Adsorption Characteristics of Combined Sulfhydryl Collector on Chalcopyrite and Arsenopyrite in Flotation of Complex Gold Ores

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Abstract

The paper presents the results of experimental study of the adsorption properties of the combined sulfhydril collecting reagent – a mixed solution of sodium diethyl-dithiocarbamate (DEDTC) and oxypropyl diethyl-dithiocarbamate ester (OPDTC) towards chalcopyrite and arsenopyrite with a view to its application as a selective collector of Au-containing sulfide minerals in flotation of complex refractory ores. Combined diethyl-dithiocarbamate solution (DEDTCc) incorporated a fixed content of anionic and non-ionic components (DEDTC:OPDTC = 1:1) and occurred variable hydrophobic effect on the surface of the basic gold-bearing sulfide minerals – chalcopyrite and arsenopyrite.

The mechanism of adsorption of the components of combined collector on the surface of chalcopyrite and arsenopyrite was identified to form characteristic molecular shape of adsorbed collector convex neoplasms and sinter chemically adsorbed film of the reactant, which is firmly anchored on the surface. The newly formed phase of the adsorbed reagent did not dissolve in water at a subsequent washing. In this case, the phase of nonionic ester OPDTC was partially removed by water and the residual adsorbed droplets changed their shape and became flatter. By X-ray microanalysis C and O bands relating to the structure of the combined DEDTCc were identified on the surface of arsenopyrite and chalcopyrite. The original technic for analyzing the liner dimension of surface images with an application of scanning laser microscopy and the software of the Analyzer was developed and the authors succeeded to provide a quantitative evaluation of the adsorption of DEDTCc on the surface of chalcopyrite and arsenopyrite.

Keywords: flotation, selective collector, gold ores

Introduction

The recovery of gold and the other precious metals from complex refractory ores that are characterized by low content of valuable components and fine impregnation of gold highly depends upon the flotation reagent modes. It may be improved by creating new combinations of novel selective reagents and conventional collecting agents providing durable hydrophobic coating on the surface of extracted minerals [1].

In IPKON RAS the novel complex collecting reagents, including modified diethyldithiocarbamate (DEDTCc) have been developed and tested for flotation extraction of sulfide minerals with emulsion gold impregnation. DEDTCc reagent is a composition which incorporates nonionic dithiocarbamic acid thioester (OPDTC) in addition to the ionic form of the main component - diethyldithiocarbamate (DEDTC) [2, 3]. There have been identified in the previous flotation and adsorption tests that nonionic OPDTC component is capable of forming a hard water-soluble gold compound on the surface of gold-containing arsenopyrite and pyrite in flotation conditions, providing selective hydrophobic coating and better floatability of gold-bearing sulfides. Introducing OPDTC nonionic component into the composition of a modified collector solution improves the conditions for its dissolution in the aqueous phase and provides better contact with the mineral surface.

A method for producing modified DEDTC solution has been developed in IPKON RAS by senior research associate Ivanova T.A., PhD [3, 4]. The method is based on the treatment of the low concentrated DEDTC solution by propylene hydrochloride to obtain a homogeneous solution of OPDTC and DEDTC in a certain ratio of the components of the solution directly before introduction into the flotation process.

The application of this reagent in a combination with xanthate and organic depressor made it possible to increase the selectivity of the separation process between auriferous pyrite and arsenopyrite, and reduce the arsenic content in the Au-pyrite concentrate [2, 5].

Due to the fact, that the choice of the optimal conditions for the formation of the hydrophobic layer of the collector on the surface of gold minerals is a determining factor in improving the recovery of precious metals from refractory ores, a detailed study of the nature of its adsorption on the surface of sulfide minerals has been performed. Arsenopyrite, which is the main gold-bearing sulfide mineral in refractory sulfide ores, and chalcopyrite – analogue of activated by copper salts arsenopyrite have been analyzed. As a result, DEDTCc adsorption on the surface of auriferous arsenopyrite and pyrite tested by UV spectroscopy was found, and the selectivity of DEDTCc compared to conventional DEDTC and xanthate flotation of gold-bearing sulfides was proved.

In this paper, analogue DEDTCc has been tested in adsorption and flotation conditions of chalcopyrite and arsenopyrite. DEDTCc was obtained by adding OPDTC into solution of DEDTC in the ratio 1: 1.

Tab. 1. The chemical composition of the mineral samples

Tab. 1. Skład chemiczny próbek minerałów

Minerals	Content, %						
	Fe	S	As	Cu	Oxides	Others	Au, ppm
Arsenopyrite	29.7	19.3	40.5	0.04	10.4	<0.1	15
Chalcopyrite	28.1	28.3	-	26.4	15.4	1.8	40

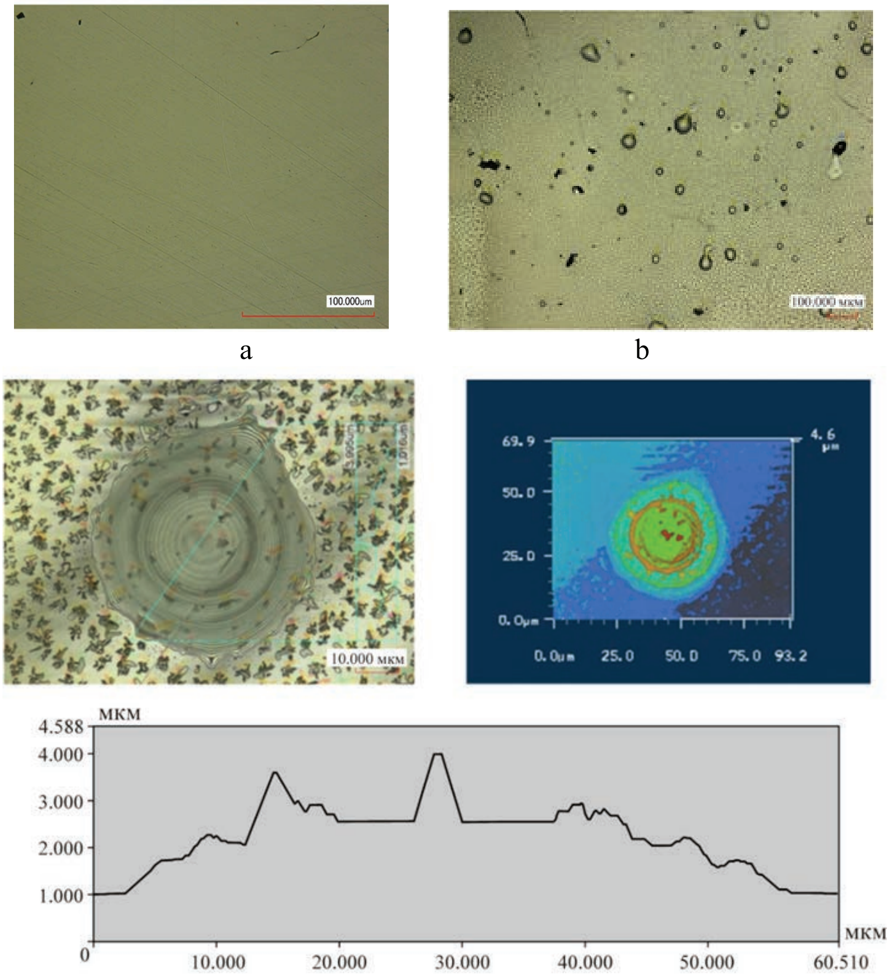


Fig. 1. Image of polished chalcopyrite before (a) and after DEDTCm treatment (P = 100 mg / l) (KEYENCE) (b) and the height of the surface roughness (the height of the connection layer, a foothold on the surface of the section) (c, Label 10 microns)

Rys. 1. Obraz szlifu chalkopirytu przed (a) i po adsorpcji DEDTCm (P = 100 mg / l) (KEYENCE) (b) i wielkość chropowatości powierzchni (wysokość warstwy łączącej, przyczółek na powierzchni sekcji) (c, Etykieta 10 mikronów)

Materials and Methods

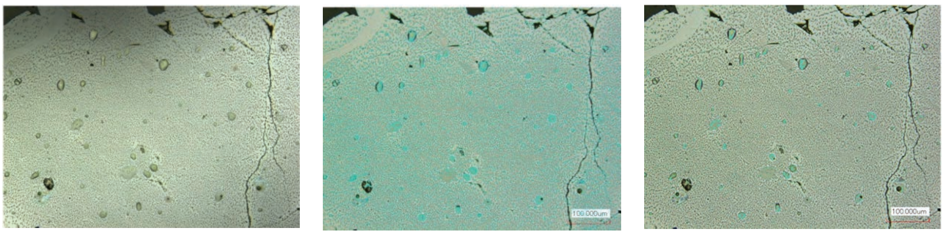
Mineral fractions of chalcopyrite and arsenopyrite were selected from samples of gold ore. The chemical composition is shown in Table 1.

Newly formed films of combined collector DEDTCc on polished sections of minerals (10x10x2 mm in size) were studied on analytical scanning electron (LEO 1420VP + INCA Oxford 350), and a laser microscope (KEYENCE VK-9700 with 1 nm resolution). Research methods are optical, confocal laser, analytical electronic, scanning probe microscopy, UV-spectrophotometry of reagent solutions, flotation of minerals. The KEYENCE scanning laser microscope with the surface analysis module VK-9700 enables making a non-contact measurement of the roughness of the surface of minerals and thus determining the height and size of the new formations obtained as a result of interaction with the reagents. The electronic microscope with energy-dispersive microanalyzer LEO-1420 VP INCA-350 allows determining the elemental composition of micro- and nanophases of reagents on the surface of minerals. UV-spectrophotometry was used to analyze the DEDTCc concentration in aqua phase of mineral suspension before and after contact with ground fractions (-0.1 + 0.063 mm) of chalcopyrite and arsenopyrite. The liquid phase was decanted after centrifugation and the residual concentration of the components of DEDTCm was analyzed by spectrophotometer SHIMADZU-1700.

Results and Discussion

The images of polished sections of chalcopyrite on analytical scanning electron (LEO 1420VP + INCA Oxford 350) and laser microscope (KEYENCE VK-9700 with 1 nm resolution) have shown that after contact with the DEDTCc solution characteristic molecular shape of adsorbed collector appeared (Fig.

a Initial polished thin section of arsenopyrite	b Filling surface covered by a reagent	c Filling drop-shaped new formations



Mineral surface area, μm^2	Surface area covered by a reagent, μm^2	Percentage of coverage by a reagent, %
499405	108091	21.6
	Drop-shaped new formations 14469.525	2.9

Fig. 2. Determining the surface area of the polished thin section of arsenopyrite coated with the DEDTCc reagent. Laser microscope KEYENCE VK-9700. Magnification of 20X

Rys. 2. Określenie pola powierzchni wypolerowanego cienkiego szlifu arsenopirytu pokrytego odczynnikiem DEDTCc. Mikroskop laserowy KEYENCE VK-9700. Powiększenie 20X

1). One can see the convex neoplasms that formed chemically adsorbed films of the reactant, which firmly anchored on the surface and did not dissolve in water at a subsequent washing.

Newly formed discrete sinter multi-phase of reactant had round shape with a diameter of 0.1 to 55 microns (Fig. 1c). Non-contact measurement of surface irregularities formed on the scanning microscope, helped to estimate the height of detected tumors, which was h = 0.1 - 0.4 mm for small phase (diameter 0.1–1.0 mm) and h = 0.65–1.85 microns to the larger formations (diameter up to 55 microns).

On the surface of arsenopyrite one could enjoy the very similar newly formed phase of the reagent after its contact with the mineral, but a little bit smaller in size and concentration (Fig. 2). Very close to round shape, a diameter of films is 0.1 to 34 microns and the height of detected tumors is about h = 0.1–0.4 mm for small phase (diameter 0.1–1.0 mm) and h = 0.65–1.65 microns to the bigger formations (diameter up to 34 microns).

In both cases, the phase reactant of nonionic component was partially removed by water and the droplets became flatter. By X-ray microanalysis, C and D picks were identified on the surface of arsenopyrite and chalcopyrite relating to the structure of the combined reagent. The different character of the adsorption phase of the combined reagent components could be explained by the chemical and the physical adsorption of combined collector. Nonionic component is attached to a mineral in the form of drop-shaped sinter tumors with a well-defined circular shape, with a diameter of 0.1 to 27.4 microns and a maximum height of 0.65 to 1.85 microns. Chemically adsorbed anionic DEDCT formed the new phase of irregularly shaped size 63–100 mm and a thickness of 10–20 microns. A combination of both phases on the surface of the sulfides is favorable for efficient flotation of associated gold from refractory ores.

In the course of the research, an original technique was developed to quantify the adsorption of DEDTCc on the surface of sulfide minerals in flotation conditions. The originality and novelty of the approach to the study of thin reagent films on the surface of mineral surfaces is to compare the numerical measurements of the unevenness of the relief of a mineral before and after a contact with the reagent solutions.

An analysis of the surface condition of sulfide minerals before and after contacting with reagent solutions is carried out using a KEYENCE VK-9700 confocal laser scanning microscope. This microscope enables making color images, conducting non-contact measurements of high definition. The short-wave laser and white light source are used simultaneously for lighting. The use of a laser beam allows the user to obtain the most accurate images of the surface relief of the object under study, as well as to perform numerical measurements of the unevenness of the relief.

Non-contact measurements were carried out by obtaining three-dimensional coordinates of the points of the sample surface relief by laser scanning. To display objects along three coordinates, a virtual manipulator and a computer mouse are used. The microscope is equipped with a revolver system of Nikon lenses, using which the researcher can adjust the magnification in the range 10X–150X. Observation and imaging is performed using the VK-Viewer software.

Measurements of the areas of the newly formed phases of the reagent on the surface of mineral polished sections were performed using the VK-Analyzer software on the basis of a color image by filling the object's selected area with a selected gradient. In other words, either the layer of the adsorbed reagent or the surface free from the reagent is highlighted in color, and the corresponding area is measured. The adsorption of the reagent according to the developed method is assessed by the degree of coverage of the surface of a mineral with a reagent (Fig. 2).

The measurements made at several fields of view (with an increase of 20X) showed that 21.6% of the arsenopyrite surface was covered by the DEDTCc reagent. The area occupied by the droplets in the neoplasms that may be presented by physically adsorbed OPDTC ester or disulfide DEDTC2, estimated 2.9% of the total area of the reagent coating (Fig. 2).

The measurements of the adsorption layer of the combined diethyl dithiocarbamate on the surface of chalcopyrite and arsenopyrite at several sites of the field showed that the degree of coverage of the surface of arsenopyrite by the DEDTCc reagent is 3 times lower than chalcopyrite, and is 21.6–27% (for chalcopyrite – 65–72,2%), which can provide preferential flotation of chalcopyrite compared to arsenopyrite into the con-

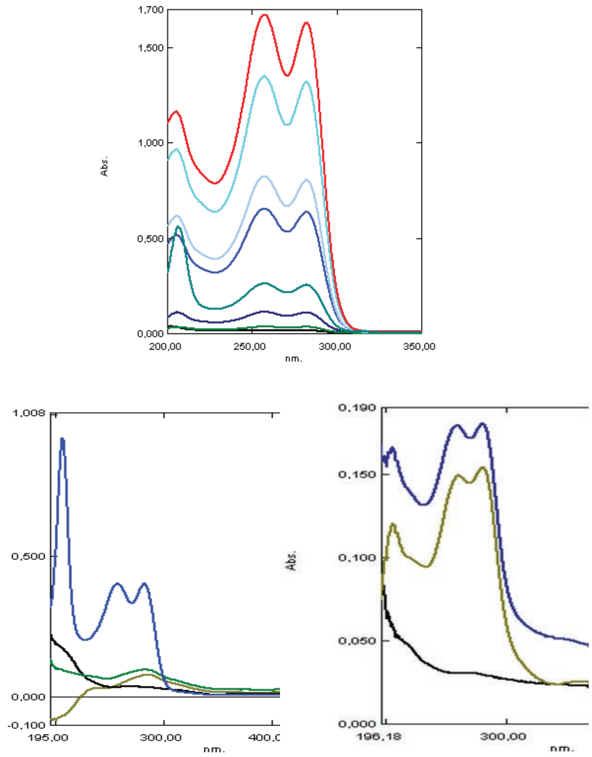


Fig. 3. UV-spectra of DEDTC initial solution (concentration 0,56–28 mg/l) (a), liquid phase of chalcopyrite suspension after DEDTC treatment (C = 10 mg/l) (b) and arsenopyrite suspension after DEDTC treatment (C = 5 mg/l) (c)

Rys. 3. Widma UV roztworu początkowego DEDTC (stężenie 0,56–28 mg / l) (a), faza ciekła zawiesiny chalkopirytu po obróbce DEDTC (C = 10 mg / l) (b) i zawiesina arsenopirytu po DEDTC leczenie (C = 5 mg / l) (c)

centrate. The total area of the tumors in the form of drops that characterize the physically sorbed component of the solution (OPDTC or DEDTC2) on the arsenopyrite was 2.9% of the total area of the coating reagent.

The predominant adsorption of DEDTCc on the chalcopyrite was quantified by UV spectroscopy of the liquid phase of mineral suspensions before and after contact of minerals with the reagent according to the difference between the initial and residual concentrations of DEDTC. Fig. 3 demonstrates UV spectra of the initial solutions of DEDTC at different concentrations (from 0.56 to 28 mg/l), on which the calibration curve was constructed, and spectra of the liquid phase of mineral suspensions after contact of the reagent with minerals are presented. By changing the optical density at the characteristic wavelengths of 257 and 282 nm, the residual concentration of the reagent and the adsorption of the reagent on the mineral were calculated. The residual concentration of DEDTCc in arsenopyrite suspenssion was 78–87% of initial concentration and adsorption was 0.02–0.04 mg/g. In the same experimental conditions the residual concentration of DEDTCc in chalcopyrite suspenssion was 19–24% of initial concentration and adsorption was 0.15–0.16 mg/g.

Conclusions

On scanning microscope from KEYENCE VK-9700 analyzer the formation of the adsorbed layer and the dimensions of newly formed phases of the combined collector DEDTCc, anchored in the surface of chalcopyrite and arsenopyrite under flotation conditions have been determined experimentally. Different newly formed phases on the surface of chalcopyrite and arsenopyrite indicated the chemical and physical nature of adsorption of the components of combined DEDTCc – anionic DEDTC and non-ionic OPDTC, respectively.

Nonionic OPDTC reagent fixed on the surface in the form of sinter drop-like neoplasms having clearly defined circular shape with a diameter of 0.1 to 27.4 microns and a maximum height of 0.65 to 1.85 microns. Combined DEDTCc formed irregularly shaped phase size 63–100 microns and a thickness of 10–20 microns, characterized by adsorption OPDTC neoplasms, which obviously explained c.

During the research it was established that for the selective separation of copper and arsenic sulfide minerals into concentrates of different kinds, it is possible to use combined DEDTCc capable to be selectively adsorbed on the chalcopyrite surface rather than on arsenopyrite. Using the laser KEYENCE VK-9700 and electronic LEO-1420 VP INCA-350 microscopy methods, it has been established that the film of a combined DEDTCc was not washed off with water and fixed firmly enough on the surface of the polished sections of chalcopyrite.

The measurements of the adsorption layer of the combined diethyl dithiocarbamate on the surface of sulfide minerals at several sites of the field showed that the degree of coverage of the surface of arsenopyrite by the DEDTCc reagent is 3 times lower than chalcopyrite, which can provide preferential flotation of chalcopyrite compared to arsenopyrite into the concentrate.

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Charakterystyka adsorpcji kombinowanego kolektora sulfhydrylowego na chalkopirycie i arsenopirycie w flotacji złożonych rud złota

W pracy przedstawiono wyniki badań eksperymentalnych właściwości adsorpcyjnych kombinowanego odczynnika zbierającego sulfhydryl – mieszanego roztworu dietyloditiokarbaminianu sodu (DEDTC) i estru oksypropylodietyloditiokarbaminianowego (OPDTC) w kierunku chalkopirytu i arsenopirytu w celu jego zastosowania selektywny kolektor minerałów siarczkowych zawierających Au w flotacji złożonych rud ogniotrwałych. Połączony roztwór dietylo-ditiokarbaminianu (DEDTCc) zawierał stałą zawartość składników anionowych i niejonowych (DEDTC: OPDTC = 1: 1) i zaobserwowano zmienny efekt hydrofobowy na powierzchni podstawowych minerałów siarczkowych niosących złoto - chalkopirytu i arsenopirytu.

Mechanizm adsorpcji składników kombinowanego kolektora na powierzchni chalkopirytu i arsenopirytu został zidentyfikowany jako charakterystyczny skład molekularny adsorbowanego kolektora chemicznie zaadsorbowanych cząsteczek reagenta, który jest mocno zakotwiczony na powierzchni. Nowo utworzona faza zaadsorbowanego odczynnika nie rozpuszczała się w wodzie podczas kolejnego płukania. W tym przypadku faza niejonowego estru OPDTC została częściowo usunięta przez wodę, a resztkowe zaadsorbowane kropelki zmieniły swój kształt i stały się bardziej płaskie. Za pomocą mikroanalizy rentgenowskiej zidentyfikowano pasma C i O dotyczące struktury połączonego DEDTCc na powierzchni arsenopirytu i chalkopirytu. Opracowano oryginalną technikę analizy wymiaru liniowego obrazów powierzchni za pomocą skaningowej mikroskopii laserowej i oprogramowania analizatora, a autorom udało się określić ilościową ocenę adsorpcji DEDTCc na powierzchni chalkopirytu i arsenopirytu.

Słowa kluczowe: flotacja, selektywny kolektor, rudy złota