



Assessment of IM-50 and TOFA Adsorbed Layer on Cassiterite in Flotation of Tin Sulfide Wastes

Tamara MATVEEVA¹⁾, Nadezhda GROMOVA¹⁾

¹⁾ Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences, (ICERM RAS), Moscow, Russia

<http://doi.org/10.29227/IM-2020-01-52>

Submission date: 14-01-2020 | Review date: 01-04-2020

Abstract

The paper presents the results of experimental study of the adsorption characteristic of the IM-50 and tall oil fatty acids (TOFA) collector reagents on cassiterite. UV-spectrophotometric method, scanning electron and laser microscopy were applied to analyze the adsorption of the reagents. SHIMADZU UV 1800 was used to obtain the UV spectra of aqueous solutions of IM-50 reagents and saponified TOFA at varied concentrations. IM-50 has not got characteristic adsorption maxima in ultraviolet and visible spectrum. TOFA has a weakly pronounced maximum absorption in the range of 233-244 nm. Microscopic photographs of cassiterite sections were obtained with LEO 1420VP INCA equipped OXFORD ENERGY 350 analyzer. Reagent IM-50 and TOFA collector reagent, Newly formed organic matter phases of IM-50 and TOFA were detected. X-ray spectra characterized the increased carbon content indicating adsorption on the surface of cassiterite IM-50 and TOFA.

By measuring the surface relief parameters of polished cassiterite, using KEYENCE VK-9700 scanning laser microscopy and VK-Analyzer software, a qualitative and quantitative assessment of the IM-50 and TOFA reagent layer on the cassiterite surface was performed. Measurements were performed in the several fields of view and showed the degree of IM-50 coating varied from 40.5 to 42.6% of the surface area, and TOFA average coating was 38.5%. Subsequent washing with water does not remove the reagents from the surface of the mineral and indicates a strong fixation of IM-50 and TOFA on cassiterite, which can have a positive effect on flotation extraction of sludge tin fractions.

Qualitative and quantitative results of the reagent adsorption helped to make a forecast of their floatability by the studied collectors. This study is supported by the Russian Science Foundation (project No. 17-17-01292).

Keywords: sulfide tin ores, cassiterite, tailings, flotation, IM-50, TOFA, adsorption

Introduction

Cassiterite is the main tin mineral. Cassiterite is found in association with quartz, muscovite, lepidolite, topaz, scheelite, fluorite, albite, tourmalines, ferro-columbite, manganocolbit, beryl, spodumene, wolframite, pyrite, arsenopyrite, pyrrhotite, sphalerite, chcryprtrum, etc., and pyrite, pyrite, arsenopyrite, pyrrhotite, sphalerite, chyrum, and ceprtrum; Cassiterite is formed in the vein and skarn deposits of W-Mo-Sn ores (hydrothermal origin); in greisens (pneumatolite-hydrothermal); forms uneven clusters in rare-metal granite pegmatites (pegmatite); as an accessory mineral in acidic rocks (igneous). Cassiterite of exogenous origin is found in zones of oxidation of deposits with tin sulfides.

The main deposits of tin sulfide type in Russia are located in the Khabarovsk Territory. At present, the recycled tails of the Solnechny Mining and Processing Plant with a tin content of 0.22–0.4% are involved in processing [1–3].

A distinctive feature of the Russian tin deposits of sulfide, less commonly silicate industrial types of the Far East is their complex mineral composition - in addition to tin, ores contain in industrial quantities copper, lead, zinc, tungsten, silver, rare and trace elements (indium, scandium, etc.). For example, in the fields of the Komsomolsk tin ore district, the ores and tailings of which are planned to be recycled in the near future, contain tin in the form of cassiterite, stannine and sulfostannat, sulphides of non-ferrous metals – copper, zinc, lead, silver, rare and trace elements (indium, scandium, etc.). At the same time, a significant proportion of sulfides is represented by pyrite, pyrrhotite and arsenopyrite, the presence

of which in concentrates of non-ferrous metals worsens their quality (for example, arsenic in copper concentrate) and complicates further metallurgical redistribution [1].

Flotation is the most effective method for sulfide-tin ores treatment. Hydroxamic acids and tall oil fat acids (TOFA) are used for flotation of cassiterite [4–6]. Application of selective collectors and modifiers may provide effective recovery of valuable metals into flotation concentrates.

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 valuable minerals is a determining factor in improving the recovery of non-ferrous metals from refractory ores, a detailed study of the nature of its adsorption on the mineral surface has been performed.

The aim of the study is to analyze the adsorbed species and percentage covering of collecting agents on cassiterite surface in flotation conditions and forecast the dosage of flotation reagents under processing of refractory tin sulfide ores

In this paper, collecting agents IM-50 and TOFA have been tested in adsorption and flotation of cassiterite from one of the sulfide-tin deposits of Russia.

Materials and Methods

Mineral fraction of cassiterite was selected from one of the sulfide-tin deposits of Russia. Microphoto and X-ray spectrum of cassiterite sample (LEO 1420VP + INCA Oxford 350) is shown Figure 1.

Newly formed species of collector IM-50 and TOFA on polished sections of cassiterite (10×10×2 mm in size) were

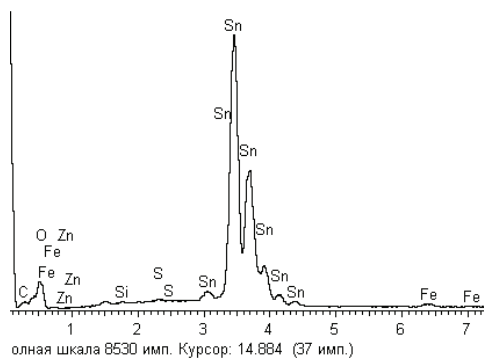
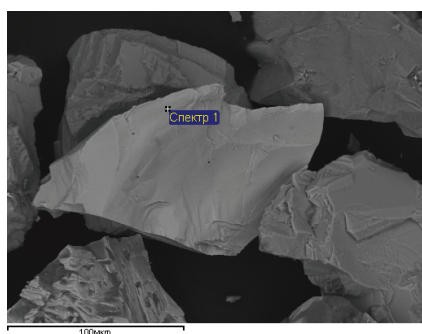
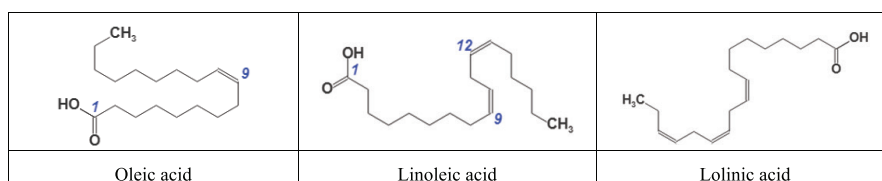
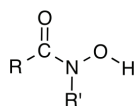


Fig. 1. Microphoto and X-ray spectrum of cassiterite sample (LEO 1420VP + INCA Oxford 350)
Rys. 1. Widmo mikrofotograficzne i rentgenowskie próbki kasyterytu (LEO 1420VP + INCA Oxford 350)



studied by 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 micro analyzer 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 IM-50 and TOFA concentration in aqua phase of mineral suspension before and after contact with ground fractions (-0.1 + 0.063 mm) of cassiterite. The liquid phase was decanted after centrifugation and the residual concentration of the components of IM-50 and TOFA was analyzed by spectrophotometer SHIMADZU-1700.

Hydroxamic acids are selective collectors for ores containing rare metals: tantalum, niobium, rare earth, etc., as well as tin. The general formula of hydroxamic acids:



Reagent IM-50 is a mixture of alkyl hydroxamic acids (C7-C9 fraction). IM-50 is a brownish-red liquid with a strongly alkaline reaction, with an ammonia smell. The technology for producing this reagent was developed at the Mekhanobr Institute, Russia. The reagent contains 75–78% hydroxamic acids, 10–12% carboxylic acids, 10–12% moisture, and up to 4.5% inorganic impurities. Hydroxamic acids are weaker than fatty acids, the pKa values for capron (C6) -, enanth (C7) - and capryl hydroxamic (C8) acids are 9.65; 9.67 and 9.69. As a result, they form much stronger complexes than fatty acids.

Tall oil fat acids (TOFA) are the oily liquid of light yellow color, consisting of a mixture of high-molecular unsaturated

organic acids (C18–C20) obtained by rectification of crude tall oil. The mixture includes oleic, linoleic, lolinic acids and their isomers. Resin acids (up to 2%), unsinkable substances (up to 2%), and also saturated fatty acids: palmitic, stearic, their isomers, etc. are present as undesirable impurities.

The spectrophotometer SHIMADZU UV 1800 was used to obtain the UV spectra of aqueous solutions of IM-50 reagents and saponified TOFA (various concentrations). On the spectra of IM-50 the characteristic maxima of absorption were not determined. The spectra of TOFA have a weakly pronounced maximum absorption in the range of 233–244 nm.

Results and Discussion

The images of polished sections of cassiterite that were observed by analytical scanning electron (LEO 1420VP + INCA Oxford 350) and laser microscope (KEYENCE VK-9700 with 1 nm resolution) have shown the characteristic molecular shape of adsorbed phase of collector after its contact with the IM-50 (Figure 1a) and TOFA (Figure 1b) solutions. Microscopic photographs of polished sections of cassiterite shows with IM-50 and TOFA reagent reveal characteristic dark round or oval spots with a diameter of 0.1 to 15 microns. X-ray spectra of the spots are characterized by an increased content of carbon C, which indicates adsorption of carbon-containing organic reagent on the surface of cassiterite.

Newly formed carbon-containing organic species of the reactant firmly anchored on the surface and did not dissolve in water at a subsequent washing.

Laser microscopy (KEYENCEVK-9700) data indicated the appearance of adsorbed IM-50 neoplasms on the surface of cassiterite in the form of films and rounded islands, the size of which is 9–29 μm in diameter, 1–1.5 μm in height, reaching a maximum height of 2 μm (Fig. 3a). After washing, the dimensions of the newly formed phases did not actually change. TOFA is fixed in the form of films and rounded droplets with a diameter of 10 μm on average and 1–2 μm in height (Fig. 3b).

Thus, as a result of the selective interaction of cassiterite with IM-50 and TOFA reagents, the surface of the mineral is modified by stable Sn-reagent complexes, namely (RR₁C-

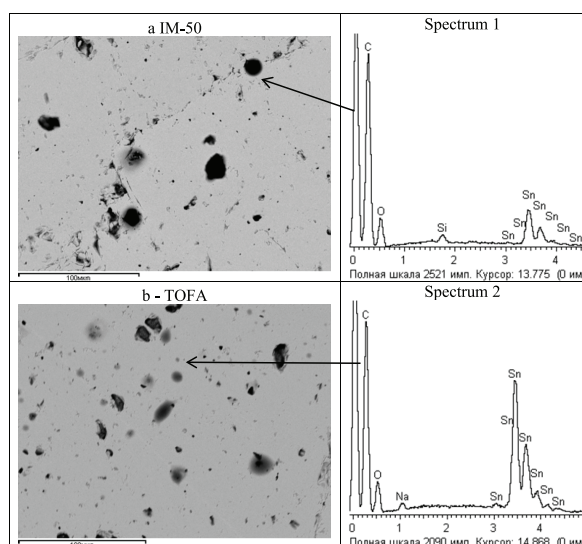


Fig. 2. Image of polished cassiterite after IM-50 (a) and TOFA (b) treatment ($C = 100 \text{ mg/l}$) (LEO 1420VP + INCA Oxford 350) (b) and X-ray spectra of adsorbed phase of collector (Label 100 microns)

Rys. 2. Obraz kasyterytu po obróbce IM-50 (a) i TOFA (b) ($C = 100 \text{ mg/l}$) (LEO 1420VP + INCA Oxford 350) (b) i widma rentgenowskie zaadsorbowanej fazy kolektora (Etykieta 100 mikronów)

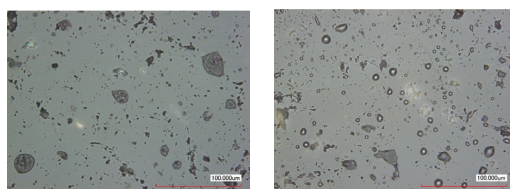


Fig. 3. Image of polished cassiterite after IM-50 (a) and TOFA (b) treatment ($C = 100 \text{ mg/l}$) (KEYENCE VK-9700) (Label 100 microns) Magnification of 50X

Rys. 3. Obraz kasyterytu po obróbce IM-50 (a) i TOFA (b) ($C = 100 \text{ mg/l}$) (KEYENCE VK-9700) (Etykieta 100 mikronów) Powiększenie 50X

Reagent	Magnification	Mineral surface area, μm^2	Surface area covered by a reagent, μm^2	Percentage of coverage by a reagent, %
IM-50	10X	2907542	1208357	41,5
TOFA	10X	3683390	1418055	38,5

NOO_2Sn , $(\text{C}_{17}\text{H}_{31}\text{COO})_n\text{Sn}$, which contributes to the efficient extraction of tin from sulfide-tin ores.

In ICERM RAS an original technique was developed to quantify the adsorption of the reagent 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 its contact with the reagent solutions [7–8].

The measurement of the surface area of the polished mineral coated with the newly formed reagent phase was made on the color image by filling the area of the object with a selected gradient. A layer of adsorbed reagent was highlighted and the corresponding area was measured. Thus, the area (μm^2) of the total mineral surface and the surface covered with the reagent were estimated. The percentage degree of coating the surface of the mineral with a reagent (%) was calculated.

The area of the newly formed reagent phases on cassiterite polished sections treated with IM-50 and TOFA was determined at various magnifications of the image (10X, 20X, 50X). Measurements were made in several areas of the field of view. The results are presented in the Table.

Measurements of the adsorption layer of reagents on the surface of cassiterite in several areas of the field of view showed that the degree of coverage with the IM-50 reagent on the surface of cassiterite with an increase of 10X and 20X is 40.5–42.6%, washing with water practically does not desorb the reagent, the degree of coverage is 41.5%, i.e. IM-50 is firmly entrenched on the surface of the mineral. The degree of coating with the reagent TOFA of the surface of cassiterite is 38.5% (with an increase of 10X).

Conclusions

Microscopic photographs of the cassiterite sections obtained using a LEO 1420VP scanning electron microscope with the INCA OXFORD ENERGY 350 energy dispersive analyzer, after being treated with IM-50 and TOFA collectors, reveal dark, round sections, whose X-ray spectra are characterized by an increased carbon content, which indicates adsorption on the surface of cassiterite carbon-containing organic reagent.

According to the method developed in ICERM RAS, which consists in comparing numerical measurements of the irregularities of the relief of a mineral before and after con-

tact with a reagent solution obtained by KEYENCE VK-9700 scanning laser microscopy using VK-Analyzer software, an IM-50 adsorption layer of reagents was measured and GCTM on the surface of cassiterite.

Measurements of the adsorption layer of reagents on the surface of cassiterite in several areas of the field of view showed that the degree of coverage with the IM-50 reagent on the surface of cassiterite with an increase of 10X and 20X is 40.5–42.6%, washing with water practically does not desorb the reagent, the degree of coverage is 41, 5%, i.e. IM-50 is

firmly entrenched on the surface of the mineral. The degree of coating with the reagent GCTM of the surface of cassiterite is 38.5% (with an increase of 10X). Qualitative and quantitative assessment of the adsorption of reagent on minerals could help to make a forecast of their floatability by the studied collectors.

Acknowledgments

This study is supported by the Russian Science Foundation (project No. 17-17-01292).

Literatura – References

1. Khanchuk, A.I., Kemkina, R.A., Kemkin, I.V., Zvereva, V.P. KRAUNZ. Earth Sciences. - 2012. - № 1 (19).
2. Yusupov, TS, Kondratyev, S.A., Baksheeva, I.I., Structural-chemical and technological properties of minerals of cassiterite-sulfide technogenic raw materials, Obogashchenie rud. - 2016. - № 5. - P. 26 - 31.
3. Gazaleeva G.I., Nazarenko L.N., Shikhov N.V., Shigaeva V.N., Boykov I.S. Development of the enrichment technology for tin-containing tails of the Solar Mining Plant // Scientific principles and practice of processing ores and technogenic raw materials: materials XIII International scientific and technical conf. - Ekaterinburg: Fort Dialog-Iset, 2018. - p. 11 - 16.
4. Leistner T., Embrechts M., Leißner T., Chehren Chelgani S., Osbahr I., Mockel R., Peuker U. A., and Rudolph M. A study of the reprocessing of fine and ultrafine cassiterite from gravity tailing residues by using various flotation techniques, Minerals Engineering. - 2016. Vol. 96 - 97. — P. 94 - 98.
5. Angadi S.I., Sreenivas T., Ho-Seok Jeon, Sang-Ho Baek, and Mishra B. K. A review of cassiterite beneficiation fundamentals and plant practices, Minerals Engineering, 2015, Vol. 70. — P. 178 - 200.
6. López F. A., García-Díaz I., Rodríguez Largo O., Polonio F. G., and Llorens T. Recovery and purification of tin from tailings from the Penouta Sn-Ta-Nb Deposit, Minerals, 2018, Vol. 8, № 1. — P. 20.
7. Matveeva, T.N., Chanturiya, V.A., Gromova, N., K., Lantsova, L., B. Study of the effect of chemical and phase composition on adsorption and flotation properties of sulfide-tin ore tails using dibutyliditiocarbamate, J Mining Science. - 2018.
8. Matveeva, T., N., Gromova, N., K., Minaev, V.A. Quantitative assessment of adsorbed layer of combined diethylditiocarbamate on chalcopyrite and arsenopyrite by measuring relief parameters, Tsvetnye metally. - 2018. - № 7. - P.27-32.

Adsorpcja kolektorów IM-50 i TOFA na kasyteryście w procesie flotacji odpadów siarczków cyny

W pracy przedstawiono wyniki badań eksperymentalnych charakterystyki adsorpcji odczynników kolektorowych IM-50 i kwasów tłuszczowych oleju talowego (TOFA) na kasyteryście. Do analizy adsorpcji odczynników zastosowano metodę spektrofotometryczną UV, skaningową mikroskopię elektronową i laserową. SHIMADZU UV 1800 zastosowano do uzyskania widm UV wodnych roztworów odczynników IM-50 i zmydlonego TOFA w różnych stężeniach. IM-50 nie ma charakterystycznych maksimów adsorpcji w widmie ultrafioletowym i widzialnym. TOFA ma słabo wyraźną maksymalną absorpcję w zakresie 233–244 nm. Zdjęcia mikroskopowe przekrojów kasyterytów uzyskano za pomocą analizatora OXFORD ENERGY 350 wyposażonego w LEO 1420VP INCA. Wykryto nowo powstałe fazy materii organicznej IM-50 i TOFA. Widma rentgenowskie charakteryzowały zwiększoną zawartość węgla wskazującą na adsorpcję na powierzchni kasyterytów IM-50 i TOFA. Mierząc parametry wypukłości powierzchni polerowanego kasyterytu, stosując skaningową mikroskopię laserową KEYENCE VK-9700 i oprogramowanie VK-Analyzer, przeprowadzono jakościową i ilościową ocenę warstwy odczynnika IM-50 i TOFA na powierzchni kasyterytu. Pomiary przeprowadzono w kilku polach widzenia i stwierdzono no stopień pokrycia IM-50 wahający się od 40,5 do 42,6% pola powierzchni, a średnie pokrycie TOFA wynosiło 38,5%. Późniejsze przemycie wodą nie usuwa odczynników z powierzchni minerału i wskazuje na silne utrwalenie IM-50 i TOFA na kasyteryście, co może mieć pozytywny wpływ na ekstrakcję flotacyjną frakcji szlamu i cyny. Jakościowe i ilościowe wyniki adsorpcji odczynników pomogły w opracowaniu prognozy ich flotowalności za pomocą badanych kolektorów. Badanie jest wspierane przez Russian Science Foundation (projekt nr 17-17-01292).

Słowa kluczowe: rudy siarczkowe cyny, kasyteryt, odpady poflotacyjne, flotacja, IM-50, TOFA, adsorpcja