

High-performance reagent modes for flotation recovery of platiniferous copper and nickel sulfides from hard-to-beneficiate ores

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Abstract. The paper presents the results of the recent research performed in IPKON Russian Academy of Sciences that deals with development and substantiation of new selective reagents for effective flotation recovery of non-ferrous and noble metals from refractory ores. The choice and development of new selective reagents PTTC, OPDTC, modified butylxanthate (BXm) and modified diethyl-dithiocarbamate (DEDTCm) to float platiniferous copper and nickel sulfide minerals from hard-to-beneficiate ores is substantiated. The mechanism of reagents adsorption and regulation of minerals floatability is discussed. The study of reagent modes indicates that by combining PTTC with the modified xanthate results in 6 – 7 % increase in the recovery of copper, nickel and PGM in the flotation of the low-sulfide platiniferous Cu-Ni ore from the Fedorovo-Panskoye deposit. The substitution of OPDTC for BX makes it possible to increase recovery of Pt by 13 %, Pd by 9 % and 2 – 4 times the noble metal content in the flotation concentrate.

1. Introduction

Platiniferous copper-nickel ores are complicated mineral raw material with thin impregnations of valuable components, close mutual intergrowth of sulfide minerals and high content of pyrrhotite in sulfide ores. Low-sulfide Cu-Ni ores are characterized by low content of copper and nickel, relatively high PGM content and gangue minerals with high floatability, like talc and other silicates.

PGM deposits are divided into three types, depending on the ratio of the sum of PGM and sulfides content in the ore [1]:

- rich-sulfide copper-nickel ores containing pyrrhotite and chalcopyrite (total sulfides content is more than 15% and the average PGM content is 1 ppm or less);
- platinum disseminated ores (sulfides content is 10 - 15% and the average content of total PGMs is 10 ppm and up);
- platinum low-sulfide ore (sulfides content is 1 - 3% and the average content of PGMs is more than 10 ppm). The proportion of disseminated ores in the overall balance of the PGMs currently stands at 70% and will increase further.

PGM Cu-Ni ores are hard-to-beneficiate raw material, because these ores are usually complex, the largest platinum-ore provinces and regions of Russia are located in the harsh climate zones, such as the Arctic zone. The prevalence of minerals of platinum metals and rich solid solutions of PGM in



pentlandite, chalcopyrite and pyrrhotite predetermines the use of gravity-flotation beneficiation circuits with the release of heavy platinum minerals in the gravity concentrate (for example, at the plant "Pechenganikel") and removing the solid soluble platinum group metals into the combined sulfide concentrate.

Most of the disseminated and low-sulfide platinum ores are characterized by fine impregnation of PGM minerals inside Cu and Ni sulfides, and a large variety of PGM mineral forms [2], resulting in high losses of fine particles of noble and non-ferrous metals into waste products. In processing circuits these specific features create certain difficulties when choosing flotation reagents and time-processing efficient reagent regimes [3].

One of the main trends in the development and rational use of Pt-Cu-Ni raw material is based on increasing the recovery of non-ferrous and precious metals and reducing production costs. It can be achieved by maximizing the selectivity of the flotation process, by controlling the parameters of the composition, creation of new effective reagents for the extraction of platinum-containing Cu-Ni sulfide minerals.

Current challenges in the design and application of effective flotation reagents for the recovery of Cu, Ni and PGMs are to produce selective reactants based on directional introduction into their molecular structure of the donor-acceptor substituents, and the ion-complexing agent, and a combination of ionic and non-ionic collectors that physically and chemically absorb on the mineral surfaces.

The methodological basis of intensification of selective flotation and the development of new flotation reagents originate from the fundamental studies of Russian and foreign scientists such as, Plaksin, Chanturiya, Kakowski, Mitrofanov, Okolovich, Ryaboy, Bogdanov, Solozhenkin, Abramov, Mantsevich, Ivankov, Vigdergauz, Gaudin, Taggart, Polling, Forssberg, O'Connor, Nagarai and others.

In our study we followed the main principle that the ability of new reagents to form water-insoluble complexes with the noble metals on the surface of minerals in flotation is the basis for selecting the compounds as collectors for extracting precious metals from hard-to-beneficiate ores. When we selected a class of reagents we also took into account their availability, simplicity of synthesis, environmental safety.

Under the guidance of the academician V.A. Chanturiya, in IPKON RAS, new class of collectors – cloud point polymers with specific functional groups of atoms like thioamine, phosphine and aminosulfide have been designed and tested for recovering platinum into nickel-pyrrhotite concentrate. These reagents owing to their complexing activity towards Cu, Ni and Pt produced high recovery of these metals but their synthesis is sufficiently expensive and complicated [4].

The main aim of the paper is the scientific substantiation of new complexing agents, produced from the conventional collectors of butyl xanthate and diethyl-dithiocarbamate, and their combinations, and on this basis to develop highly efficient reagent regimes to extract platinum-sulfide minerals from refractory ores.

2. Objects and methods

In this paper cyclic propylene tri-thiocarbonate (4-methyl-1, 3-dithiolan-2-thione) (PTTC) and oxypropyl ether diethyl-dithiocarbamate acid (OPDTC) were used as new selective flotation reagents towards Cu-Ni and PGMs minerals. Due to their ability to form a coordination bond with noble metals these compounds produce sparingly soluble compounds of non-ionic molecule structure and water-repelling properties [5, 6].

The use of S-dithiocarbamic acid esters, dithiocarbamates and cyanate-ethylene compounds in the flotation of copper-nickel and copper-molybdenum ores is known to have positive effects [7]. The other advantage of PTTC and OPDTC is that these reagents may be prepared and added into flotation cell as individual compounds or incorporated into modified collector solutions composed of xanthate or dithiocarbamate as the products of their reaction with propylene chlorhydrin. This technique was worked out in IPKON RAS by T.A. Ivanova (Ph.D., senior research associate) [8] and the authors highly appreciated her assistance in this study. The advantage of using modified reagent solutions

directly before being added into the flotation cell instead of adding them as separate components is that this technique avoids additional dissolution procedure.

The mineral fractions of pyrrhotite, chalcopyrite and pentlandite were from the Monchegorsk ore and the sample of low-sulfide ore was from the Fedorova Pana deposit in Russia. The chemical composition of these mineral samples is presented in table 1. The pentlandite sample incorporated the impurities of pyrrhotite and chalcopyrite, and the chalcopyrite sample had about 16.6 % of silicates.

Table 1. Chemical composition of mineral samples.

Mineral sample	Content							
	Au	Pt	Pd	Ni	Cu	Fe	S	Oxides
	ppm				%			
Pentlandite (pyrrhotite, chalcopyrite)	0.15	0.9	7	16.3	4.7	42.9	32.6	3.2
Pyrrhotite	—	—	—	0.03	0.04	59.0	38.1	2.8
Chalcopyrite (silicates)	0.15	0.9	1.2	0.6	26.4	28.1	28.3	16.6

Qualitative and quantitative analyses of the aqueous solutions of the reagents studied PTTC, OPDTC, BXm and DEDTCm before and after their contact with ground mineral samples ($-0.1 + 0.063$ mm), as well as the organic (hexane) extracts of aqueous and solid (mineral) phases after reagent-mineral contact were performed by UV-spectrophotometry using a SHIMADZU UV-1700 spectrometer. The amounts of reagents adsorbed on the surface of sulfides were obtained from the difference between the initial and final concentrations of the reactants in the liquid phase, taking into account the amount of reactant desorbed into the organic solvent from the surface of the mineral.

Mineral polished sections were studied by scanning electron microscopy (SEM, LEO 1420VP microscope) with X-ray microanalysis (EPMA, energy dispersive spectrometry INCA Oxford 350), optical microscopy (OM, Olympus BX51 microscope), laser microscopy (KEYENCE VK-9700) and X-ray diffraction (Rigaku D/MAX-2200). Mathematical statistics methods were used for the analysis of the results.

3. Results and discussion

The efficiency of flotation reagents applied for sulfide minerals extraction using both traditional and new collectors is largely dependent on the formation of certain hydrophobic compounds on the surface of the sulfides.

The results of tests on the adsorption of PTTC, OPDTC and BX on mineral samples by UV extractive spectroscopy have shown that cyclic propylene trithiocarbonate (PTTC) incorporated into the modified butylxanthate solution and OPDTC incorporated into the modified diethyl-dithiocarbamate solution, have shown different values of adsorbed reagent onto the surface of Cu-Ni-Pt sulfide minerals [9]. A maximum PTTC adsorption of 23×10^{-6} g/g was measured on pentlandite with chalcopyrite and PGM impurities and of 4.6×10^{-6} g/g on chalcopyrite. There was no PTTC absorbed on pyrrhotite which is free of Cu, Ni and PGM impurities (table. 2).

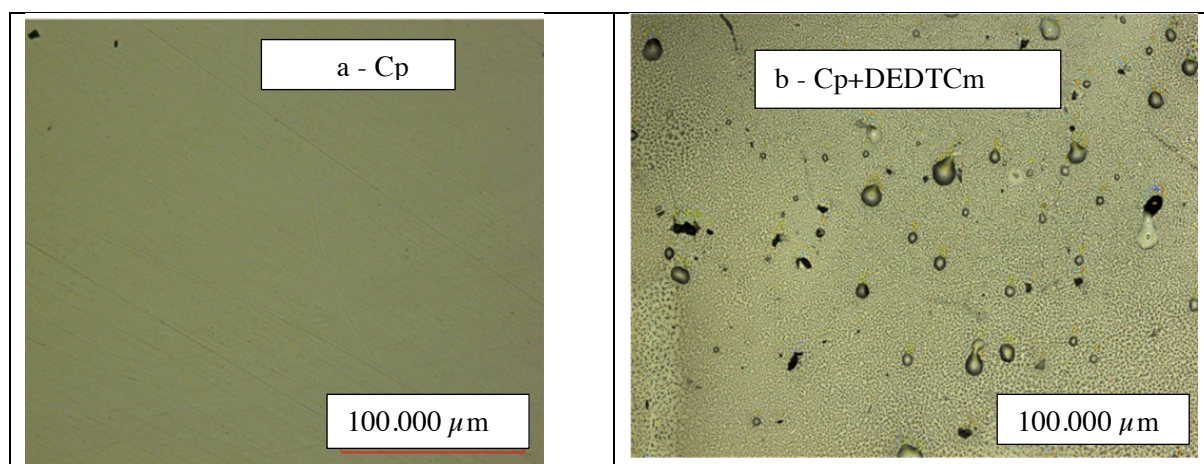
OPDTC showed the same trend of adsorption on the surface of the Pt-Cu-Ni sulfides with highest adsorption on pentlandite (73×10^{-6} g/g), medium adsorption on chalcopyrite (20.7×10^{-6} g/g) and lowest adsorption on pyrrhotite (4.6×10^{-6} g/g) (see table 2). For comparison, the adsorption of butylxanthate (BX) on all studied samples under identical concentrations was much higher than those of PTTC and DEDTCm with adsorption of 1.33×10^{-3} g/g on pentlandite (100% of initial BX), 1.01×10^{-3} g/g on chalcopyrite (79.6% of initial BX), and 46.8 % adsorption on pyrrhotite .

Table 2. PTTC, OPDTC and BX adsorption on mineral samples (UV extractive spectroscopy).

Mineral sample	Adsorption					
	PTTC		BX		OPDTC	
	10^{-6} g/g	% init.	10^{-3} g/g	% init.	10^{-6} g/g	% init.
Pentlandite (pyrrhotite, chalcopyrite)	23	31.6	1.33	100	73	16.5
Chalcopyrite (silicates)	4.6	6.3	1.01	79.6	20.7	4.7
Pyrrhotite	0	0	0.66	46.8	4.4	1.0

Such a high adsorption of BX on pyrrhotite may explain why it is difficult to separate Cu-Ni sulfides from pyrrhotite using this collector. The designed reagents of PTTC and OPDTC demonstrated higher selectivity to Cu and Ni sulfides compared to pyrrhotite, which makes them potential collectors for selective flotation of Cu-Ni-Pt minerals.

The study of newly formed films of combined collector DEDTCm (that incorporates OPDTC and DTC), on polished sections of chalcopyrite by ASEM (LEO 1420VP INCA Oxford 350) and ALM (KEYENCE VK-9700) indicated that after contact with the reagent solution characteristic molecular shape of adsorbed collector appeared on the Cu-Ni mineral surface. For example, figure 1 and 2 demonstrate the presence of DEDTCm on chalcopyrite.

**Figure 1.** Laser microscopy images of polished chalcopyrite (Cp) samples before (a) and after (b) contact with DEDTCm (OPDTC+DTC) solution ($C = 100$ mg/l, $t = 5$ min).

One can see the convex neoplasms that fixed onto very small chemically adsorbed species of the reactant (figure 1b and figure 2a). Adsorbed species have differential shape sizes: the largest species is about $60.5 \mu\text{m}$ in diameter and about $4.0 \mu\text{m}$ in height, and the smallest species are less than $1.0 \mu\text{m}$ in diameter and less than $0.1 \mu\text{m}$ in height (figure 2d, 2c). It was found that the amount of adsorbed species depended on the initial reagent concentration, and that they firmly anchored on the surface and did not dissolve in water after subsequent washing.

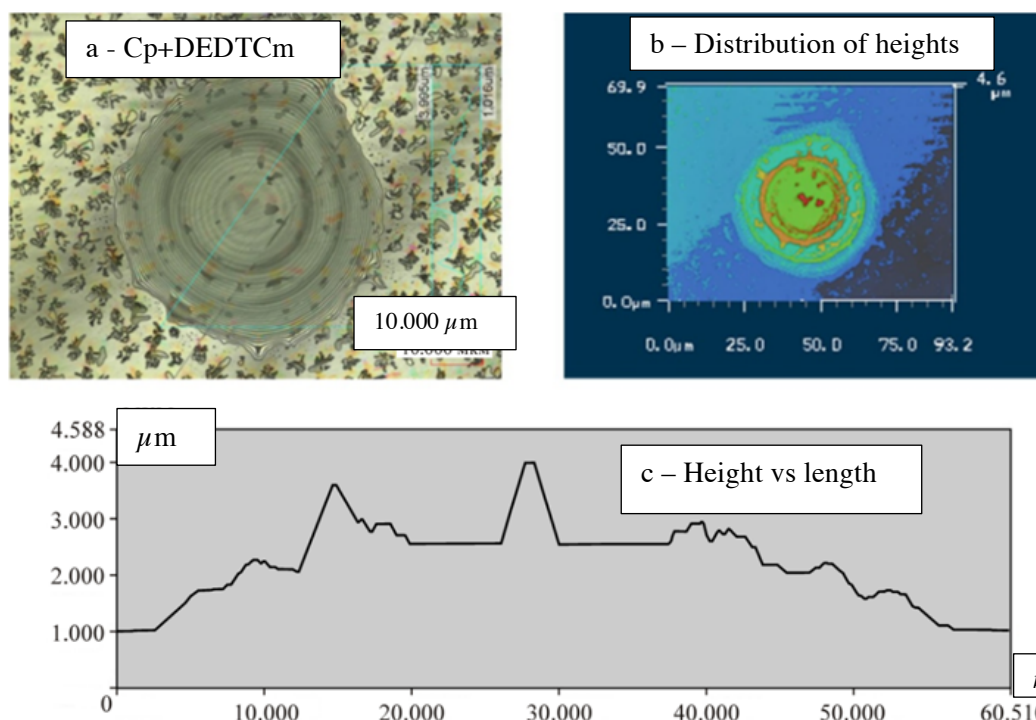


Figure 2. Laser microscopy images of polished chalcopyrite (Cp) samples after DEDTCm (OPDTC+DTC) treatment ($C = 100 \text{ mg/l}$) (a), distribution of heights (b) and size of the reagent species on Cp surface (c).

Flotation tests on a sample of low-sulfide platinumiferous copper-nickel ore of the Fedorova-Pana deposit showed the effectiveness of the modified xanthate solution, in which cyclic PTTC was included, instead of the conventional collector (butyl xanthate). Ore sample was ground to a particle size of 80% - 0.074 mm and floated in a single-stage operation. Using modified xanthate together with dithiophosphate in the proportion of 1:1 improved the quality of Cu - Ni concentrate and provided a total gain of recovering copper and nickel of 6 - 7% [10].

Laboratory tests of new reagent schemes of combination of OPDTC and BX were also performed on a Pt-Cu-Ni low-sulfide ore sample from the Fedorova-Pana deposit ground to 80% - 0.074 mm.

Using butyl xanthate (BX 100 g/t), isopropyl dithiophosphate (DTC 50 g/t), tannin depressor (300 g/t) and methyl-isobutyl carbinole as a frother (MIBC 60g/t) in a conventional reagent scheme produced a recovery of PGMs not exceeding 72 – 74% (Table 3).

Table 3. Results of low-sulfide ore flotation (Fedorova-Pana field) using OPDTC and BX (PGMs extraction)

Reagents, g/t	Product	Yield, %	Content, ppm		Recovery, %	
			Pd	Pt	Pd	Pt
BX-100, DTP-50	Concentrate	13.33	3.88	1.02	73.97	72.33
Depressor-300	Tails	86.67	0.21	0.06	26.03	27.67
MIDC-60	Ore	100	0.7	0.19	100	100
OPDTC-150	Concentrate	7.59	10.14	4.24	82.23	85.31
Depressor-300	Tails	92.41	0.18	0.06	17.77	14.69

MIBC-60	Ore	100	0.93	0.38	100	100
Table 4. Results of low-sulfide ore flotation (Fedorova-Pana field) using OPDTC and BX (Cu and Ni extraction)						
Reagents, g/t	Product	Yield, %	Content, ppm		Recovery, %	
			Cu	Ni	Cu	Ni
BX-100, DTP-50	Concentrate	13.33	0.56	0.43	83.09	71.65
Depressor-300	Tails	86.67	0.017	0.026	16.91	28.35
MIBC-60	Ore	100	0.09	0.08	100	100
OPDTC-150	Concentrate	7.59	1.018	0.8	85.84	76.02
Depressor-300	Tails	92.41	0.014	0.021	14.16	23.98
MIBC-60	Ore	100	0.09	0.08	100	100

Application of OPDTC instead of combination of BX and DTP helped to achieve a higher flotation performance. Compared to the conventional scheme, Pt recovery increased by 13%, Pd recovery increased by 9% and the content of noble metals in the flotation concentrate increased 2 - 4 times (table 3).

Recovery of Cu and Ni was about 83 and 71 %, respectively under the conventional reagent scheme (Table 4). When the new reagent OPDTC was used, the recovery of non-ferrous metals increased by 2.7 – 4.6 % and the content of Cu and Ni in the flotation concentrate increased 2 times.

4. Conclusions

The new reagents-collectors, PTTC, OPDTC, modified BX, and modified DEDTCm were obtained and tested for the recovery of PGM, Cu and Ni from refractory ores.

Experimental studies of the physical and chemical effect of the new reagents on the surface of chalcopyrite, pentlandite and pyrrhotite using analytical methods helped to determine the conditions for the formation of adsorption layer of new reagents-collectors and shows that these reagents selectively adsorbed on the surface of micro- and nanoparticles of Pt, Cu and Ni metals and provide improved recovery of PGMs, Cu and Ni by 2-13% in ore flotation.

It is found that the cyclic PTTC, being a part of the modified xanthate solution, exhibits selectivity with respect to the Pt-containing Cu and Ni sulfide minerals and increases the floatability of these minerals in the flotation of a low-sulfide ore from the Fedorova Pana deposit. Using modified xanthate in conjunction with dithiophosphate at a ratio of 1:1 led to better quality of the Pt - Cu - Ni concentrate and provided a total increase in Cu, Ni and PGMs recovery by 6 - 7%.

The selectivity of OPDTC as additional collector to xanthate in the flotation of Pt-containing minerals is confirmed by its selective adsorption on the surface of copper and nickel sulfides, which provides 82 - 85% recovery of PGM metals from the Pt-Cu-Ni ore.

Designed reagent modes with new selective reagents (PTTC, OPDTC, BXm and DEDTCm) are recommended for the flotation of Cu, Ni and PGMs sulfide minerals from refractory ores.

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