

THE USE OF NEW DEPRESSOR IN LEAD-COPPER CONCENTRATES SEPARATION

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ABSTRACT

The rational choice of flotation reagents is one of the main facilities for selective mineral separation. As a result of investigations with application of flotation, electrochemical, FT-IR and electronic spectroscopy as well as some other methods it has been established that dyes of azine group can be used as an additional efficient depressor for copper sulphides in lead-copper concentrates separation with cyanide.

Efficiency of azine compounds is proved by their selective interaction with copper sulphide surfaces. Nigrosine doesn't adsorb on galena and doesn't change its surface properties.

INTRODUCTION

The analysis of modern reagent regimes of lead-copper concentrates selective flotation testifies to present reserves of their more efficient use as at the expense of recovery increasing of metals presented by the own mineral forms as at the expense of use of low-toxic selective reagents-modifiers allowing to replace sodium cyanide partially or completely having raised thus ecological cleanliness of the process.

The rational choice of flotation reagents is one of the main control facilities of selective mineral separation; therefore steadfast attention is given recently to questions of selective reagents collection and finding out their action mechanism. The available representation in this area has received a new explanation due to attraction of coordination compounds chemistry laws.

At the present time of according to modern flotation theory, nucleophilic reagents chemisorption on mineral surfaces in general form is considered as a process of mixed coordinated-type surface compounds formation, proceeding on donor-acceptor (acid-basic) mechanism (Bogdanov et al., 1990). The role of acid Lewis's adsorption centres are performed by partially charged metals cations located on mineral surfaces, which are not saturated coordinately relative to

dispersed environment. Steric accessible atoms perform the role of solidophilic functional centres of nucleophilic reagents or groups characterised with excessive density of electronic charge. Chemisorbed flotation reagent forms internal coordinational sphere of metal-complexing agent on mineral surface equally to crystal lattice anions.

Proceeding from modern representations about coordination mechanism of flotation reagents adsorption, which are in accordance with the principle of hard and soft Pearson's acids and bases and concept of characteristic nuclear groups (CNG), intensification action on depression of copper sulphides flotation may be connected to presence in reagent structure electron-donating nitrogen-containing CNG as active solidophilic agents; for providing necessary hydrophobic degree, a reagent should contain appropriate groups (Ryaboi, 1982).

From among these compounds water-soluble nitrogen, concerning to a group of azine dye was chosen as rather cheap, little toxic and produced in industrial scales reagent. Nigrosine isn't individual compound (Stepanov, 1984).

The intermolecular polarization analysis of nigrosine (NG) molecules electronic density has shown that structure of NG-entering compounds and steric accessibility N- and O- donor atoms correspond with solidophilic activity condition of characteristic atomic dye groups: -N= groups of heteroaromatic cycle, imido -NH- groups of phenylamine fragments and sulpho -SO₃- groups. The preliminary laboratory tests have confirmed rather high efficiency of NG application in selective lead and copper sulphides flotation process (Yushina et al., 1996).

EXPERIMENTAL RESULTS

NG action studies on flotation of sulphide minerals - galena, chalcopyrite and chalcocite - have been carried out by frothless flotation method on powders having (-125 + 44) microns size.

The main aim of laboratory tests was determination of influence such factors as consumption of the collector (butyl potassium xanthate - BPX), NG, sodium cyanide and pH values on minerals floatabilities of a mineral suspension liquid phase were investigated.

The results of carried out researches have shown that copper sulphides depression is followed by increase of the NG consumption and depends on the collector concentration and the medium pH value (Fig.1). Chalcopyrite flotation is depressed most efficiently while galena is depressed insignificantly, down to the value of 15-20 mg/l NG concentration in solution. The further increase of NG concentration is not low-efficient because the increase of galena recovery into cell product is observed and the process selectivity is disturbed.

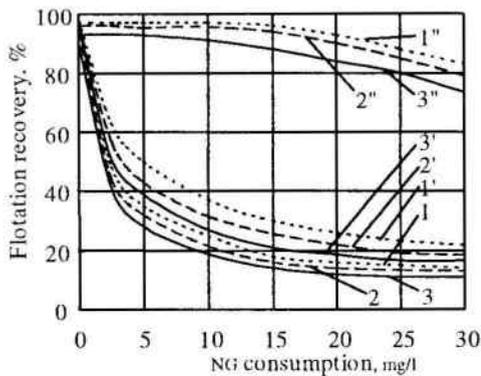


Figure 1. Flotation of chalcopyrite (1-3) chalcocite (1'-3') and galena (1''-3'') with 5 mg/l BPX: influence of NG consumption and pH: 1,1'-pH 7,5; 2,2',2''-pH 9; 3,3',3''-pH 10.

The study of NG attachment firmness on sulphide mineral surfaces and its influence on the following adsorption activity of the collector tests were carried out under conditions of changed sequence of reagents feeding. Results of these researches which have been conducted within pH 7-9 region, where the copper sulphides greatest depression by NG is obtained, have shown, that with increase of the dye concentration in solution sulphides recovery in cell product, especially appreciable for chalcopyrite and chalcocite, raises. While 20 mg/l NG concentration, minerals depression is characterized by the following figures (in %): chalcopyrite - 80-85, chalcocite - 70-75, galena - 7-9.

Flotation researches of "mineral-xanthate-NG-cyanide" systems have shown, that copper minerals treatment with NG provides the same results of depression by cyanide as well as in case of copper sulphide flotation depression by single sodium cyanide but twice concentration.

The study of quantitative NG sorption laws and exchange sorption between collector and dye ions on

lead and copper sulphides surfaces was carried out using electrochemical spectrophotometric method. It has been established that NG adsorption increases in a row: $PbS \ll Cu_2S < CuFeS_2$. At mineral treatment with NG solution up to 100 mg/l concentration, complete rectification of isotherms isn't observed (Fig.2a). Maximum NG adsorption on chalcopyrite and chalcocite surfaces is observed in neutral and slightly alkaline solutions; this fact is quite in accordance with results of monomineral suspension flotation researches. It has been established that even insignificant sorbed NG amount evokes essential change of copper minerals surfaces condition, promoting to sharp collector adsorption reduction in a range of NG concentrations up to 20 mg/l. Further decrease of xanthate adsorption on minerals is observed under condition of increase of NG amount adsorbed by surface (Fig.2b). Reduction of BPX sorption on minerals depending on NG concentration to the following (in % from BPX sorption by clean surface): galena - 9,0-9,5, chalcopyrite - 60-63, chalcocite - 40-42.

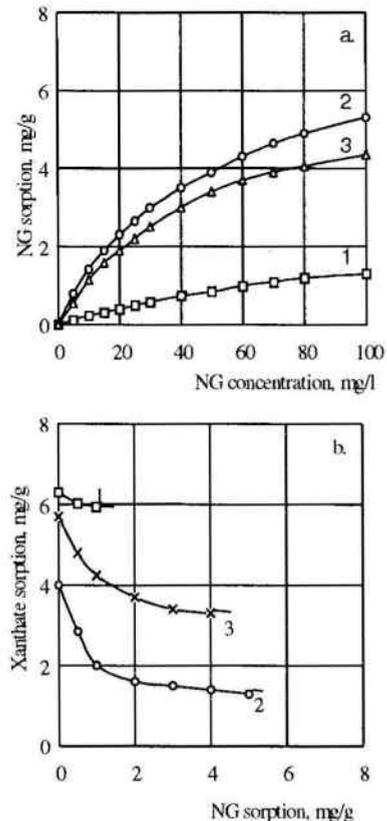


Figure 2. Isotherms of reagent adsorption on galena (1), chalcopyrite (2), chalcocite (3) at pH 8: a) NG concentration influence on its sorption on minerals b) influence of previous treatment with NG on BPX sorption (BPX concentration is 30 mg/l).

The researches, which have been carried out on lead and copper sulphides, previously treated with BPX of various concentrations, have shown that NG displays desorbed properties in relation to collector sorbed on mineral surface, especially appreciable in relation to chalcopyrite and chalcocite. The xanthate replacement by NG from chalcopyrite surface almost in 7 times (and from chalcocite surface in 4,5 times) is higher than from galena surface.

As a result of electrochemical researches it has been established, that the cathode shift of chalcopyrite electrode potential reaching the greatest value ($\Delta\phi_{\text{NG}}^{\text{CuFeS}_2} = -25$ mV) in slightly alkaline media (pH=7,5-9) is observed under NG introduction into "mineral-water" system; the value of galena electrode potential thus remains practically constant ($\Delta\phi_{\text{NG}}^{\text{PbS}} = -0,5-1,5$ mV). The observable change of chalcopyrite electrode potential in cathode area reaching maximum significance's within the first five minutes after NG feeding, is irreversible and allows to consider the reagent as a donor of electrons while its adsorption on copper sulphides, that is as a nucleophilic agent. The skip value of the chalcopyrite electrode potential ($\Delta\phi_{\text{NG}}^{\text{CuFeS}_2} = 20-25$ mV) testifies of chemisorbed interaction without covalent bonds formation.

For estimation of mineral surface wettability change the researches on determination of air bubble detaching force from mineral electrode treated with NG were carried out by attachment indemnification with elevating force of a float with bubble. All the researches on mineral wettability studies were carried out in a borate buffer solution (pH=9,18). Wettability change of researched mineral surfaces, depending on collector concentration, was determined first. The least surface wettability was observed at 150 mg/l collector concentration for chalcopyrite and since 50 mg/l for galena (Fig.3, curves 1). The values of stationary electrode potentials of researched minerals thus are shifted in negative area, what confirms xanthate sorption (Fig.3, curves 2).

Significant reduction of air bubble detaching force value from surfaces of chalcopyrite electrode was observed at various NG concentrations dosing in "sulphide mineral - collector" system (Fig.3, curves 3). For the galena electrode in the researched dye concentrations range (0-20 mg/l) essential changes of detaching force values in comparison with these ones without NG wasn't observed at xanthate 50 mg/l concentration. The restrictions in NG solutions concentrations (<20 mg/l) were carried out by visual

observation difficulties of processes of air bubble placing and detaching on mineral electrode surface in consequence of deep black-blue colour of dye solutions having concentrations more than 20 mg/l.

The received results have confirmed our assumption concerning NG adsorption on surfaces of copper sulphides accompanying with formation of difficulty-soluble hydrophilic compounds.

Products composition researches devoted to sorption interaction between NG and chalcopyrite and galena surfaces were carried out using FT-IR spectroscopy method. The received FT-IR spectra of NG surface compounds on chalcopyrite are reproduced well in all the range of pH values conforming to conditions of reagent intensive adsorption on copper minerals without and after treatment them with xanthate (Yushina and Abramov, 1996).

The appearance on the spectrum of chalcopyrite treated with NG an intensive 470 cm^{-1} absorption bend conforms to metal-nitrogen valence oscillations frequency; absorption bend shifting conforms to valence oscillations of C-N- and C=N-groups and SO_2 - groups in more low-frequency spectrum area on $40-85\text{ cm}^{-1}$, and pendulum and deformation oscillation of -NH- groups in more high-frequency area on $50-130\text{ cm}^{-1}$ testify to a metal-nitrogen coordination bond. The presence of several characteristic absorption bends corresponding -N-H-group oscillations indicates existence of a number of these groups' conditions differing by interaction (hydrogen bonds) and orientation. The absent of the characteristic for dixanthogen (1265 cm^{-1}) bend on the spectrum of chalcopyrite treated sequentially with BPX and NG testifies about dixanthogen desorption. The appearance of the -OH groups valence oscillations bend (3472 cm^{-1}) indicates the presence of coordinated-bound water on mineral surface (Nakamoto, 1986).

The electronic spectra analysis of combined NG solutions conforming lead, copper and iron soluble salts and BPX has shown absence of chemical interaction in systems "NG - lead nitrate" and "NG - BPX". At Fe(III) salts dosing into NG solutions instant change of color from blue-black to gray-yellow occurs, the solution becomes colloidal and black amorphous precipitate formation is observed. The filtrate spectrum points to NG absence in the solution; i.e. NG interactions with Fe (III) cations with formation of highly hydrated multinuclear NG-aquacomplexes of iron. The X-ray researches of precipitate has confirmed this assumption.

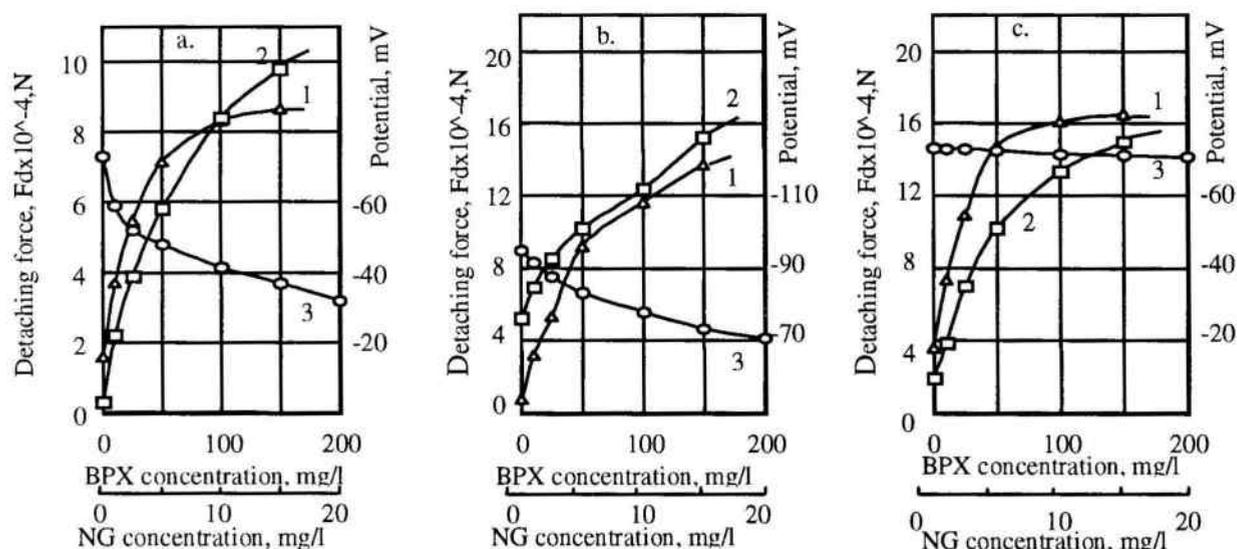


Figure 3. Influence of xanthate (1) and nigrosine (3) concentrations on change of air bubble detaching force from chalcopyrite (a), chalcosine (b), galena (c) surfaces and their electrode potentials (2). -at 50 mg/l xanthate concentration.

At mixing NG solutions and copper sulfate the deepening of solution color is observed, and significant bathochromic shift of NG characteristic maximum $\lambda^{max} = 580$ nm on 15-40 nm, hyperchromatic shift to the side of optical density increasing on 10-20 % and absorption bend geometric area increasing in comparison with NG spectra of similar concentrations are observed on the spectrum depending on components concentrations ratio. Proceeding from the complexing theory of organic heterocyclic compounds with metals, it is possible to make a conclusion about the chelate copper-NG complex formation at the expense of covalent-coordination binding of a copper cation with nitrogen and oxygen atoms of two NG molecules with stable six-members cycles formation.

DISCUSSION

Analysing the researches results of FT-IR, electronic and X-rays spectroscopy, it is possible to make a conclusion that NG in water solutions interacts as with a clean chalcopyrite surface as with the mineral previously treated with collector. In this case chemisorbed NG layer formation coordinated by cations of mineral surface and physical co-adsorbed NG molecules ensuring sufficient surface hydrophilic as a whole by coordinate-bound water with conforming CNG not participating in coordination is observe. In the case of consecutive chalcopyrite surface treatment with the

collector and NG, the last one desorbs dixanthogen from the sorption layer changing the collector sorption forms ratio; and also interacting with acid Lewis's sorption centres of mineral surface free from the collector (a NG ion may be coordinated simultaneously at least by two metal cations) "blocks" the collector action increasing total surface hydrophilicity. The flat structure and structural complementation of dye molecules also provides physical co-adsorption at the expense of hydrogen bonds and weak intermolecular interactions of NG molecules as free as in the form of volumetric complexes with metals from the solution (back-directed layer) what also promotes surface hydration increase and mineral depression (Yushina and Abramov, 1996).

On the basis of the received results of regularities and azine group reagents action researches with lead and copper sulphides selective flotation, the reagent regime of their selection using NG was developed and confirmed under laboratory conditions at industrial lead-copper concentrates. The results of laboratory researches at industrial concentrates have shown that the increase of collective lead-copper concentrates selection process indexes with complex polymetal ores processing can be achieved by selective flotation reagent regime perfection based on NG using as a copper sulphides additional depressor.

Advantages of the developed regime are preservation of basic, accepted at plant selection technology of collective lead-copper concentrates; an opportunity of NG feeding to the concentrate preparation cycle; the

small NG consumption, what allows to use the developed regime at the plant with insignificant capital expenses. Thus it is necessary to take into account, that the developed regime use allows to reduce dissolved copper, gold and silver losses with copper thickener overflows sharply (Table 1).

CONCLUSIONS

1. It has been established that as an additional depressor of primary and secondary copper sulphides with lead-copper concentrates cyanide selection it is necessary to use reagents of the azine dyes group. Azine compounds interact with copper sulphides surface on the coordination mechanism. NG doesn't adsorb on galena and doesn't change its surface properties.

Table 1: Ion composition of pulp liquid phase in the scavenging flotation operation.

Regime	Grade, mg/l				
	CN ⁻ _{fr}	CNS ⁻	Au	Ag	Cu
With NaCN use	90	80-120	0,2-0,6	6-10	210-250
With NG and NaCN use	10-20	30-40	0,03	0,8-1	50-70

2. The following processes passing cause azine compounds depression action:

- NG chemisorption on copper sulphide surfaces on coordination mechanism with difficulty-soluble hydrophilic compounds formation;

- partial dixanthogen desorption, causing collector sorption forms ratio change and mineral surface hydrophobic reduction.

3. At NG presence the copper cations leaching processes by cyanide are slowed down and "copper-cyanide" optimal ratio in flotation pulp liquid phase is supported.

4. The developed regime of lead-copper concentrations separation using NG has been tested under pilot-scale conditions at plant. The tests results have shown an opportunity of metals recoveries increase in the same concentrates by 1,5% with copper concentrate quality improvement by 0,5-0,7% and high toxic sodium cyanide by 50-70 %, and also will allow to reduce dissolved metals losses with copper thickener overflow, to raise ecological cleanliness of processes and improve ecological conditions in the plant action area.

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