

KINETICS OF REAGENT OXIDATION OF MOLYBDENUM SULFIDE IN SULPHATE ELECTROLYTES

Sitorabonu RASULOVA, Vitaliy GURO

Institute of General and Inorganic Chemistry of Uzbekistan Academy of sciences, Tashkent, Uzbekistan

sitora_r91@mail.ru, vpquro@gmail.com

<https://doi.org/10.37904/metal.2019.915>

Abstract

The sulphide phase of ore minerals is subject to passivation in oxidizing conditions. The kinetics of dissolution of polycrystalline sulfide minerals - the raw material of hydrometallurgy of molybdenum, copper, under conditions of variable hydrodynamics of interaction with the medium, is adequately described by the method of a rotating disk of dissolved material with a surface equally accessible to the diffusion of reagents. Overcoming the passivation of their surface is described by kinetic equations based on model representations. Objective: on the example of the behavior of Mo-concentrate in nitrate and hypochlorite electrolytes to describe the nature of the resulting products and the kinetics of their dissolution. Samples of Mo-concentrate (38 % Mo in MoS₂ phase) were used. The concentration of Cu (II), Fe (III), Mo (VI), Re (VII) ions in solutions was determined photocolometrically and spectrometrically (AAS Perkin-Elmer 3030B, ICP- Aligent 7500 ICP MS); thermal analysis was carried out by dilatography, and microscopy of samples was carried out on scanning electron microscopes: SEM-EDS EVO-MA (Carl Zeiss Instrum) and JCM - 6000 Neoscope II (JEOL); spectral analysis - on a Nicolet iS50 FT-IR spectrophotometer (Thermo Scientific, USA), diffuse reflection electronic spectra - on a UV-2600 spectrophotometer (Shimadzu); structural and phase analysis - on an XRD Empyrean X-ray diffractometer (PANalytical), kinetic measurements were performed on powder samples of sulfide concentrates, t:W = 1:7 and 1:75. For example, oxidation of Mo-concentrate samples in a sulfate-hypochlorite electrolyte, during 1800 seconds, the destruction of the phase of Mo, Cu sulfide compounds was established, with the transformation of their share into the oxide-sulfate phase. The kinetics of oxidation of a number of minerals in a sulfate-hypochlorite electrolyte was studied in the temperature range 20-40-70 °C, at atmospheric pressure. The samples of the solid phase after their leaching were studied by the methods of thermal analysis, optical, UV and IR spectroscopy, X-ray diffraction, electron microscopy, and probe microanalysis of the surface areas of the grains.

Keywords: Sulfide minerals, Mo-concentrate, reagent, oxidation, leaching

1. INTRODUCTION

The sulfide phase of natural minerals is subject to passivation under oxidizing conditions [1]. Overcoming it in the stage of leaching of metals is achieved by the choice of reagents and modes, based on kinetic calculations. An increase in temperature and pressure accelerates leaching, but if the autoclave technology is justified for ore concentrates, it is not economically feasible for low-grade ores.

The mechanisms for passivating the surface of sulphides are poorly understood, however, it has been established that they apply to known minerals [2]. These include sulfides in the composition of refractory Au-containing ores of the state-owned enterprise Navoi Mining, and Cu, Mo ores of JSC "Almalyk MMC". The previous approaches [3] to the development of their hydrometallurgical processes did not affect the specifics of the raw materials associated with its tendency to passivation, catalytic activity with respect to the Redox processes. However, the emergence of the rotating disk (RD) method [4-7], which reliably describes the kinetic characteristics of the processes of interaction of sulfide compounds and minerals with solutions, ensuring equal accessibility of the surface of the soluble substance under controlled convection, made it possible to quickly develop adequate hydrochemical technologies.

2. OXIDATION AND PASSIVATION OF SULFIDE ORES

2.1. Methodological bases

Samples of the molybdenite concentrate (38 % Mo in the MoS₂ phase) were used, as well as of synthetic copper sulfide (100 % CuS) [8, 9] and of Coqpatas fields flotation Au-containing concentrate (with pyrite and arsenopyrite - up to 97 % in the sulfide part). ORP (Redox- potential) was measured potentiometrically (EV-74 potentiometer; PI-50-1 potentiostat) on Pt, relative to saturated Ag/AgCl electrode. Concentrations of Cu(II), Fe(III), Mo(VI) and Re(VII) in solution were detected photocolometrically (KFK-2) or by means of spectrometers (AAS Perkin-Elmer 3030B, ICP-Aligent 7500 ICP MS). Thermal analysis of samples is recorded on the Paulik-Erdey derivatographic system at a speed of 10 degrees per min applying a sample of 0.177-0.180 g with sensitivity of T-900, TG-200, DTA-1/10, DTG-1/10 galvanometers, at atmospheric pressure, holder served as a platinum tiger with a diameter of 10 mm without a cap, with the standard Al₂O₃. Sample microscopy was performed on scanning electron microscopes with an energy dispersive probe element microanalysis system: SEM-EDS, EVO-MA (Carl Zeiss, Germany, Oxford Instrum, UK, with a resolution of 3 nm) and JCM - 6000 Neoscope II (Jeol, Japan, W-electron source operating in the magnification range of 10-60000 times, with a resolution of up to 30 nm). Spectral analysis of the composition of molecular compounds in powders was performed on a Nicolet iS50 FT-IR spectrophotometer (Thermo Scientific), with an internal reflection attachment and a Continuum microscope in the range $\nu=50-13500\text{ cm}^{-1}$. Electronic diffuse reflectance spectra achieved at a UV-2600 spectrophotometer (Shimadzu) with an ISR-2600 Plus diffuse reflectance attachment were recorded relative to BaSO₄ in the range of $\lambda=220-1400\text{ nm}$, for which samples were placed in a quartz cell with an optical path length 2 mm, where the spectra of the LMS were recorded. Kinetic measurements were performed on powder samples of sulfide concentrates, weighing 1 g, S:L = 1:7 and 1:75, with stirring suspensions at a speed of 300 rpm, a temperature of 20 °C, and a RD (\varnothing 18 mm) made of Mo concentrate and copper sulphide, in teflon, with an angular rotation speed (ω) of 0-200 rpm [4-7]. 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).

2.2. Results and their discussion

Mo-concentrate, crushed to a class of 0.074 mm, 75 %, bulk density 1.12 g/cm³, composition wt%: 38 Mo; 0.7 Re; 2.5 Cu; 0.009 P; 0.025 Sb; 0.05 WO₃; 25.2 S; 10.8 SiO₂; 0.42 humidity (**Figure 1**).

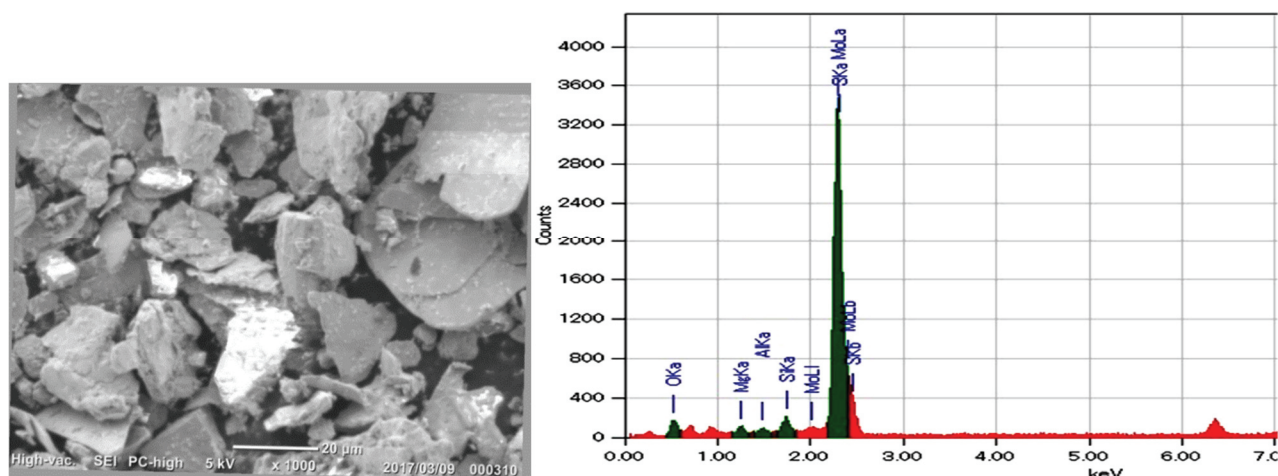


Figure 1 The sample's surface of Mo-concentrate (SEM Jeol JSM-6000)

Figure 2 shows the results of thermal analysis of samples of Mo-concentrate, subjected to various exposures of oxidative leaching in a solution of sodium hypochlorite (18 %) against the background of 5% H₂SO₄ electrolyte, in the time range: 0-1800 s (**Figure 2**).

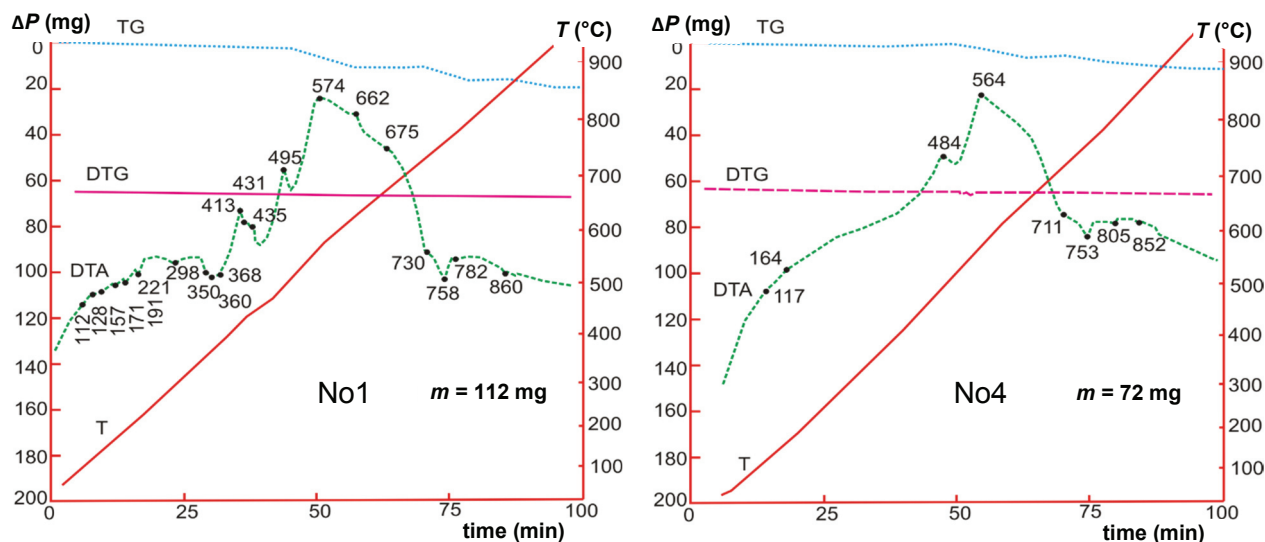


Figure 2 Derivatograms of samples No 1, 4. *Designation:* exposure in sodium hypochlorite solution:
No 1 - 0 s; No 4 - 1800 s

The thermal behavior of the studied samples showed that the magnitude of the decrease in mass of the samples during thermal analysis depends on the preliminary "history" of the samples: the composition and temperature of the electrolyte, and the exposure of the samples to it. The thermal stability of the substance of samples No 1-4 increased in the series: No 1 (15.18 %), No 4 (13.89 %), No 2 (13.40 %), No 3 (8.40 %), which is natural: samples of maximum stability: No 1 and No 4, respectively, the initial Mo-concentrate (not subjected to oxidation in hypochlorite) and the same, after oxidative leaching for 1800 s (mostly of stable mineral composition). Samples No 2 and No 3 are of intermediate state.

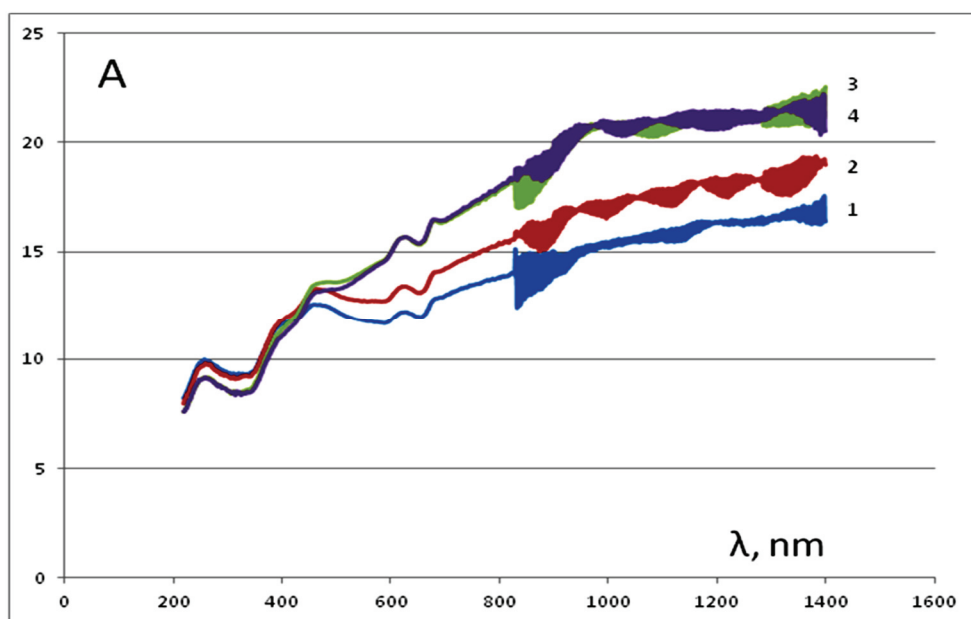


Figure 3 UV spectra of samples No 1-4

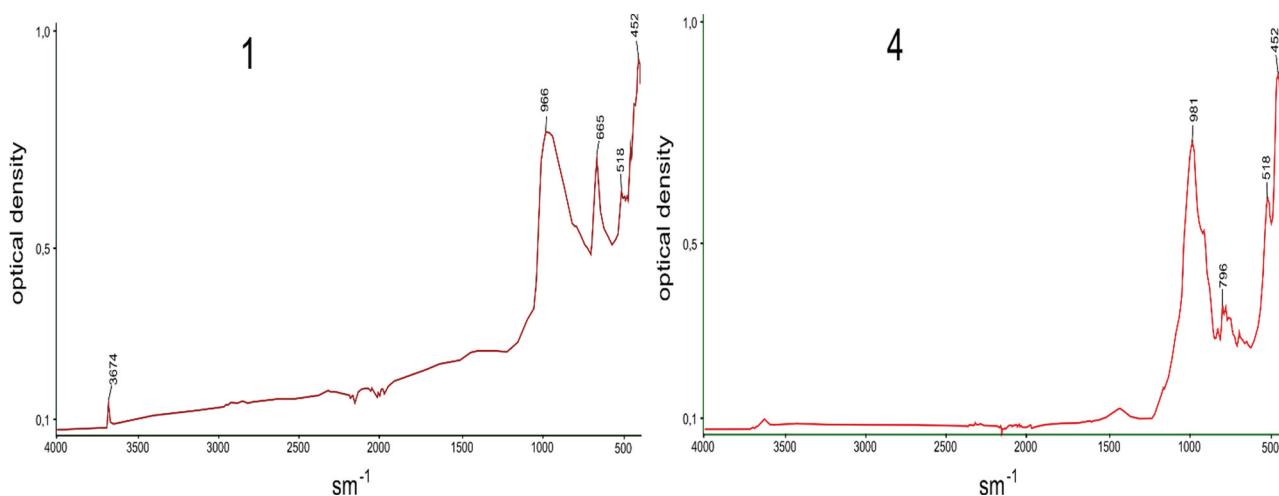


Figure 4 IR spectra of samples No 1-4

The established nature of the thermal stability of samples No 1-4 correlates with the UV and IR spectra of the same samples (**Figure 3**, **Figure 4**).

It follows from them that as the proportion of sulphides in the samples decreases, during 0-1800 seconds, when they are exposed to sodium hypochlorite solution, the main qualitative change in the nature of bonding: from Mo-S to Mo-O occurs in the series No 1 - No 2; the spectra of samples No 3 and No 4 are hardly distinguishable, which means that the oxidation of molybdenite is complete in a time longer than 600 sec.

The designation in **Figures 3-4**: exposure of samples in sodium hypochlorite solution, sec: No 1 - 0; No 2 - 60; No 3 - 600; No 4 - 1800. The IR spectra of the sample No 1 does not practically differ from No 2-3, in contrast to the spectrum of sample No 4. The most intense vibration bands for the samples No 1 was found in the range of 966 and 664 cm^{-1} (**Figure 4**). According to literature data [10], these peaks correspond to symmetric stretching vibrations ν (S - S).

Obviously, oxidation should lead to a shift in the vibration bands and the appearance in the spectra of symmetric and asymmetric stretching vibrations of S - O, deformation vibrations of O - S - O, symmetric stretching vibrations (O - S - O), as well as $[\text{MoO}_4]^{2-}$ [11].

Despite the fact that samples No 2-3 undergo oxidation, the above changes in the IR spectra associated with oxidation were observed only for sample No 4, which manifested itself in the appearance of new vibration bands in the 981, 796, 517, 452 cm^{-1} regions. In addition, unlike sulfides, oxygen metal compounds have different types of hydrogen bonds in the crystal structure and are characterized by wide vibration bands in the region of 3600 cm^{-1} and O - H bonds (1670 cm^{-1}), characteristic of stretching and deformation vibrations. These data confirm that, in addition to metal sulfides, components oxidized to sulfates or sulfites and molybdates are also present in sample No 4.

At the same time, the electronic reflection spectra are more sensitive with respect to the oxidation of the samples, as indicated by the gradual shift of the reflection bands.

Molybdenum sulfide compounds exhibit a d - d transition at 1000-588 nm, followed by charge transfer (from Mo to S) in the region from 588 to 333 nm [12]. The spectra of oxidized samples No 3-4 are almost identical and are characterized by a shift in the charge transfer transition to the long wavelength region.

There is a gradual "loss" of Mo and copper from the crystalline matrix of the material, as a result of the oxidative leaching of the sulfides of these metals from it, in a series of samples No. 1 to No. 4 (**Figure 5**), as follows from the data of their surface monitoring by scanning electron microscopy, with probe microanalysis of selected sites.

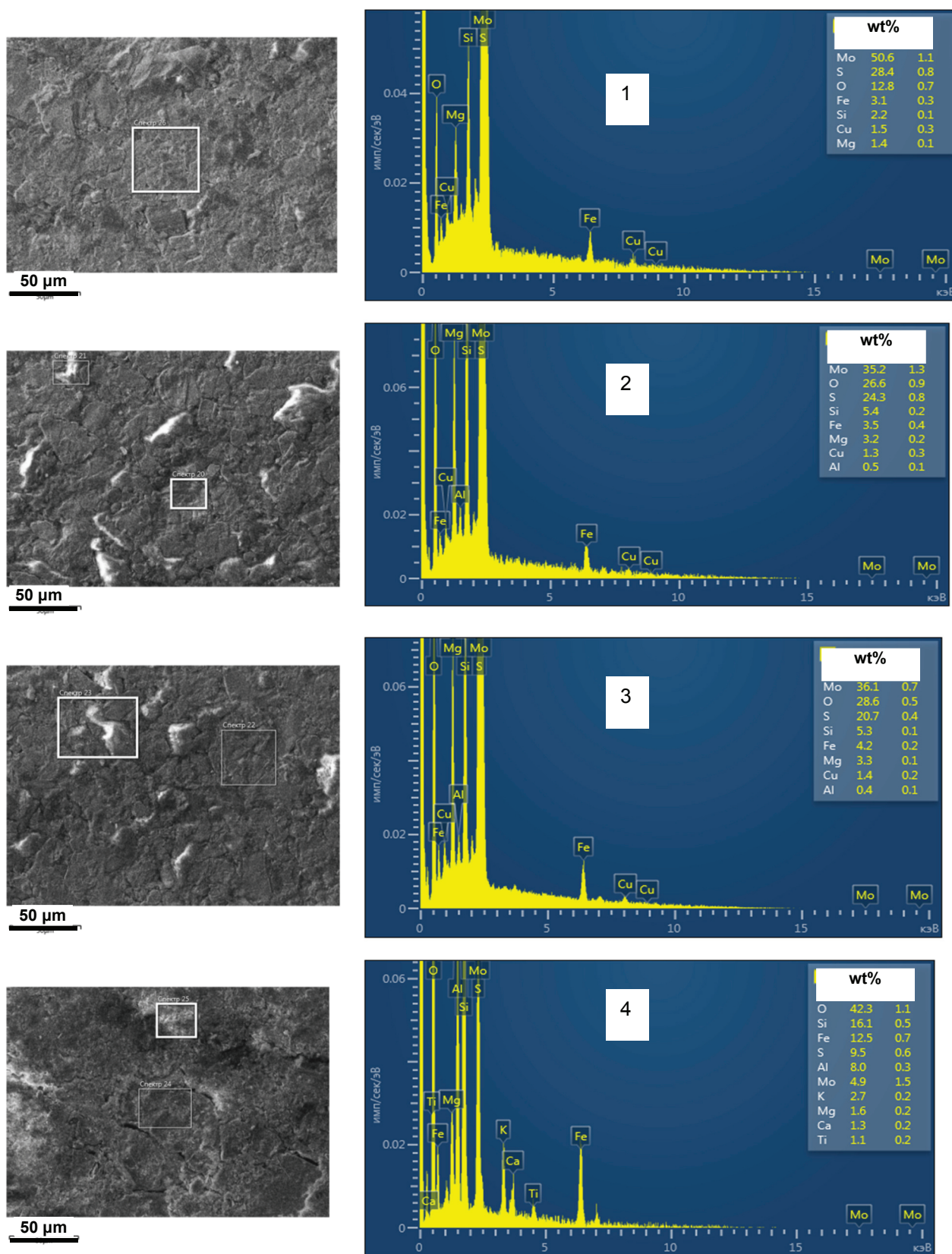


Figure 5 Surface of SEM-EDS specimens, brands EVO-MA (Carl Zeiss, Germany, Oxford Instrum, UK)
Designation: similarly to **Figures 1-4**

The distribution of the main elements in the solid matrix of polycrystallites, as the oxidative treatment of the suspension of Mo-concentrate powders in the sulphate-hypochlorite electrolyte, occurs over time, as follows (see **Table 1**).

Table 1 The change in the composition of the samples of Mo-concentrate during their oxidative leaching in sulphate-hypochlorite electrolyte

Sample No.	Sulfide oxidation time (s)	The content of elements in the solid phase (wt%)				
		Mo	S	Si	Cu	O
1	0	50.6	28.4	2.2	1.5	12.8
2	90	35.2	24.3	5.4	1.3	26.6
3	600	36.1	20.7	5.3	1.4	28.6
4	1800	4.9	9.5	16.1	0	42.3

It follows from the table that as oxidative leaching of samples No 1-4 in the sulphate-hypochlorite electrolyte took place, from 0 to 1800 seconds, the content of the following elements decreased: Mo from 50.6 to 4.9 %, Cu from 1.5 to 0 %, sulfur - from 28.4 to 9.5 %, but increased for the following elements: Si - from 2.2 to 16.1 %, oxygen - from 12.8 to 42.3 %. As follows from **Figures 5 - 6** and the tables, the time of oxidative leaching of Mo-concentrate in the above shown system - 1800 seconds, was insufficient for 100 % extraction of molybdenum into a solution and conversion of sulfide compounds of metals to oxide-sulfate. Nevertheless, the dynamics of this process is quite clearly demonstrated in the model of 4 samples of the specified system.

3. CONCLUSION

Using the example of oxidative leaching of powder samples of Mo-concentrate in an aqueous sulfate-hypochlorite electrolyte, up to 1800 seconds, in the study of the solid phase formed after such reagent exposure to them, by thermal analysis, optical, UV and IR spectroscopy, X-ray, electron microscopy with probe microanalysis of the surface areas of the grains of their material, the almost complete destruction of the phase of molybdenum sulfide compounds of copper, with the transition of most of them into solution, and the transformation of their remaining fractions from the sulfide phase to the oxide-sulfate phase is established.

ACKNOWLEDGEMENTS

Authors are grateful for T.3-18 Uzbekistan governmental Fund of Fundamental researches support

REFERENCES

- [1] RASULOVA, S., GURO, V., IBRAGIMOVA, M. and SAFAROV, E. Oxidation and passivation of sulfide ores in gold and molybdenum hydrometallurgy. In *METAL 2018: 27th International Conference on Metallurgy and Materials*. Ostrava: TANGER, 2018. pp. 1442-1447.
- [2] PUGAEV, D., NICOL, M. and SENANAYAKE, G. The mechanisms of the passivation of sulfide minerals in oxidative leaching processes. In *Proceedings of 6th Southern African Base Metals Conference*, 2011. pp. 39-48.
- [3] BOGACHEVA, L.M. and ISMATOV, K.R. *Hydrometallurgical Processing of Copper-Bearing Minerals*. Tashkent: Fan publishing house, 1989. 116 p.
- [4] POTASHNIKOV, Y.M., LUTSIK, V.I. and CHURSANOV, Y.V. Study of the interaction of molybdenite with nitric acid. *Proceedings of the Universities. Nonferrous Metallurgy*. 1984. no. 1, pp. 57-61.
- [5] LUTSIK, V.I., POTASHNIKOV, Y.M. and LUTSIK, V.A. Extraction of molybdenum from sulfide ore with an alkaline solution of sodium hypochlorite. *Izv. Sib. Dep. Academy of Sciences of the USSR. Ser. Chemical Sciences*. 1985. vol. 4, no. 11, pp. 49-54.

- [6] PLESKOV, V. and FILINOVSKY, V.Y. *Rotating Disk Electrode*. Moscow: Science Publ House, 1972. 225 p.
- [7] LEVICH, V.G. *Physico-Chemical Hydrodynamics*. Moscow: Fizmatgiz publ house, 1959. 699 p.
- [8] KLAUBER, C. Review of liquid ferric acid sulphate dissolving acid. *International Journal of Mineral Processing*. 2008. vol. 86, no. 1-4. pp. 1-17.
- [9] *Manual on Inorganic Synthesis*. Ed. G. Brower, vol. 5, Moscow: Mir Publ. House, 1985. pp. 1652-1653.
- [10] ANDRONIC, L., ISAC, L. and DUTA, A. Photochemical synthesis of copper sulphide / titanium oxide photocatalyst. *Journal of Photochemistry and Photobiology A: Chemistry*. 2011. vol. 221, no. 1. pp. 30-37.
- [11] NAKAMOTO, K. IR spectra and Raman spectra of inorganic and coordination compounds. Moscow: Mir Publ. House. 1991.
- [12] LIVER, E., GREENBERG, J.H. and TULCHINSKY, M.L. *Electron Spectroscopy of Non-organic Compounds*. Moscow: Mir Publ. House. 1987.