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Substantiation of New Reagent Compositions for the Effective Extraction of Rhenium in the Processing of Complex Molybdenum Ores

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Abstract: Modern trends in technological improvement for producing high-quality rhenium-containing molybdenum concentrates are aimed at developing environmentally friendly solutions compared to traditional ones, involving a reduction in consumption or complete replacement of toxic substances and the use of plant reagents and microorganisms and make it possible to eliminate energy-intensive processes of steaming and roasting. It is known that up to 25%–30% of Mo, Cu and Re goes to rough flotation tailings and is lost in wastes. Those losses are a consequence of the ore composition variability, chalcopyrite–molybdenite ratio, an increase in the proportion between primary copper sulfide and finely disseminated molybdenite and the recovery of floating pyrite. High rates of valuable metal recovery into bulk concentrate can be achieved by using new compositions of flotation reagents that selectively change the hydrophobic properties of the target minerals. The application of new reagent compositions, including novel chemicals—dithiopyrylmethane (DTM), composite reagent (CR) and conventional butyl xanthate (ButX)—was theoretically and experimentally substantiated for the effective rhenium extraction in the processing of hard-to-beneficiate complex molybdenum ores. It is identified that DTM forms a complex DTM–Re compound and chemically adsorbed on rhenium-containing molybdenite providing an increase in Re recovery into the bulk Cu–Mo–Re concentrate by 17%, reducing by two times the loss of rhenium with flotation tailings, and the subsequent 97.6% Re extraction of the molybdenum concentrate by autoclave leaching.

Keywords: molybdenum ores; molybdenite; flotation; reagents; dithiopyrylmethane; rhenium; reagent composition



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1. Introduction

The main source of rhenium products is molybdenum concentrates and by-products obtained during the enrichment of porphyry copper–molybdenum ores [1,2]. Rhenium does not have its own ore deposits. It is isomorphically included in some sulfide minerals (chalcopyrite, molybdenite) [3–5]. The average content of molybdenum in the ore is 0.003%–0.01%, rhenium 0.02–0.5 ppm [6,7]. In the ore beneficiation process, rhenium is concentrated in the bulk flotation concentrate, and in selective flotation up to 80 wt.%, Re goes to molybdenum concentrate, and up to 20 wt.% follows to copper concentrates. The total extraction of rhenium in molybdenum (copper–molybdenum) ores treatment is relatively low—up to 45 wt.%. This is due to the large metal losses with flotation tailings. Molybdenum concentrates obtained during the enrichment of porphyry copper ores contain 0.02%–0.17% rhenium [8]. The largest Re producer is the Chilean company MolyMet [9,10]. Re world production over the past 5 years is about 40–50 t [11].

In terms of Re reserves, Russia is in the third place after Chile and the United States [12].

A vital task in the rare metal production is to reduce the losses of valuable metals with dressing tailings and metallurgical treatment that often reach up to 50%–70% only for rhenium. In this regard, increasing the extraction of rhenium into copper–molybdenum and molybdenum concentrates, additional extraction of rhenium processing tailings is the most important task to increase the production of this strategic metal.

Copper–molybdenum ores belong to very hard-to-beneficiate mineral resource due to low content of valuable metals, the variability of the mineral composition, uneven and relatively large inclusions of molybdenite and pyrite, fine inclusions of copper minerals and a high content of flotation active pyrite. That is why the high amounts of Mo, Cu and Re go to the tailings just on the first stage of bulk sulfide flotation [13]. This circumstance necessitates the use of multi-staged enrichment schemes. After a relatively coarse first-stage ore grinding to 45%–55% less than 0.074 mm, a bulk Cu–Mo concentrate and tailings are obtained. Then, Cu–Mo concentrate after regrinding to 90%–95% less than 0.074 mm goes to the separation into the copper concentrate (21%–32% Cu with recovery of 75%–95%) and molybdenum concentrate (40%–57% Mo with a recovery from 45%–55% to 80%–86%) [4,5]. Copper and molybdenum rhenium-containing concentrates and by-products are exposed to oxidative roasting while sublimating rhenium, sintering molybdenum concentrate with soda or sodium sulfide, followed by leaching and precipitation. Mo–Re concentrate may be subjected to nitric acid autoclave leaching without roasting, and rhenium is extracted on selective sorbents from the leaching solutions [14–17].

In bulk copper–molybdenum flotation, xanthates or their mixtures with different hydrocarbon radical lengths, dithiophosphates and thionocarbamates are used as collectors [10,18]. Most of the dressing plants use several collectors or compositions of individual collectors in bulk, cleaning and scavenger flotation operations [19,20]. Non-polar reagents (diesel fuel, kerosene, engine oil, etc.) together with xanthates are used as molybdenite collectors.

Summarizing the above, we can conclude that the effective Re, Mo and Cu recovery rates into flotation concentrates can be achieved by using new types of flotation reagents that selectively change the hydrophobic and flotation properties of the target minerals [21–25]. The improved rhenium extraction into copper–molybdenum and molybdenum concentrates will decrease its high losses in flotation tailings during Cu–Mo processing of hard-to-beneficiate ores.

This paper aimed at studying the novel reagents and their compositions to improve rhenium extraction in flotation processing of hard-to-beneficiate copper–molybdenum ores.

2. Materials and Methods

Monomineral samples of molybdenite (MoS_2) 4 by 8 mm in size, polished sections of chalcopyrite and pyrite 10 by 10 mm in size, and ground fractions of molybdenite, chalcopyrite and pyrite with a particle size of 0.063–0.1 mm were used.

Scanning electron microscopy (LEO 1420VP, ZEISS Group, Oberkochen, Germany) equipped with an energy dispersive microanalyzer (Oxford INCA ENERGY 350, Oxford Instruments, Abingdon, UK) and laser scanning microscopy (KEYENCE VK-9700, KEYENCE Corporation of America, Itasca, IL, USA) were used to study the morphology and element composition of adsorbed reagent phases (thin films) on the mineral surface. SEM analysis makes it possible to identify the presence of mineral and organic phases on the mineral surface in the initial state and after contact with reagents by the presence and intensity of absorption peaks [26–28].

Scanning electron LEO 1420 VP INCA 350 microscope operates by the line-by-line moving (scanning) of a focused electron beam along the sample surface. The image is formed sequentially by points and is the result of the electron beam interaction with the sample. As a result of this interaction, a group of radiations is formed, including reflected, secondary electrons and characteristic X-ray radiation. Low-energy secondary electrons are mainly responsible for the formation of a pattern that reflects the shape of the sample surface. The intensity of reflected electrons signal directly relates to the density

(average atomic number) of the target at the point of the primary electron beam incidence. The quantum energy of characteristic X-ray radiation is strictly determined by the type of electron transition in a particular atom. The number of quanta of this energy in the summary spectrum of X-ray radiation is proportional to the number of atoms of this type (element). Qualitative elemental analysis is carried out by an INCA-300 X-ray energy-dispersive spectrometer (Oxford Instruments, Abingdon, UK). Analysis is possible both at a point 2–5 microns, and over an arbitrarily specified area. Range of registered elements: Be4–U92. Electron microscopic observation and analysis of thin-film objects (especially organic ones with low average atomic numbers) on a massive substrate has a number of methodological limitations. Based on interaction of the primary electron beam with the sample, the generated zone of the characteristic X-ray radiation for light elements is more than 3–7 μm , depending on the accelerating voltage of the electron microscope. Since the thickness of the reagent's coating is often much less than these values, the intensity of the peaks of its constituent components (carbon, oxygen, nitrogen, and phosphorus) in the summary energy-dispersive spectrum of the sulfide substrate and the film will be low. High-energy reflected electrons weakly interact with a thin layer of reagent. Therefore, the image contrast in reflected electrons is extremely weak. Low-energy secondary electrons interact with the surface layer much stronger. As a result, the areas covered with reagents accumulate an electronic charge that leads to the appearance of bright zone in secondary electrons images.

Additionally, qualitative and quantitative verification of the adsorbed collecting reagents on sulfide minerals was performed by UV spectrophotometric method. The optical densities of the reagent solutions before and after their contact with ground mineral fraction were measured on a Shimadzu UV-1800 spectrophotometer. The spectrophotometer allows receiving data in the form of a graphical spectrum. The error of determination is ± 0.002 Abs (at 0.5 Abs), ± 0.004 Abs (at 1.0 Abs), ± 0.006 Abs (at 2.0 Abs). The solution was prepared as follows: a sample of a mineral weighing 1 g was placed in a glass (volume 50 mL), a reagent solution (0, 5, 10 and 15 mg/L) was added and stirred for 5 min, then filtered. The filtrate was put in a cuvette, and the UV spectrum (190–360 nm) was obtained. The adsorption of the reagent on the mineral was determined by the difference between the initial and residual concentration of the reagent in the liquid phase in accordance with the Bugger–Lambert–Behr law.

Mineral flotation on pure minerals is carried out in a small 20–50 mL cell and on a small sample weight 1–5 g in order to evaluate the flotation activity of the mineral. Ore flotation is performed in 0.75 L cells.

The sample of the copper–molybdenum rhenium-containing porphyry ore from one of the Russian deposits was selected for ore flotation tests. The initial content of copper, molybdenum and rhenium in the sample according to the chemical analysis was 0.54% Cu, 0.0055% Mo and 0.13 ppm Re, respectively. Chemical analyses were performed in the certified Stuart Geochemical and Essay, Ltd. by the analytical method of inductively coupled plasma mass spectrometry after ore sample decomposition in a mixture of concentrated nitric HNO_3 and hydrochloric HCl acids at a volume ratio 1:3. Each probe was duplicated. Definition range was 0.001–50 ppm Re, 0.05–10,000 ppm Mo, 0.2–10,000 ppm Cu. Cu content in the concentrate was analyzed by oxidative decomposition in three acids followed by inductively coupled plasma atomic emission analysis (definition range 0.005%–40% Cu). The original ore sample with a size of $-10 + 0$ mm was crushed in a cone crusher to a class of -2 mm. Then, by quartering, the sample was divided into portions weighing 250 g and crushed to 70% of the class -0.071 mm in a laboratory ball mill at the ratio solid–water–ball 1:0.5:6. Flotation tests were performed according to the direct bulk flotation scheme obtaining the concentrate and tailings in a laboratory mechanical flotation machine MEKHANOBR (0.75 L).

Butyl xanthate (ButX), kerosene, a novel composite reagent (CR), which is a finely emulsified kerosene solution with a dialkyldithiophosphinate (S–P-containing agent) [29,30], and dithiopyrilmethane (DTM) that belongs to the pyrazole group chemicals, were used

as collectors [31,32]. For the depressing rock minerals, liquid glass was used 300 g/t, frother-pine oil 50 g/t. New reagent compositions were tested at variable dosages.

3. Results and Discussion

3.1. Research of a Novel Composite Reagent CR

Electron-donor sulfur and phosphorus atoms in the CR structure predetermine its ability to complex formation and selective adsorption, while alkyl radicals provide a high collecting activity with respect to the extracted sulfides. In contrast to S–P–O-containing reagents that are well-known and used in flotation practice of non-ferrous and noble metal ores with a high pyrite content, CR reagent has a high selectivity to non-ferrous minerals [29,30]. Laser scanning microscopy (ASEM) and scanning electron microscopy were used to obtain surface images of polished mineral sections. Energy-dispersive spectra of the surface covered by adsorbed CR phase and reagent-free before and after contact with the reagent's solutions were measured and analyzed. On molybdenite, newly formed phases of adsorbed CR appeared after its contact with CR solution. They formed the dark plates of regular shape, evenly distributed on the mineral surface (Figure 1c). Phosphorus, carbon peaks in the energy dispersive spectrum of newly formed phases indicated the CR fixation on the molybdenite surface (Figure 1d).

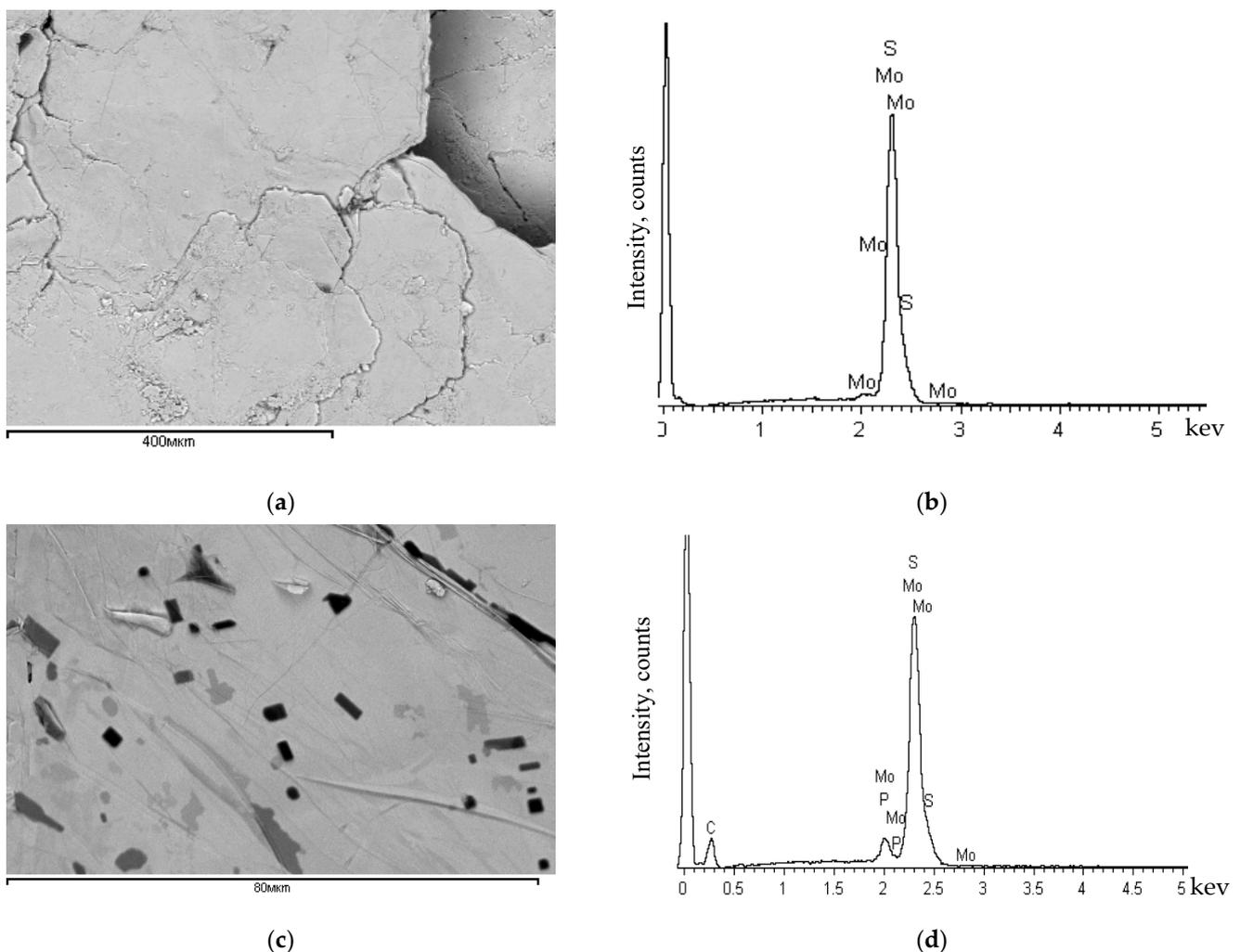


Figure 1. SEM image of molybdenite surface before (a) and after (b) contact with the reagent's solutions and energy-dispersive spectrum of the surface areas before (c) and after (d) contact with the reagent's solutions.

The energy spectrum of a clean mineral surface before its contact with the reagent's solution (Figure 1a) showed only S and Mo peaks that belong to the MoS_2 mineral, but no other organic elements were detected like in the spectrum of the mineral that was in contact with the reagent's solution (Figure 1b). A similar determination was observed on the chalcopyrite sample. Figure 2a demonstrates the surface image before adding the reagent, and the energy dispersion spectrum had Cu, Fe and S peaks of chalcopyrite CuFeS_2 (Figure 2b). After chalcopyrite contacted the CR solution, the needle-like spots of the reagent, rather evenly distributed over the surface (Figure 2c,d), appeared on the mineral surface, and C and P peaks in the energy-dispersive spectrum of those spots proved the CR adsorption (Figure 2e).

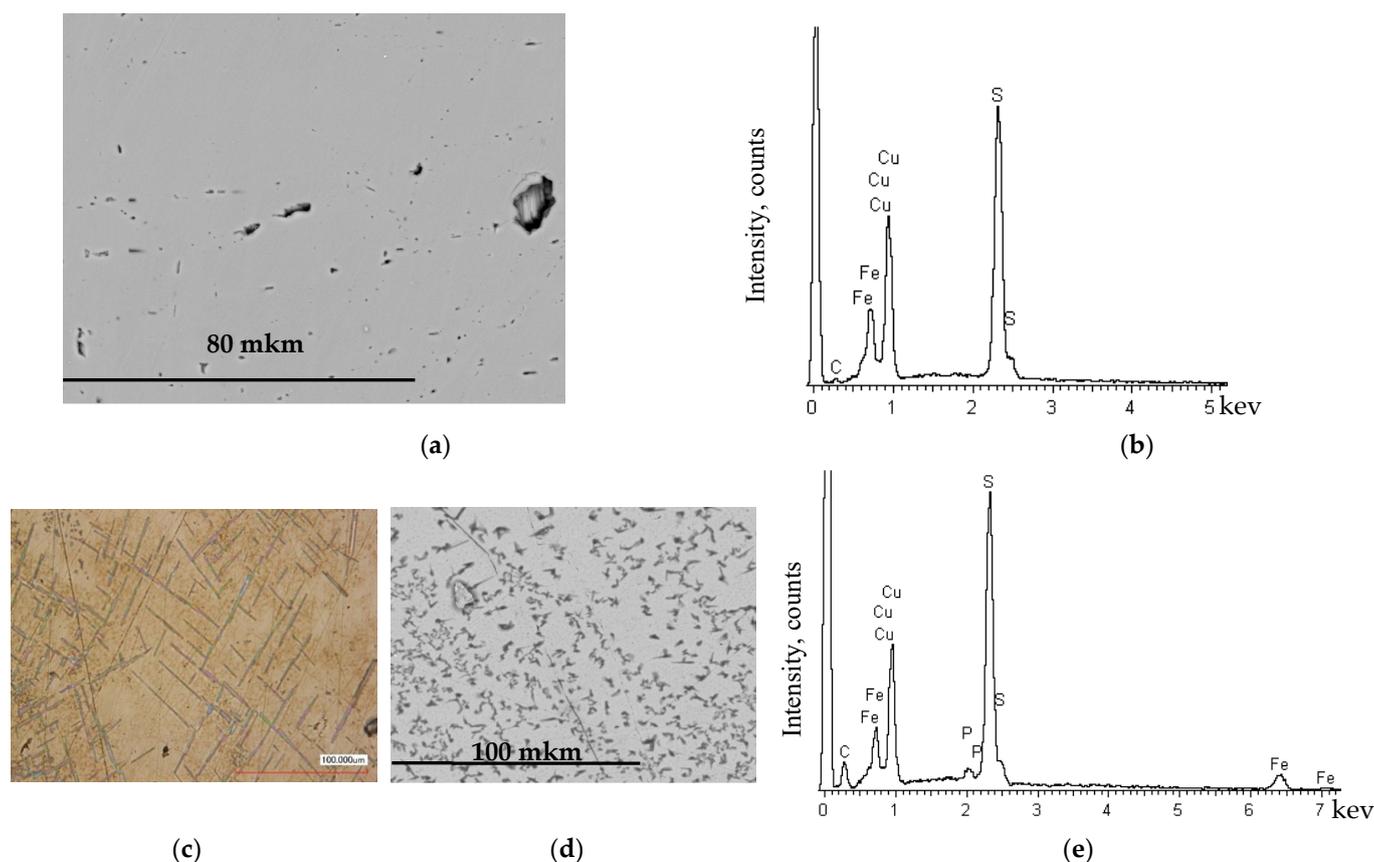


Figure 2. SEM image of the chalcopyrite surface (a) and energy-dispersive spectrum (b) before its contact with the CR; surface image of the chalcopyrite by laser scanning microscopy (c), SEM image (d); and energy-dispersive spectrum (e) after contact with the CR.

Repeated washing by distilled water did not change the surface images that demonstrated a reserved reagent covering, thus proving the stable CR fixation on molybdenite and chalcopyrite. This fact indicated strong chemical interaction of the reagent with the mineral surface. There was no CR phase determined on the pyrite sample, indicating that the CR reagent did not adsorb on the pyrite surface.

UV spectroscopy was applied to determine the adsorbed CR quantitatively on ground fractions of pyrite, chalcopyrite and molybdenite. The CR solutions had characteristic absorption peaks in the UV spectrum at a wavelength 232 nm (Figure 3a) that made it possible to measure its concentration before and after contact with minerals. Measuring the difference between the initial and residual concentrations of the reagent, in accordance with the Bugger–Lambert–Beer law, the CR adsorption after 5 min contact with the mineral suspension was calculated. It was found that at 10 mg/L concentrations, CR demonstrated 60 μg/g adsorption on chalcopyrite and 160 μg/g on molybdenite. The maximal absorption

activity 108 mg/g on chalcopyrite and 170 µg/g on molybdenite CR showed at the concentration 15 mg/L. It was identified that CR did not interact with pyrite at the concentrations 0–20 mg/L. The sorption activity of CR with respect to chalcopyrite and molybdenite can be explained by its interaction with copper and molybdenum atoms forming stable complex compounds on the mineral surface.

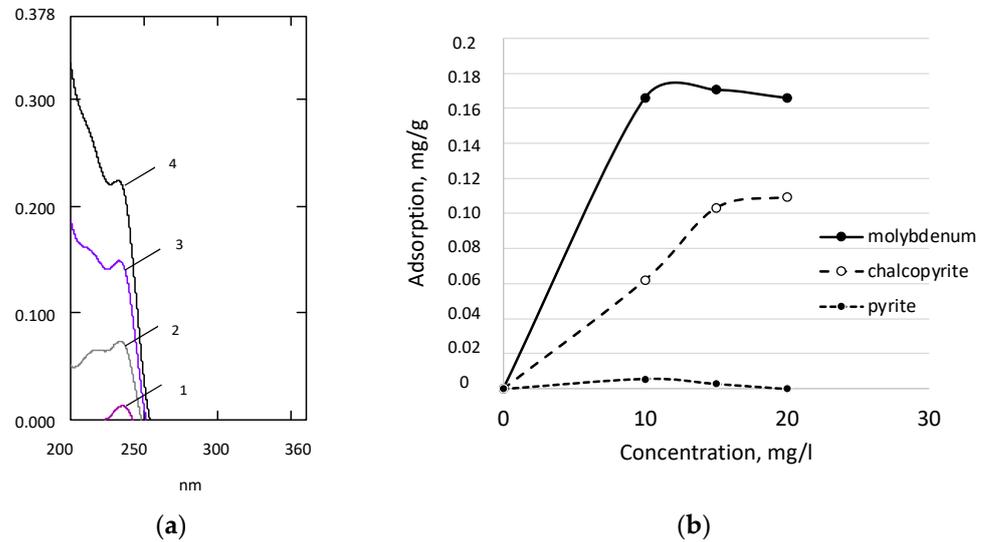


Figure 3. UV Spectra of the composite reagent CR at variable concentrations: 5 (1), 10 (2), 15 (3) and 20 (4) mg/L (a); CR adsorption curves via CR concentration (b).

Molybdenite, chalcopyrite and pyrite floatability by CR reagent was studied in comparison with conventional kerosene monomineral flotation at a variable collector concentration (Figure 4). Monomineral flotation was carried out on the ground fractions of molybdenite, chalcopyrite and pyrite with a particle size of 0.063–0.1 mm.

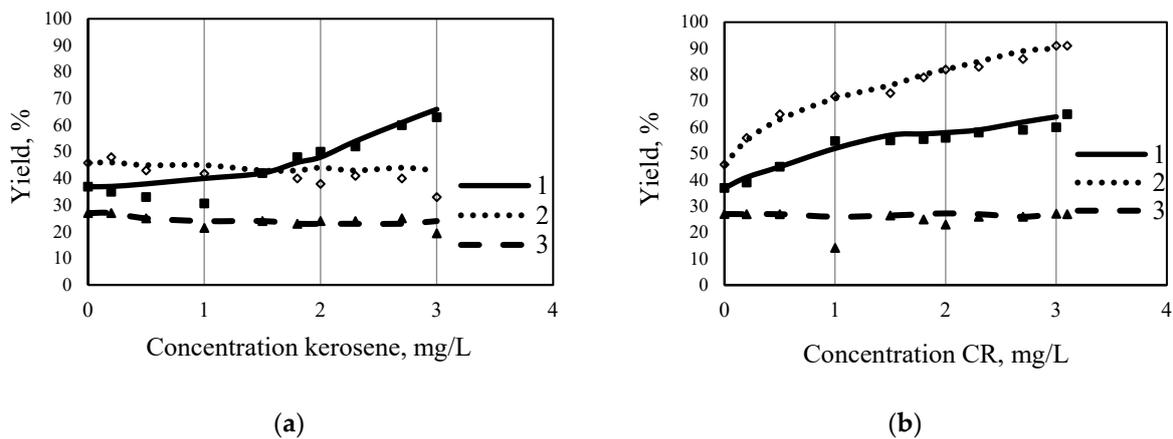


Figure 4. Floatability curves of molybdenite (1), chalcopyrite (2) and pyrite (3) via kerosene (a) and CR (b) concentration.

Floatability curves analysis (Figure 4b) showed that CR composite reagent exhibits selective collecting properties towards Cu and Mo sulfides and did not float pyrite: at 1 mg/L concentration, 53% molybdenite and 70% chalcopyrite floated into the concentrate. At the CR concentration of 3 mg/L the floatability of molybdenite and chalcopyrite increased to 64% and 90%, respectively, while kerosene helped to raise only molybdenite recovery to 62%. An important advantage of the composite reagent CR is that CR did not increase

the floatability of pyrite that might give a positive effect on the quality of both the bulk Cu–Mo–Re concentrate and individual Mo–Re and Cu–Re concentrates in ore flotation.

3.2. Study of the Reagent Dithiopyrilmethane

The reactive center in the heterocyclic DTM molecule is the N–C=S group, which has a high polarity and complex-forming ability towards non-ferrous, noble and rare metals [31,32]. UV spectrophotometry tests showed the quantitative dependence of DTM adsorption on natural molybdenite as a function of reagent concentration (Figure 5).

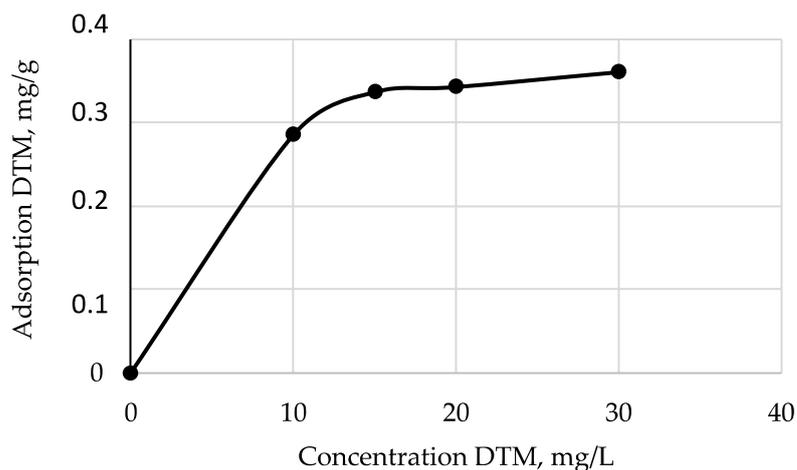


Figure 5. DTM adsorption isotherm on molybdenite.

The DTM adsorption on molybdenite sharply increased to 0.34 mg/g when the reagent concentration grew to 15 mg/L; the maximum DTM adsorption was 0.36 mg/g at 20–30 mg/L. The results of scanning electron microscopy confirmed that dithiopyrilmethane fixed on the molybdenite surface.

A SEM image of the mineral surface after its contact with a DTM solution revealed the appearance of dark-colored irregularly shaped neoplasms in the energy-dispersive spectra of which there are both Mo and S peaks (Figure 6), characteristic of molybdenite, and C and N peaks of organic substance appeared, indicating the DTM adsorption on molybdenite.

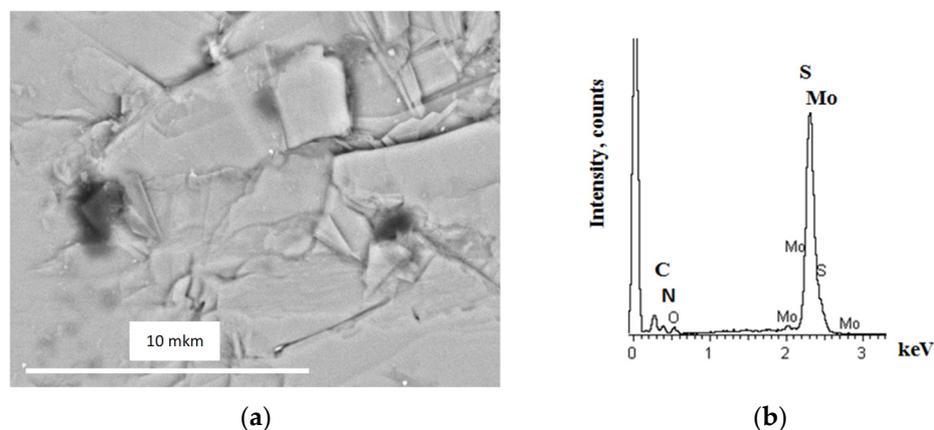


Figure 6. SEM image of molybdenite surface after its contact with a 0.1% DTM solution—(a); and energy-dispersive spectrum of dark spots/areas with adsorbed reagent—(b).

The preservation of newly formed reagent phase on molybdenite after repeated washing confirmed strong DTM adsorption on the mineral surface that may be justified by the chemical interaction between the reagent N–C=S group and Re-containing molybdenite.

Interaction between DTM and Re in an aqueous ammonium perrhenate (NH_4ReO_4) solution in the presence of ammonium thiocyanate (NH_4CNS) was tested by UV spectrophotometry at variable ratios of the components. UV spectra of the starting compounds and the reaction mixture are shown in Figure 7a. UV spectrum of NH_4ReO_4 has the absorption peak at wavelength 230 nm (Figure 7 curve 1) and UV spectrum of DTM—at 288 nm (Figure 7a curve 2). UV spectrum of a combined DTM and NH_4ReO_4 solution demonstrated a decrease of the optical density at 288 nm (Figure 7a curve 3). At the same time, the UV spectrum of DTM and NH_4ReO_4 solution that was taken relative to a starting DTM solution showed a new absorption maximum at 240 nm (Figure 7a curve 4) that may belong to a newly formed DTM–Re complex compound.

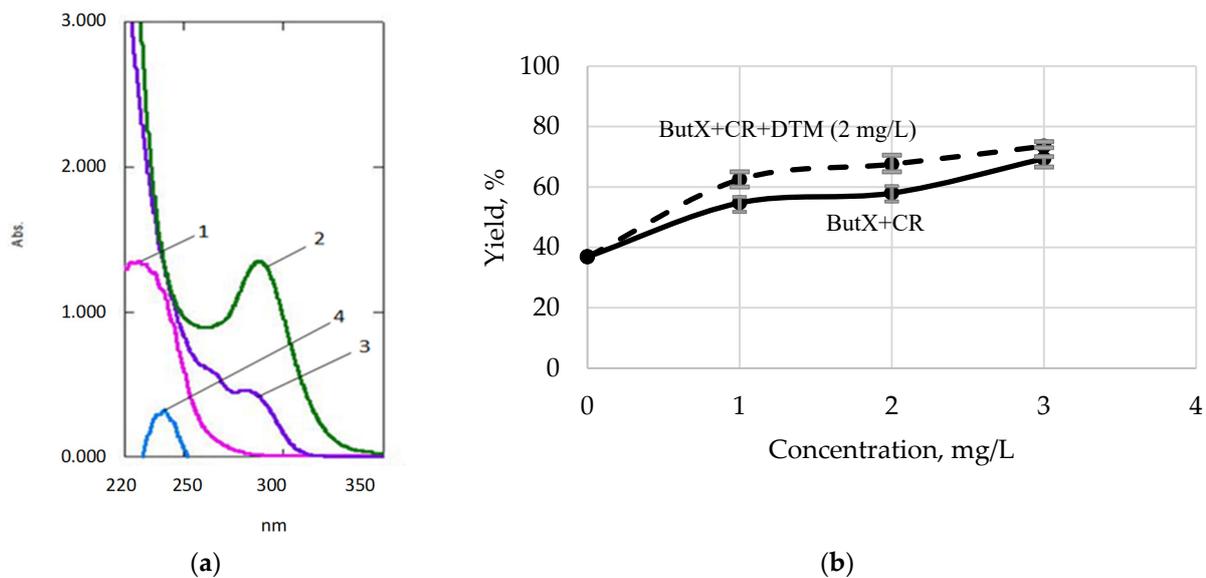


Figure 7. UV spectra of reagent solutions: NH_4ReO_4 (100 mg/L)—1, DTM (50 mg/L)—2, DTM (50 mg/L) with NH_4ReO_4 (100 mg/L)—3, DTM with NH_4ReO_4 relative to DTM solution—4—(a); results of comparative monomineral molybdenite flotation by ButX + CR 1:1 (solid line) and ButX + CR (1:1) and dithiopyrylmethane DTM (const = 2 mg/L) (dashed line)—(b).

The results of comparative monomineral molybdenite flotation by DTM:ButX:CR reagent composition (Figure 7b) showed that at ButX:CR (1:1) and in the variable dosage of DTM:ButX:CR (0.5–2:1:1), the flotation yield demonstrated an increase of 4.1%–9.5%. The highest floatability was recorded at a ratio of DTM:ButX:CR (1:1:1).

3.3. Ore Flotation

The technological results of the ore sample flotation are presented in Table 1.

The use of a composite reagent CR and ButX at a dosage of 10 g/t and a ratio 1:1 led to an increase in Cu recovery from 83.1% to 87.9%, Mo recovery from 81.0% to 82.2% and Re recovery from 80.0% to 81.1%. The higher dosage 20 g/t CR and 20 g/t ButX helped to raise the recovery up to 96.7% Cu, 83.8% Mo and 83.8% Re. The highest increase in flotation recovery by 14.9% Cu, 3.4% Mo and 6.8% Re was recorded at the reagent mode using DTM:ButX:CR (1:1:1) at 10 g/t dosage of each component. The obtained bulk concentrate was further subjected to Cu–Mo separation and the obtained Mo concentrate was leached and a subsequent 97.6% extraction of rhenium from molybdenum concentrate by autoclave leaching was achieved (20% HNO_3 , T—130 °C, S:L—1:10, process duration—5 h, pressure in the autoclave—63 atm.).

Table 1. Results of copper–molybdenum–porphyry ore bulk flotation.

Dosage, g/t	Product	Yield, %	Content			Recovery, %		
			Cu, %	Mo, %	Re, ppm	Cu	Mo	Re
Kerosene 10 ButX 10	Concentrate	12.7	3.73	0.0351	0.825	83.1	81.0	80.0
	Tails	87.3	0.11	0.0012	0.030	16.9	19.0	20.0
	Total	100.0	0.57	0.0055	0.131	100.0	100.0	100.0
CR 10 ButX 10	Concentrate	12.2	4.18	0.0364	0.864	87.9	82.2	81.1
	Tails	87.8	0.08	0.0011	0.027	12.1	18.7	18.9
	Total	100.0	0.58	0.0054	0.130	100.0	100.0	100.0
CR 20 ButX 20	Concentrate	12.1	4.40	0.0373	0.900	96.8	83.8	83.8
	Tails	87.9	0.02	0.0010	0.024	3.2	16.2	16.2
	Total	100.0	0.55	0.0054	0.130	100.0	100.0	100.0
DTM 10 g/t, CR 10 g/t, ButX 10 g/t	Concentrate	12.6	4.54	0.0375	0.909	97.1	84.4	86.8
	Tails	87.4	0.02	0.0010	0.020	2.9	15.6	13.2
	Total	100.0	0.59	0.0056	0.132	100.0	100.0	100.0

4. Conclusions

The application of new reagent compositions, incorporating novel chemicals—dithiopyrylmethane (DTM), composite reagent (CR) and conventional butyl xanthate (ButX)—was theoretically and experimentally substantiated for the effective rhenium extraction in the processing of hard-to-beneficiate complex molybdenum ores. Mechanism of dithiopyrylmethane (DTM), composite reagent (CR) and potassium butyl xanthate (ButX) action towards rhenium-bearing molybdenite consists of the formation of a complex compound DTM–Re and chemical adsorption of DTM and CR on the molybdenite surface. The method for flotation extraction of copper and molybdenum was developed (RU patent 2775219 C1). The new composition of reagents provided an increase in the extraction of rhenium into the bulk concentrate by 6.8% with a 1.5-fold reduction in rhenium losses with flotation tailings. The obtained bulk concentrate was further subjected to Cu–Mo separation. The obtained Mo concentrate was leached and a subsequent 97.6% extraction of rhenium from molybdenum concentrate by autoclave leaching was achieved. Results obtained may be used to improve the efficiency of the flotation recovery of hard-to-beneficiate copper–molybdenum ores.

5. Patents

Chanturiya V.A., Matveeva T.N., Getman V.V., Karkeshkina A.Yu., Gromova N.K. Method for flotation extraction of copper and molybdenum Patent for an invention RU 2775219 C1, 28 June 2022. Application № 2021131047, 25 October 2021.

Author Contributions: Conceptualization, T.N.M., V.A.C. and V.V.G.; methodology, T.N.M., V.A.C. and V.V.G.; writing—original draft preparation, V.V.G., A.Y.K. and N.K.G.; writing—review and editing, T.N.M. and N.K.G. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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