Analysis of the reasons for molybdenite losses and improvement of recirculating water conditioning regimes in the process of copper-molybdenum ore flotation

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Copper-molybdenum ore flotation at closed water circulation system is accompanied by significant losses of molybdenum, recovery of which often does not exceed 50%. The losses are often caused by changing ion composition of the pulp aqueous phase, and primarily accumulation of copper and calcium ions, causing the change in the state of mineral surface. The probability of molybdenite activation by copper cations under conditions of copper-molybdenum ore milling was determined by thermodynamic calculations and confirmed by spectral studies. It was demonstrated that the activation of molybdenite by copper ions increases floatability in the bulk flotation circuit, but causes depression and increase in molybdenite losses in the selective flotation circuit, that leads to decreasing the recovery into commercial concentrates. Kinetic parameters of the interaction of molybdenite with copper cations under milling conditions were experimentally determined, and the boundary concentration of copper cations (0.175 mg/l) was determined. The reasons for molybdenite flotability decline at elevated concentrations of calcium ions and molybdate ions were determined: the formation of calcium molybdate on the mineral surface under conditions of bulk flotation, which is transformed to hydrophilic calcium carbonate at pH above 9.5. The flotation studies established the maximum permissible concentration of copper ions (0.6 mg/l) and calcium (350 mg/l) in recirculating water, exceeding of which leads to deterioration of the process performance. Regime of joint conditioning of filtrates saturated with copper and utility fluids was developed, at the medium pH maintained at 7.5–7.8 by lime adding, providing reducing concentration of dissolved copper and technical fatty acids in the purified recirculating water to 0.4 mg/l and 0.55 mg/l, respectively. The developed conditioning regime for heavily polluted effluents of Erdenet GOK industrial cluster made it possible to increase the recovery of copper and molybdenum by 0.35% and 0.5%, respectively, when the effluents are involved in the water circulation system.

Key words: copper-molybdenum ores, molybdenite, activation, filtrates, effluents, wastewater, copper and calcium cations, flotation, recirculating water, conditioning.

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Introduction

Recovery of molybdenum in copper-molybdenum ore processing rarely exceeds 50%. At most processing plants, where mass fraction of molybdenum in ore is 0.01–0.02%, this element is considered to be accompanying and no special measures are taken to increase its recovery. However, in the case of Erdenet GOK, where the mass fraction of molybdenum rises to 0.03%, the cost of this metal amounts to up to 8% of the cost of marketable products, and the enterprise profitability substantially depends on its recovery. To increase the processing performance, it is necessary to determine the effect of the recirculating water components on the state of the surface and floatability of minerals [1–2]. When copper-molybdenum ores are processed using recirculating water system, copper, iron, calcium, and other ions accumulated in the pulp aqueous phase, and many of which negatively affect the flotation process [3-4]. Particularly noticeable decrease in the process performance takes place when the recirculation system involves pit, under-waste dump and under-dam waters, saturated with heavy metal ions, as well as utility fluids with high content of fatty acids [5-6].

The effect of copper ions on flotation of many sulfide minerals has been well studied; however, insufficient attention has been paid to the interaction of molybdenite with copper ions, although the fact of decreased recovery of molybdenite from mixed ores was noted by many researchers [7–8]. In a number of studies, it is noted that the decrease in molybdenite floatability is due to increase in the concentration of calcium ions [9–10].

When lime is used for depression of pyrite, significant decrease in molybdenite flotability is also observed [11-12]. The decrease in molybdenite flotability when adding lime in the milling process stage is connected with the processes occurring on the surface of minerals [13].

As the experience of using recirculating water system at Erdenet GOK showed, the use of tailings storage facility filtrate, saturated with metals, is accompanied by decreasing the process performance [14]. Therefore, in recent years, the enterprise operated a system of partial recirculating water supply, which provided for returning only a part of the filtrate to the processing plant [15]. A simple and effective way to improve the recirculating water technological properties by chemical bonding of heavy metal ions into insoluble compounds was then implemented. This method was implemented by mixing the filtrate having maximum concentration of heavy metal ions with ion-precipitators, presented, for example, in the form of carbonate, fatty acid, and hydroxyl ions, contained in utility waters and ash dump drainage [16]. However, the required decrease in the concentration of metal ions and fatty acids was not always achieved due to changes in the flow rate and properties of the mixed flows that required the development of more efficient regime of low-reagent conditioning.

1. The research materials and methods

Thermodynamic calculations of the mineral surface state and the processes of ion and molecular components interaction in the recirculating water conditioning processes were carried out using classical methods described in detail by Kakovsky I. A. and Abramov A. A. [17–18]. The method used involves the calculation of Gibbs energies and equilibrium constants of probable chemical reactions and determination of component ratios under equilibrium conditions. For electrochemical reactions, the probability of examined process was determined by the ratio of equilibrium and measured electrode potential of a mineral.

Kinetic analysis of the reactions in the studied systems was carried out using electrochemical measurements of the rate of sulfide mineral oxidation and the duration of activation process, measured by the potential drop technique [19]. For the electrochemical measurements, P40-X potentiostat — galvanostat with three-electrode cell was used.

To study the composition of compounds on the mineral surfaces, we applied the method of *X*-ray diffraction analysis using ADP2-01 instrument. The *X*-ray photograms were processed automatically using PDWin software. The composition of chemical compounds in the systems under consideration and the collector adsorption on the surface of molybdenite was determined by IR spectroscopy method using SPECORD 75 IR instrument.

Chemical analysis of the pulp liquid phase, recirculating water and conditioning products was carried out using traditional methods. The concentration of copper and molybdenum ions was measured by Nexion 300D atomic adsorption analyzer. The concentration of calcium ions was measured by gravimetric method. The medium pH was measured by potentiometric method.

Mineral floatability studies were carried out using a non-frothing flotation unit. Flotation experiments for ore and concentrates were carried out using mechanical flotation machines with cell volume of 0.1 to 3 liters. Milling ore before flotation was carried out in mills with steel grinding media. The finished milled ore fineness class was separated by the method of dry sieving.

Minerals and ore for the research were provided by the Erdenet GOK research department. The technological testwork for ore and concentrates was carried out in the pilot laboratory of the enterprise.

The research on recirculating water conditioning was carried out using a special installation in the pilot laboratory of the enterprise. In the installation, maintenance of operating mode was achieved using a system for automatic maintaining the medium alkalinity. Samples of the recirculating water for the research were mixed artificially or taken directly from the production water circulation system.

2. Investigation of the effect of copper and calcium ions on the state of molybdenite surface

Analysis of the aqueous phase ionic composition measurements in the ball-milling process stage at the Erdenet GOK processing plant showed that it contains noticeable concentrations of copper, iron, calcium, and molybdenum ions [15]. The sources of these ions are both milling processes accompanied by dissolution of oxidized minerals and recirculating water [1, 6]. In the copper-molybdenum bulk flotation, the medium alkalinity is significantly higher due to lime adding, however, even under these conditions, there are detectable concentrations of copper and iron ions, and the concentration of soluble molybdenum in the form of predominantly molybdate ions remains practically unchanged [16].

Thermodynamic calculations show that under milling and flotation conditions, the final product of molybdenite oxidation is molybdate ion [12–13]. This is consistent with the data of the pulp liquid phase assay at the Erdenet GOK processing plant, according to which noticeable amount of molybdenum in dissolved form (4-7 mg/l) is contained in the pulp liquid phase in the milling and flotation operations. However, the oxidation of molybdenite proceeds very slowly that leads to the presence, on the mineral grain surface, of both the initial molybdenite and molybdenum dioxide, which is relatively stable intermediate product of the oxidation reaction.

The reactions of molybdenite activation by copper ions are accompanied by redox processes. Considering the staged proceeding of the activation reactions and the mismatch of concentrations in the liquid medium volume and on the mineral surface, three groups of the activation reactions are assumed, which are presented in

Reactions of molybdenite activation by	y copper ions and values o	f the thermodynamic parameters
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No.	Reactions	∆G ⁰ , kJ/mol	E ⁰
1.	$MoS_2 + 2Cu^{2+} + 4H_2O = 2CuS + H_2MoO_4 + 6H^+ + 2e$	83.571	0.433
2.	$MoS_2 + 2Cu^{2+} + 4H_2O = 2CuS + HMoO_4^- + 7H^+ + 2e$	115.023	0.596
3.	$MoS_2 + 2Cu^{2+} + 4H_2O = 2CuS + MoO_4^{2-} + 8H^+ + 2e$	150.196	0.778
4.	$MoS_2 + 2Cu^{2+} + 2H_2O = 2CuS + MoO_2 + 4H^+$	-4.56	lg <i>K</i> = 3.35
5.	$MoS_2^+ (CuOH)_2CO_3^+ 2H_2^- = 2CuS^+ 3H^+ + HMoO_4^- + H_2CO_3^- + 2e$	102.245	0.529
6.	$MoS_2^+ (CuOH)_2CO_3^+ 2H_2O = 2CuS + 4H^+ + MoO_4^{2-} + H_2CO_3^- + 2e$	87.846	0.455
7.	$MoS_2 + (CuOH)_2CO_3 + 2H_2O = 2CuS + 5H^+ + MoO_4^{2-} + HCO_3^- + 2e$	124.256	0.644

Table 1. The first group of the reactions (1-3) involves the interaction of Cu²⁺ ions with molybdenum and the oxidation-exchange reaction with the formation of H₂MoO₄, HMoO₄⁻, MoO₄²⁻. The second group of the reactions involves the interaction of Cu²⁺ ions with molybdenite and the formation of MoO₂ by the exchange reaction 4. The third group of the reactions involves the interaction of Cu²⁺ ions with molybdenite, when the ions are in equilibrium with the precipitated form of Cu, (CuOH)₂CO₃, and the oxidation-exchange reaction with the formation of HMoO₄⁻ and MoO₄²⁻ (reactions 5–7).

The thermodynamic analysis show that molybdenite can interact with copper ions both under the milling conditions and in the conditions of bulk copper-molybdenum flotation. Moreover, as the activation mechanisms, all the considered processes may be considered.

The results of thermodynamic calculations are valid for systems that are in equilibrium, achieved with relatively long proceeding of the reactions in the system under consideration. To transfer the results of the thermodynamic calculations to real systems, an experimental verification was carried out.

For the experimental verification, the experiments were carried out on the interaction of the slurry class molybdenite ($-5 \mu m$) with solutions containing copper ions (in the form of copper acetate). The duration of the interaction of the mineral with copper ions was 20 minutes that is comparable with the time of the ore milling or flotation.

Based on the ratio of the amounts of absorbed copper and the released molybdenum in molar terms, the conclusion was drawn about the exchange-oxidation nature of the reaction. The analysis of the ratio of the absorbed and released moles of the dissolved copper and molybdenum, taking into account natural oxidation of the minerals, indicates the likelihood of reactions 1-3 in Table 1 with the formation of covellite CuS on the molybdenite surface.

To confirm the calculation results, X-ray-phase quantitative analysis of the copper compounds on the molybdenite surface was carried out using ADP2-01 computerized instrument. The X-ray photograms were processed automatically using the PDWin software. The results of the X-ray phase analysis showed that the copper that left the solution is fixed on the molybdenite surface with formation of a sulfide compound similar in crystal lattice parameters to covellite.

Copper sulfides formed on the surface of molybdenite, most likely covellite, are highly adsorption-active to the collector that is confirmed by the IR spectrophotometry of molybdenite, which underwent initial treatment with copper ions and then was used as collector by allyl ether of amyl-xanthic acid in the flotation process. On the IR spectra of the treated molybdenite, increased absorption of IR radiation in the range of wave numbers of 1020– 1150 cm^{-1} , 2916 cm⁻¹, characteristic of this compound, is distinctly observed.

To determine the conditions of the molybdenite activation processes, the kinetic method was used, according to which the oxidation time of the mineral monolayer was compared with the activation process duration. The activation process duration was taken equal to the time of the transition process of changing the mineral electrode potential when copper ions were introduced into the solution. In fact, with this technique, the kinetic probability of the oxidation and activation processes is compared, since shorter duration of one of these processes increases the likelihood that this process will prevail on the mineral surface.

The duration of the transition process of changing the mineral electrode potential when copper ions are introduced into the solution was measured by the potential drop technique according to the procedure described in [17]. The measurement was carried out in the amperestatic conditions (I = 0), created by the P40-X potentiostat-galvanostat with three-electrode cell. The activation process duration was taken equal to the half-period of the "potential drop" observed when the copper salt was fed.

The results of the measurements at various pH show that the duration of the molybdenite activation process at close to the average copper ion concentrations (2 mg/l) is 4.1–6.9 s. The duration of the mineral monolayer oxidation was calculated from the density of the corrosion current, obtained by the method of potentiodynamic curves, recorded using the P40-X potentiostat-galvanostat.

Comparison of the mineral monolayer oxidation duration and the time of its activation by copper ions shows that these values are close to each other in magnitude and



Fig. 1. The dependence of the potential drop of the molybdenite (*a*) and pyrite (*b*) electrode when copper salt solution is supplied on the calculated concentration of copper ions (*I*) and the calculated boundary concentrations of copper ions (*2*)

lg[Ca²⁺]



Fig. 2. Diagram of thermodynamic stability of calcium compounds in presence of molybdate ions in $lg[Ca^{2+}] - pH$ coordinates: M — the area of pH and concentration of calcium ions under milling conditions; F — the area of pH and concentration of calcium ions under flotation conditions; the solid line — $[H_nMoO_m] = 10^{-5} \text{ mol}/1$, $[H_nCO_3] = 10^{-3} \text{ mol}/1$; the dashed line — $[H_nMoO_m] = 3 \cdot 10^{-5} \text{ mol}/1$, $[H_nCO_3] = 10^{-4} \text{ mol}/1$. Spectral verification results: \bigcirc — calcium molybdate; \oslash — calcium carbonate

the activation of molybdenite by copper ions is kinetically quite achievable.

The results of the measurements of the mineral potential drops upon activation were used to determine the necessary (boundary) concentration of copper ions for molybdenite and pyrite activation under the milling conditions (pH = 8.5). For this purpose, the dependence of the potential drop (ΔE) of molybdenite and pyrite electrodes on the copper concentration was built.

The results showed that the dependence built in semilogarithmic coordinates ($\Delta E = \text{flg} [\text{Cu}^{2+}]$) is close to straightforward (Fig. 1, *a*, line 1) and cuts off the copper concentration on the abscissa curve equal to 0.175 mg/l for molybdenite (Figure 1, *a*, point 2) and 0.3 mg/l for pyrite (Figure 1, *b*, point 2). The result obtained is quite important, since it indicates greater tendency for molybdenite to be activated by copper ions compared to pyrite.

The obtained concentrations of copper ions are ten times higher than those calculated by the thermodynamic method (0.001-0.01 mg/l) and are close to those measured in the pulp liquid phase in the milling operation.

The cations of calcium and anions of molybdic acid contained in the pulp liquid phase are brought in with the recirculating water or when adjusting the medium alkalinity. To determine their influence on the state of molybdenite surface, diagrams of thermodynamic stability of calcium compounds inw the volume of the pulp liquid phase and on the surface of molybdenite were built.

To assess thermodynamic probability of such process, the reactions of interaction of the molybdenum products with calcium ions were considered and the diagram of thermodynamic stability of the compounds in pH - log[Ca²⁺] coordinates was built (Fig. 2).

Analysis of the calculation results presented in the calcium compound stability diagrams in Fig. 2 shows that under the milling conditions, the concentrations of calcium cations and molybdic acid anions are sufficient for the formation of calcium molybdate in the volume of the pulp liquid phase and on the surface of molybdenite. It should be noted that the likelihood of calcium molybdate formation on molybdenite is higher in lower alkalinity medium, whereas that of calcium carbonate formation, in higher alkalinity medium (pH above 8-9.3).

In the process of bulk copper-molybdenum flotation, both the shift in the aqueous phase pH to the alkaline zone and increasing the concentration of calcium ions due to adding lime as the medium pH regulator is observed. In addition to the characteristic increasing the concentration of calcium ions, the concentration of molybdate ions also increases that indicates the decomposition of calcium molybdate.

The results of X-ray spectral studies confirmed the calculation results and showed that, in the zone of pH = 6.7-8.5, calcium molybdate is identified on the surface of molybdenite; at pH = 9.2, a mixture of molybdate and calcium carbonate; at pH = 10.3, calcium carbonate.

The effect of calcium ions and molybdic acid on the surface properties of molybdenite was also investigated by electrochemical method. Potentiodynamic curves were recorded by the P40-X potentiostat-galvanostat using three-electrode circuit. Analysis of the potentiodynamic curves shows that the replacement of sodium hydroxide with calcium hydroxide as the regulator of pH reduces the molybdenite oxidation rate in 2.5 times. The decrease in the molybdenite oxidation rate in presence of calcium ions is the consequence of blocking the surface with insoluble products of the mineral oxidation and corresponds to the discussed mechanism of action of calcium ions on the surface of molybdenite.

The obtained results confirmed the fact that under the milling conditions at high concentrations of calcium, on the surface of molybdenite, calcium molybdate forms, which, with increasing the medium pH, turns into calcium carbonate, which causes decreasing the floatability of molybdenite.

3. Selection of requirements for recirculating water composition to maintain the flotability of molybdenite in the process of copper-molybdenum ore processing

The effect of molybdenite activation is manifested in wide range of copper ion concentrations (Fig. 3) in neutral and slightly alkaline solutions (8.5). However, the effect of increasing the flotability of molybdenite decreases with increasing pH; when molybdenite is activated in alkaline solution with pH of 10.3, the effect of increasing flotability is not observed. The results confirm the conclusion that molybdenite propensity to activation by copper ions decreases with increasing the solution alkalinity.

To assess the effect of the activation process on the flotability of molybdenite in the selective flotation circuit, the flotation concentrate was re-floated after conditioning in sodium sulfide solution. The results of laboratory flotation experiments showed that the activation of molybdenite by copper ions reduces its recovery into molybdenum concentrate by 3-12% (Fig. 4).

The selectivity of the molybdenite separation from copper minerals significantly decreases. The results obtained allow broadly interpreting activating effect of copper ions on molybdenite in milling and bulk flotation as negative, since the losses of molybdenite in the selective circuit exceed the growth of its recovery in the bulk flotation circuit.

To evaluate the effect of calcium ions on the flotability of molybdenite, laboratory experiments were carried out, in which calcium acetate producing near-neutral medium, or calcium hydroxide producing alkaline medium, were added into the conditioning processing stage before flotation.

The experimental results shown in Fig. 5 demonstrated that the addition of calcium acetate to the milling processing stage decreases the recovery of molybdenite by 3-7%. If the addition is carried out in the form of calcium hydro-

ide, then the decrease in molybdenum recovery is much larger and reaches 23% at calcium ion concentration of 400 mg/l (Fig. 5, curve 2).

To clarify the effect of calcium ions or compounds on the flotation of molybdenite, flotation experiments were performed on copper-molybdenum ore, subjected to processing at the Erdenet GOK processing plant. The crushed ore was floated in bulk copper-molybdenum flotation regime, similar to that used at the GOK processing plant, at pH of 10.2 to 10.35 and Aeromix-5140 collector concentration of 15 g/t, using MIBK reagent as frothing agent. To the ore milling operation, before flotation, calcium acetate or calcium hydroxide was added with concentration of calcium ions of 100–600 mg/l at different pH. In a number of the experiments, ammonium molybdate was separately or additionally fed into the pulp. In some other



Fig. 3. Dependences of the molybdenite recovery on the concentration of copper ions (calculated); treatment: 1 - at pH = 6.5; 2 - at pH = 8.5



Fig. 4. Dependences of the molybdenite recovery (1, 2) and copper recovery (3) on the consumption of sodium sulfide in the separation of copper-molybdenum concentrate:
1, 3 – basic experiment; 2 – with preliminary activation by copper salts (10 mg/l Cu²⁺)



Fig. 5. Dependences of the recovery of molybdenite on the concentration of calcium ions in the aqueous phase:

I — when adding calcium acetate into the milling process; 2 — when adding calcium hydroxide into the milling process; 3 — when adding calcium acetate and sodium molybdate; 4 — when adding calcium hydroxide and sodium molybdate into the milling process

experiments, the effect of iron compounds and organic compounds (fatty acids) on the flotation performance was investigated.

When adjusting the flotation pH by lime, increasing copper recovery and decreasing iron recovery are observed. When adding ammonium molybdate to the milling process stage, decreasing floatability of all sulfides is observed. Noticeable change in the floatability of minerals is observed at joint adding calcium acetate and ammonium molybdate to the milling process operation. The decrease in molybdenite recovery reaches 10.3%, that of copper and iron sulfides, 2.5-3%.

When lime is added to ore milling process stage (to pH = 9.8), decreasing the floatability of all sulfides by 2.5–6% is observed. Similar results were obtained when co-adding calcium hydroxide and ammonium molybdate into the milling process.

The results obtained are in principle consistent with the results of the mineral flotation and show that increasing the concentration of calcium ions in the pulp aqueous phase above 300 mg/l contributes to the surface hydrophilization and decreasing molybdenite floatability. The greatest decrease in the flotability of molybdenite is observed at simultaneous increasing the concentrations of calcium ions and molybdate.

Concurrently, the studies have shown that the addition of soluble iron salts in concentration above 0.3 mg/l reduces the recovery of all sulfide minerals. Increasing the concentration of industrial fatty acids above 0.5 mg/l leads to deterioration of the bulk concentrate quality due to the extraction of rock-forming minerals into it.

Thus, the results of the laboratory and enlarged flotation studies on the minerals and ores made it possible to determine the limiting concentrations of copper and calcium ions (0.3 and 300 mg/l, respectively) in the aqueous phase of the pulp. Taking into account the mixing of the recirculating water that underwent the conditioning operation and the TSF clarification pond discharge water, maximum concentrations of copper and calcium ions in the circulating waters are 0.6 and 350 mg/l, respectively.

4. Development of recirculating water conditioning regimes

Many nonferrous metallurgy enterprises face acute shortage of process water. To solve this problem, they involve non-traditional sources, including heavily polluted industrial effluents and utility fluids [20]. For Erdenet GOK, the problem of expanding the resource base of water sources is solved by involving industrial effluents and utility fluids in the water-recycling system. This is due to significant losses of recirculating water from the TSF and the inability to use natural water from the Selenga River [15].

Attempts to expand the TSF flow rate by diverting to it the discharge waters from the treatment plant were unsuccessful due to worsening technological properties of the recirculating water and decreasing the beneficiation performance. A promising way for optimizing water recirculating systems is mixing heavily polluted waters of different composition. For example, when mixing TSF filtrates and municipal treatment plant discharge water, dissolved copper interacts with fatty acids, resulting in formation of insoluble precipitating compounds.

To determine the conditions for binding of copper ions and fatty acids to produce insoluble compounds, we used thermodynamic modeling of chemical processes of the mutual deposition.

Analysis of the precipitation composition shows that when concentration of oleic acid ions and compounds in the discharge waters exceeds 10^{-6} mol/l (0.3 mg/l), they interact with copper ions to produce normal copper oleate. The reaction proceeds in low-acidic and neutral solutions. At lower concentration of copper ions and oleic acid, copper oleate does not form. As pH increases to low alkaline level, copper oleate passes into copper hydroxidecarbonate and the concentration of oleate ions increases.

To select the best deposition conditions, a combined diagram of copper and calcium compounds stability was considered. Under the considered conditions, in the pH range from 5 to 9, the simultaneous formation of copper and calcium oleates is possible (Fig. 6).

To describe the conditions for the co-deposition of calcium and copper oleates, reaction 1 was considered:

$$2Ca^{2+} + 2Cu(Ol)_{2} + HCO_{3}^{-} + 2H_{2}O =$$

= (CuOH)_{2}CO_{3} + 3H^{+} + 2Ca(Ol)_{2} (1)

This equation, in fact, presents the resulting reaction that describes the equilibrium in the calcium oleate - copper oleate system.

Table 2.

The maximum permissible concentrations of ion/molecular components and the achievable ones with lime conditioning in the recirculating water

lkom	Ion/molecular components				
item	[Cu ²⁺]	[Fe ²⁺]	MoO ₄ ^{2–}	Ca ²⁺	[OI ⁻]
Maximum permissible concentration	0.3	0.3	4.5	350.0	0.5
Achievable concentration with lime conditioning (pH = 7.8–8.0)	0.15	0.1	2.5	360.0	0.4

The conditions for simultaneous proceeding of the considered processes (the co-deposition process) are described by the following equation:

$$lg[HCO_3^{-}] = 12.36 - 2 lg[Ca^{2+}] - 3 pH;$$

(6.36 \le pH \le 10.34) (2)

After substituting the mean values of ion concentrations to equation 2, analytical equation was obtained for the relationship between the variable parameters of the thermodynamic stability diagrams describing the conditions for the simultaneous binding of oleate ions into oleates of copper and calcium. This is characteristic for the conditions of the recirculating water conditioning when mixing filtrates of the TSF, treatment plants, and HPP ash dump.

$$pH = 4.12 - 0.67 \, lg[Ca^{2+}] - 0.33 \, lg[HCO_3^{-}]$$
(3)

Based on the data on the actual concentration of bicarbonate ions in the recirculating waters $(10^{-5}-10^{-4} \text{ mol/l})$, the optimal pH range (7.2–8.0) was established, at which the most complete deposition of oleate ions is achieved at high degree of copper ion deposition.

The specified pH range is achieved by mixing the discharge waters in the following ratio: the TSF filtrate -1, discharge waters from the municipal treatment plants -0.8, discharge waters from the HPP ash dump -0.2, with calcium ions added in the form of lime. When using Ca(OH)₂, increasing pH results in greater decrease in the concentration of copper ions than when using NaOH. The dependence of changing the concentration of oleate ions on pH when using Ca(OH)₂ demonstrates the range of pH, from 6.5 t to 7.8, in which minimum concentration of fatty acids is maintained. This corresponds to the thermodynamic modeling results for the reactions of oleate ions binding into copper and calcium oleates in the indicated range of pH.

The results obtained are indicative of the fact that small addition $(50-100g/m^3)$ of lime to the mixed discharge waters (low-reagent conditioning) enables simultaneously decreasing the concentration of both copper ions and oleate ions (Ol⁻). In this pH range, the recommended concentrations of the unwanted ions in the recirculating water are achievable (Table 2).

The developed conditioning regime for heavily polluted discharge waters was tested and implemented at the Erdenet GOK processing plant. When switching to the





the ion concentrations under the conditions of co-deposition

developed low-reagent technology for the recirculating water conditioning, significant increasing the contribution of these new water sources to the enterprise's recirculation water system is achieved (up to 7%), as well as increasing the basic flotation performance, in particular, increasing copper and molybdenum recovery by 0.35%and 0.5%, respectively.

Conclusion

The calculations and experimental studies have established the feasibility of molybdenite activation by copper cations in the conditions of copper-molybdenum ore milling. It was demonstrated that the activation of molybdenite by copper ions causes depression and increase in molybdenite losses in the selective flotation circuit. The reasons for molybdenite flotability decreasing by calcium ions and molybdate ions were determined: the formation of calcium molybdate on the mineral surface under conditions of bulk flotation, which passed into hydrophilic calcium carbonate at pH above 9.5. The maximum permissible concentrations of copper ions (0.6 mg/l) and calcium (350 mg/l) in the recirculating water are determined. Exceeding these levels leads to deterioration of the flotation process performance. The regime of joint conditioning of the filtrates and utility fluids was developed, providing reducing concentration of dissolved copper in the purified recirculating water to 0.55 mg/l and technical fatty acids to 0.35 mg/l. This allowed increasing the volume of heavily polluted discharge water used and raising the recovery of copper and molybdenum by 0.35% and 0.5%, respectively.

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