Mechanism of selective operation of 1-phenyl-2,3-dimethyl-4-aminopyrazolone-5 in the process of flotation separation of sphalerite and pyrite

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There was carried out the research of mechanism of operation of new reagent AMD (АМД) (1-phenyl-2,3-dimethyl-4-dimethylaminopyrazolone-5), which is intended for flotation separation of sphalerite and pyrite during the flotation of auriferous copper-zinc pyrite-containing ores. There are established the reasons of reagent AMD selectivity concerning sphalerite and pyrite in alkaline medium:
 – capability of this compound for formation of stable hydrophobic complex compound with zinc on the sphalerite surface;
 – oxidation of AMD by ferric iron ions on the pyrite surface with formation of hydrophilic oxidation products.
For the purpose of identification of compound, which was formed during the flotation on the sphalerite surface, there was synthesized the complex compound of AMD with zinc, which formation rate is increased in the presence of thiocyanate-ions. Identification was carried out, using the UV- and IR-Fourier spectroscopy. It is shown that pyrite surface can catalyze the oxidation of AMD by ferric iron ions with formation of hydrophilic oxidation product in alkaline medium and removal of hydrophilic oxidized films from the surface of pyrite particles in acid medium.

Key words: selective flotation, sulfides, flotation reagents, pyrite, sphalerite, copper-zinc sulfide ores, collecting agent.

Separation of pyrite from other sulfide minerals is one of the most important tasks in the process of concentration of copper-zinc ores. High-selective collecting agents and modifiers are required for the solution of this task. Butyl potassium xanthate is a powerful but non-selective reagent, which is the main collector during the flotation of pyrite copper-zinc ores at Russian concentration plants. Separation of sphalerite from iron minerals is usually carried out in strongly alkaline lime medium. Copper (II) sulfate is introduced into pulp before the zinc flotation. According to this, copper (II) sulfate activates sphalerite, but at the same time, reacts with xanthate, decreasing the concentration of collector in pulp and increasing its wastage [1].

It is also known, that efficient collectors of sphalerite are sparingly soluble xanthates of higher alcohols [2], and reagent МКОР (МКОП), obtained on the basis of mother liquor of xanthate production, taken with xanthate and aeroflot [3, 4]. The reagent Z-200 or mercaptobenzothiazole are applied at foreign plants during the flotation of sphalerite, activated by copper cations.

Possibility of selective separation of sphalerite and pyrite in the presence of new flotation reagent AMD (АМД) and complexing regulators has been earlier researched [5, 6]. Reagent AMD is a pyrazolone-5 derivative. It is used as an analytic reagent in color chemistry, as well as a component of medical products, well-known as aminophenazone (amidozone, amidopyrine, pyramidon, pyrazon etc.) [7, 8].

This article researches the mechanism of functioning of new reagent AMD during the separation of sphalerite from pyrite in zinc flotation cycle.

Objects and methods of researches

The following substances were applied in the researches:
— freshly manufactured water solutions of white crystalline 1-phenyl-2,3-dimethyl-4-dimethylaminopyrazolone-5 (reagent AMD);
— $C_{13}H_{17}N_3O$ (molar weight is 231);
— ammonium thiocyanate NH_4SCN;
— iron chloride $FeCl_3$.
AMD has the following structural formula:
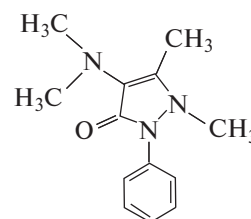
For the purpose of identification of compound, formed during the flotation on the sphalerite surface, there was carried out the synthesis of compound of AMD with zinc by analogy with the methodology, presented in the reference [9]. Carrying out of this synthesis was at room temperature in water solution in alkaline medium, containing $ZnCl_2$, AMD and intensifier of complexing of ammonium thiocyanate with molar ratio equal to 1:2:2. With the help of UV- and IR-spectrophotometry, the released sediment was researched on analytic scanning electron microscope LEO 1420VP, equipped with X-ray energy dispersive microanalyser INCA 350.

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Material for researches included monomineral fractions of pyrite and sphalerite (deposits of South Urals) with the coarseness of −0.08+0.045 mm. The value of sorption on minerals was defined by the residue concentration of reagent AMD (5–60 mg/l) in water filtrate of mineral suspension with the ratio of S:L = 1:10 after 5 minutes of mixing, filtration and centrifugation of filtrate. For the purpose of identification of surface-fixed compound, the mineral powder after the drying process was mixed with organic solvent, which was subsequently researched with the help of spectrophotometry. Optical density of solutions was measured on spectrophotometer UV-1700 Shimadzu in the area of adsorption maximum of 230–264 and 300–600 nm, characteristic for AMD and products for its interconnection with metals. IR-Fourier spectrums of complexes with AMD and its compounds with zinc in the range of 4000–400 cm^{-1} were obtained on spectrophotometer "Ifralyum FT-8" ("Ифралюм FT-8"). Morphology and elementary composition of solid residues and reagent films on minerals' sections was researched on laser scanning microscope KEYNCE with VK-9700 and analytic scanning electron microscope LEO 1420VP.

Discussion of results

Flotation researches on monomineral fractions of minerals in acid and neutral medium established the aggregative activity of AMD, concerning both sphalerite and pyrite. Selective properties of this reagent occur in alkaline medium. With the value of pH = 9.0–10.5, pyrite flotability in the presence of AMD is decreased to the level of natural flotability, while the significant decreasing of flotability of sphalerite is observed only with the value of pH > 10.5. Difference in extraction of pyrite and sphalerite in this area of pH reaches 50% with AMD consumption of 500 g/t (Fig. 1).

Together with the AMD consumption of 100 g/t and introduction of reducing agent (NH$_4$SCN), extraction of sphalerite is increased to 80–90%, and the difference in extraction reaches 75–85%.

Results of research of mechanism of interconnection of AMD and sphalerite

Photometric method established the adsorption of reagent AMD ($C_{initial}$ = 20 mg/l) on sphalerite. Sorption of reagent AMD without ammonium thiocyanate was decreased from 0.04 to 0.006 mg/g with increasing of pH value from 3.5 to 10.5. At the same time, sorption of reagent AMD in the presence of ammonium thiocyanate was decreased from 0.054 to 0.008 mg/g respectively.

Obviously, established adsorption of reagent on sphalerite is the consequence of formation of stable hydrophobic complex compound of AMD with zinc on mineral surface. Capability of derivatives of pyrazolone-5 for formation of com-
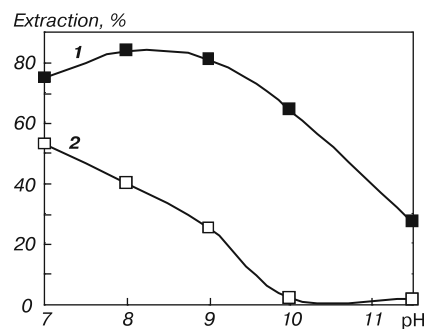

Fig. 1. Influence of pulp alkalinity on flotability of sphalerite (*1*) and pyrite (*2*) in the presence of AMD (500 g/t)

plex compounds is substantiated by the presence of donor atoms of N and O in molecule. The composition of complexes includes two ligands: ambidentate thiocyanate-ion (SCN$^-$) and bidentate AMD. Stable complex Zn[C$_{13}$H$_{17}$ON$_3$]$_2$(SCN)$_2$ is formed in neutral medium in the presence of thiocyanate-ions. Another composition complex [C$_{13}$H$_{17}$ON$_3$·H]$_2$[Zn(SCN)$_4$] is formed by AMD and zinc in acid medium [9, 10]. There are not found any data about interconnection of AMD with zinc in alkaline medium. However, results of flotation and sorption experiments, which were carried out on sphalerite with pH = 7.5–10.5, correspond intermediately about the possibility of formation of hydrophobic compound with zinc on sphalerite in alkaline medium.

Obtaining and research of complex compound of AMD with zinc ions

Interconnection is observed even in low concentration water solutions in the range of pH = 6–10 in the alkaline medium at room temperature in water solution, containing ZnCl$_2$, AMD and intensifier of complexing of ammonium thiocyanate with molar ratio of 1:2:2. Formation of fine-crystalline sediment accompanies the interconnection. The ratio of reaction is decreased during the increasing of alkalinity, as well as in the absence of NH$_4$SCN. Obtained solid fine-crystalline substance, hardly soluble in water, is dissolved in chloroform and carbon tetrachloride.

According to the results of analytic scanning electron microscope analysis, the sediment can belong to organic compound with zinc, because the peaks of Zn, S, O and C are present at the spectrums of sediment particles area (Fig. 2).
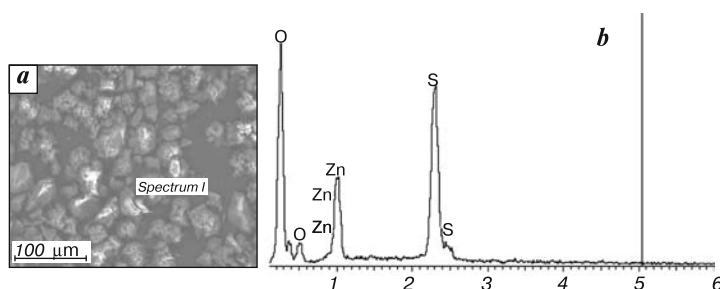

Fig. 2. Synthesized complex compound of AMD with zinc and ammonium thiocyanate (1:2:2):
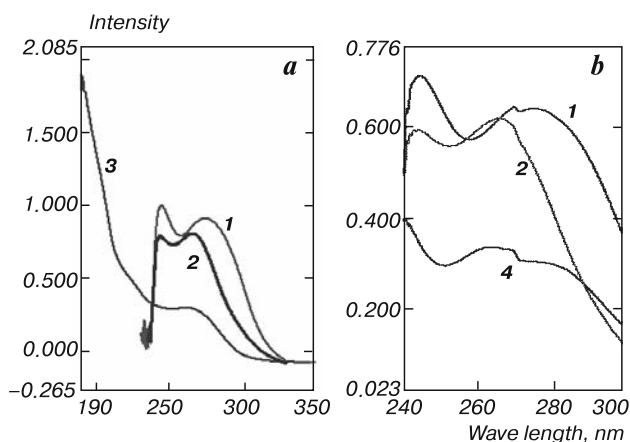*a* — microphotography with mark; *b* — X-ray spectrum of compound of AMD with zinc

Fig. 3. UV-spectrums of ADM (*1*) and complex compound of AMD with zinc (*2*, *3*) in chloroform (*1*, *2*); in water (*3*); substance, washed from the surface of sphalerite by chloroform (*4*)

IR-Fourier spectrums of AMD and its compounds with zinc were photographed in chloroform in the area of 400–4,000 cm^{-1}. Particles of carbonyl CO-group and exocyclic amines are the most important for AMD. The following phenomena are observed in IR-Fourier spectrums of obtained complex:

– decreasing of frequency of stretch vibrations of CO-group by 30 cm^{-1} relatively to the spectrum of initial AMD (1,655 and 1,984 cm^{-1} respectively);

– less signified shift of frequency of stretch vibrations of CN-group (1,309 and 1,300 cm^{-1}; 1,125 and 1,133 cm^{-1}).

Formation of complex compound can be confirmed by the comparative data of compound spectrum, where SCN-group is coordinated with zinc through nitrogen atom, and AMD is a bidentate ligand, forming the five-term chelate ring. Lines assignment was carried out taking into account the reference [10].

In UV area, the maximums in absorption spectrum in chloroform, which are typical for initial AMD with the wave length of 277 and 245 nm, are offset for the left near the complex to the area of lower values and appeared with the wave length of 266 and 243 nm. In water, the adsorption maximum, typical for AMD with the wave length of 264 nm, appeared in complex with the wave length of 259 nm (Fig. 3, *a*).

Thereby, it is substantiated that formation of compound of AMD with zinc is also possible in alkaline medium in the conditions, close to flotation.

Identification of synthesized complex compound and compound, strongly allocated on the surface of sphalerite after mixing of mineral with AMD solution, was carried out by the comparison of their adsorption spectrums in ethanol or chloroform. UV spectrums of both compounds in ethanol practically coincide with the spectrum of AMD itself. Spectrums in chloroform turn out to be more informative. Characteristic frequencies in absorption spectrums of compound, washed from the surface, are practically the same. In both cases, these frequencies are situated to the left of maximum, typical for the spectrum of AMD in chloroform with 277 and 252 nm (Fig. 3, *b*).
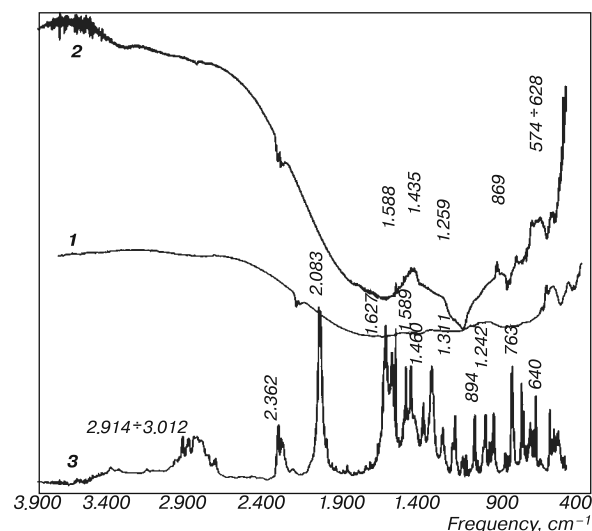

Fig. 4. IR-Fourier spectrums of sphalerite:
1 – before the processing; *2* – after the processing by AMD solution (30 mg/l, pH = 10); *3* – compound of AMD with zinc in chloroform

The lines of 1,259 and 869 cm^{-1} frequency appeared on IR-Fourier spectrum of sphalerite after agitation with AMD. These lines correspond to stretching vibrations of interconnections of C−N and C−S respectively, in the content of complex of AMD with thiocyanate and zinc. The line of 1,588 cm^{-1} frequency can be referred to the frequency of stretching vibrations of CO-group. The range of differences, which were found during the comparison of this spectrum with the spectrum of complex compound of AMD with zinc in chloroform, is obviously explained by different state of matter in solution and on the sphalerite surface. Spectrums of sphalerite after mixing with water solution of AMD (30 mg/l) with pH = 10 are significantly different from the spectrums of mineral after mixing in water (Fig. 4), which can also be an evidence of sorption of organic substance on its surface.

Experimental data are the evidence about the fact that the strongly allocated substance, which spectrums are similar to the spectrums of synthesized complex of AMD with zinc, is left on sphalerite after the contact with reagent AMD.

Results of research of mechanism of interconnection of AMD with pyrite

Low flotability of pyrite (hydrophilic nature of particles) by reagent AMD in alkaline medium can be the consequence of absence of sorption of collector on its surface or the consequence of formation on the surface of hydrophilic compounds.

During the research of sorption activity of AMD on pyrite after the contact of reagent with mineral in the interval of pH = 3.5−10.5 (as well as on the sphalerite), there is defined the decreasing of concentration of reagent in water phase of suspension (Fig. 5, *a*). Residue concentration of AMD in solution ($C_{AMD}^{initial}$ = 20 mg/l) after 5 minutes of mixing with pyrite with pH = 6 and pH = 10.5 was 13.5 and 14.7 mg/l, respectively. Such a non-significant difference in the value of reagent adsorption could not lead to
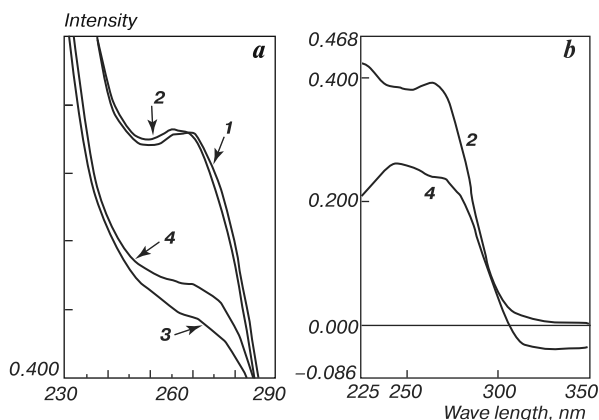
Fig. 5. UV-spectrums:
1 − solution of AMD with pH = 6; *2* − solution of AMD with pH = 10; *3* − filtrate of water phase of suspension after mixing of AMD with FeS$_2$ with pH = 6; *4* − filtrate of water phase of suspension after mixing of AMD with pH = 10;
a − C_{AMD} = CNH_4SCN = 20 mg/l; S:L − 1:10; *b* − C_{AMD} = 10 mg/l; S:L = 1:5

such a notable difference in pyrite flotability (~60%) with pH = 6 and 10.5 (Fig. 1).

Besides, the maximums, typical for AMD, were not revealed in the spectrum of absorption of substance, removed by chloroform from the surface of pyrite after its processing by AMD and water washing.

There are given the data about interconnection of AMD with Fe^{3+} in acid medium. In contrast to the zinc ions, during the influence of ferric iron, AMD is instantly oxidized with formation of the range of intermediate blue-violet-colored products. The maize-yellow substance − dioxyamidopyrine − is formed with further oxidation of these products. Dioxyamidopyrine is acyclic compound, which has the hydrophilic oxygen groups near the outside atoms of carbon:
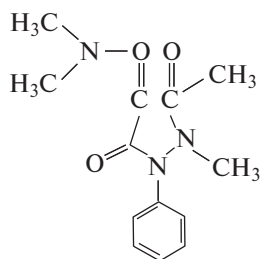
At the same time, oxidation process in acid medium is different from this process in alkaline medium [7, 8, 11, 12].

Increased reactive capacity of pyrite causes its intensive oxidation in processes of grinding and flotation with formation of areas of surface of mineral particles, containing ferric iron [11]. In connection with this, it is expected, that being rather active reducer, the reagent AMD is oxidized by Fe^{3+} ions during the interconnection with pyrite.

It has been experimentally found that after intensive mixing of AMD solution (10 mg/l) with mineral powder of pyrite (S:L = 1:5, pH = 10) during 5 minutes, the typical maximums with the wave length of 225 and 264 nm disappear in spectrums of water suspension filtrate. However, the maximum in the area of the wave length of 230−240 nm appears on the spectrum instead of these typical maximums (Fig. 5, *b*). After agitation of pyrite with AMD solutions in the conditions of sorption experiments, its absorption spectrum was also changed (Fig. 5, *a*).

AMD was oxidized by FeCl$_3$ solutions in acid and alkaline medium for the purpose of identification of substances, formed in water. Analysis of spectrums in UV-area has shown, that oxidation leads to the gradual decreasing of optic density of solution with the wave length of 264 nm, disappearance of maximum with the wave length of 225 nm and its appearance with the wave length of 242 nm (Fig. 6). In acid medium, solution immediately obtains the stable blue color, characteristic for intermediate product of oxidation of AMD [7]. The maximum appears with the wave length of 320 nm and the maximum of AMD appears with the wave length of 568 nm in visual area of solution spectrum (Fig. 7).

The process of oxidation of AMD in alkaline medium is slower. The maximums with the wave length of 320 and 568 nm are also revealed in the spectrum of solution (Fig. 6). After that, the color of solution is quickly changed to maize yellow, which is accompanied with appearance of maximum in the area of 230−240 nm and disappearance of maximums with 320 and 568 nm (Fig. 7), which is in good agreement with the data, presented in the reference [12].

It is obvious that the compound, characterized by maximum in the adsorption spectrum with the wave length of 230 nm, is the final product of AMD oxidation − dioxyamidopyrine.

In a parallel way, there was carried out the reaction with iodine (oxidizer, which does not contain iron). It is substantiated, that solutions of AMD with pH = 5 and 10 during the oxidation by iodine are analogue − colors are the same, and spectrums of solutions are identified. These data confirm that during the interconnection with pyrite, there takes place the
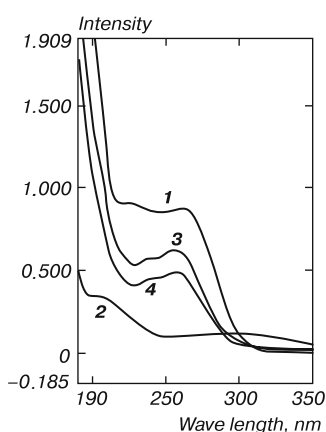

Fig. 6. UV-spectrums:
1 − solution of AMD (0.003 mole/l); *2* − FeCl$_3$ (0.003 mole/l); *3* − solution of AMD with FeCl$_3$ in equimolar quantities with pH = 10; *4* − solution of AMD with FeCl$_3$ in equimolar quantities with pH = 5

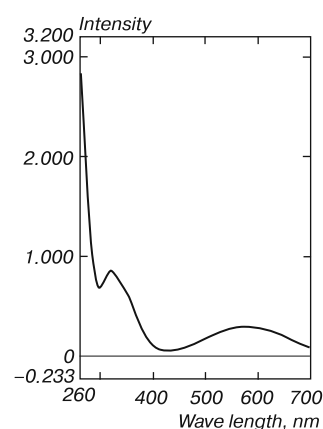**Fig. 7.** Spectrum of adsorption of AMD solution in visible area after formation of intermediate oxidation product $C_{AMD}^{initial}$ = 100 mg/l, pH = 6
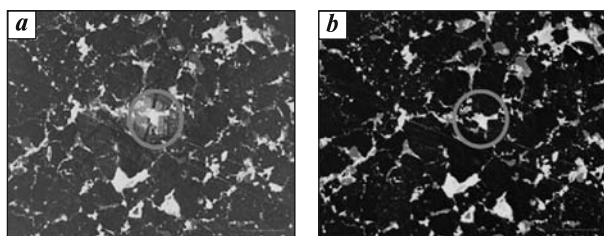
Fig. 8. Section of copper-zinc ore of Ural region:
a − pyrite is covered by the iron oxides' film. Mark is 100 μm; *b* − the same area of the section after processing of AMD (pH = 6) without the iron oxides' film. Mark is 100 μm

process of oxidation, not reaction of complex formation of AMD with iron.

By all appearances, results of flotation of pyrite in acid medium (Fig. 1), corresponding about its hydrophoby, are the consequence of intensive interconnection of AMD from the surface of pyrite and removement of oxidized hydrophilic films from the surface. This is corresponded by the data of comparative researches of the surface of ore section of pyrite, obtained with the help of laser microscopy before and after the contact of section surface with solution of AMD in acid medium (Fig. 8). Oxidized film was saved during the processing of section by AMD solution in alkaline medium.

As it is known, possibility of formation of complex compound of AMD with iron is not confirmed by literature data. Authors could not also obtain the complex compound, in spite of the change of the solution color with interconnection of AMD and iron. Thus, on the basis of experimental and literature data, there can be made a conclusion about the fact that decreasing of AMD concentration in water phase of pyrite suspension was not caused by adsorption of AMD on its surface.

Thus, it is obvious that surface of pyrite can catalyze the oxidation of collector of AMD by ions of ferric iron with formation of hydrophilic product of oxidation (dioxyamidopyrine) in alkaline medium and removal of hydrophilic oxide film from the surface of pyrite particles in acid medium.

Nowadays, there is carried out the research and is prepared the publication about interconnection of reagent AMD with copper cations, copper sulfides and with the surface of sphalerite, activated by copper cations.

Conclusions

The reason of reagent AMD selectivity, concerning sphalerite and pyrite in alkaline medium, is the availability of this compound to formation of stable hydrophobic complex compound with zinc on the sphalerite surface and oxidation of AMD by ferric iron ions on the pyrite surface with formation of hydrophilic oxidation products.

References

1. Bogdanov O. S., Maksimov I. I., Podnek A. K., Yanis N. A. *Teoriya i tekhnologiya flotatsii rud* (Theory and technology of ore flotation). Moscow : Nedra, 1980. 363 p.

2. Dudenkov S. V., Shubov L. Ya. et al. *Osnovy teorii i praktika primeneniya flotatsionnykh reagentov* (Basis of theory and application practice of flotation reagents). Moscow : Nedra, 1969. 273 p.

3. Ivanova T. A., Zaslavskaya N. N., Tyurnikova V. I. Poluchenie, svoystva i primenenie novogo flotatsionnogo reagenta MKOP (Obtaining, properties and application of new flotation reagent MKOP). *Metallurgicheskie tekhnologii pri pererabotke rud i kontsentratov tsvetnykh metallov : sbornik nauchnykh trudov Gintsvetmet* (Metallurgical technologies in the processing of ores and concentrates of non-ferrous metals : collection of scientific proceedings Gintsvetmet). Moscow, 1993. pp. 119−123.

4. V. I. Tyurnikova, T. A. Ivanova, V. M. Bogomolov et al. *Sposob obogashcheniya polimetallicheskikh rud* (Method of concentration of polymetallic ores). Certificate of Authority USSR, No. 1457232. Accepted from: August 28, 1987.

5. Ivanova T. A., Chanturiya E. L., Zimbovskiy I. G. Issledovanie vozmozhnosti povysheniya effektivnosti izvlecheniya tsennykh komponentov iz medno-tsinkovykh rud s ispolzovaniem novogo reagenta (Research of the possibility of increasing of efficiency of extraction of valuable components from copper-zinc ores, using new reagent). *Materialy Mezhdunarodnogo soveshchaniya "Plaksinskie chteniya − 2010". Kazan, 13−18 sentyabrya 2010* (Materials of International meeting "Plaksin`s readings − 2010". Kazan, September 13−18, 2010). Moscow, 2010. pp. 55−64.

6. Chanturiya E. L., Ivanova T. A., Zimbovskiy I. G. Vliyanie kompleksoobrazovatelya AMD na flotatsionnoe razdelenie sulfidov medo-tsinkovykh rud (Influence of AMD complexing compound on the flotation separation of copper-zinc ores` sulfides). *Materialy Mezhdunarodnogo soveshchaniya "Plaksinskie chteniya − 2011". Verkhnyaya Pyshma, 19−24 sentyabrya 2011* (Materials of International meeting "Plaksin`s readings − 2011". Verkhnyaya Pyshma, September 19−24, 2011). Ekaterinburg : "Fort Dialog-Iset", 2011. p. 170.

7. Busev A. I., Akimov V. K., Gusev S. I. *Uspekhi khimii − Russian Chemical Reviews.* 1965. Vol. XXXIV, Iss. 3. pp. 565−583.

8. Kramarenko V. F. *Toksikologicheskaya khimiya* (Forensic chemistry). Kiev : Vysshaya shkola, 1989. 225 p.

9. Mikhaylenko Yu. A., Katkova O. V. *Polzunovskiy vestnik − Polzunov Bulletin.* 2008. No. 3. pp. 19−21.

10. Cherkasova T. G., Katkova O. V. *Khimiya i khimicheskaya tekhnologiya − Chemistry and chemical technology.* 2005. Vol. 48, Iss. 1. pp. 76−77.

11. Chanturiya V. A., Fedorov A. A., Matveeva T. N. *Tsvetnye Metally − Non-ferrous metals.* 2000. No. 8. pp. 9−12.

12. Lodzinska A, Golinska F., Rozploch F., Jesmanowicz A. Polish Journal of Chemistry. 1986. Vol. 60, No. 4/6. p. 389.

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