manganese arsenate is a result of parallel reactions of interaction of sulfate ions with manganese ions with the formation of a sulfate complex, interaction of the manganese sulphate complex with arsenate ions with the formation of manganese hydroarsenate, and the transition of hydroarsenate to manganese arsenate.

Keywords: copper electrolyte, manganese oxide (IV), arsenic; arsenates, hydroarsenate, manganese arsenate, stochastic determined design of experiments.

Introduction

The deterioration in the quality of raw materials, the need to ensure the selective extraction of all its valuable components and the toughened requirements for environmental protection have revealed huge volumes of various technological solutions that require processing. Technological solutions of electrolytic refining of copper have a great interest. They contain significant amounts of copper and nickel sulfates, sulfuric acid, arsenic, antimony and other components of the copper electrolyte. Decrease in the quality of cathode copper due to excessive accumulation of arsenic in the electrolyte, as well as high toxicity of arsenic compounds, determine arsenic as one of the dangerous impurities of copper electrolyte.

In works [1, 2] pyrolusite, which is a mineral based on manganese oxide (IV), is used as an oxidizer of trivalent arsenic to pentavalent. Considering that manganese arsenate is a compound with a low solubility value, the role of manganese as an arsenic precipitant in the form of arsenates from copper electrolyte, where it is found both in anionic and cationic forms, has become a matter of interest.

According to the literature data [3, 4], during the electrorefining of copper from the anode, 60–80 % of arsenic passes into the electrolyte, the rest goes to the sludge. The distribution of arsenic between the electrolyte and sludge, as well as its form of stay in solution depends on electrolyte's composition and the mode of electrolysis. For example, the presence of As and Sb with different valencies in the electrolyte leads to the precipitation of antimony-arsenic (Sb^{3+} - As^{5+}) and antimony-arsenic (Sb^{5+} - As^{3+}) precipitates. The introduction of zinc sulphide into the strongly acid copper electrolyte [5] led in precipitation of 40 % of arsenic in the form of sulfides.

The physicochemical analysis of multicomponent systems with the participation of arsenic, antimony, and bismuth carried out by us [6, 7] showed that these elements in the form of arsenates, antimonates and bismuths are stable compounds, both in the water and in the oxidizing and reducing media.

Materials and methods

A technological solution of JSC «Kazakhmys» (Balkhash town) with the content of components is used to investigate the process of precipitation of arsenic from copper electrolyte, g/l: Cu — 50,7; Ni — 7,75; As — 7,4; H_2SO_4 — 200,0 and others.

Experiments on the deposition of arsenic from a copper electrolyte were carried out in a reaction thermostated cell with a capacity of 150 cm³. A sample of manganese oxide (IV), taken in the required

amount, was injected into a solution of a copper electrolyte with a predetermined temperature. The temperature of the experiments was maintained with an accuracy of ± 2 °C. The deposition process was carried out with continuous mixing with the duration dictated by the condition of the experimental matrix. After a predetermined time, the precipitate was separated by filtration, the residual arsenic content was determined in the filtrate by the bichromate method after separation of potassium hypophosphite from the hydrochloric acid solution [8]. The solid precipitates were subjected to differential thermal and IR spectroscopy using LABSYSTMEVOTG, DTA, DSC 1600 °C, FSM 1201 Infrared Fourier spectrometer.

Investigation of the process of arsenic precipitation from copper electrolyte with manganese oxide (IV) was carried out by the method of probabilistic determination of the experiment [9, 10] at four levels. The following factors were chosen as factors: the multiplicity of precipitator dosage (MPD) — this is the number of portions into which the planned weight of the precipitant is divided; the ratio of precipitant to arsenic (Mn:As) — this ratio of the required weight parts of the precipitant to the weight part of arsenic (this value is not calculated mathematically and has no dimension); process temperature (t , °C); the concentration of sulfuric acid (H_2SO_4 , g/l); duration of experiment (time, min). For planning the experiment, Table 1 was used.

Table 1

Levels of variable factors in the precipitation of arsenic by manganese oxide (IV)

No. factor	Factor	Definition	Level of factors			
			1	2	3	4
1	MPD	X_1	1	2	3	4
2	Mn:As	X_2	1	1.5	2	2.5
3	t , °C	X_3	25	40	50	60
4	H_2SO_4 , g/l	X_4	120	150	175	200
5	time, min	X_5	15	30	45	60

Results

Using the most common matrix of the probabilistic-deterministic plan of the five-factor experiment, a plan was drawn up (Table 2), in which the level numbers are replaced with their values from Table 1. The column on the right includes the results of the extraction of arsenic (α_e , As) into the precipitate.

Table 2

The plan-matrix layout and the results of the five-factor experiment at four levels of arsenic precipitation with manganese oxide (IV)

No. of experiment	MPD (x_1)	Mn:As (x_2)	t , °C (x_3)	H_2SO_4 , g/l (x_4)	Time, min (x_5)	α_e , As %
1	1	1	25	120	15	47.25
2	1	1.5	40	150	30	55.80
3	1	2	50	175	45	50.40
4	1	2.5	60	200	60	51.95
5	2	1	40	175	60	46.80
6	2	1.5	25	200	45	48.70
7	2	2	60	120	30	66.00
8	2	2.5	50	150	15	72.40
9	3	1	50	200	30	46.40
10	3	1.5	60	175	15	61.30
11	3	2	25	150	60	27.60
12	3	2.5	40	120	45	52.00
13	4	1	60	150	45	45.40
14	4	1.5	50	120	60	31.50
15	4	2	40	200	15	52.85
16	4	2.5	25	175	30	64.40

In order to construct particular dependences of the degree of arsenic deposition with manganese (IV) oxide, the results of the experiments for each factor were averaged using the geometric mean (Table 3).

Table 3

Sampling for the construction of particular dependencies of the degree of arsenic deposition by manganese oxide (IV) in solutions from the considered factors

Factors		Levels of factors				The mean α_c (geometric)
		1	2	3	4	
x_1	α_c	51.35	58.48	46.83	48.54	51.0
x_2	α_c	46.46	49.33	49.21	60.19	
x_3	α_c	46.99	51.86	50.18	56.16	
x_4	α_c	49.19	50.30	55.73	49.98	
x_5	α_c	58.45	58.15	49.13	39.46	

The average values of the arsenic deposition were used to find the approximating function with calculation of the correlation coefficient and significance (Table 4).

Table 4

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

Function	R	t_R	Significance
$\alpha(x_1) = 56.36 \cdot 0.96x_1$	0.1	0.1	Insignificant
$\alpha(x_2) = 38.93 \cdot 1.17x_2$	0.79	2.98	Significant
$\alpha(x_3) = 42.24 \cdot 1.004x_3$	0.83	3.70	Significant
$\alpha(x_4) = -887.7/x_4 \cdot 57.01x_4$	0.22	0.33	Insignificant
$\alpha(x_5) = 0.44x_5 + 67.795$	0.1	0.1	Insignificant

The statistical description of particular dependences is represented by the generalized Protodyakonov equation. For the precipitation process of arsenic with manganese (IV) oxide:

$$Y_p = (38.93 \cdot 1.17x_2) \cdot (42.24 \cdot 1.004x_3) \cdot 51.0^{-2}$$

The correlation coefficient of equation $R = 0.80$, and its significance $t_R = 7.86$.

Figure 1 shows the graphical dependencies of the degree of arsenic deposition on all studied factors.

An increase in the multiplicity of precipitator dosage (MPD) to 4 (Fig. 1, a) leads to a decrease in the degree of arsenic precipitation, which is associated with an increase in the rate of the competing manganese sulfate formation reaction.

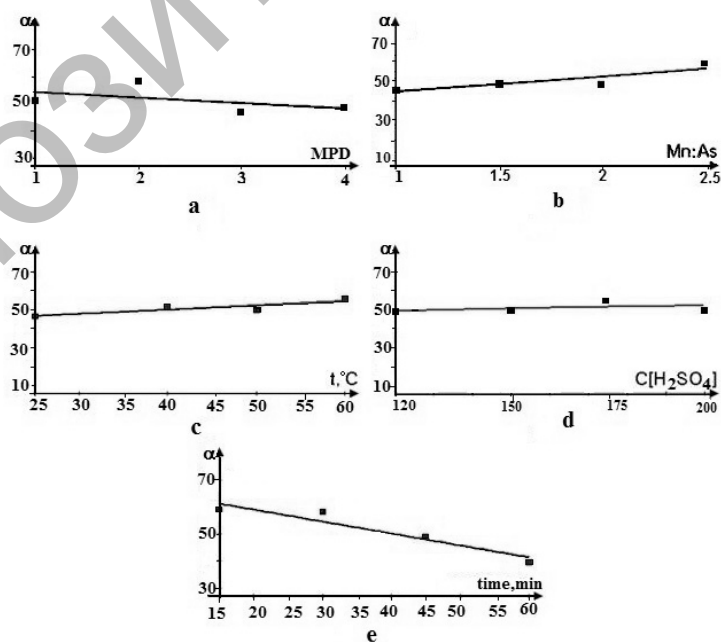


Figure 1. Particular dependencies of arsenic deposition on: the multiplicity of precipitator dosage (a), the ratio of Mn:As (b), temperature (c), the content of sulfuric acid (d), the duration of the experiment (e)

The amount of precipitator (Fig. 1, *b*) positively affects the degree of extraction of arsenic in the sediment, which confirms the sorption nature of the process of its deposition. Factors such as temperature and sulfuric acid concentration (Fig. 1, *c*, *d*) do not significantly influence the transition of arsenic to the solid phase, due to the complexity of the internal processes of formation of the arsenic-containing precipitate. Similar processes were analyzed in [11], where the formation of hydrated complexes of arsenic with iron in acidic solutions was studied.

With an increase in the time of the experiment (Fig. 1, *e*), the decrease in the degree of arsenic precipitation when using manganese oxide (IV) is observed more significantly by 5–10 % every 15 minutes. This is due to the desorption of the cationic form of arsenic from the surface of the precipitant.

To confirm the results of our experiments on the deposition of arsenic by manganese oxide (IV) in the form of arsenate, we analyzed the IR spectrum of the solid precipitate of experiment 8 (Table 2). Analyzing the literature sources [12, 13] in which the data on IR absorption spectra of metal arsenates are given, it is possible to compare data given by the authors with the IR spectrograph obtained by us (Fig. 2).

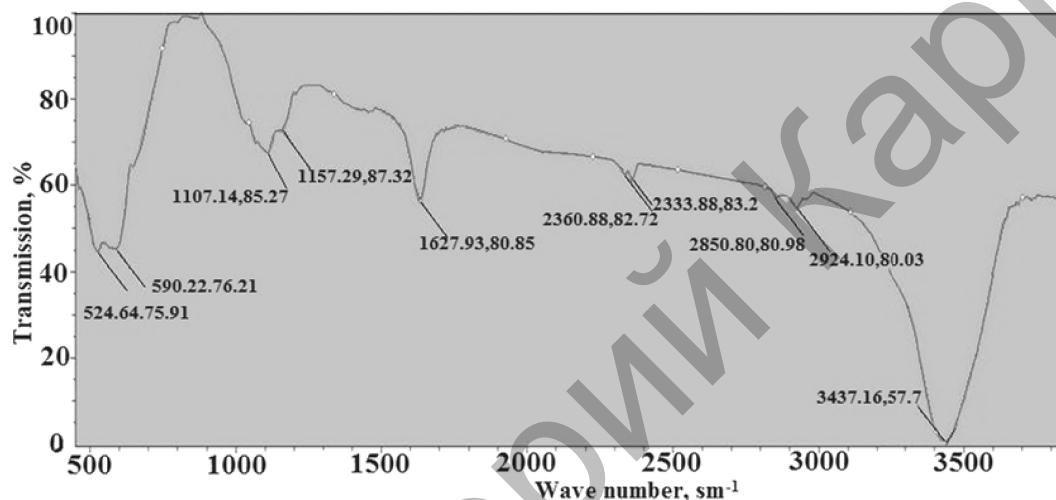


Figure 2. IR spectra of the solid precipitate of the arsenic precipitation experiment with manganese oxide (IV).

The absorption bands at 500–600 cm^{-1} indicate vibrations of the (As-O-As) bridge, and at 800–900 cm^{-1} — (As-O) bridge, i.e. for the presence of manganese arsenate ($\text{Mn}_3(\text{AsO}_4)_2 \cdot 7\text{H}_2\text{O}$) in the investigated solid sediments. In the same intervals, absorption bands of manganese hydroarsenates are observed [12]. The presence of maxima in the spectra in the interval 1130–1080 cm^{-1} indicates the content of manganese sulfate in the composition of the analyzed samples.

The authors of [13] established that manganese hydrosarsenate ($\text{MnHAsO}_4 \cdot 4\text{H}_2\text{O}$) is stable in acidic aqueous solutions in the temperature range 25–75 °C. It is also noted that for manganese phosphates, as for manganese arsenates, acid salts are in equilibrium with strongly acidic solutions.

The $\text{AsO}_4^{3-} \cdot 7\text{H}_2\text{O}$ arsenate ion is characterized by an intense absorption band at 590 cm^{-1} , due to the low symmetry of the $\text{AsO}_4^{3-} \cdot n\text{H}_2\text{O}$ ions. In addition to the intense absorption band of the $\text{AsO}_4^{3-} \cdot 7\text{H}_2\text{O}$ ion, the author [14] presents data on the IR absorption spectra of metaarsenates characterized by the presence of complex intense absorption bands of $\nu(\text{AsO})$ stretching vibrations of the AsO bonds in the 600–850 cm^{-1} region.

Thus, by comparing the above data on the absorption spectra of arsenates with the obtained spectrogram, we confirmed the presence of arsenate ions (AsO_4^{3-}) in the analyzed sample.

To study the kinetics of the process of arsenic precipitation with manganese oxide (IV), a differential thermal analysis of the solid precipitate obtained under the following experimental conditions was carried out: MPD-3; Mn:As = 2.5:1; t , °C — 40; $C(\text{H}_2\text{SO}_4)$, g/l — 120; time, min. — 45.

As can be seen from Figure 3, the kinetic curve consists of three stages, and each of the stages is represented by an S-shaped line. This form is explained by the fact that at first the reaction rate increases due to an increase in the rate constant by the Arrhenius equation, and then the rate of destruction decreases in connection with the completion of the decomposition of the test sample.

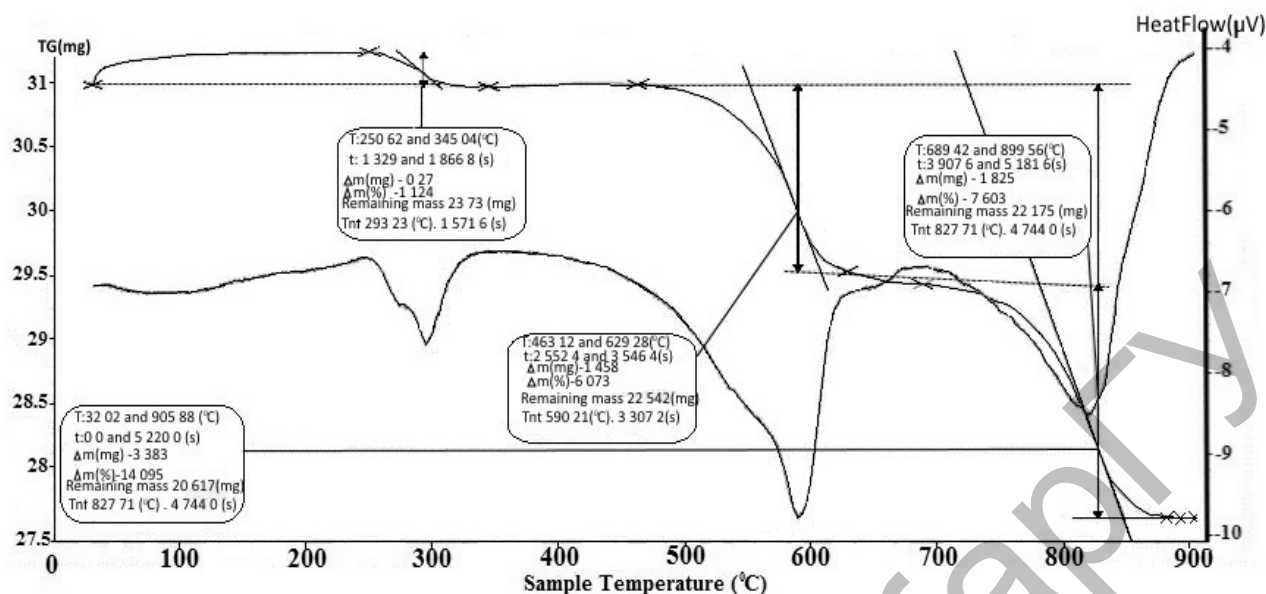


Figure 3. Curve of volatile substances during thermal destruction of solid arsenic-containing precipitate.

Further, the kinetic curve of thermal destruction was subjected to mathematical processing by the method [15]. The data obtained are presented in Table 5.

Table 5

Results of mathematical processing of the kinetic curve of thermal destruction of solid arsenic-containing precipitate

No.	τ , min	m , mg	$m_{i, \max} - m_i$, mg	r_i , mg/min	$r_i / (m_{i, \max} - m_i)$	$-\ln[r_i / (m_{i, \max} - m_i)]$	t , °C	$10^3 / T$, K ⁻¹
1	—	0	—	—	—	—	35	3.25
2	22.10	0	0.27	0.02	0.08	2.53	250	1.91
3	23.99	0.05	0.22	0.04	0.18	1.71	270	1.84
4	25.89	0.14	0.12	0.05	0.42	0.87	290	1.78
5	27.79	0.24	0.025	0.03	1.33	-0.29	310	1.72
6	29.69	0.27	0.001	0.003	3.40	-1.22	330	1.66
7	31.59	0.28	—	—	—	—	350	1.61
8	43.22	0	1.46	—	—	—	470	1.35
9	45.18	0.02	1.43	0.02	0.02	4.09	490	1.31
10	47.14	0.08	1.38	0.04	0.03	3.51	510	1.28
11	49.11	0.17	1.28	0.07	0.05	2.97	530	1.25
12	51.12	0.33	1.12	0.10	0.09	2.44	550	1.22
13	53.13	0.57	0.88	0.16	0.18	1.69	570	1.19
14	55.13	0.99	0.46	0.20	0.44	0.83	590	1.16
15	57.14	1.36	0.09	0.12	1.23	-0.21	610	1.13
16	59.18	1.46	—	—	—	—	630	1.11
17	65.18	0	1.83	—	—	—	690	1.04
18	68.18	0.04	1.78	0.02	0.01	4.34	720	1.01
19	71.20	0.14	1.69	0.06	0.03	3.41	750	0.98
20	74.20	0.36	1.46	0.12	0.08	2.54	780	0.95
21	77.30	0.85	0.98	0.19	0.20	1.62	810	0.92
22	80.30	1.55	0.27	0.16	0.59	0.53	840	0.90
23	83.30	1.80	0.02	0.04	1.88	-0.63	870	0.87
24	86.40	1.83	—	—	—	—	900	0.85

As can be seen from the obtained results, the first stage of thermal destruction takes place in the temperature range from 250 °C to 350 °C, then the change in mass in the temperature range from 350 °C to

470 °C is negligible. The second stage proceeds in the temperature range from 470 °C to 630 °C, the third stage — from 690 °C to 900 °C.

Further, after mathematical processing of the results, graphs of the dependences $-\ln[r_i/(m_{i, \max} - m_i)]$ from $10^3/T$ were plotted (Fig. 4).

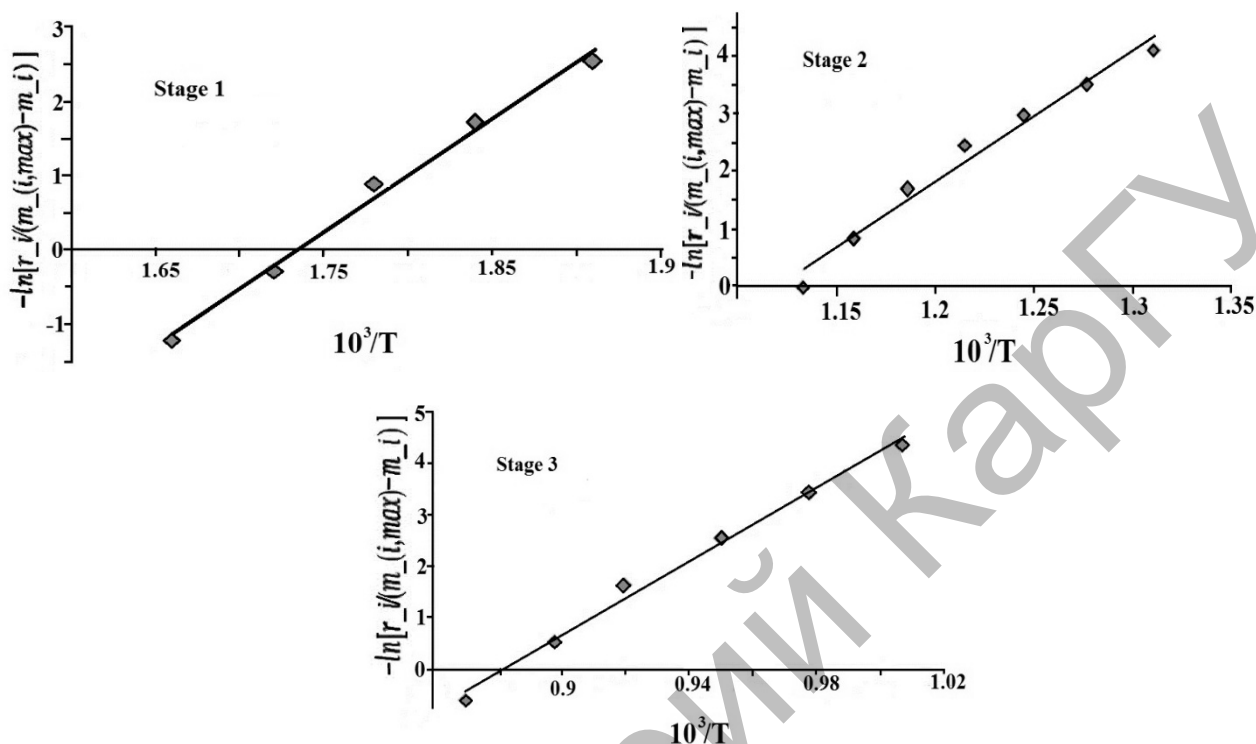


Figure 4. Linearization of the temperature dependence of the rate of thermal destruction of arsenic-containing precipitate

The processing of the obtained direct lines of dependencies of all three stages yielded the following results:

- the first stage refers to the diffusion region — the value of the activation energy is 15.28 kJ/mol;
- the value of the activation energy of 24.81 kJ/mol and the linear dependence of the total arsenic deposition rate on temperature (Fig. 4) suggest the commensurability of the diffusion rate and chemical reaction of the second stage, and indicate the course of the process in the transition region, which is characteristic of the mixed kinetics of heterogeneous processes;
- the third stage refers to the kinetic region — the value of the activation energy is 37.43 kJ/mol.

For the first stage, flowing in the range from 250 °C to 350 °C, corresponds a peak with a temperature value of 300 °C, while the crystallization water is removed.

For the second stage, flowing in the range from 470 °C to 630 °C, there corresponds a peak with a temperature of 600 °C, corresponding to the decomposition of manganese hydrogenarsenate according to the source [16] and further decomposition of manganese oxide (IV) [17].

The third stage, running in the range from 690 °C to 900 °C, corresponds to a peak with a temperature of about 840 °C, at which the process of decomposition of manganese arsenate proceeds [16, 18].

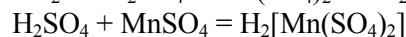
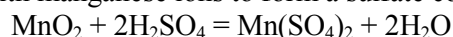
Conclusion

From the analysis of the experimental data on the process of precipitation of arsenic from copper electrolyte with manganese oxide (IV), follows that the highest indices of arsenic extraction into sediment (66.0–72.4 %) are achieved with a relatively short duration of the experiment (15–30 min) and large ratios of precipitant to arsenic (2.0–2.5:1).

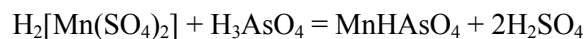
Analysis of the partial dependencies of arsenic deposition from copper electrolyte with manganese oxide (IV), obtained as a result of five-factor experiments (factors: multiplicity of the precipitator dosage, Mn:As ratio, temperature, sulfuric acid concentration, duration of the experiment), the results of differential

thermal analysis and IR spectroscopy of the obtained solid precipitates showed the complexity of the formation of manganese arsenate, which can be represented as a result of parallel reactions:

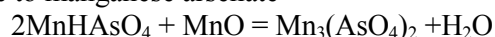
- interaction of sulfate ions with manganese ions to form a sulfate complex



- interaction of manganese sulfate complex with arsenate ions with formation of manganese hydroarsenate



- transition of hydroarsenate to manganese arsenate



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Мыс электролитінен марганец (IV) тотығымен күшәланы тұндыру үрдісін зерттеу

Мақала экспериментті төрт деңгейлі ықтималды-детерминирленген жоспарлау әдісті қолдануымен марганец (IV) тотығымен мыс электролитінен күшәланы бөліп алу үрдісін зерттеуге бағытталған. Таңдалған факторлар болып келесілер табылады: тұндырғышты мөлшерлеу дәрежесі, тұндырғыштың күшәлаға қатынасы, үрдістің температурасы, күкірт қышқылының концентрациясы, эксперименттің ұзақтығы. Күшәланы тұндырудың жеке тәуелділіктерінің сараптамасы бойынша тұндырғыштың мөлшері мен эксперименттің ұзақтығы ұлғаюы үрдістің өтуіне зор әсері көрсетілді. Қатты тұнбаның ИҚ-спектроскопия нәтижелері тұнбада AsO_4^{3-} арсенат-иондарының бар екендігін көрсетті. Қатты тұнбаның дифференциалды-термиялық талдауының кинетикалық сызығы оның ыдырау үрдісі сатылап өтетінін сипаттайды — кристалданған судың бөлінуі (250 °C бастап 350 °C дейін), марганецтің гидроарсенаты ыдырауы (470 °C бастап 630 °C дейін) және де марганец арсенатының ыдырауы (690 °C бастап 900 °C дейін). Марганец арсенатының түзілуі параллельді реакцияларының нәтижесі болатыны анықталған: сульфат-иондарының марганец иондарымен әрекеттесу нәтижесінде сульфаты комплексін түзілуі, марганец сульфаты комплексінің арсенат иондарымен әрекеттесу барысында марганецтің гидроарсенатын түзілуі және дегидроарсенаттың марганец арсенатына өзгеруі.

Кілт сөздер: мыс электролиті, марганец (IV) тотығы, күшәла, арсенаттар, гидроарсенат, марганец арсенаты, эксперименттің ықтималды-детерминирленген жоспарлауы.

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Исследование процесса осаждения мышьяка из медного электролита оксидом марганца (IV)

Статья направлена на исследование процесса осаждения мышьяка из медного электролита оксидом марганца (IV) с использованием метода вероятностно-детерминированного планирования эксперимента на четырех уровнях. Выбранными факторами являются: кратность дозирования осадителя, отношение осадителя к мышьяку, температура процесса, концентрация серной кислоты, продолжительность эксперимента. Анализ частичных зависимостей осаждения мышьяка показал, что увеличение количества осадителя и продолжительность эксперимента оказали значительное влияние на ход процесса. ИК-спектроскопия твердого осадка показала присутствие в нем арсенат-ионов AsO_4^{3-} . Кинетическая кривая дифференциально-термического анализа твердого осадка характеризует процесс его разложения как ступенчатый процесс — удаление кристаллизованной воды (от 250 °C до 350 °C), разложение гидроарсената марганца (от 470 °C до 630 °C) и разложение арсената марганца (от 690 °C до 900 °C). Установлено, что процесс образования арсената марганца является результатом параллельных реакций: взаимодействия сульфат-ионов с ионами марганца с образованием сульфатного комплекса, взаимодействия комплекса сульфата марганца с ионами арсената с образованием гидроарсената марганца и переход гидроарсената в арсенат марганца.

Ключевые слова: медный электролит, оксид марганца (IV), мышьяк, арсенаты, гидроарсенат, арсенат марганца, вероятностно-детерминированное планирование эксперимента.

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