METALS RECOVERY FROM MOLYBDENITE CONCENTRATE BY ELECTROOXIDATION AND LEACHING

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Abstract. Mineral resources today are increasingly determined by the concept of "persistent". The reason for their difficult opening is in the composition of sulfide nature, leading to passivation of the surface and inhibition of hydrometallurgical processes. The way out in practice was found in oxidative firing and some other technologies. The work compares the results of leaching of molybdenite concentrate of Almalyk MMC JSC according to the schemes: the existing calcining-ammonia and non-calcining with nitric acid, hypochlorite opening and leaching. Non-calcining with hypochlorite opening and leaching scheme is not only ecologically cleaner in compare with pyro-metallurgy, but it relocates quantitatively to the solution not only molybdenum, rhenium, but gold and silver as well.

1. Introduction

Sulfide minerals are susceptible to surface passivation under oxidizing conditions [1]. Its overcoming is achieved through: 1 - oxidative roasting, 2 - in an autoclave, 3 - hydrometallurgical methods.

Firing is used in the processing of molybdenite concentrates (MoC) [2], containing Re [3]. Its disadvantages inherent in pyrometallurgy include the burden on the environment and high capital costs. MoC is oxidized in an autoclave with the addition of an HNO₃ catalyst [4]. An increase in temperature and pressure accelerates leaching in autoclave, but it is not feasible for low grade ores.

Hydrometallurgical processes are considered traditional, but also promising, due to the relative minimization of environmental threats. With the exception of bio-oxidation (carried out in H₂SO₄), sulfide minerals are opened in various solutions using oxidizing agents: chlorine [5], oxygen [6], HNO₃ with O₂ [7], salts of Fe (III) [8], ozone [9], sodium peroxodisulfate [10], bubbling air into a solution of HCl + MgCl₂ [11], reagent hypochlorite [12], hypochlorite generated in viva by electrolysis of 10% NaCl [13-16].

The mechanism of surface passivation of sulfides is extended to known minerals in the composition of the Mo-concentrate of Almalyk MMC JSC [17]. According to the technology existing there, it is granulated with kaolin (8-10% by weight), burned in a drum furnace with sublimation of rhenium oxide, ammonia leaching of the cinder [18]. To eliminate the effect of dilution of Mo caused by kaolin, an organic binder was proposed instead, with firing in a fluidized bed furnace [19-20]. Meanwhile, the hydrometallurgical processing of molybdenite concentrate remains an alternative to this technology [21]. One of its promising areas is hypochlorite electrochemical oxidation and
leaching [22-23].

2. Methods

Samples of molybdenite concentrate (38% Mo in the MoS\textsubscript{2} phase) were used. The concentrations of Cu (II), Fe (III), Mo (VI), Re (VII) were determined photocolorimetrically (KFK-2) and spectrometrically (AAC Perkin-Elmer 3030B, ICP-Aligent 7500 ICP MS).

Microscopy of the samples was performed on SEM-EDS scanning electron microscopes: EVO-MA (Carl Zeiss, Germany, Oxford Instrum, UK, with a resolution of 3 nm) and JCM-6000 Neoscope II (Jeol, Japan, in the range of 10-60000 times and a resolution of up to 30 nm).

Kinetic measurements were performed with Mo-concentrate powders weighing up to 6 g, s : w = 1: 7 and 1:75, with stirring, 300 rpm, and a temperature of 20-70 ° C. Firing of Mo-concentrate granules (with kaolin or an organic binder) was carried out in furnaces: industrial drum and laboratory, fluidized bed. Hypochlorite leaching of MoC was carried out in solutions: 12% hypochlorite reagent (GOST 11086-76) and in a solution of 10% NaCl by electrooxidation, generating hypochlorite on the anode of the electrolyzer (Figure1).

![Figure 1. Scheme of electrooxidation of Mo-concentrate in a solution of 10% NaCl. Designation: 1-potentiostat PI-50-1, 2-pH meter, 3-magnetic stirrer, 4-thermostat, 5-cell, 6-anode, 7-capillary Luggin, 8-electrode silver chloride, 9-cathode, 10-thermometer.](image1)

![Figure 2. Scheme of the pilot installation of a fluidized bed furnace (FB) for firing MoC. Designation: 1-gas burner; 2-boiler; 3 - zone loading granules MoC; 4 - viewing window of the hearth of the firing zone; 5 - pipeline of gas products of firing; 6 - scrubber for absorption of rhenium oxide and SO\textsubscript{2}; 7 - filter; 8 - water refrigerator, 9 - pump.](image2)

3. Results

Given the purpose of the work, it was of interest to compare the efficiency of the extraction of valuable metals from molybdenum concentrate under conditions of preliminary oxidative firing, changes in temperature, nature and concentration of the leaching agent, the process time (Table 1).
Table 1. Comparison of the degrees of extraction (in solutions) of metals from cinder and MoC (total initial raw materials). Designation: 1-12 - a cinder of firing MoC (570 °C): 1-3, 7-9 in a fluidized bed furnace; 4-6, 10-12 in a rotary kiln, in both - with O₂ access, 13-16 - MoC without firing, leaching: 13-15 - in ammonia after nitrate opening, 16-18 - opening and leaching at 12% hypochlorite, pH 11-12.

| Sample, No. | Binder | Reagent leaching, % | T, °C | Leaching time, min | Extraction degree (%) | Cu | Mo | Re | Au | Ag |
|-------------|--------|---------------------|-------|--------------------|----------------------|----|----|----|----|----|
| 1- calcine  | organic | NH₄OH | 90   | 90             | 95.5  | 93.0 | 97.0* | - | - |
| 2- calcine  | organic | 25% | 20 | 180 | 96.8  | 94.0 | 98.0* | - | - |
| 3- calcine  | organic | 270 | 20 | 90 | 96.9  | 97.6 | 99.7* | - | - |
| 4- calcine  | kaolin | 20 | 180 | 91.4  | 93.8 | 99.5* | - | - |
| 5- calcine  | kaolin | 270 | 92.5 | 95.8 | 99.3* | - | - |
| 6- calcine  | organic | NaClO | 20 | 90 | 47.7  | 99.7 | 99.5* | 94.6 | 73.3 |
| 7- calcine  | organic | 12% | 180 | 55.3 | 99.8 | 99.6* | 95.3 | 79.4 |
| 8- calcine  | organic | 270 | 64.5 | 99.8 | 99.9* | 96.5 | 99.0 |
| 9- calcine  | Kaolin | 20 | 90 | 66.4 | 99.6 | 99.3* | 92.3 | 72.0 |
| 10- calcine | organic | 180 | 68.4 | 99.8 | 99.7* | 93.5 | 77.3 |
| 11- calcine | organic | 270 | 98.2 | 99.9 | 99.6* | 95.1 | 97.5 |
| 12- calcine | None | NH₄OH | 70 | 90 | 73.5  | 98.0 | 93.8 | - | 70.8 |
| 13- MoC     | None | HNO₃ 56% | 180 | 75.5 | 98.5 | 94.0 | - | 72.0 |
| 14- MoC     | None | 25% | 270 | 88.6 | 98.6 | 99.9 | - | 94.0 |
| 15- MoC     | None | NaClO | 40 | 90 | 83.5  | 98.1 | 99.9 | 93.8 | 81.0 |
| 16- MoC     | None | 12% | 180 | 84.5 | 98.3 | 99.9 | 94.0 | 83.0 |
| 17- MoC     | None | 270 | 84.5 | 98.7 | 99.9 | 94.5 | 84.0 |  |  |

Note: * - extraction of rhenium - total: in the gas (in the form of Re₂O₇) and liquid phases.

Figure 3. Change in the concentration of active chlorine in a 2-chamber membrane electrolyzer, galvanostatic mode I = 2.45 mA, 10 (mA/V), solution volume 75 cm³. Over 60 min, the concentration of NaNClO = 0.06% was achieved.

Figure 4. Change in the concentration of active chlorine in a 1-chamber electrolyzer, galvanostatic mode, I = 109.9 mA, 0.1 (A/V), the solution volume is 75 cm³. Over 360 min, the concentration of NaNClO = 1.13%.
Figure 5. Change in the concentration of active chlorine in a 1-chamber electrolyzer, galvanostatic mode, $I = 109.9$ mA, 0.1 (A/V), solution volume 75 cm$^3$. Over 360 minutes, NaClO concentration = 5.12% was reached.

Figure 6. Change in the concentration of active chlorine in a 1-chamber electrolyzer, galvanostatic mode, $I = 109.9$ mA, 0.1 (A/V), solution volume 75 cm$^3$. Over 360 minutes, NaClO concentration = 10.0% was reached.

From Table 1 it follows: 1) from the cinder (samples 1-12), the extraction of Cu, Mo, Re - almost completely takes place in an ammonia medium in 90 minutes, in 12% hypochlorite, copper reaches the same level of extraction in only 270 minutes, Mo is already complete in 60 minutes; precious metals in ammonia are not extracted, in nitric acid, Au - is not extracted, Ag - partially; in hypochlorite: Au - completely in 90 minutes; Ag - completely in 270 min.

The material of the MoC binder granules did not affect the degree of metal extraction, with the exception of Au and Ag: the organic binder gave better results than kaolin. 2) from MoC: in nitric acid: Cu - completely in 270 minutes, Mo and Re — completely in 90 minutes, Ag - partially; in hypochlorite: Au - completely in 90 minutes; Ag - completely in 270 min.

The next task was to search for the generation modes at the anode of the hypochlorite electrolyzer in an electrolyte of 10% NaCl. Two types of synthesis were tested with pH control: in a two-chamber diaphragm electrolyzer with a volume of 90 cm$^3$, and in it in a 1-chamber (without membrane); electrodes - graphite, the ratio of the areas of the anode / cathode, varied: from 1:1 to 100: 1, temperature 20 °C, stirring on a magnetic stirrer, 300 rpm. The concentration of active chlorine generated in the cell was determined according to GOST 11086-76 (Figures 3-6). By increasing the ratio of the anode/cathode areas (from 1:1 to 100:1), the hypochlorite concentration in the 1-chamber electrolyzer was increased from 1.13% (Figure 4) to 5.12% (Figure 5) and 10.0 (Figure 6).

Table 2. The degree of Mo extraction by electrooxidation of MoC sulfides in the electrolyte (C NaClO = 1.03-10.0%) T: W = 1:7 (75 cm$^3$ of 10% NaCl electrolyte).

| №  | Time (hour) | Extraction rate of Mo [%] in the electrolyte with NaClO concentration: |
|----|-------------|---------------------------------------------------------------------|
|    |             | 1.13%                  | 5.12%                  | 10%   |
| 1  | 6           | 4                      | 17                     | 27    |
| 2  | 24          | 4.7                    | 29.3                   | 64.6  |
| 3  | 48          | 8.4                    | 48.5                   | 98.5  |

The next objective of the study was the leaching of MoC in 3 variants of electrooxidation: in medium 1.13; 5.12; 10.0% NaClO, which was achieved by adding MoC to the electrolytes to the ratio S:W = 1:7; continuous electrolysis, stirring suspensions on a magnetic stirrer, 300 rpm (Table 2).
The distribution of elements in MoC matrix, as the suspension of the powder in the sulfate-hypochlorite electrolyte is oxidized, occurs as follows (table 3).

**Table 3.** Change in the composition of samples of Mo-concentrate as they oxidatively leach in a sulfate-hypochlorite electrolyte, over time.

| No. sample | Sulfide oxidation time, sec. | Content of elements in the solid phase, mass. % |
|------------|------------------------------|-----------------------------------------------|
|            |                              | 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| 0.0 | 42.3 |

**Figure 7.** UV spectra of samples 1-4.

**Figure 8.** IR spectra of samples 1-4.

The designation in fig. 10-11: exposure of samples in a solution of sodium hypochlorite, sec: No. 1 - 0; No. 2 - 60; No. 3 - 600; No. 4 - 1800 (right).

**Figure 9.** Radiographs (XRD Empyrean PANalytical) of samples No. 1-4. *Designation:* similar to figures 7-8.
4. Discussion

The IR spectra of samples No. 1-3 do not differ from each other, in contrast to the spectrum of sample 4. The most intense vibration bands for samples No. 1-3 were found in the range of 966 and 664 cm\(^{-1}\) (Figure 7). These peaks correspond to symmetric stretching vibrations (S – S). Obviously, oxidation should lead to a shift of the vibrational bands and the appearance in the spectra of the bands of symmetric and asymmetric S–O stretching vibrations, O–S–O deformation vibrations, symmetric O–S–O vibrations, and [MoO\(_4\)]\(^{2-}\) vibrations [fourteen].

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 was manifested in the appearance of new vibration bands in the range 981, 796, 517, 452 cm\(^{-1}\). In addition, unlike sulfides, oxygen compounds of metals 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, in sample No. 4 there are also components oxidized to sulfates or sulfites, molybdates.

At the same time, electronic reflection spectra are more sensitive to the ongoing oxidation of the samples, as indicated by a 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. The spectra of oxidized samples No. 3-4 are almost identical and are characterized by a shift in the transition of charge transfer to the long-wavelength region.

The data of X-Ray phase analysis of samples No. 1-4 (Figure 9) also indicate significant changes in the structure and phase composition. In the diffraction patterns, in addition to peaks of molybdenite, pyrite peaks are observed (5-7%), impurities of quartz and natural silicates. From the diffraction patterns it is seen that sample No. 3 is characterized by a small number of diffraction peaks, in addition to peaks of molybdenite, which can serve as confirmation of the destruction of the crystal structure of the initial Mo-concentrate. For sample No. 4, growth of new crystalline phases was observed, which formed oxidation products in a heterogeneous system: “Mo-concentrate powder - Na-hypochlorite solution”, during the interaction time of 1800 sec, at room temperature and atmospheric pressure.

A gradual “loss” of Mo and copper from the crystalline matrix of the material is observed, as a result of oxidative leaching of the sulfides of these metals from it, in the number of samples No. 1-No. 4 (Figure 10), as follows from the data of their surface control by scanning electron microscopy, with probe microanalysis of selected sites.

Which is consistent with the previously obtained results on the leaching of chalcopyrite in the presence of an oxidizing agent [2]: the dissolution of sulfide minerals is presented in the sequence: dissolution of the outer layer of the mineral at the beginning of the process leads to a short high speed...
of the process; - diffusion of Cu, Fe – ions from the bulk of the mineral, with their depletion of the surface of the solid phase; - enrichment of the mineral interface with sulfur, leading to a drop in the diffusion coefficients of metals; - continued thickening of the diffusion layer from the surface into the mineral.

From table 3 it follows that as the oxidative leaching of samples of samples No. 1-4 in a sulfate-hypochlorite electrolyte, over a period of 0-1800 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%, increased for the following elements: Si - from 2.2 to 16.1%, oxygen - from 12.8 to 42.3%. As follows from Figures 8-10 and Table 3, the time of oxidative leaching of MoC in 1800 sec was insufficient for 100% extraction of Mo into a solution and oxidation of sulfates to oxide-sulfate compounds. Nevertheless, the dynamics of the process are quite clearly demonstrated in the model of 4 samples of this system.

5. Conclusions

The results of leaching of molybdenite concentrate of JSC Almalyksky MMC are compared according to the schemes: the existing calcining-ammonia and non-calcining with nitric acid, hypochlorite opening and leaching. Preliminary oxidative firing was carried out both in the existing drum furnace of the enterprise (MoK granules with kaolin) and in the pilot fluidized bed furnace (granules with an organic binder, leveling the dilution of the cinder according to Mo). In addition to reagent hypochlorite leaching of MoC samples, MoC electrooxidation was used in a non-diaphragm electrolyzer charged initially with 10% NaCl, and the electrolysis time was up to 49 hours. In all cases, complete (> 97%) molybdenum recovery was achieved. In ammonia, Au Ag completely passed into a cake, and in hypochlorite - into solution. Nitric acid leaching led to an intermediate state: Au — in cake, Ag — partially in solution. By the example of oxidative leaching of samples of Mo-concentrate in a hypochlorite electrolyte, for up to 1800 sec, when studying the solid phase formed after reagent exposure, the destruction of sulfide compounds of molybdenum, copper, with the transition of most of them to a solution and the transformation of the remaining fraction from the sulfide to the oxide-sulfate phase, was established.

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