

PROCESSING OF CAKE OF MOLYBDENUM MINING AND METALLURGICAL PRODUCTION BY ELECTROOXIDATION IN CHLORIDE-CONTAINING SOLUTIONS

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Abstract

One of the types of technogenic metal-containing raw materials of Almalyk MMC JSC (Uzbekistan) is waste processing of molybdenite concentrate of previous years, based on nitric acid opening of sulfide concentrate: cakes stored in the tailings of the plant, allowing to some extent to increase the output of the plant's main products. In their composition, wt%: 4.1 Mo; 2.0 Fe, 3.87 S, 78.98 SiO₂, 5.26 CaO, others 4.79 (including Au 20-25 g/t). *Purpose:* development of technology for the extraction of Mo. Au, other components from molybdenum cakes by electrooxidation in hydrochloric acid medium. Interest in the method is caused by the modernization of hydrometallurgical technologies, due to the increase in environmental requirements for them, and also due to the emergence of new hydrometallurgical equipment. We used a two-chamber electrolysis plant for Mo-cake leaching, with a membrane, a direct current source, 20 A, generating active chlorine: hypochlorite ions at the anode. Mo(VI), Au(III), Cu(II) ions were analyzed by photocolometric and spectrometric methods (ICP - Agilent 7500 ICP MS). The concentration of NaClO was determined according to the State Standard 18190-72, free chlorine was determined by titration with methyl orange. The behavior of gold in Mo-cake in contact with hypochlorite ions is considered. The oxidation of Mo cakes in a hydrochloric acid medium by hypochlorite ions generated anode at the anode has been studied, the parameters of their electrooxidation have been calculated, and the leaching products have been studied. The method of electrooxidation, in the presence of HCl, on the basis of 3-factor planning of the experiment, regression equations were obtained. Checking their adequacy, according to the Fisher criterion, by comparing the calculated and experimental data on the degree of extraction of these metals, showed the adequacy of the proposed process models. A technology for the electrooxidation of molybdenum cake has been developed, which is an alternative to the existing scheme of oxidative roasting of molybdenite concentrate, followed by soda leaching of molybdenum from the cinder, with cyanide processing of cake for gold. It has been established that the electrooxidation of Mo-cakes makes it possible to process them efficiently, with through extraction of gold up to 90%, molybdenum - up to 72.6%.

Keywords: Sulfides, molybdenum, gold, cinder, cake

1. INTRODUCTION

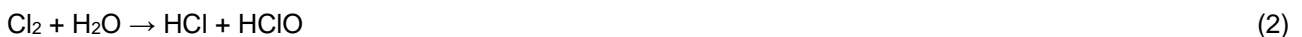
Previously, the production of molybdenum at the Scientific Production Association "Production of rare metals and hard alloys" (SPA PRM&HA) JSC "Almalyk MMC" was based on nitric acid opening of molybdenite concentrate (MoC) [1-3], later replaced by oxidative roasting followed by ammonia [4], then soda [5] by leaching the cinder [6]. The Mo cakes tailings [7] accumulated in the tailings are not yet processed, although the concentration of gold in them is higher than in gold-bearing ore [8] processed by oxidative leaching in solutions of cyanide, ferric chloride [9], and hypochlorite [10]. The last reagent, due to chemical instability, is anodically generated directly in the pulp (electrooxidation method) [11–12], in a 10% NaCl, H₂O, Na₂CO₃ medium [13]. For Mo concentrate, in this case, it is known that the product yield depended on: NaCl concentration, temperature, stirring, L:S (liquid:solid) ratio, pH, anode current density (hypochlorite

concentration), pH [14]. When the solution was acidified, $\text{MoO}_3 \cdot (\text{H}_2\text{O})_x$ precipitated (together with Re). The low emission of chlorine made it possible to consider the process environmentally friendly, and the leaching of Mo concentrate [15] is the result of its interaction with chlorine, and not with the anode current. However, Mo-cake, sharply depleted in Mo, is more attractive only as a gold-bearing raw material, for which it is expedient to replace Na_2CO_3 , as a Mo(VI) leaching agent, with HCl, as an agent leaching Au^{3+} ions. It should be noted that interest in the electrooxidative processing of Au-, Mo-containing raw materials [16] is caused by the modernization of hydrometallurgical technologies, due to increased environmental requirements for them, and also due to the emergence of new hydrometallurgical equipment.

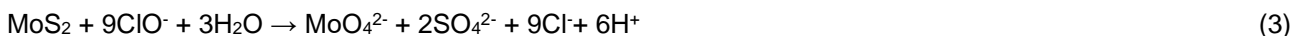
Purpose: Evaluation of the efficiency of Mo-cake proc processing in hypochlorite hydrochloric acid electrolyte using the experimental design method.

2. RESULTS AND ITS DISCUSSION

During the electrolysis of chloride solutions, chlorine is released at the anode (1), which, upon hydrolysis, forms hypochlorous acid (2):



which is also a strong oxidizing agent (3):



it is possible to oxidize molybdenite MoS_2 directly with chlorine:



The task of the stage of work was to optimize the Mo-cake electrooxidation process in terms of the following parameters: anode current density i_a , concentration of sodium chloride, hydrochloric acid, L:S ratio, duration, solution-pulp temperature. It was performed using the *Matlab program* by planning a three-factor experiment with variation intervals: X_1 , X_2 , X_3 and calculating their effect on the extraction of Mo (Y_1 , %) and Au (Y_2 , %) into solution (**Table 1**), where:

X_1 – concentration of sodium chloride: 100-250 g/dm³;

X_2 – anode current density: 100-200 mA/cm²;

X_3 – concentration of hydrochloric acid: 10-100 g/dm³.

moreover, in view of the fact that Mo cake is a middling product poor in Mo, and dilution of the pulp with electrolyte (an increase in L:S value) is favorable from the point of view of increasing the completeness of the extraction of valuable components from it, but it is not economically feasible due to the increase in filtration costs, pulp pumping, electricity, then for the 3-factor experiment a fixed ratio L:S = 10:1 was chosen.

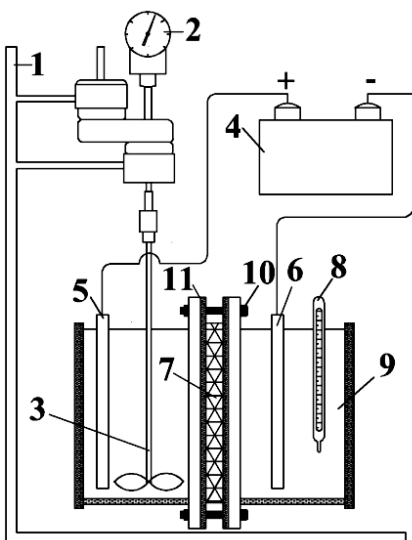


Figure 1 Plant for molybdenum cake leaching in hypochlorite-anodically generated solutions. *Designation:* 1 - stand, 2 - tachometer, 3 - stirrer, 4 - direct current source, 5 - anode, 6 - cathode, 7 - membrane, 8 - thermometer, 9 - electrolytic bath, 10 - bolt tie, 11 - teflon gasket

The regression equations for Mo (5) and Au(6) are calculated:

$$Y_1 = 72.26 + 2.381 X_1 + 5.701 X_2 + 8.594 X_3 \quad (5)$$

$$Y_2 = 58.266 + 3.188 X_1 + 4.273 X_2 + 11.851 X_3 \quad (6)$$

Analyzing the regression equations (5) and (6), we see that the extraction of molybdenum and gold in solutions was positively affected by all three factors, although to a different extent. Y_1 depended to the greatest extent on the concentration of hydrochloric acid X_3 , somewhat less on the anodic density current i_a (factor X_2): an increase in i_a led to an intensification of chlorine release, stimulating the mechanism (4) of MoS₂ oxidation by atomic chlorine.

For the extraction of Au (6), the growth of X_3 is more significant than X_3 in (5). Given that in a hypochlorite-chloride electrolyte, the electrooxidation of gold proceeds according to the reaction equation (7), the role of chloride ions is to shift its equilibrium to the right:



Table 1 Matrix of a three-factor experiment for Mo and Au leaching from Mo-cake in HCl solution, when generating hypochlorite in it, $\tau = 6$ h, samples initial weight is 100 g

Experiment No	Factors			Optimization parameters	
	X_1	X_2	X_3	Y_1	Y_2
1	+ 250	- 100	- 10	48.20	38.55
2	- 100	+ 200	- 10	65.16	52.10
3	- 100	- 100	+ 100	47.50	77.65
4	+ 250	+ 200	+ 100	72.83	80.10
5	- 100	+ 200	+ 100	66.21	85.73
6	+ 250	- 100	+ 100	50.70	75.00
7	+ 250	+ 200	- 10	68.45	48.00
8	- 100	- 100	- 10	45.25	35.25

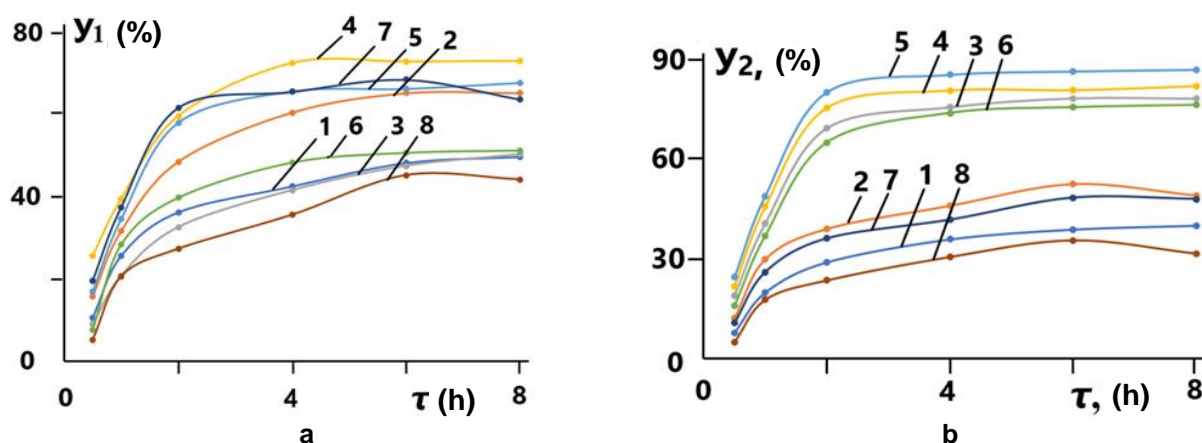


Figure 2 Kinetics of extraction of Mo (Y_1 , %) (a) and Au (Y_2 , %) (b) from hypochlorite-anodically generated solutions, composition (g/dm³): HCl 10.0-100.0; NaCl 25-250; in mode: i_a , (mA/cm²): 100-200; τ , hours: 0.5-8.0. *Designation:* curves: from 1 to 8, correspond to the values of Y_1 , Y_2 , in experiments No 1-8, at fixed values of τ , hours: 0.5; 1.0; 2.0; 4.0; 6.0; 8.0.

Due to the maximum value of the coefficient at the X_3 factor in (6), the HCl concentration makes the maximum contribution to the growth of the Y_2 value. A slightly lower value than in (6), the X_3 factor influenced the extraction of Mo (5). The presence of Fe(III) ions from the cake in the solution-pulp, in the form of chloride, as follows from (5), does not significantly affect the value of Y_1 . The larger value of the coefficient in front of X_2 in

(5) as compared to (6) indicates the predominance of the effect of the anode current density i_a on Mo leaching as compared to Au. The positive sign of the coefficients at X_1 in (5) and (6) indicates that an increase in the NaCl concentration increases the degree of extraction of Mo, Au from hypochlorite-chloride electrolytes by Mo-cake electrooxidation.

The next task was to study the kinetics of Mo, Au leaching. The data of **Figure 2** revealed the role of factors X_1 , X_2 , X_3 in the extraction of Mo (Y_1 , %), and Au (Y_2 , %) in leaching solutions, over time. There are two groups of curves: the first - No 4, 7, 5, 2; the second - No 1, 6, 3, 8 in **Figure 2a**; the first - No 5,4,3,6; the second - No 2, 7, 1, 8 in **Figure 2b**, respectively, of which the former correspond to the maximum values of Y_1 and Y_2 , and the latter correspond to the minimum values of Y_1 and Y_2 . The reason for such differences is the following. In **Figure 2a** the maximum Y_1 corresponds to large values of i_a ; in **Figure 2b** the Y_2 maximum corresponds to large values of the HCl concentration. The extraction rates of Mo (Y_1) and Au (Y_2) increased sharply for the first 2 hours, after which, in the subsequent period, up to 8 h, they changed little.

Table 2 Dependence of extraction degree, %: Mo (Y_1), Au (Y_2) on the concentration of HCl (X_3), at fixed: values L: S = 10:1; $\tau = 6$ h, $C_{NaCl} = 175$ g/dm³; $i_{an} = 150$ mA/cm²; $T = 25$ °C

Values	HCl concentration, g/dm ³							
	0.0	10.0	32.5	55.0	77.5	100.0	122.5	145.0
Encoding, X_3	-1.5	-1.0	-0.5	0.0	+0.5	+1.0	+1.5	+2.0
Calculation, Y_1	11.41	19.69	27.98	36.26	44.55	52.84	61.12	69.41
Experiment, Y_1 (avg.)	3.50	15.55	29.31	49.91	54.87	57.57	57.85	58.33
Relative error, Y_1 (%)	1.15	2.70	1.91	2.47	4.48	1.48	0.88	1.02
Calculation, Y_2	13.46	26.20	38.94	51.68	64.41	77.15	89.88	97.62
Experiment, Y_2 (avg.)	0.61	25.65	47.46	60.80	69.17	81.62	89.46	90.32
Relative error, Y_2 , %	3.43	1.56	1.17	0.57	0.74	0.87	1.07	0.77

The next task of the study was to assess the adequacy of models (5) and (6). It was performed by comparing the experimental data Y_1 (ex), Y_2 (ex) and data from the substitution of experimental conditions in (5) and (6) (**Table 2** and **Figure 3a, b, c**). The dependences of Y_1 (ex), Y_2 (ex) on the concentration of NaCl (**Figure 3a**), HCl (**Figure 3b**), i_a (**Figure 3c**) were obtained at fixed values of 2 of the 3 factors, with a variable 3th value, which varied in a wider range of variation than with mathematical planning (**Table 1**). **Figure 3a** shows a reduced level of Y_1 (ex) and Y_2 (ex), in comparison with the calculation. When moving to the lower boundary of the X_1 variation interval, the discrepancy between them increased. With an increase in the concentration of NaCl (**Figure 3a**) in the range: 25-138 g/dm³, an increase in Y_2 (ex) from 45.8 to 61.5% was observed, caused by the intensification of chlorine release and pulp saturation with it. But a further increase in X_1 led to a decrease in the concentration of Cl₂ in the solution and a drop in the recovery of Au.

Table 3 Dependence of extraction degree, %: Mo (Y_1), Au (Y_2) on i_a (X_2), at L:S=10:1; $\tau = 6$ h, $C_{HCl} = 55$ g/dm³; $C_{NaCl} = 175$ g/dm³; $T = 25$ °C

Values	Anode current density, i_a (mA/cm ²)								
	50	75	100	125	150	175	200	225	250
Encoding, X_2	-2.0	-1.5	-1.0	-0.5	0.0	+0.5	+1.0	+1.5	+2.0
Calculation, Y_1	33.01	38.82	44.63	50.45	56.26	62.07	67.88	73.70	79.52
Experiment, Y_1 (avg.)	25.57	39.33	46.65	53.57	59.81	66.03	70.733	71.85	72.63
Relative error, Y_1 (%)	2.93	1.62	1.46	0.96	1.39	1.02	1.01	0.10	0.62
Calculation, Y_2	30.30	35.57	40.84	46.11	51.38	56.65	61.92	67.18	72.46
Experiment, Y_2 (avg.)	20.60	31.45	42.50	55.35	60.73	62.50	62.80	63.20	63.30
Relative error, Y_2 (%)	2.88	1.91	1.58	0.98	1.74	1.49	0.78	0.88	0.73

The effect of i_a on $Y_1(\text{ex})$, $Y_2(\text{ex})$ (**Figure 3b**, **Table 3**) was considered: their monotonic increase with increasing i_a was established and at the lower boundary of the X_2 variation interval, a significant discrepancy between $Y_1(\text{ex})$, $Y_2(\text{ex})$ with the calculated data (with a lag of the first from the second), but when moving upwards within the interval, up to 200 mA/cm², the indicated discrepancy was leveled, then increased again. An increase in the HCl concentration increased the recovery of Au (**Figure 3c**, **Table 2**), both in accordance with the calculation and in the experiment. Moreover, in the absence of HCl in the pulp, $Y_1(\text{ex})$, $Y_2(\text{ex})$ are much less than the calculated ones and are minimal: 3.5% Mo and 0.5% Au, respectively.

An increase in the L:S index increased $Y_1(\text{ex})$, $Y_2(\text{ex})$ up to 70–80% (**Figure 3e**) only in the initial section, up to L:S= 10:1, but did not further increase the values of $Y_1(\text{ex})$, $Y_2(\text{ex})$: dilution of the pulp more than 10:1 did not cause a noticeable increase in the extraction of Mo and Au.

To check the adequacy of the obtained regression equations (5) and (6) in addition to the visual convergence of curves $Y_1(\text{ex})$ and $Y_2(\text{ex})$ with the calculated dependences (curves 1, 3), confirming their adequacy to each other, was of interest to compare the values of the residual and selected variances. The multiple correlation index reflects convergence: it takes into account the combined influence of factors on the result. Unlike the paired correlation coefficient, which can take negative values, the multiple index takes values from 0 to 1. Therefore, the correlation coefficient $r^*(X_i)$ (**Table 4**) cannot be used to interpret the nature of the relationship. The closer to each other the calculated Y_1 , Y_2 and the actual values of $Y_1(\text{ex})$ and $Y_2(\text{ex})$ (2.4), relative to the regression line, the smaller the residual variance and, therefore, the greater the value of the multiple correlation coefficient $r^*(X_1, X_2, X_3)$. Thus, with a value of r^* close to 1, the regression equation better describes the actual data and the factors X_1 , X_2 and X_3 have a greater effect on the result. With an r^* value close to 0, the regression equation does not describe the actual data well.

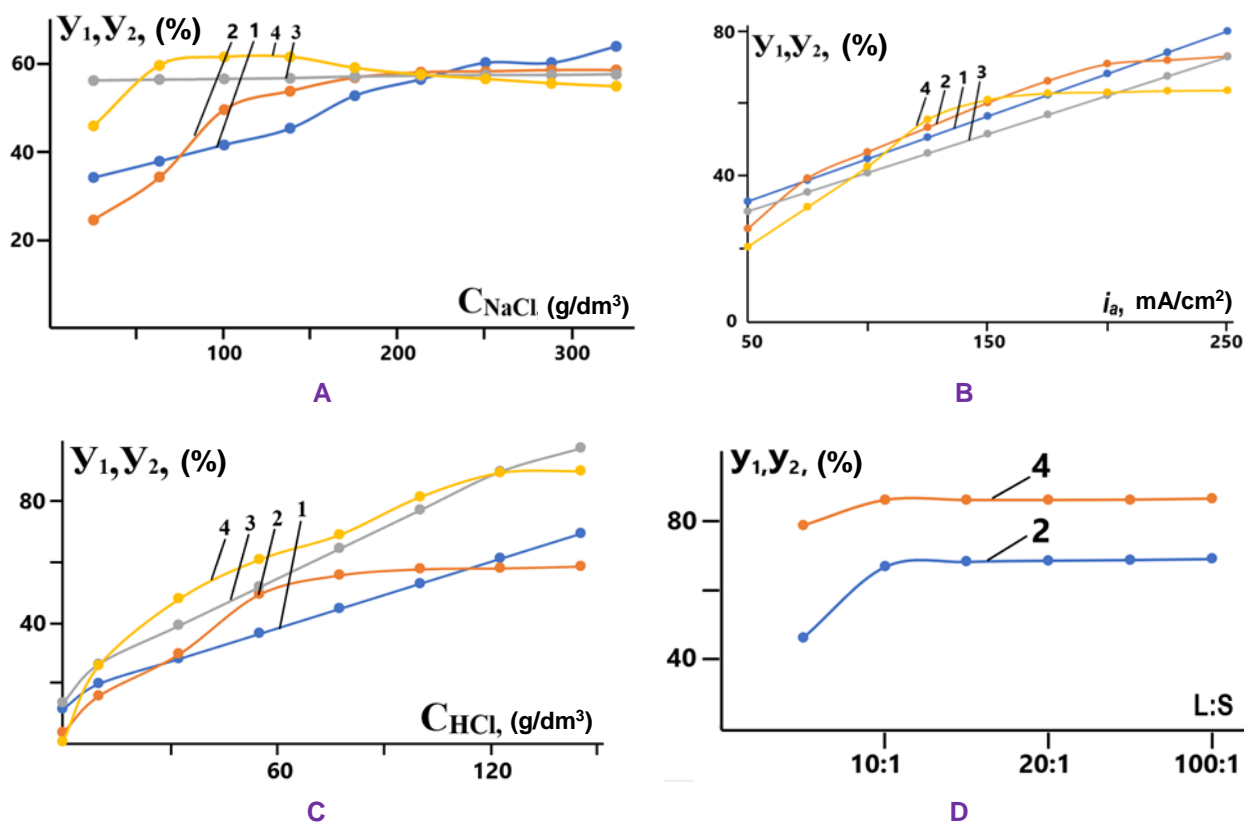


Figure 3 Dependences of extraction degree of Mo (1.2) and Au (3.4) on: C_{NaCl} (a), L:S=10:1; $i_a = 150$ mA/cm²; $\tau = 6$ h, $C_{\text{HCl}} = 55$ g/dm³; i_a (b); C_{HCl} (c); ratio L:S (d), at: $i_a = 200$ mA/cm²; $\tau = 6$ h, $C_{\text{NaCl}} = 100$ g/dm³; $C_{\text{HCl}} = 100$ g/dm³; $T = 25$ °C; V of the solution = 1 dm³; 1,3 - calculated data; 2,4 - experimental

Table 4 Correlation coefficients $r^*(X_i)$

Values	$r^*(X_1)$	$r^*(X_2)$	$r^*(X_3)$	$r^*(X_{av})$
Y_1	0.87	0.96	0.93	0.92
Y_2	0.96	0.97	0.98	0.97

The value of the correlation coefficient for (5) and (6) is close to unity, so the relationship between Y and X is close to linear: $Y_1 r^*_{av} = 0.92$, $Y_2 r^*_{av} = 0.97$. The adequacy variance was calculated for (5) and for (6). The adequacy of equations (5) and (6) was successfully checked by the Fisher criterion [17-18]. Statistical analysis showed that the mathematical models for (5) and (6) are adequate.

3. CONCLUSION

The efficiency of leaching of molybdenum and gold from the Mo-cakes of "Almalyk MMC JSC" in NaCl solutions was studied by electrooxidation in the presence of HCl, based on 3-factor experiment planning, regression equations were obtained. Checking their adequacy according to the Fisher criterion, by comparing the calculated and experimental data on the degree of extraction of these metals, showed the adequacy of the proposed models. It has been established that the electrooxidation of Mo-cakes makes it possible to process them efficiently, with through extraction of gold up to 90%, molybdenum - up to 72.6%. Optimal process conditions are: L:S = 10:1; T = 25 °C; $C_{HCl} = 100 \text{ g/dm}^3$; $C_{NaCl} = 100\text{-}138 \text{ g/dm}^3$; $i_a = 150\text{-}200 \text{ mA/cm}^2$; $\tau = 6 \text{ h}$. It is advisable to continue the study by extending the technology of Mo-cake leaching in NaCl solutions to other supporting electrolytes.

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