

KINETICS OF THE REAGENT OXIDATION OF MOLYBDENUM DISULFIDE BY NITRIC ACID

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Abstract

In the production of molybdenum compounds, JSC "Almalyk MMC" (Republic of Uzbekistan), for a long time used the method of nitric acid opening of raw material, replaced by the scheme of ammonia, then soda leaching of the cinder of the industrial product of molybdenum after oxidative roasting. In view of the improvement of technologies and equipment, there is an interest in environmentally friendly hydro-oxidative methods for their processing based on a strong oxidizer. Molybdenum disulfide in the composition of molybdenite concentrate is subject to surface passivation under the oxidizing conditions of processing the cinder of an industrial molybdenum product. The use of a strong oxidizing agent, nitric acid, makes it possible to overcome it in the hydrometallurgical process of oxidative leaching. The purpose of the study: to study the kinetics of the reaction of oxidative leaching of molybdenite concentrate of industrial production of molybdenum in nitric acid solutions, with the regeneration of nitric acid in them. Used samples of molybdenite concentrate, composition, wt%: 38.0 Mo; 2.5 Cu; 13.8 Fe; 0.7 Re; 0.009 P; 0.025 Sb; 0.05 WO₃; 25.2 S; 10.8 SiO₂; 0.42 H₂O; in solution, %: HNO₃ 0-25, H₂SO₄ 5, O₂. Kinetics of reagent oxidation of a sulfide mineral in nitric acid solutions, in the temperature range of 24-70 °C, at atmospheric pressure. was studied by the rotating disk method with control of the mass of the disk and the concentration of Cu(II), Fe(III), Mo(VI), Re(VII) ions in solutions. Kinetic measurements were performed on powder samples of Mo disulfide concentrate pressed into discs, 10 mm in diameter. Elemental analysis of samples was performed spectrometrically by methods of potentiometry, pH-metry, atomic absorption and optical emission (ICP-Agilent 7500 ICP MS), IR- (Nicolet iS50 FT-IR spectrophotometer, ThermoScientific), X-ray phase (XRD Empyrean X-ray diffractometer PANalytical).and X-ray fluorescence analysis (Rigaku NEXCGEDX RF Analyzer), scanning electron microscopy (SEM-EDS EVO-MA, Carl Zeiss Instrum). The parameters of the kinetic equation of the leaching process are obtained, the order of the reaction in terms of the concentration of the oxidizing agent, the activation energy of the process of solid-phase diffusion of molybdenum (VI) ions from the crystal lattice of the mineral into the liquid phase of the solution are calculated.

Keywords: Molybdenite concentrate, oxidation, nitric acid

1. INTRODUCTION

Previously, in the production of molybdenum compounds by Research and Production Association for the Production of Rare Metals and Hard Alloys (RPA PRM&HA) of "Almalyk MMC" JSC (former UZKTJM), Uzbekistan, the method of nitric acid opening of molybdenite concentrate (MoC) was used, replaced due to the increased environmental requirements for the process by the scheme of ammonia, then soda leaching middling cinder after molybdenite concentrate oxidative roasting [1-2]. In view of the improvement of technologies and equipment, an interest in hydro-oxidative methods application revived, such as generated hypochlorite [3] or nitric acid in autoclave [4] processing. However, the latest method is ineffective. Environmental safety in the latter case could be ensured by a closed cycle of nitric acid regeneration by

absorption of nitrous gases by water. It was of interest to study the kinetics of MoC leaching reactions in nitric acid and propose a highly efficient method for its regeneration.

Purpose: to obtain data on kinetics of molybdenite concentrate leaching by the rotating disk method in nitric acid with its regeneration for the development of schemes for the MoC hydrometallurgical processing.

Object of the study: MoC, containing, wt%: 38.0 Mo; 2.5 Cu; 13.8 Fe; 0.7 Re; 0.009 P; 0.025 Sb; 0.05 WO₃; 25.2 S; 10.8 SiO₂; 0.42 H₂O in solution, %: H₂SO₄ 5,0; HNO₃ (the range of HNO₃, %: 0-55).

2. METHODS AND MATERIALS

The kinetics of MoC dissolution [5] in HNO₃ was studied by rotating disc (RD) method (disc \varnothing 18 mm made of MoC, in Teflon), with an angular rotation speed 0-840 rpm [6-8] with the control of the RD mass and concentration of Cu(II), Fe(III), Mo(VI) ions in the liquid phase detected photocolorimetrically (KFK-2) 'or by means of Agilent 7500 ICP MS. We studied the dependence of the specific amount of metal passing into the solution from the disk surface (Q , mol·dm⁻²) on: reagent concentration (C , mol·dm⁻³), temperature (T): 20-40-70 °C, disk rotation frequency (ω , s⁻¹), duration (τ , s). Dissolution specific speed of compactly packed molybdenite concentrate pressed into a disk, designated as $W = dQ/d\tau$, is found from the first time derivative of Q . The HNO₃ regeneration method was tested using an ozonator (**Figure 1**).

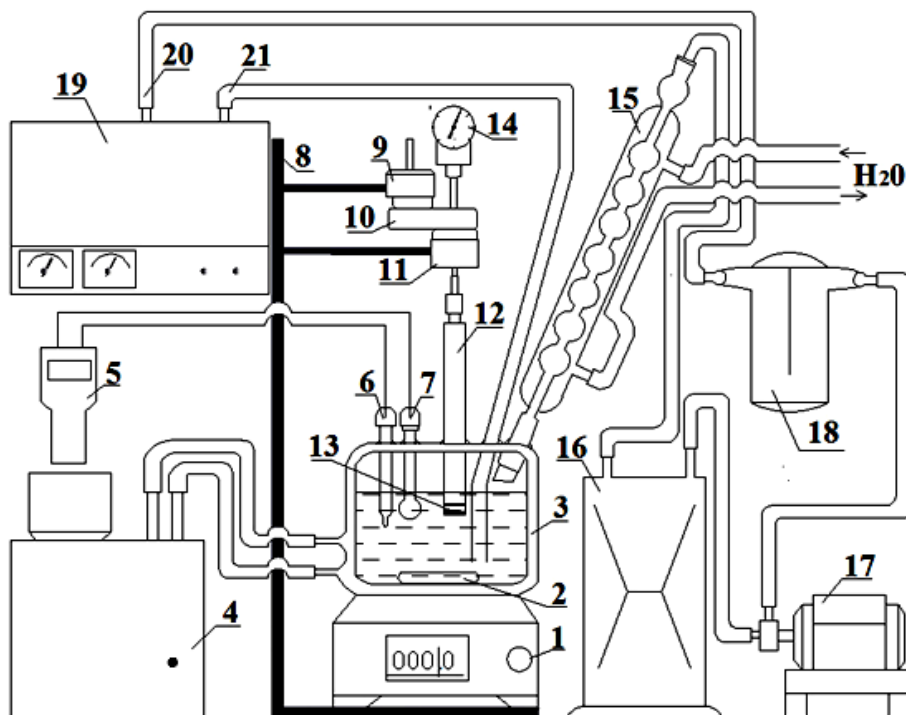


Figure 1 Reagent MoC leaching laboratory plant: 1, 2 - magnetic stirrer, 3 - reactor; 4 - thermostat; 5 - pH meter for Redox control; 6- silver chloride reference electrode; 7 - Indicator electrode; 8- tripod; 9- electric motor; 10- reducer; 11- bearings; 12 - teflon; 13 - disk; 14 - tachometer; 15 - cooler; 16 - drop eliminator; 17 - gas blower; 18 - receiver; 19 - ozonizer; 20 - gas enriched with NO; 21-gas enriched with NO₂

3. RESULTS AND DISCUSSION

3.1 The kinetics of MoC dissolution in HNO₃

The kinetics of MoC dissolution in HNO₃ is presented as dependences: W - ω (0 - 840 rpm) (**Figure 2**); W - τ (60-1800 s) (**Figure 3**); W on temperature T (24-70 °C) (**Figure 4**), based on Mo(VI) control in the solution.

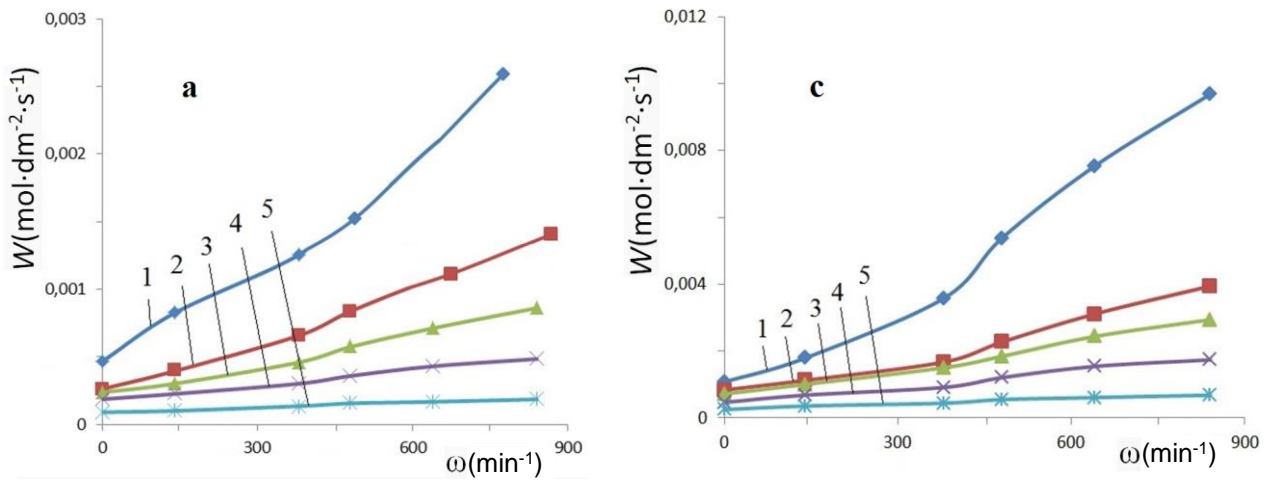


Figure 2 Dependence $W-\omega$, designation, $T(^{\circ}\text{C})$: 24.0 (left); 70.0 (right); duration τ is indicated as 1-6; 2-180; 3-300; 4-600; 5-1800 (s)

According to [10], Q is in a power-law (exponential for T) dependence on the variable factors of the dissolution process, in the general case:

$$Q = k \cdot C^n \cdot \omega^m \cdot \tau^p \cdot \exp(-E_{act} / RT), \quad (1)$$

where: k - rate constant, E_{act} - activation energy; R is the gas constant, T is the absolute temperature; n is the order of the reaction according to the HNO_3 concentration C ; where m , p - are power exponents: rotation speed (ω); duration (τ). Logarithm of (1) gives (2):

$$\ln Q = \ln k + n \cdot \ln C + m \cdot \ln \omega + p \cdot \ln \tau + q/T \quad (2)$$

The dependence $Q_i = f(\tau)$ was built, W was found from the tangent of its slope:

$$W = dQ/d\tau = p \cdot k \cdot C^n \cdot \omega^m \cdot \tau^{p-1} \cdot \exp(-E_{act}/RT) \quad (3)$$

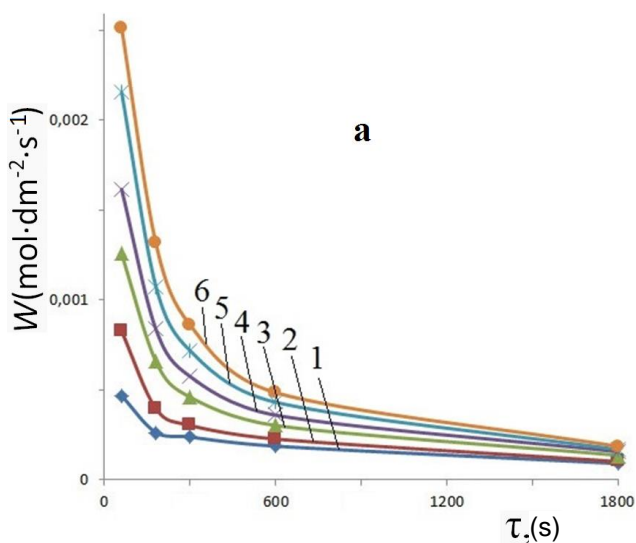


Figure 3 $W-\tau$, at $T=24^{\circ}\text{C}$ and ω , rpm: 1-0; 2-140; 3-380; 4-480; 5-700; 6-840

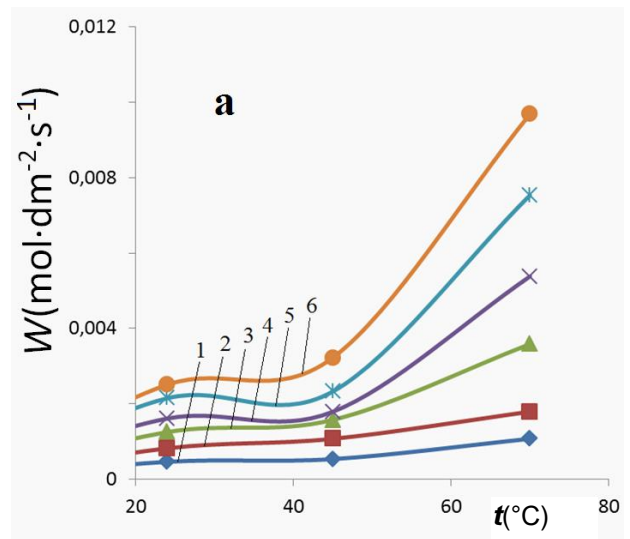


Figure 4 $W-T$, $T=24^{\circ}\text{C}$, $\tau=60$ s, and ω , rpm: 1-0; 2-140; 3-380; 4-480; 5-640; 6-840

3.2 Kinetic equation, limiting stage, reaction order

According to the VD theory [7, 10], W in (3) is presented in a general form. At $\tau^{p-1}=0$ and $\omega^{m=0}$ we obtain

$$W = k \cdot C^n \cdot \omega^{m=0} \cdot \exp(-E_{act}/RT) \quad (4)$$

as a special case - the kinetic regime, in contrast to the case $\omega^{m=0.5}$, when the diffusion mode (5) is realized:

$$W = k \cdot C^n \cdot \omega^{0.5} \cdot \exp(-E_{akm}/RT) \quad (5)$$

To identify the limiting stage under experimental conditions, it makes sense to refer to the form of the kinetic curves at **Figure 2**. First of all, as follows from it ($W-\tau^{p-1}$ series) at $\omega \rightarrow \max$ (0÷840 rpm), we see that the exponent " $p-1$ " changes from "-1" to "-0.5", and further $(p-1) \rightarrow 0$, therefore, there is a mixed kinetics of the process with the priority of the external diffusion mode at the maximum speed of the disk.

The mixed control regime is also confirmed by the data at **Figure 2** (series $W-\omega^m$), from which the change in the exponent " m " of the function ω from $m = 1$ to $m \rightarrow 0$, at $\tau \rightarrow \max$ (1800 sec), and $m \neq \text{const}$, follows.

The order in $\omega(m)$ ranging from 0 to 0.5 and fractional in C ($n=0.9$, see below) also indicates a mixed mode of the dissolution reaction [9]:

$$W = k \cdot C^{n=0.9} \cdot \omega^m \cdot \exp(-E_{act}/RT) \quad (6)$$

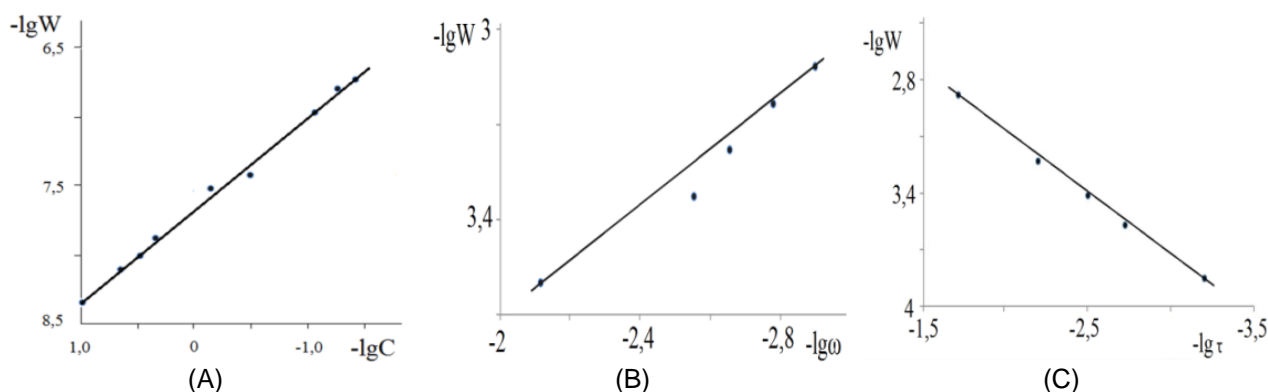


Figure 5 Dependences in the aerated solution, %: HNO₃ 0-55, H₂SO₄ 5, calculation for Mo at $T=297$ K, (A): $-\lg W$ from $-\lg C$ at $\omega = 380$ rpm; (B): $-\lg W$ from $-\lg \omega$, at $\tau=300$ s; (C): $-\lg W$ from $-\lg \tau$.

As follows from the series $W \sim \tau^{0.5}$, the dependences of W on the time indicator $\tau^{0.5}$ are directly proportional, especially clearly at high disk revolutions, parameters indicate the predominance of the limiting stage of internal diffusion.

Of interest was the order of the reaction with respect to the HNO₃ concentration. We proceeded from the fact that MoC in HNO₃ is oxidized according to the equation:



To calculate the exponent of concentration C^n in (3), the dependence " $-\lg W$ on $-\lg C$ " was built in the selected concentration range at a temperature of 297 K (**Figure 5**). The first derivative of the function W with respect to C (after taking the logarithm) determined the experimental value of the reaction order with respect to the HNO₃ reagent: $n = 0.9$. Similarly to the above experimental dependence " $-\lg W$ on $-\lg C$ ", other pair effects are distinguished: " $W-\omega$ ", " $W-\tau$ ", and on their basis the remaining orders of the parameters of the kinetic equation (3) are calculated. Graphs of functional dependence of $-\lg W$ on $-\lg \omega$ are constructed: in the range ω (rpm, 0;

140; 380; 480; 640; 840), as well as $-\lg W$ on $-\lg \tau$, in the range τ (60-1800 s). Reaction orders are obtained, respectively: $m = 0.56$ (**Figure 5-B**), and $p-1 = -0.62$ (**Figure 5-C**).

As a result, by substituting these values of the reaction orders: by C ($n=0.9$), by ω ($m=0.56$), by τ ($p-1 = -0.62$) into (3), a kinetic equation of the form was obtained:

$$W = p \cdot k \cdot C^{0.9} \cdot \omega^{0.56} \cdot \tau^{-0.62} \cdot \exp(-E_{act}/RT) \quad (8)$$

Calculating its right side gives:

$$0.38 \cdot k \cdot [300]^{-0.62} \cdot \exp(-34.7476/8.314 \cdot 297) = 0.38 \cdot k \cdot [300]^{-0.62} \cdot \exp(0.0373) = k \cdot 0.01066 \quad (9)$$

where: $E_{act} = 34.7476 \text{ J} \cdot \text{mol}^{-1}$ taken from **Table 1** for Mo, $\omega = 380 \text{ rpm}$, $\tau = 300 \text{ s}$.

The calculation of the left side of (8) is based on the **Table 1** data for Mo, when extrapolating W to its value at $\omega = 1 \text{ rpm}$ and $C = 1 \text{ mol}$. Eventually:

$$W = 2.69 \cdot 10^{-4} = k \cdot 0.01066 \quad (10)$$

3.3 Activation energy of the MoC oxidation reaction

Based on the dependence of the leaching rate of Fe(II), Cu(II), Mo(VI) (**Table 1**) from MoC into HNO_3 solution, at 24 and 70 °C temperature, angular velocity 0-380-700 rpm, in the range 0-1800 s duration, the values of the activation energy E_a of the reaction (7) were calculated using the Arrhenius equation, according to (11):

$$E_{act} = \frac{(\ln W_{45} - \ln W_{22}) \cdot 2.3R}{\left(\frac{1}{T_{22}} - \frac{1}{T_{45}}\right)} = \frac{(\ln W_{45} - \ln W_{22}) \cdot 7.314}{(0.00025)} \quad (11)$$

The experimental value of the activation energy of the MoC dissolution reaction is one of the criteria for describing its regime: for diffusion it is 12-17 $\text{kJ} \cdot \text{mol}^{-1}$, for kinetic it is 40-80 $\text{kJ} \cdot \text{mol}^{-1}$ [7]. Since our values of E_{act} (**Table 1**) occupy an intermediate position, this fact confirms its mixed kinetic-diffusion character. For comparison, at 60-80 °C it proceeds in the kinetic mode, at 90 °C - in the mixed mode ($E_{act} = 85.7-98.6 \text{ kJ} \cdot \text{mol}^{-1}$ and 16.7-18.8 $\text{kJ} \cdot \text{mol}^{-1}$), respectively [10].

3.4 Rate constant of the MoC oxidation reaction

The calculation of the rate constant of the MoC oxidation reaction was performed for the case: $C[\text{HNO}_3] = 1 \text{ mol} \cdot \text{dm}^{-3}$ and $\omega = 1 \text{ s}^{-1}$, $T = 298 \text{ K}$. From equation (10): $2.69 \cdot 10^{-4} = k \cdot 0.01066$, we get (for 298 K): $k_{298} = 2.5 \cdot 10^{-2} [\text{dm}^{1.9} \cdot \text{mol}^{-0.9} \cdot \text{s}^{0.18}]$.

3.5 Regeneration of nitric acid during the oxidation of MoC

It was of interest to develop a laboratory HNO_3 recovery device (**Figure 1**), which turns the nitric acid scheme of MoC processing into a closed cycle technology that reduces the consumption of HNO_3 to almost zero. For comparison, the industrial rate of its consumption in the same process of an open cycle is 8 tons of 54% HNO_3 per 1 ton of 50% MoC, with a theoretical indicator of 3.2 tons [10]. Its other advantage, along with high profitability, is environmental safety. The nitrous gases emitted in the reactor (position 1) during nitric acid leaching of MoC (7) are returned to the process after oxidation (NO to NO^2) in the ozonator (position 8). The achieved effect is the saving of the reagent, maintaining the value of the Redox potential in the reactor at the proper level (**Table 2**), preventing the release of nitrous gases into the atmosphere.

Table 1 Activation energy E_{act} ($J \cdot mol^{-1}$) of the reaction of MoC dissolution in the aerated solution, HNO_3 0-55%, H_2SO_4 5 %; $\omega = 0-380-700$ rpm, $T: 24.7$ °C

$T(^{\circ}C)$	Duration τ for different ω and elements that have passed into the liquid phase								
	60 s			300 s			1800 s		
	Fe	Cu	Mo	Fe	Cu	Mo	Fe	Cu	Mo
$W(mol \cdot dm^{-2} \cdot s^{-1}), \omega = 0rpm$									
24	$6.15 \cdot 10^{-4}$	$2.69 \cdot 10^{-4}$	$4.66 \cdot 10^{-4}$	$3.69 \cdot 10^{-4}$	$1.61 \cdot 10^{-4}$	$2.37 \cdot 10^{-4}$	$1.64 \cdot 10^{-4}$	$3.58 \cdot 10^{-5}$	$8.96 \cdot 10^{-5}$
70	$1.23 \cdot 10^{-3}$	$6.46 \cdot 10^{-3}$	$1.08 \cdot 10^{-3}$	$7.01 \cdot 10^{-4}$	$1.72 \cdot 10^{-3}$	$7.17 \cdot 10^{-4}$	$4.91 \cdot 10^{-4}$	$3.58 \cdot 10^{-4}$	$2.51 \cdot 10^{-4}$
E_{act}	20259.8	92976.9	24463.1	18774.3	69259.2	40549.0	32140.9	67363.7	30119.5
$W(mol \cdot dm^{-2} \cdot s^{-1}), \omega = 380rpm$									
24	$12.30 \cdot 10^{-4}$	$10.6 \cdot 10^{-4}$	$12.6 \cdot 10^{-4}$	$7.4 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$	$4.6 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$9.0 \cdot 10^{-5}$	$13.5 \cdot 10^{-5}$
70	$2.46 \cdot 10^{-3}$	$8.6 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$	$17.2 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$	$15.1 \cdot 10^{-4}$	$6.6 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$
E_{act}	20271.5	60836.5	30712.4	24790.1	47078.1	34747.6	24194.8	49336.0	34664.6
$W(mol \cdot dm^{-2} \cdot s^{-1}), \omega = 700rpm$									
24	$16.14 \cdot 10^{-4}$	$19.9 \cdot 10^{-4}$	$21.5 \cdot 10^{-4}$	$11.1 \cdot 10^{-4}$	$5.9 \cdot 10^{-4}$	$7.2 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$	$12.5 \cdot 10^{-5}$	$16.7 \cdot 10^{-5}$
70	$4.31 \cdot 10^{-3}$	$12.4 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	$20.9 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	$24.4 \cdot 10^{-4}$	$9.0 \cdot 10^{-4}$	$5.9 \cdot 10^{-4}$	$6.19 \cdot 10^{-4}$
E_{act}	28697.8	53454.3	36650.1	18604.8	46550.2	35800.9	24665.8	45364.7	37823.2

Table 2 Dependence of the Redox potential of the leaching medium on the concentration of HNO_3 (Liquid: Solid=1:75, in the aerated solution 5% H_2SO_4 , HNO_3), the weight of the powder sample MoC was 1.000 g

% HNO_3	$\tau(s)$	Temperature ($^{\circ}C$)	$\Delta m, g$	Weight loss rate, $10^4 \cdot j_k(g/s)$	Redox (mV)
without bubbling ozone-oxygen O_3/O_2 mixture					
5	900	24	0.1463	1.63	+ 840
15	1800	24	0.1598	0.89	+ 930
25	1800	35	0.1811	1.00	+ 960
35	1800	35	0.1968	1.09	+ 985
45	1800	35	0.2055	1.14	+ 1000
55	1800	35	0.2198	1.22	+ 1030
with bubbling ozone-oxygen O_3/O_2 mixture					
35	900	24	0.1686	1.87	+ 1105
35	1800	24	0.2215	1.23	+ 1120

CONCLUSION

Against the background of most publications on the topic of the research, performed on powder samples of molybdenite concentrate which do not allow correct interpretation of the measured kinetic characteristics, the used RD method provides controlled conditions for controlled convection of the "nitric acid - MoC" system. On its basis, the kinetic equation for the oxidation reaction of the sulfide phases of the components: molybdenum, iron, copper compounds was derived. Ideas are obtained about the limiting stages of the process, the values of the activation energy of oxidation reactions, their orders in terms of parameters: oxidant concentration, disk rotation speed, medium temperature, interaction duration. They are in good agreement with the theoretical and practical data on the oxidation of sulfide minerals and will form the basis of the closed cycle technology for nitric acid processing of molybdenite concentrate.

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