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PROMISING REAGENTS FOR THE EXTRACTION OF PRECIOUS METALS FROM REFRACTORY MINERAL RAW MATERIALS

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Abstract: The mining and processing industry is increasingly in need of new specialized reagents due to the declining quality of the ores being processed. The low gold content (below 0.5-1.0 g/t) and finely dispersed gold inclusions (0.1-10.0 microns) in ores, combined with the similar characteristics of separated minerals, significantly hinder flotation performance when traditional reagents are used. This often results in considerable losses of valuable metals in the enrichment tailings. Expanding the selection of domestic flotation reagents, informed by the latest advancements in fundamental research, is essential for mitigating the negative effects of the raw material's mineral composition and maximizing the recovery of strategic metals from challenging ores. Utilizing modern research techniques—such as scanning electron and laser microscopy, UV spectrophotometry, XRF, and chemical analysis—has allowed for the visualization of the adsorption layer of new collector reagents, specifically various dithiocarbamates, on gold-containing sulfides. The experimental determination of the quantity of adsorbed reagents on mineral surfaces revealed unique fixation characteristics that led to optimized consumption ratios in the flotation process. These scientifically tailored reagent protocols resulted in a 5-6% increase in gold concentration in the concentrate and a reduction in gold losses in the tailings during the flotation enrichment of refractory ore from the Malinovskoe deposit.

Keywords: gold-bearing minerals; challenging ores; flotation reagents; morpholindithiocarbamate; cyanethyl-diethyldithiocarbamate; plant modifier; extraction.

Introduction.Mineral raw materials that are difficult to process, including low-grade ores and man-made resources, are significant sources of strategic metals. The mining and processing sectors in the country face an imbalance due to the disparity between available raw materials and the level of mineral processing technology, resulting in substantial losses of valuable components—up to 30% for traditional ores and even more for hard-to-recover and man-made resources. As the content of valuable metals in feedstock continues to decline, along with the fine intergrowth of ore minerals and host rocks, new technologies are being developed to enhance the extraction of strategic metals. These technologies often incorporate combined approaches, with flotation being a critical component. Current flotation reagents have limitations and do not always achieve high enrichment rates, prompting research into new chelating reagents that are both more effective and cost-efficient. This research involves not only synthesizing new compounds but also examining their properties, determining optimal application conditions, and assessing their impacts on flotation process parameters. Relying on traditional reagent methods can lead to reduced concentrate quality and increased production costs. Therefore, it is essential to develop and implement new environmentally friendly domestic reagents that can significantly improve the extraction of valuable metals from challenging mineral raw materials. A variety of organic and inorganic reagents are employed in flotation, with some having stood the test of time while newer options address evolving industry needs. These new and enhanced reagents align with both technological and environmental standards. The Russian market for flotation reagents includes major domestic manufacturers such as OOO Kvadrat Plus, AO Volzhsky Orgsintez, OOO MBI-Sintez, OOO Flotent Chemicals Rus, OOO NPP QVALITET, and AO UK BHH Orgkhim, offering a range of products including dithiophosphates, xanthates, dithiocarbamates, and thionocarbamates. Despite this variety, xanthates remain the dominant choice in processing plants. Given the current push for intensified flotation and processing of complex multicomponent ores, there is a pressing need to create and implement new collecting reagents that offer improved efficiency and selectivity. Research in this field is actively conducted by several institutions, including the Empress Catherine II Saint Petersburg Mining University, the National Research Technological University "MISIS," the Institute of Mining SB RAS, and others. Recent developments include selective collectors based on thionocarbamates that enhance gold recovery from pyrite copper-zinc ores, as well as new reagents derived from acetylene alcohols aimed at recovering gold from porphyry copper ores. The kinetics of collector-mineral interactions have been studied, highlighting the role of the physical form of sorption during flotation. Ongoing research is focused on selecting effective collectors for extracting non-ferrous and rare metals from complex ores. International studies have proposed using humates and hypochlorites for the selective depression of arsenopyrite and the separation of chalcopyrite from galena, as well as exploring various combinations of sulfhydryl collectors and organic modifiers for polymetallic ore flotation.

Under the guidance of Academician V.A. Chanturia, systematic research has been conducted on developing and testing new targeted reagents for extracting gold, platinum, copper, and other valuable metals from challenging mineral raw materials. For instance, solutions of dithiocarbamic acid salts—such as morpholindithiocarbamate sodium and cyanethyl diethyldithiocarbamate—have been tested both alone and in combination with potassium butyl xanthogenate. Hogweed extract has also been investigated as a surface modifier for gold-containing sulfides, leveraging its complexing properties to enhance selectivity in flotation. The hogweed extract contains tannins, essential oils, coumarins, and other compounds, with the coumarins being of particular interest due to their ability to form complexes with metals. The objective of this work is to advance scientific understanding of the mechanisms by which chelating reagents—specifically dithiocarbamate derivatives and an organic modifier—interact with gold-containing sulfide minerals, and to evaluate their potential use both individually and in combination with butyl xanthogenate for improving the extraction of strategic metals from challenging mineral raw materials.

Methods: Surface scanning of gold-bearing sulfide minerals and ore samples from the Malinovskoe deposit was conducted using laser (KEYENCE VK-9700) and electron (LEO 1420VP) microscopy. This combination of methods enabled the identification of key areas and evaluation of differences in images before and after interaction with reagent solutions. The morphology of the adsorbed organic phase on mineral surfaces was visualized through microscopy, allowing measurement of its dimensions.

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During the study, linear dimensions and areas of reagent deposits on mineral surfaces were quantified. Images obtained from laser microscopy post-reagent treatment were analyzed to determine the area covered by the reagent and the extent of mineral coating. The ore from the Malinovskoe deposit is classified as gold sulfide-quartz type, with gold (1.4 g/t), silver (50.3 g/t), and copper (1.3%) being the primary economic components. The sulfide minerals present include FeAsS, FeS2, CuFeS2, and FenSn+1, with lesser amounts of MoS2, CaWO4, ZnS, PbS, FeO·Fe2O3, and native gold. The average sulfide content is between 10-15%. According to chemical analysis, arsenic, iron, lead, and tungsten are present in the ore at levels of 1, 8.6, 0.05, and 0.08%, respectively, with gold associated with chalcopyrite and arsenopyrite. Chemical analysis of the ME-ICP06 ore sample indicates that quartz comprises over 60% SiO2, with approximately 14% Al2O3 and around 20% total iron, potassium, and magnesium oxides. X-ray phase analysis identifies quartz (67.2%), chlorite (11.5%), and muscovite (7.5%) as the main rock-forming minerals. For mineralogical characterization, the Mineral C7 analytical complex (Olympus BX51 optical microscope) was utilized to automatically determine mineral composition, grain size, and mass fractions within aggregates. The study involved both Anschlift analyses and microphotography using a laser microscope. UV spectroscopy was employed to determine the characteristic absorption maxima and reagent concentration in solution. The quantity of the adsorbed reagent on the mineral was evaluated after mixing its solution with crushed mineral fractions sized between -0.1 and +0.063 mm.

where $V_{l.p.}$ – the volume of the liquid phase, ml; C_{in} – the initial reagent concentration, mg/l; C_{res} – the residual reagent concentration, mg/l; P – the weight of the mineral sample, g.

Flotation Conditions of the Malinovskoe Ore Deposit. An ore sample, crushed to 90% of a size less than 0.071 mm, was placed in the chamber of a laboratory flotation machine (FML 1, model 237 FL). Flotation was conducted for 5 minutes with varying reagent consumption. The gold content in the flotation samples was analyzed through assay methods, followed by atomic absorption spectrometry at the accredited laboratory LLC Stewart Geochemical and Assay.

Discussion of Results: The UV spectroscopy method indicated the formation of chelate complexes between the new reagents and gold. UV spectroscopy is commonly used to investigate chemical reactions, including how different reagents interact with gold. In this study, the absorption spectra of the solutions were analyzed in the UV range (see Table 1). Table 1 displays the wavelengths (λmax) where the absorption peaks of the tested chemical compounds occur, along with their optical density (D) values as measured by a spectrophotometer. Notable changes in the electronic spectrum were observed when mixing a solution of morpholindithiocarbamate with a gold-containing solution. The UV spectrum of morpholineDTC exhibited distinct absorption peaks at 261.2 nm and 285.2 nm, which changed significantly following its interaction with hydrogen.

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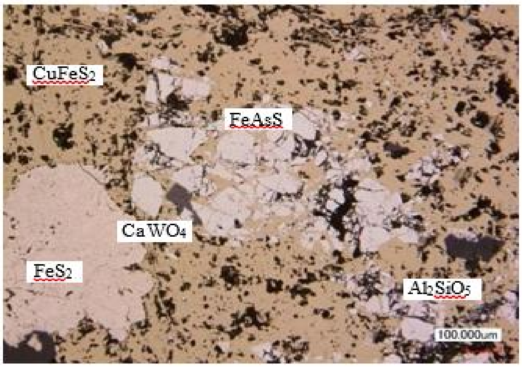
Table 1

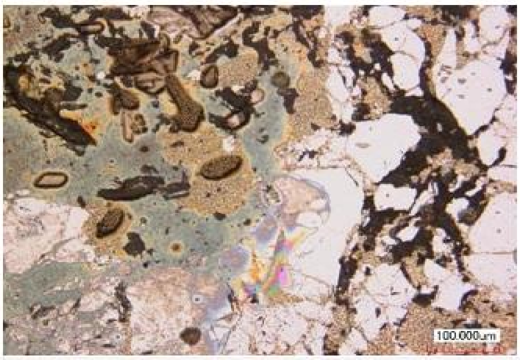
The results of the analysis of UV spectra of solutions of the studied chemical compounds

Chemical compound	λ_{max}, nm	D
Hydrogen tetrachloroaurate(III)	223.1 302.4	0.56 0.73
MorpholineDTC	261.2 285.2	0.39 0.41
MorpholineDTC Complex with Au	275.6 313.5	0.62 0.55
CEDEDTC	223.0 251.7 274.3	0.38 0.45 0.52
CEDEDTC Complex with Au	254.3 318.1	0.47 0.16

a



b



Analysis of Tetrachloroaurate(III) new absorption maxima at 275.6 nm and 313.5 nm were identified in the presence of tetrachloroaurate(III), which are not present in the electronic spectra of the original solutions. The electronic spectrum of the mixture showed changes in optical density values that differed from the additive sum of the initial substances, indicating that an interaction occurs between the components, resulting in the formation of a morpholineDTC complex with gold. Similar alterations were observed with CEDEDTC when interacting with a gold-containing solution. The initial cyanethyldiethyldithiocarbamate solution displayed peaks at 251.7 nm and 274.3 nm. Following the addition of hydrogen tetrachloroaurate(III), new peaks emerged at 254.3 nm and 318.1 nm, while the absorption peak at 274.3 nm disappeared. These observations confirm the formation of a CEDEDTC complex with gold. The adsorption of morpholineDTC onto the surface of minerals with artificially deposited gold was studied using sulfide fractions crushed to a size of –0.1+0.063 mm. The criterion for evaluation was the change in reagent concentration, calculated using UV spectra. Experimental results showed that after 5 minutes of conditioning a morpholinedithiocarbamate solution (C = 20 mg/l) with gold-containing arsenopyrite and chalcopyrite, the concentration in the suspension decreased to 2.5 mg/l, confirming the adsorption of morpholineDTC on the sulfide surfaces. Calculations indicated that the adsorption of morpholindithiocarbamate was 0.7 mg/g, meaning that 87.5% of the morpholineDTC was retained on the minerals. Data from UV spectroscopy are crucial for understanding the interaction mechanisms of gold with the reagents morpholineDTC and CEDEDTC, as well as the adsorption processes on gold-bearing minerals, which is essential for developing methods for gold extraction from ores**.**

Laser microscopy analysis: Laser microscopy was employed to capture images (Fig. 1) of the surface of the initial ore anshliff from the Malinovskoe deposit, as well as after conditioning with solutions of morpholindithiocarbamate and hogweed extract. The adsorption of reagents on the minerals in the ore sample exhibited distinct characteristics: a light brown film of morpholineDTC covered the entire surface of CuFeS2, while brown grow

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the appeared on FeS2, indicating that morpholineDTC was

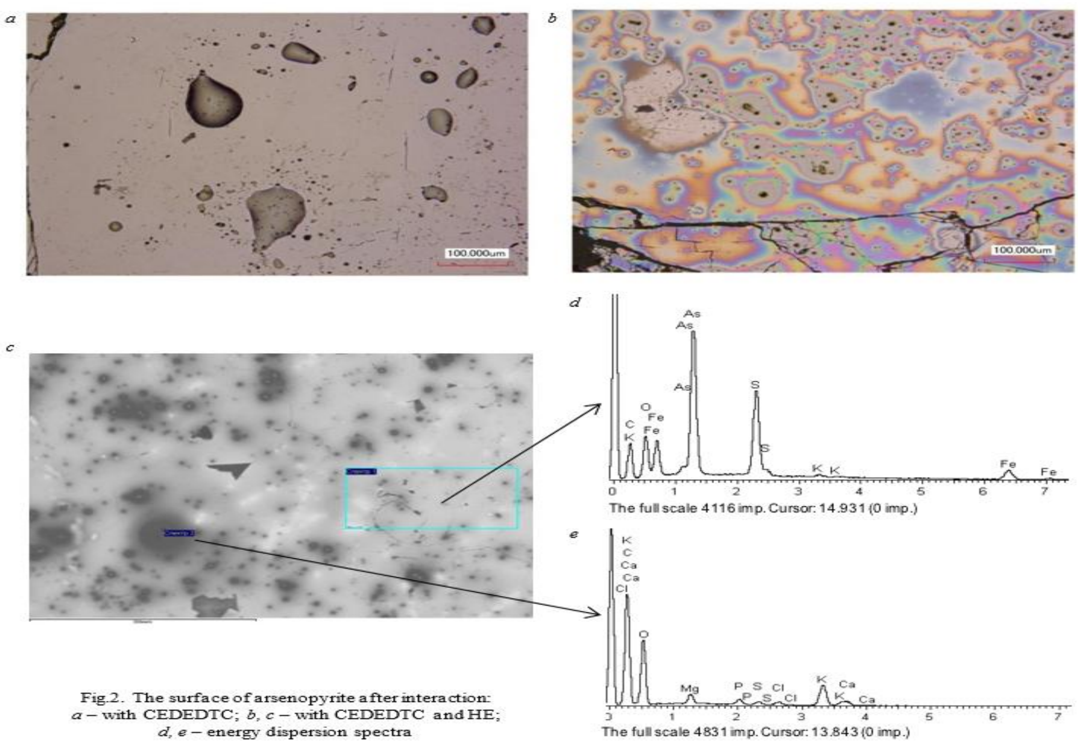

Fig.2. The surface of arsenopyrite after interaction: *a* – with CEDEDTC; *b, c* – with CEDEDTC and HE; *d, e* – energy dispersion spectra

not adsorbed onto other ore minerals. A pale blue film of hogweed extract was found to overlay the morpholineDTC on chalcopyrite and pyrite. The energy dispersion spectrum of the hogweed extract film on the minerals matched that of the initial extract. Previous studies have also noted the unique formation of the adsorption layer of chelating reagents on monomineral anshlifts. The newly formed phases remained intact after rinsing the anshlift with water, confirming the stable fixation of the reagent on the mineral surfaces. Images of the surfaces of FeAsS, CuFeS2, and CuFeS2 with gold deposited, treated with the CEDEDTC reagent, were analyzed according to the established method. The image analysis revealed that the degree of surface coverage with cyanethyldiethyldithiocarbamate was 8% for FeAsS, 12% for CuFeS2, and 20.8% for CuFeS2 with gold deposited. Experiments conducted under similar conditions showed variability in the degree of coating, which could inform selective separation during flotation. Notably, chalcopyrite with gold exhibited the highest surface coverage among the minerals studied, indicating its greater capacity to adsorb the reagent, which may enhance gold extraction from ore. After exposure to the CEDEDTC solution, chalcopyrite and arsenopyrite displayed teardrop-shaped growths on their surfaces (Fig. 2a). Subsequent treatment with hogweed extract resulted in the formation of an iridescent film on the surface (Fig. 2b).

Table 2

The results of flotation enrichment of the Malinovskoe deposit ore

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Reagent mode	Products	Output, %	Au content, g/t	Au extraction, %
PBX	Concentrate	17.04	11.57	85.30
	Tailings	82.96	0.41	14.81
	Ore	100	2.31	100
CEDEDTC, PBX	Concentrate	17.22	12.12	87.67
	Tailings	82.78	0.35	12.33
	Ore	100	2.38	100
CEDEDTC, HE, PBX	Concentrate	17.30	12.25	91.34
	Tailings	82.7	0.24	8.66
	Ore	100	2.32	100

Micrograph analysis. Micrographs from the LEO 1420VP electron microscope reveal black islands on the surface of FeAsS (Fig. 2c), with the energy dispersion spectrum (Fig. 2d, e) matching that of the hogweed extract (HE). Besides peaks for carbon (C) and oxygen (O), the spectrum displayed strong peaks for potassium (K) and calcium (Ca), along with weaker peaks for magnesium (Mg), phosphorus (P), sulfur (S), and chlorine (Cl). A thorough investigation of the inclusions in ore minerals and low-dimensional mineral aggregates provided insights into the types of mineral associations and the morphological characteristics of the grains. This study highlighted the significant impact of the adsorption layer formed by chelating reagents (dithiocarbamates and organic extracts) on the flotation properties of mineral aggregates. Results from the flotation enrichment of refractory gold-bearing ore from the Malinovskoe deposit indicated (Table 2) that substituting part of the butyl xanthogenate with cyanethyldiethyldithiocarbamate increased the gold content in the concentrate by 0.55 g/t and improved extraction by 2.4%.

Incorporating a plant modifier enhanced the synergy of the collectors, boosting gold extraction by 6% to 91.3%, while reducing the gold content in the tailings from 0.41 g/t to 0.24 g/t compared to the baseline experiment.

Conclusion. In today's fast-evolving high-tech landscape, the demand for strategic metals has surged. There is a pressing need to expand the range of domestic flotation reagents that match the efficiency of foreign counterparts. The development and scientific validation of new flotation chelating reagents and their combinations are rooted in fundamental research on phase and chemical transformations occurring on mineral surfaces during reagent interactions. Reliable findings can only be achieved through modern high-resolution physical and chemical analytical techniques. Understanding these processes is crucial for creating selectively acting reagents. This research has confirmed the unique fixation characteristics of chelating reagents—specifically, dithiocarbamate derivatives (MDTC and CEDEDTC)—on gold-bearing sulfide minerals found in the multicomponent ore of the Malinovskoe deposit. The formation of stable complex compounds significantly enhances gold extraction into the flotation concentrate. The replacement of part of the butyl xanthogenate with CEDEDTC increased the gold content in the concentrate by 0.55 g/t and improved extraction by 2.4%. The adsorbed plant modifier further amplified the effects of the collector combination, leading to a 6% increase in gold extraction, reaching 91.3%, while the gold content in the tailings decreased by 1.7 times. The advancement of flotation chelating reagents and their compositions is a scientifically significant endeavor with practical implications for the mining industry. Ongoing research in this area utilizes cutting-edge technologies to develop environmentally friendly and highly effective solutions, aiming to minimize the loss of strategic metals during the processing of difficult-to-enrich mineral raw materials.

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