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RESEARCH ON STUDY OF MINERALOGICAL COMPOSITION OF PRODUCTS OF FIRING OF SULFIDE CONCENTRATES OF MOLYBDENUM

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ABSTRACT

The article deals with the formation of oxidized particles during oxidative roasting of molybdenum sulfide concentrates and cakes, as well as under-oxidized cinders and dust of molybdenum production. In the course of the work, various factors influencing the oxidative roasting process, parameters and requirements for the supplied and discharged material were investigated. The results of the analyzes are summarized and conclusions based on them are drawn.

KEYWORDS: *Multiple Hearth Furnace, Intensive Roasting, Cinder, Sulfides, Molybdenum, Cake, Soda Leaching, Oxidative Roasting, Concentrate, Desulfurization, Oxidation State.*

INTRODUCTION

An industrial method for extracting molybdenum includes roasting its concentrate, purifying the obtained calcine by a hydrometallurgical method to MoO_3, and reducing trioxide with hydrogen to metal. Although this method is the main method for the production of molybdenum and has been used for a long time in the industry, research on its application to various concentrates, as well as the kinetics and mechanism of roasting, is ongoing. still in short supply [1]. However, as a result of the well-known disadvantages of pyrometallurgical extraction of molybdenum, hydrometallurgical processes are becoming more and more attractive. Among them, nitric acid

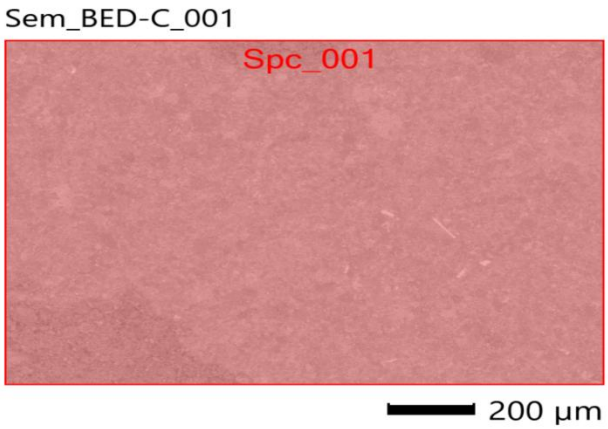
leaching, pressure oxygen leaching, electro oxidative extraction, sodium chlorate and hypochlorite leaching, and bioleaching are more popular. [2].

Objects and methods of research

We have studied the kinetics and mechanics of the solid-state reaction between MoS_2 and MoO_3 for the formation of MoO_2 in an atmosphere with a nitrogen content of 450-700 ° C using untreated samples of molybdenum production, pressed melange samples and pure MoS_2 and MoO_3 dumplings with the contacting side. The results show that, for untreated samples, the reaction reaches a maximum conversion of 67.3% at 650 ° C in 75 minutes, while for compressed samples, the conversion under similar conditions reached 96.1% in 75 minutes, which reflects the effect of physical conditions of both types of experiments on reaction kinetics [3]. The calculated values of the activation energy for the two experimental conditions are coherent with an average value of -44.2 ± 1.9 kJ, which is in the range of reactions in the solid state, controlled by diffusion [4]. For samples with a contacting face above 923 k, the results seem to indicate that molecular diffusion in the solid state and MoO3 in opposite directions in the newly formed crystal structure of MoO_2 can occur with the established diffusion coefficients of MoS_2 in MoO_2 and MoO_3 in MoO_2 at 923 to 1.08 x 10^{-6} and 7.78 x 10^{-6} cm^2 / s, as well as with constant diffusion coefficients of MoS_2 in MoO_2 and MoO_3 in MoO_2 at 650 °C 1.08 x 10^{-6} and 7.78 x 10^{-6} cm^2/s 973 kde 10^{-5} and 1.13 x 10^{-5} cm^2/s, respectively[5].

RESULTS AND DISCUSSION

There are four known molybdenum sulfides: Mo_3S_4, Mo_2S_3, MoS_2, and MoS_3. Sulfide Mo_3S_4 is formed from aqueous solutions and decomposes at about 120°C to MoO_3^-•nH_2O and sulfur. Trisulfide MoS_3 usually contains an excess of sulfur in the form of MoS_3 + x, in which x = 0-0.7. When heated in an inert atmosphere between 527 and 573K, it decomposes into MoS_2 and sulfur. Molybdenite (MoS_2) decomposes to Mo_2S_3 and gaseous sulfur in a neutral atmosphere above 1673 K [6]. There are two known molybdenum oxysulfides, MoO_2S and MoS_2, but they are very unstable and decompose to MoS2 and oxygen. Several molybdenum oxides have been identified with oxidation states from 2 to 6, most of which are non-stoichiometric, and only two (MoO_2 dioxide and MoO_3 trioxide) are stoichiometric, stable compounds.



Some others, such as Mo_5O_{12}, Mo_3O_8, Mo_2O_5, Mo_4O_{11} and Mo_9O_{26}, have been found in small amounts in multi-hearth furnaces and appear to be solid solutions of MoO_2 and MoO_3 in various proportions [6-8].

A general chemical analysis of samples was carried out over the entire surface of each sample to determine the possible components of the studied objects, which are shown below in the figures below..

Fig. 1. General elemental analysis of the entire surface of the soda leach sludges

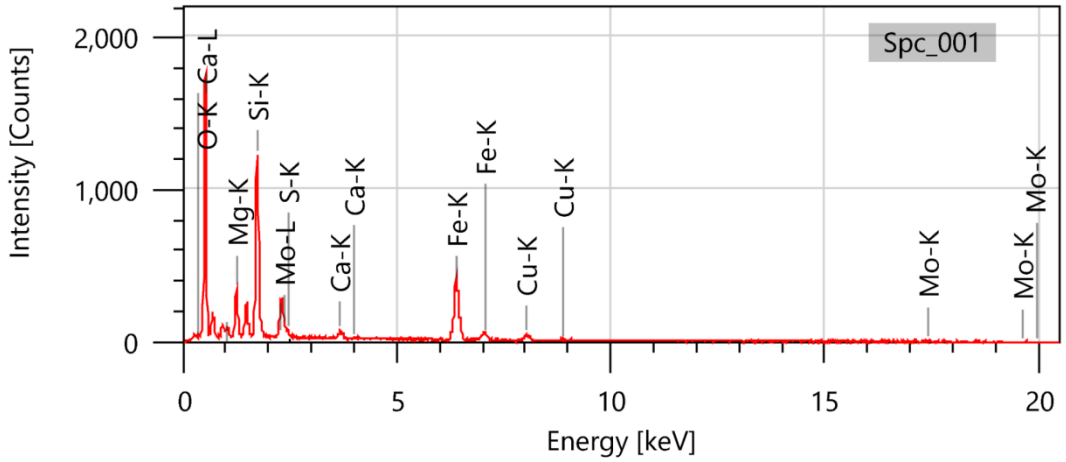


Fig. 2. Results of the analysis of the leaching sludge sample

TABLE 1 ELEMENTARY COMPOSITION OF THE TOTAL AREA OF THE LEACHING SLUDGE SAMPLE

Element	Line	Mass%	Atom%
O	K	42.10 ± 0.41	62.95 ±0.61
Na	K	1.37 ± 0.11	1.43 ± 0.12
Mg	K	4.92 ± 0.15	4.84 ± 0.14
Al	K	3.27 ± 0.12	2.90 ± 0.11
Si	K	16.62 ± 0.24	14.15 ± 0.20
S	K	2.80 ± 0.13	2.09 ± 0.10
Ca	K	0.85 ± 0.07	0.51 ± 0.04
Fe	K	20.83 ± 0.36	8.92 ± 0.16
Cu	K	3.23 ± 0.21	1.22 ± 0.08
Mo	L	4.01 ± 0.34	1.00 ± 0.08
Total		100.00	100.00
Spc_001			Fitting ratio 0.0357

The results of the analysis show that the leaching cake sample contains mainly different iron oxides, and molybdenum sulfides is 6.8%. This proves that after soda leaching of molybdenum concentrates, up to 4% of molybdenum remains in the sludge.

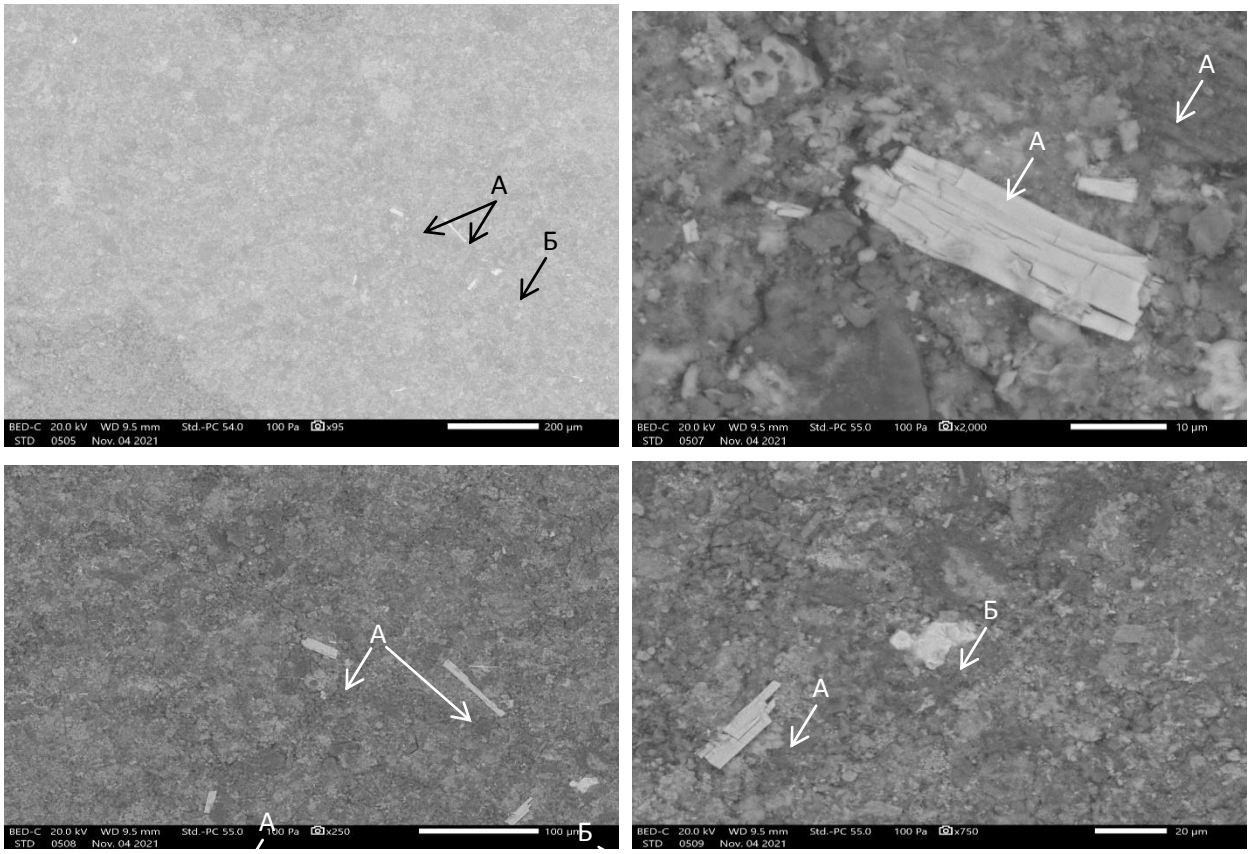


Fig. 3. Scanning eíectron microscope images (leaching sludge)

Figure 3 shows images of a scanning electron microscope of the leach cake. The figure shows molybdenum particles bound by oxygen and sulfides, and the main part of the surface is filled with iron oxides. Determined by the values of A - molybdenum oxides, B - sulfide particles of molybdenum, and the rest, mainly iron oxides. In a scanning electron microscope, heavy particles are shown brighter, since the brighter the particles, the heavier. From the above, it can be concluded that the main surface of the sample is iron oxides. These conclusions are confirmed by the data in Table 1. Table 1 shows that the sample contains 20.83% Fe and 42.10% oxygen.

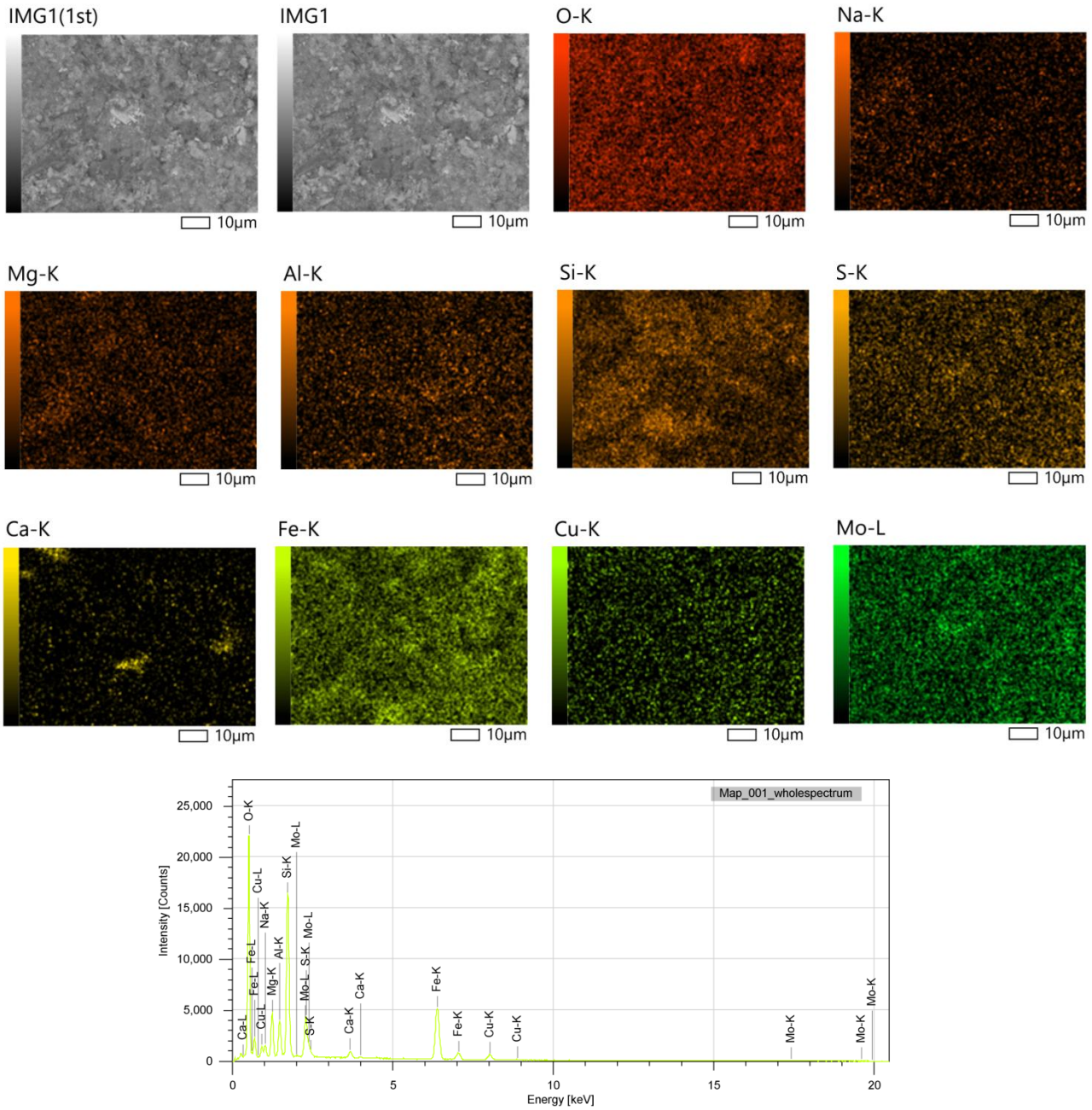


Fig. 4. Results of EMF analysis of leaching cake samples

Next, an EDS analysis was performed to study the complete surface map (mapping method) (Figure 4.). This method determines in what part of the sample the constituent elements are located. Figure 4. states that the sample contains mainly oxygen, and where there is oxygen, the signals of Fe and Si shine through. The signals of molybdenum and sulfur are very close, so the patterns of the L-line of molybdenum and the K-line of sulfur are almost the same. The energy resolution of the energy dispersive spectrometer is 130 eV. But the difference between the Lα

line of molybdenum and the Kα line of sulfur is almost 14 eV[7]. Therefore, when analyzing an energy dispersive spectrometer, it shows molybdenum and sulfides in one peak.

A general analysis of a sample of a molybdenum middling product was carried out to determine the elemental composition.

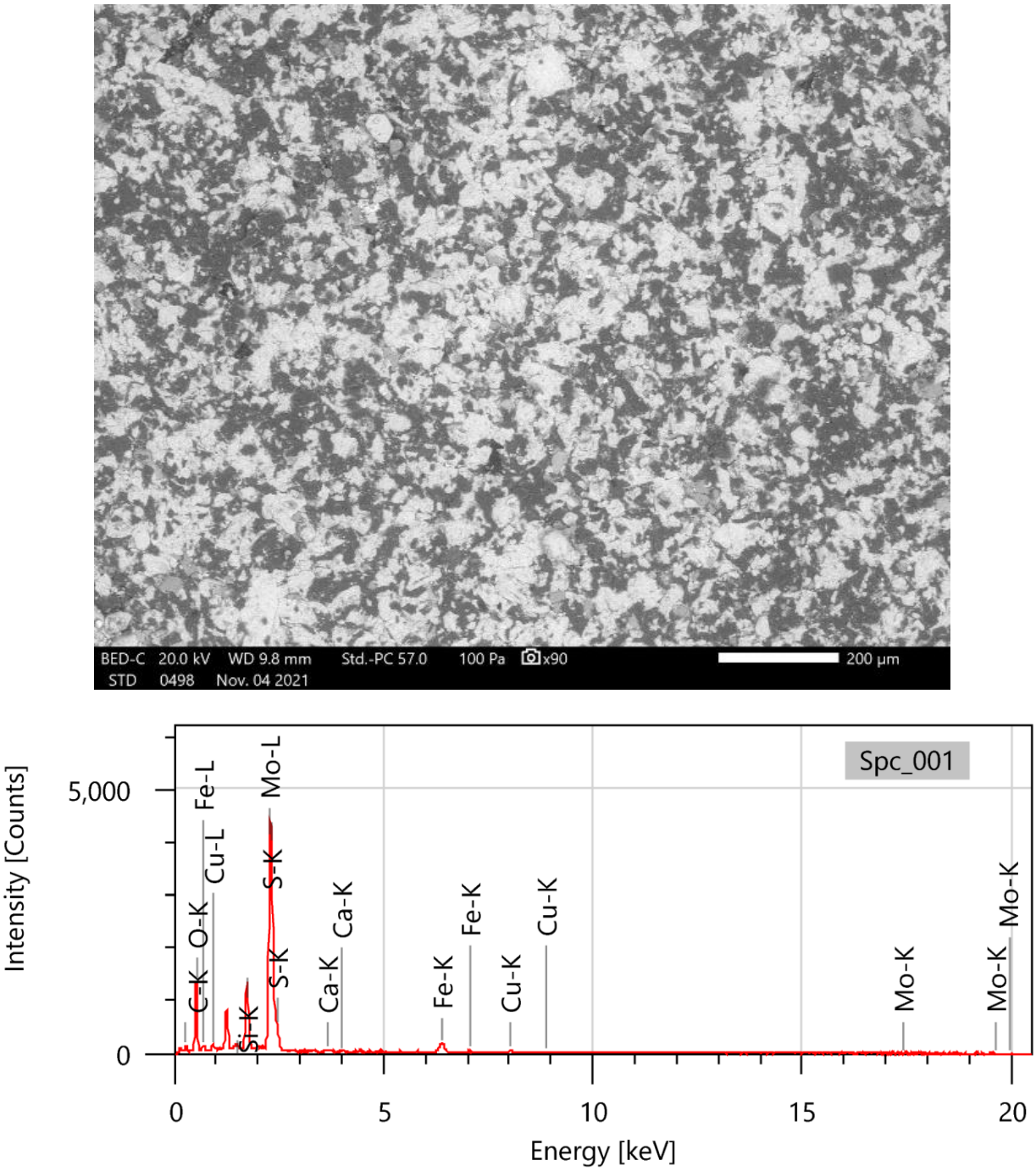
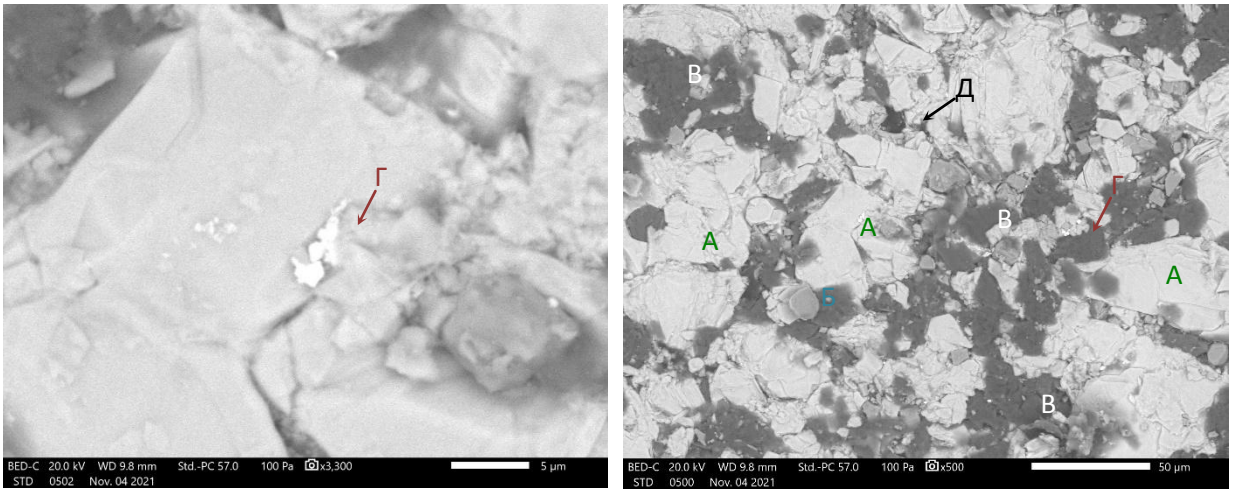


Fig. 4 General elementary analysis of the entire surface of a sample of molybdenum production middlings.

As a result of the analysis, the elementary composition of the molybdenum middling product was determined. Based on the analysis results, it can be seen that molybdenum in the sample is 25.5%, S - 18.54%, Si - 6.12%, Cu - 8.9%, O - 31.18%, Fe - 3.74 %. For a more accurate determination of the structure of samples of middlings of molybdenum production, several images were taken in different magnified states from 90x to 3300x.

The work of Sooeun Shin and Eunsoo Kim [8-12] shows the structural analysis of molybdenum oxides, which shows the mineral is an acicular state. Based on the literature data on the structures of minerals, it is possible to determine visually which minerals are in the sample based on the table of data on the elemental composition of the analyzed object.



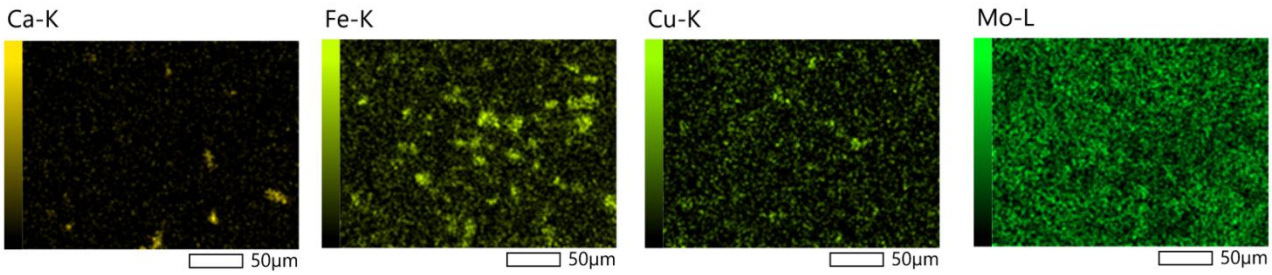
А) 3300x Б) 500x

Fig. 5. Images of a scanning electron microscope with a magnification of 90x and 500x

From the images and the data table, it can be determined that the sample of molybdenum middling contains mainly molybdenum sulfides, chalcopyrite, pyrite and various iron sulfides, as well as SiO_2 and iron oxides. The 500x image definitely showed which particles are at which points on the surface. For example, A - molybdenum sulfides, B - silicates, C - iron oxides (hematite, goethite, etc.), D - possible heavy metals (Pb, Pd), E - carbon compounds. Figure 5. And for a detailed determination of heavy metal, the image was enlarged to 3300x and the elementary composition of this area was determined.

The elemental composition of this area shows that there is 17.38% Pb in this area.

Further, by the mapping method, the state of the elements in the object under study is determined.



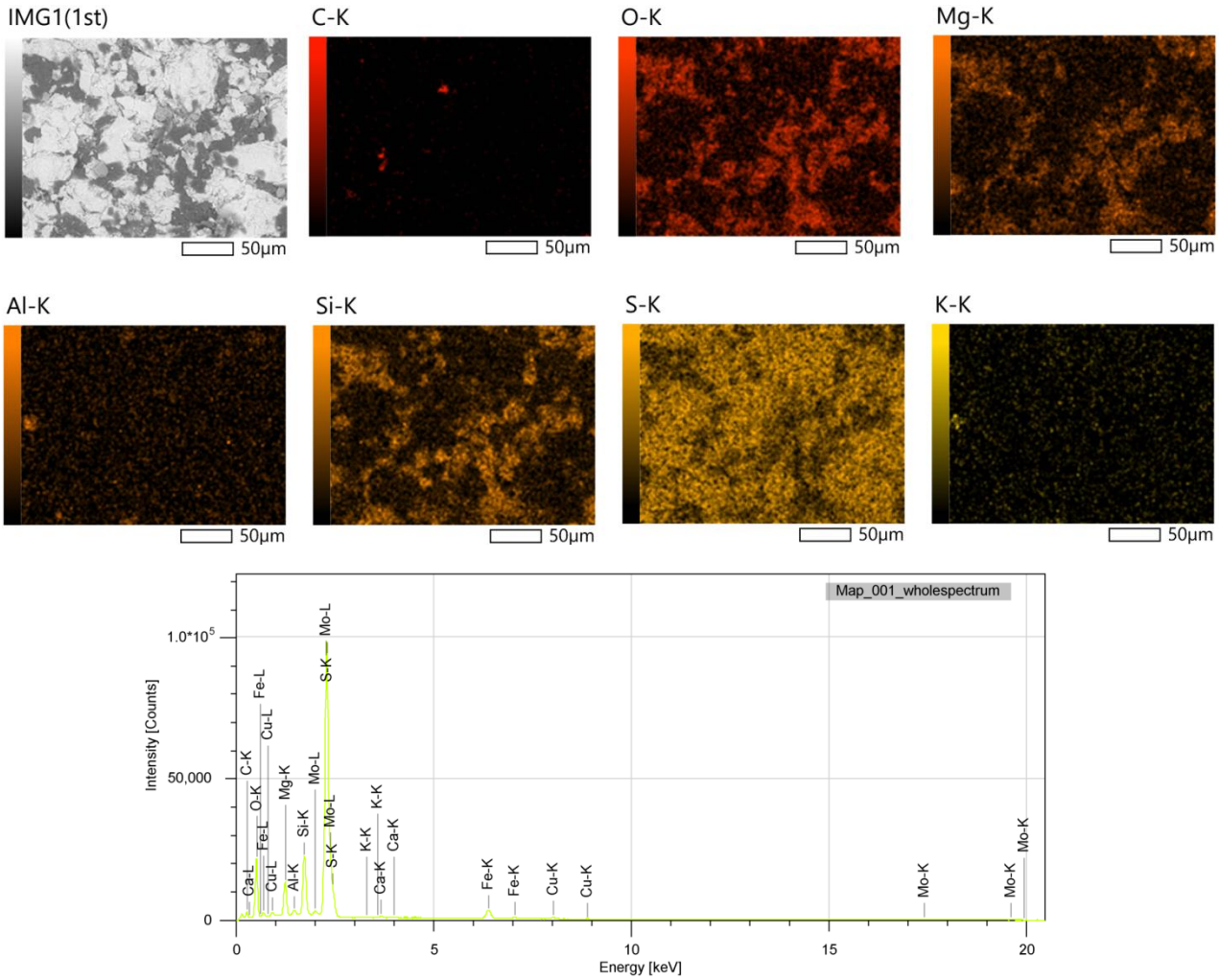


Fig.6. Results of EDS analysis of samples of molybdenum middlings

The above analyzes state that a sample of molybdenum middlings contains molybdenum in sulfide compounds and Al, Fe, Mg and Si in the form of oxides. When determining the structure of molybdenum middlings, the content of chalcopyrite, pyrite and iron sulfides was determined. Analyzes of individual sample sites for the determination of heavy metals are presented in the appendices.

Analyzes for determining the elemental composition of a sample of cinders of molybdenum production middlings have been carried out. In the course of the work, images of the scanning electron microscope of the sample were obtained.

In contrast to the middlings of molybdenum production in cinders, the bulk of molybdenum sulfides is formed by molybdenum oxides. From Figure 2.8. it can be seen that bright particles expressing molybdenum compounds are shown as an acicular structure and this states that the main part of sulfides during oxidative roasting is oxidized.

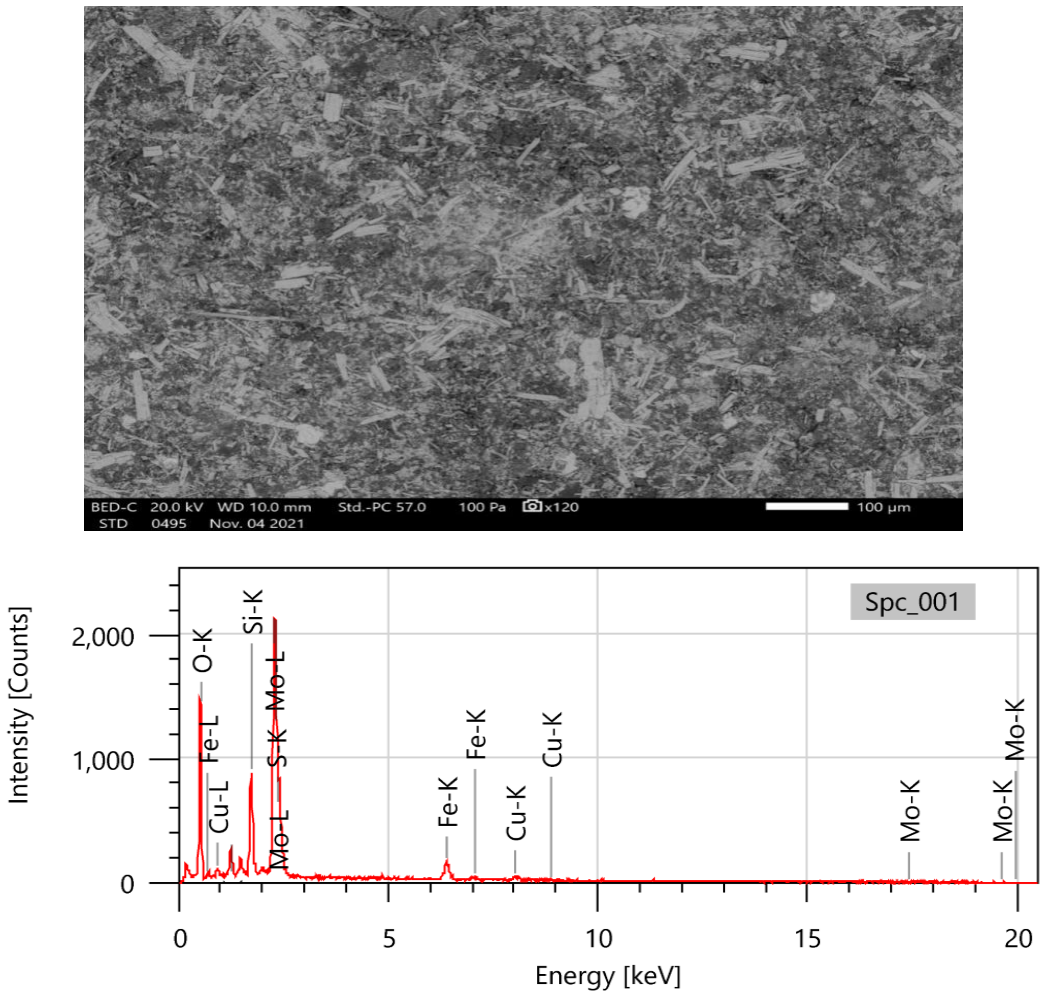


Figure 7. General elementary analysis of the entire surface of the sample of the middlings of molybdenum production

Figure 7. shows that oxidized molybdenum particles have a size of up to 100 µm. However, the presence of molybdenum sulfide compounds is also impossible to refuse. In Table 1 it is possible to compare the sulfur and molybdenum contents, which indicate the oxidation of sulphide particles. Table 2 it is shown that the sulfur content in the middlings of molybdenum production is 18.54%, and 4.69% sulfur remains on the cinder (Table 2.).

TABLE 2 ELEMENTARY COMPOSITION OF THE TOTAL AREA OF THE SAMPLE OF CINDERS OF MOLYBDENUM MIDDLING PRODUCT

Element	Line	Mass%	Atom%
O	K	42.45 ± 0.45	73.12 ±0.82
Mg	K	1.84 ± 0.07	1.34± 0.10
Al	K	1.03 ± 0.05	2.20± 0.09
Si	K	5.94 ± 0.11	1.52± 0.07
S	K	4.69 ± 0.16	6.10± 0.12
Fe	K	4.26 ± 0.13	4.29± 0.10

Cu	K	2.00 ± 0.13	0.77± 0.06
Mo	L	37.79 ± 0.49	10.67± 0.11
Total		100.00	100.00
Spc_001		Fitting ratio 0.0478	

Figure 8 shows the change in the structure of molybdenum middlings after oxidative firing. An increase in the mass fraction of oxygen and a decrease in sulfides indicate the quality of the oxidative roasting process. By studying the mechanisms of oxidation and determining the parameters of oxidative firing, it is possible to determine the optimal firing conditions, this is discussed in the following chapters of the thesis.

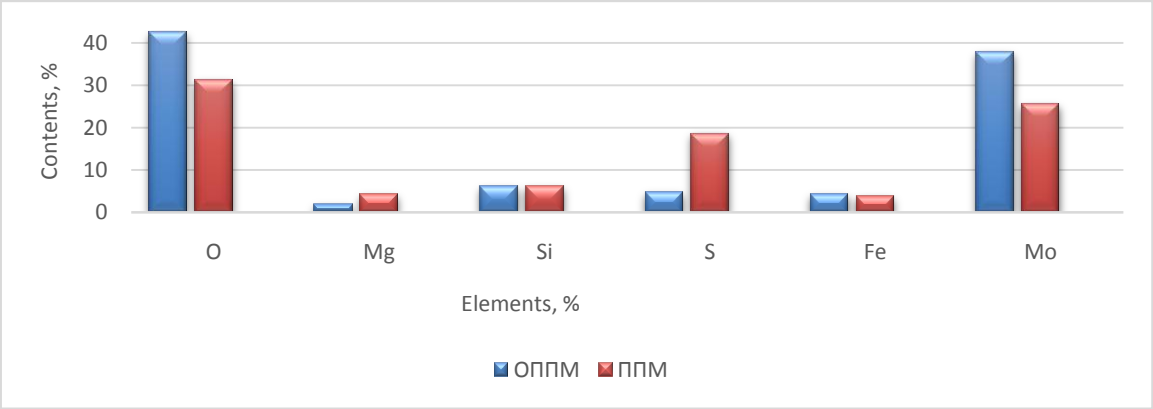
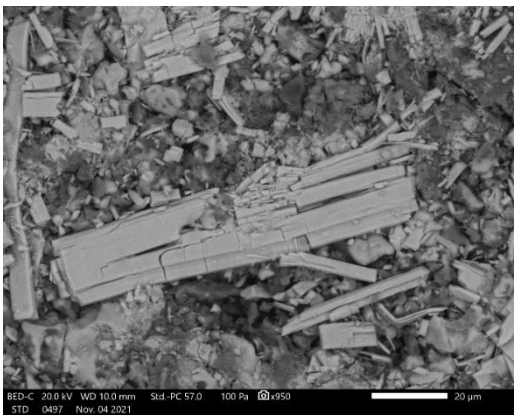
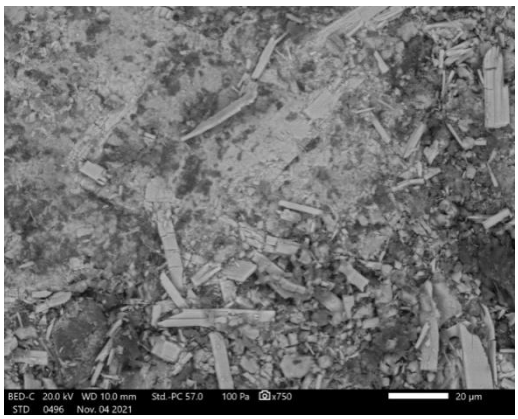


Fig. 8 Changes in the structure of molybdenum middlings during oxidative firing.

Figure 9. shows the structures of an oxidized sample, sulfide particles are contained in an insignificant amount. The main part of the sample is covered with molybdenum oxides, also in table 2 it is indicated that the sample contains 42.45% oxygen and 37.79% molybdenum, up to 5-6% additional components such as Fe, Cu, Si, Al and Mg.



А) 950x



Б) 750x

Fig 9. Images of a scanning electron microscope with a magnification of 90x and 500x

Several photographs and elementary analysis of dust samples from oxidative roasting of molybdenum production were made. Below, in Figure 10. a 60x enlarged photograph of molybdenum dust under an accelerating voltage of 20.0 kV and low vacuum is presented.

The elemental composition of the dust was determined to further clarify the shape of the state of the elements in the sample. The composition of the dust contains much more sulfur than cinders of molybdenum middlings. This is due to the fact that the volatilized dust is under-oxidized, molybdenum in it remains in the sulfide form up to 7-8%. To refine the analysis results and find the shape and structure of minerals in the sample, electron dispersive spectral analysis was performed using a JEOL IT200 scanning electron microscope.

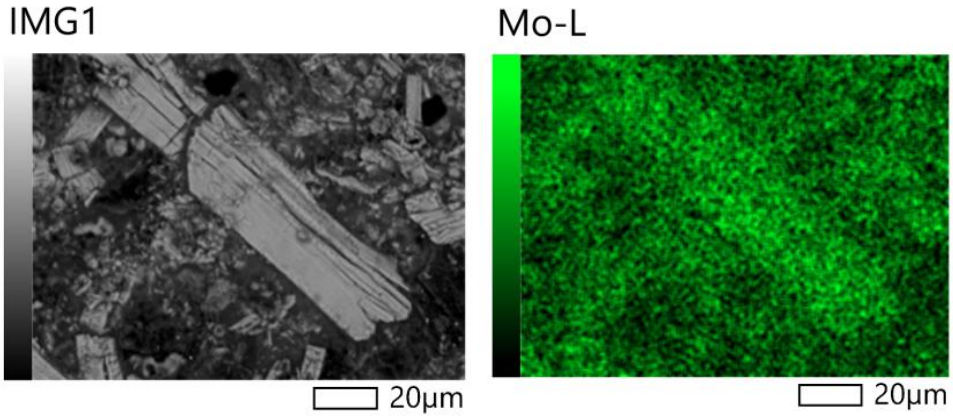


Fig. 10. Determination of mineral particles by the EDS method

Figure 10 shows that the large acicular particle contains molybdenum as a whole, and the particle is brighter than the rest of the areas. The needle-like structure of this mineral means that this mineral is molybdenum oxide, now you can compare the results of oxygen indicators, since the picture with oxygen may confirm this opinion. Figure 12 compares the signals of the Lα line of molybdenum and the Kα line of oxygen.

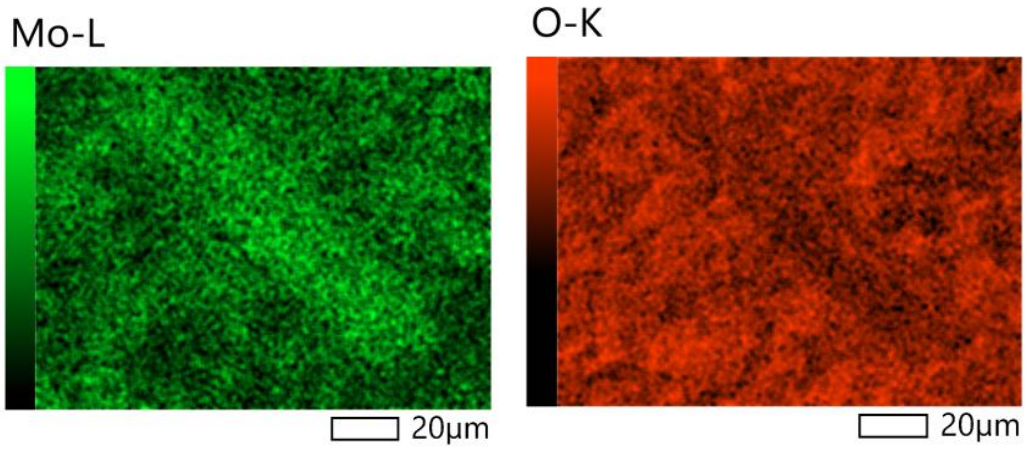


Fig. 12. Comparison of mineral particles by the EDS method (Mo-O)

The traces of the selected particle are almost the same in both figures, which means that in this area of the sample, oxygen and molybdenum are bound, or it can be inferred that molybdenum is in an oxidized state here.

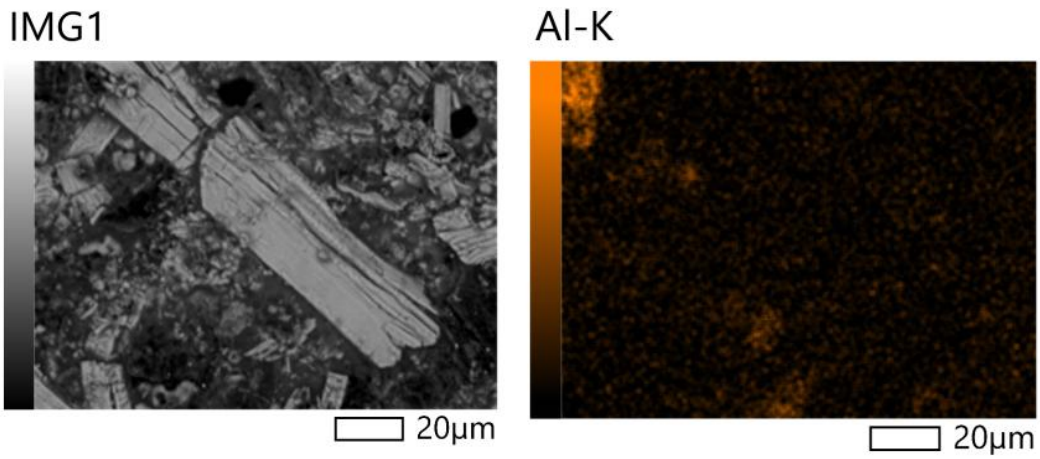


Fig.13. Determination of the form of finding aluminum by the EDS method

By comparing the pictures, you can see the points where the aluminum is. Aluminum is a lightweight non-ferrous metal, so it appears darker in images.

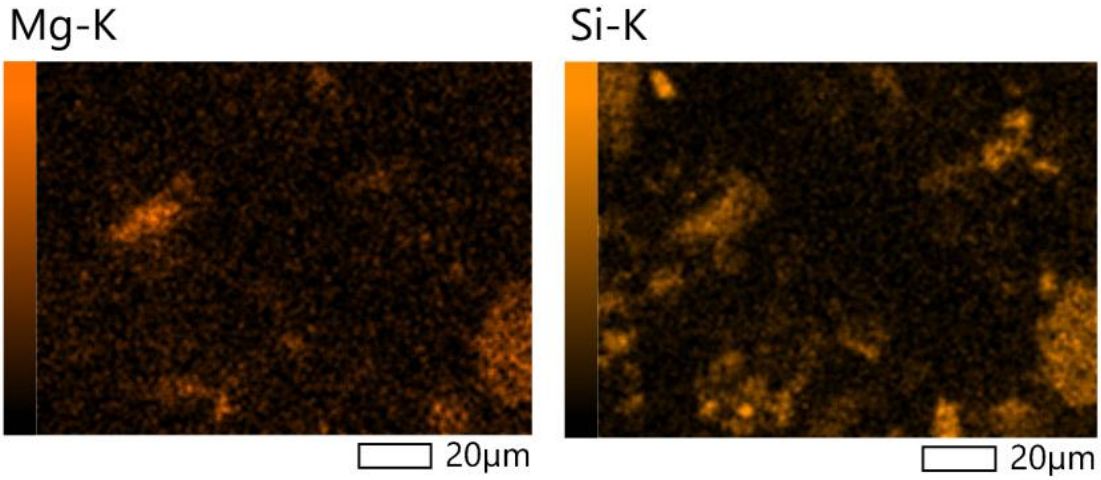


Fig. 13. Determination of the form of finding minerals Mg-Si

Figure 13 indicates the presence of talc (Mg3Si4O10 (OH) 2) in the sample. Translucence of magnesium and silicon is located in basically the same places on the surface.

CONCLUSIONS

The kinetics and mechanism of the solid state reaction between MoS_2 and MoO_3 with the formation of MoO_2 in a nitrogen atmosphere between 450 and 700°C were studied using bulk mixed samples, mixed compressed granules and pure granules of MoS_2 and MoO_3 with a single contacting surface. The results show that for bulk samples the reaction reaches a maximum conversion of 67.3% at 650 ° C in 75 min, while for compressed samples the conversion under similar conditions reaches 96.1%, which indicates the effect of the physical characteristics of both types of experiments on diffusion coefficient of MoS_2 and / or MoO_3 through the newly formed crystalline layer of MoO2. The calculated activation energies for both experimental

conditions agree with an average value of -44.2 ± 1.9 kJ, which is in the range of diffusion-controlled reactions. The literature has not reported any other value for this reaction.

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