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INVESTIGATION OF THE MECHANISM OF MOLYBDENITE OXIDATION BY NITRIC ACID

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Abstract. This paper provides a detailed examination of the oxidation of molybdenite (MoS_2) by nitric acid. It explains how molybdenite interacts with the acid, which chemical reactions occur at different stages of the process, and which substances are formed as a result. Particular attention is paid to the conversion of sulfur, which is part of molybdenite, into oxidized compounds, as well as to changes in the chemical state of molybdenum during the reaction. The influence of the main technological parameters on the oxidation rate is also analyzed. The paper considers how changes in nitric acid concentration, process temperature, and ore particle size affect the completeness of reagent interaction and the degree of molybdenum extraction. In general, an increase in temperature and a decrease in particle size accelerate the reaction because they improve the conditions for interaction between the acid and the mineral surface. However, the specific effect depends on the ore composition and process conditions. The formation of intermediate compounds that appear during oxidation and may affect the subsequent course of the reaction is also considered. In addition, the passivation of the molybdenite surface is examined. This phenomenon involves the formation of a layer of reaction products on the particle surface, which hinders access of nitric acid to the unreacted mineral and slows its further oxidation.
Keywords: molybdenite; MoS_2; nitric acid; oxidation; mechanism; kinetics; passivation; hydrometallurgy; molybdic acid; molybdenum oxide; sulfuric acid; sulfide ores.

Introduction. In recent years, hydrometallurgical methods have increasingly been considered for processing molybdenum concentrates and industrial products. This is due to the gradual depletion of high-grade molybdenum ore reserves and the declining quality of extracted raw materials and the concentrates produced from them. As a result, conventional processing methods, particularly roasting, do not always provide the required efficiency and are not suitable in every case for processing such raw materials [1, 2].

Hydrometallurgical methods are based on treating mineral raw materials with aqueous solutions of chemical reagents. Their use makes it possible to transfer molybdenum and other valuable components into solution and then recover them from the resulting liquid phase. One advantage of these methods is the possibility of comprehensively processing raw materials and recovering not only molybdenum but also associated rare and precious metals.

Despite their advantages, the hydrometallurgical processing of low-grade molybdenum concentrates and industrial products presents certain difficulties. These include the instability of chemical reactions, insufficiently high recovery of molybdenum and associated metals, and the lack of adequately substantiated recommendations for selecting and controlling technological parameters. Effective process control requires consideration of the chemical and mineralogical composition of the raw material, reagent concentration, temperature, treatment duration, and particle size. One of the main reasons for the existing limitations is the insufficient understanding of the theoretical principles governing the hydrometallurgical processing of molybdenite-containing materials [3, 4].

In this regard, the study of the decomposition of molybdenite (MoS_2) by nitric acid is of particular interest. Nitric-acid leaching makes it possible to oxidize sulfide compounds and change the chemical forms of the mineral components, creating conditions for subsequent molybdenum recovery. However, the efficiency of this process depends on the mechanism of interaction between the mineral and the acid, the nature of intermediate reaction products, and the possible formation of a surface layer that impedes further interaction between the reagents.

This work is one stage in the investigation of the mechanism and chemical principles of nitric-acid decomposition of molybdenite-containing industrial products. The main objective is to establish the patterns of interaction between molybdenite materials and nitric acid and to identify ways to improve the nitric-acid leaching process by developing its theoretical foundations. The results may provide a scientific basis for the well-founded selection of technological conditions for processing molybdenum-containing raw materials and increasing the recovery efficiency of valuable components.

Results and Discussion. Molybdenum is a strategically important metal used in metallurgy, the chemical industry, and catalyst production. Its main industrial mineral is molybdenite (MoS_2). One effective method for processing molybdenum-containing concentrates is hydrometallurgical treatment, in particular oxidation with nitric acid. However, this process occurs in several stages and is accompanied by the formation of oxide and sulfide films, which complicates its kinetics [5, 6].

Nitric-acid leaching of molybdenite concentrates and intermediate products is carried out at the Uzbek Combine of Refractory and Heat-Resistant Metals. In this method, molybdenite (MoS_2) is oxidized by nitric acid; the sulfide ion is converted into sulfates, while molybdenum passes into soluble molybdate forms. As a result, molybdenum is oxidized to form water-soluble molybdates. This process creates favorable conditions for recovering molybdenum from concentrates and for subsequent stages of metallurgical processing.

However, because the chemistry of nitric-acid oxidation of molybdenite and its associated minerals has not been sufficiently studied, controlling the technological process under industrial conditions remains a complex task. This requires a detailed investigation of the chemistry and mechanism of the process.

Stages of nitric-acid leaching of molybdenite concentrates [7, 8, 9]:

1. Concentrate preparation. Molybdenite concentrate (MoS_2) and intermediate products are dried, ground, and classified by particle size to increase the reactive surface area.

2. Preparation of the reaction mixture. The concentrate is charged into an acid-resistant reactor. Concentrated nitric acid (HNO_3) is added. If necessary, water is added to adjust the acidity and achieve the optimum reaction temperature.

3. Oxidative leaching. Upon heating and stirring, MoS_2 reacts with HNO_3. Molybdenum sulfide is oxidized:

$$\mathbf{MoS_2 + 6HNO_3 \rightarrow H_2MoO_4 + H_2SO_4 + 6NO} \quad \mathbf{(1)}$$

4. Filtration and phase separation. After the reaction is complete, the mixture is cooled. Insoluble solid residues (gangue minerals) are separated by filtration. The liquid phase contains molybdenum in the form of soluble molybdates.

5. Solution concentration and purification. Evaporation and precipitation are carried out to recover ammonium molybdate or other intermediate molybdenum compounds. If necessary, impurities (Fe, Cu, Pb, Zn, etc.) are removed by neutralization or selective precipitation.

6. Production of the final product. Ammonium paramolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) is obtained from the purified solution. It is then calcined to form pure MoO_3, which is used as a raw material for producing metallic molybdenum and alloys.

Thus, at high HNO_3 concentrations, the reaction proceeds intensively and is accompanied by the release of brown gases (NO_2). In dilute solutions, the process is slower, but the formation of a passivating oxide film is less pronounced. An increase in temperature accelerates the reaction; however, it may lead to the formation of a dense MoO_3 layer that hinders further interaction [10, 11].

The particle size distribution of molybdenite plays a key role: the smaller the particles, the higher the degree of oxidation. The experiments were carried out in a thermostatically controlled cell with automatic temperature regulation. The nitric acid concentration, reaction duration, and temperature were varied. Molybdenum concentrations in the solutions, the volumes of gases released, and their evolution rates were determined. The experiments were conducted at a liquid-to-solid ratio (L:S) of 50:1. The MoS_2 sample mass was 1 g. A molybdenite concentrate containing 52% molybdenum was used.

Preliminary experiments showed that, in order to determine the volume of gases released, it was necessary to select a liquid for the intermediate vessel that would practically not absorb NO and NO_2. Water and saturated NaCl solution are known to absorb very little NO. We found no literature data on liquids that do not absorb NO_2. Therefore, solutions and liquids that do not absorb NO_2 were selected empirically. It was established that organic solvents (TBP, kerosene) cannot be used for this purpose because they interact with NO_2. For subsequent determination of the NO_2 volume, 60% nitric acid saturated with nitrogen dioxide was used. When NO was the predominant gas released, the intermediate vessel was filled with water or saturated NaCl solution.

Table 1

Dependence of the molybdenum content in solution on temperature (τ = 30 min, HNO_3 = 207 g/L, L:S = 50:1)

T, °C	Gas volume, mL	Molybdenum content in solution, g/L	Degree of molybdenum oxidation, %
60	88	1,91	20,0
70	424	4,36	45,4
80	832	5,72	58,3
90	1166	7,72	78,8

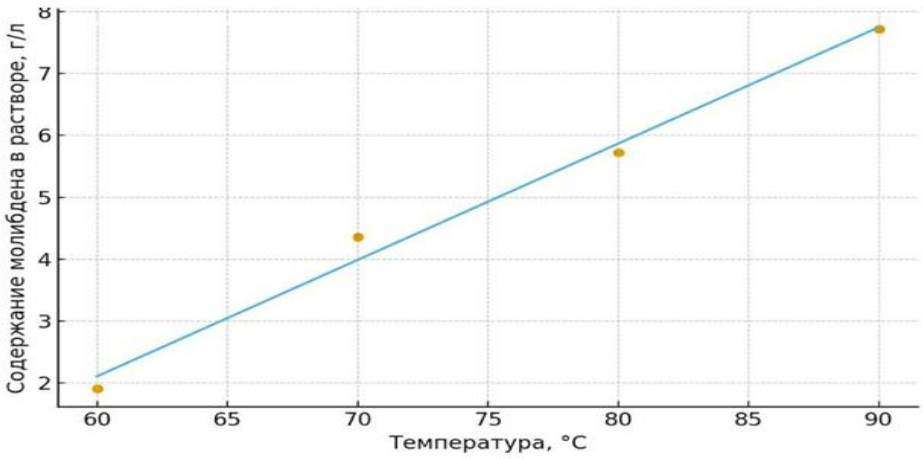


Fig. 1. Dependence of the molybdenum content in solution on temperature (τ = 30 min, HNO_3 = 207 g/L, L:S = 50:1)

The data obtained show that at relatively low temperatures (60–70 °C), the experimentally measured volumes of gas released are significantly lower than the values theoretically calculated from the reaction at the corresponding molybdenum concentrations in solution. In contrast, when the temperature increases to 80–90 °C, the experimental and calculated values show almost complete agreement within the experimental error. Thus, at low temperatures there is a discrepancy between the amount of gas released and the molybdenum content in solution, indicating that the oxidation process is slow and probably involves side-reaction stages.

The effects of several salts ($NaNO_3$, Na_2SO_4, and NH_4NO_3) on the oxidation of molybdenite by nitric acid were investigated. The salts were added to the initial nitric-acid solution containing 400 g/L HNO_3. The concentration of each added salt was 100 g/L. The experiments were conducted at 90 °C. The distribution of oxidized molybdenum between the solid and liquid phases and the total amount of oxidized molybdenum were determined. The experimental results obtained in the presence of Na_2SO_4 are presented in Table 2 and Fig. 2.

Table 2

Dependence of the molybdenum content in solution and in the precipitate on treatment time in the presence of Na_2SO_4

Duration, min	Solution volume, mL	Mo content in solution		Precipitate mass, g	Mo content in precipitate		Total amount of Mo, g
		g/L	g		g/L	g	
15	74	24,8	1,83	-	0	0	1,83
30	80	27,1	2,17	-	0	0	2,17
60	82	29,4	2,41	1,69	7,1	0,12	2,53
120	88	26,2	2,31	1,77	20,4	0,36	2,67

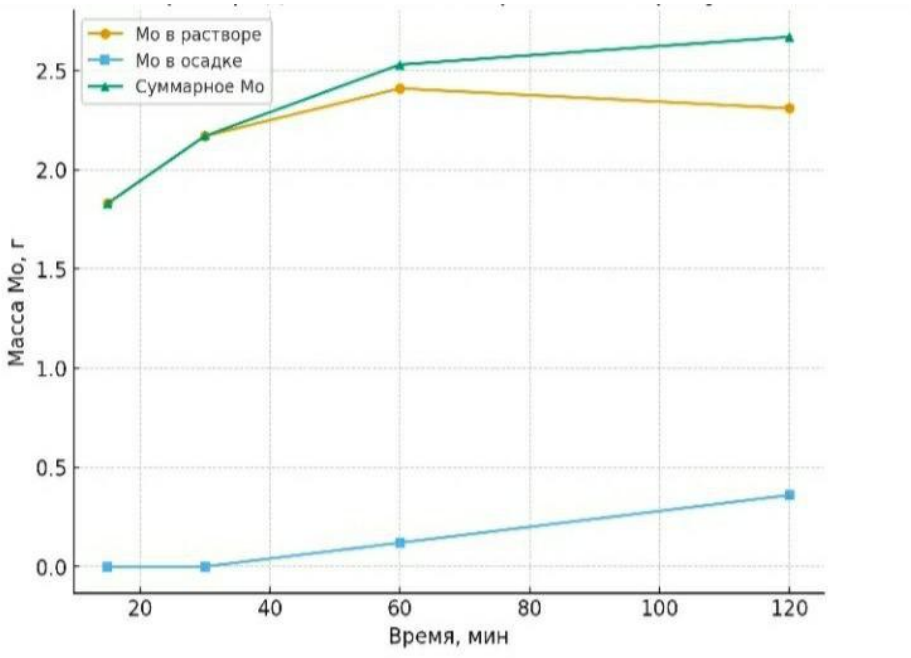


Fig. 2. Dependence of Mo distribution on time in the presence of Na_2SO_4

The investigation of the distribution of molybdenum between the solution and the solid phase in the presence of Na_2SO_4 showed that the metal-recovery process is distinctly multistage. In the initial stages (15–30 min), molybdenum is almost entirely present in solution, indicating active dissolution of the mineral phase. With a further increase in treatment time (60–120 min), redistribution of molybdenum is observed: its concentration in solution decreases, while its content in the precipitate increases substantially. At 120 min, the molybdenum mass fraction in the precipitate reaches 20.4%, indicating the transfer of part of the metal from solution to the solid phase, probably in the form of sparingly soluble compounds or coprecipitation products.

The total amount of molybdenum in the system increases from 1.83 g (15 min) to 2.67 g (120 min), indicating that leaching of the raw material intensifies over time, although the process is close to equilibrium by this point. The results confirm the importance of treatment time and the role of the sulfate ion in determining the phase distribution of molybdenum during nitric-acid decomposition.

Conclusion. The investigation of the mechanism of molybdenite (MoS_2) oxidation by nitric acid examined the main patterns of the mineral's chemical interaction with an oxidizing medium, the features of reaction product formation, and the factors determining the rate and efficiency of the process. It was established that the nitric-acid oxidation of molybdenite is a complex physicochemical process involving successive transformations of the mineral components and changes in the composition of the solid and liquid phases.

An important area of the study is the formation of molybdenum and sulfur compounds during oxidation. When molybdenite reacts with nitric acid, molybdenum changes its oxidation state from +4 to +6, while sulfur is oxidized to compounds in higher oxidation states. Depending on the process conditions, molybdenum transformation products may include molybdenum oxide (MoO_3) and molybdic acid (H_2MoO_4); deep oxidation of sulfur may produce sulfuric acid (H_2SO_4) or sulfates. The formation and relative proportions of these compounds depend on the nitric acid concentration, temperature, treatment duration, and composition of the initial raw material.

It was also established that the efficiency of molybdenite oxidation is determined by the combined influence of technological parameters. An increase in temperature generally accelerates chemical reactions; an increase in nitric acid concentration changes the oxidizing conditions of the process; and a decrease in particle size increases the specific contact surface area between the mineral and the reagent. However, an excessive increase in acid concentration or temperature does not always result in a proportional improvement in efficiency, since surface passivation, oxidant consumption, and the characteristics of the mineral raw material may have a significant effect.

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