UDC 622.765:622.793

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ASSESSMENT OF ECOLOGICAL SAFETY OF FLOTATION AGENTS IN HEMATITE ORE PROCESSING

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RIVS accomplishes a whole range of work aimed at improvement of iron ore dressing technology and equipment. The scope of work includes flotation of magnetite concentrates toward enhancement of their quality, including production of super concentrates, and development of efficient processing technology for ferruginous quartzites.

Cationic amine-bearing surface active substances (CABS) are widely used in hematite ore dressing. It is required to control CABS residual content as these substances are highly toxic and hazardous for the environment. The measurement of concentrations of flotation agents used spectrophotometric analysis (a simple, inexpensive but low selective method) and more selective technique of gas-liquid partition chromatography based on the certified procedures. It is recommended to carry out the production ecology monitoring using selective methods for estimating concentrations of flotation agents, including calculation of standards for allowable wastewater discharges in surface bodies or onto local terrain. The authors show that flotation-opposite process of CABS desorption can take place in tailings pulp slurry, which results in higher concentration of CABS in recirculated water. However, CABS undergo chemical transformation with time, and their concentration in recirculated water and in water phase in tailings ponds reduces. Decomposition of CABS runs more intensive under higher temperature.

RIVS Science and Production Association carries out a wide range of work aimed at improvement of iron ore dressing technology and equipment. The scope of work embraces flotation of magnetite concentrates toward their quality refinement and production of superconcentrates, and development of efficient technology for oxidized ferruginous quartzite dressing.

Concentration of hematite ore uses cation amine-containing surface active agents (AC SAA). It is required to control the remaining content of highly toxic and ecologically hazardous AC SAA. Concentration of flotation agents was measured using the spectrophotometric method (simple, inexpensive but less selective) and the selective method of gas–liquid partition chromatography based on certified procedures. The industrial environmental monitoring advises to use the selective methods to estimate concentration of flotation agents, including calculation of effluents treated to standard quality. The article shows that desorption of AC SAA can run in pulp slurry, which results in higher concentration of AC SAA in the recycling water. However, in the course of time, AC SAA undergo chemical transformation and their content in the recycling water and liquid phase of tailings reduces. The process of AC SAA decomposition intensifies under higher temperature.

Key words: *hematite ore, flotation, amine-bearing surface active substances, flotation agents, spectrophotometric analysis, gas-liquid partition chromatography.*

The world iron ore production is substantial as compared with the other minerals. Some projects produce annually 120–150 Mt of ore (e.g., Hawsons Iron, Australia; Minas Rio, Brazil). The world metal market becomes currently more dynamic. Metallurgists place higher demands on the initial ore quality. The best preferable raw material is blast-furnace pellets with the content of 65–66% Fe_{total} and not higher than 4–4.5% SiO_2, while the direct reduction process requires 2–3% SiO_2 content. This pre-conditions introduction of after-treatment of magnetite concentrate by reverse cationic flotation. Flotation can be used as a finishing operation in the high-quality magnetite concentrate production and as the dominant full-scale technology of oxidized (hematite-bearing) ore processing.

RIVS has undertaken a range of works on improvement of iron ore processing technology and equipment. The scope of works involves flotation of magnetite concentrates in order to enhance their quality, including production of super concentrates, and development of an efficient processing technology for oxidized ferruginous quartzites.

The iron ore flotation technology uses reagents most of which belong in the category of surface active substances, which is dictated by the need to control surface phenomena in disperse systems. At the present time, the range of various purpose surfactants covers hundreds of names and their consumption makes hundreds of thousands of tons. Majority of the surfactants in use are synthetic composites having no natural analogues, which complicates estimation of the behavior in the ambient medium, the character of their composition

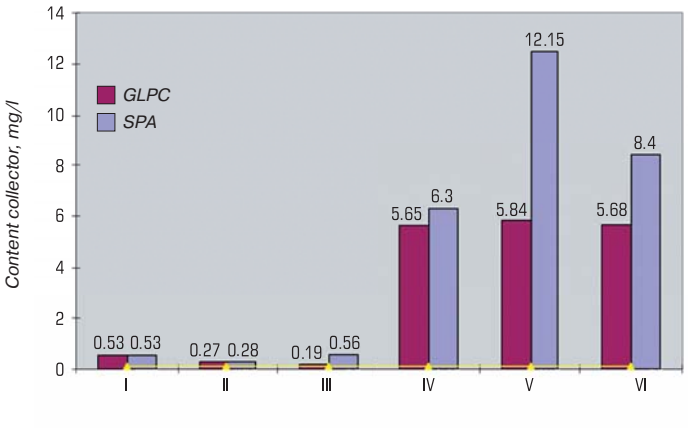

Fig. 1 The content of aminecontaining collectors in the aqueous phase of the pulp as a result of determining GLPC method and SPA method:
I, II, III — pulp iron concentrate after thickener, reagent 1, 2, 3 respectively; IV, V, VI — pulp tailings, reagent 1, 2, 3 respectively; MAC — the maximum allowable concentration collectors in water of water bodies of drinking and household water use 0,1 mg/l

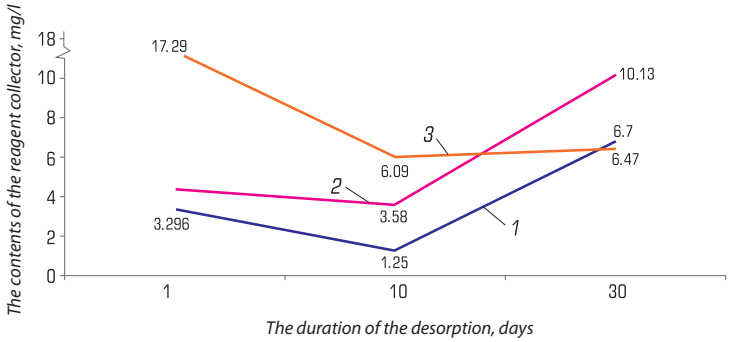

Fig. 2. The dependence of the content in the eluate collecting agents (notably by GLPC) on the duration of their desorption with flotation tailings tap water (with the change of eluent through 1, 10 and 30 days):
1, *2*, *3* — reagents 1, 2, 3 respectively

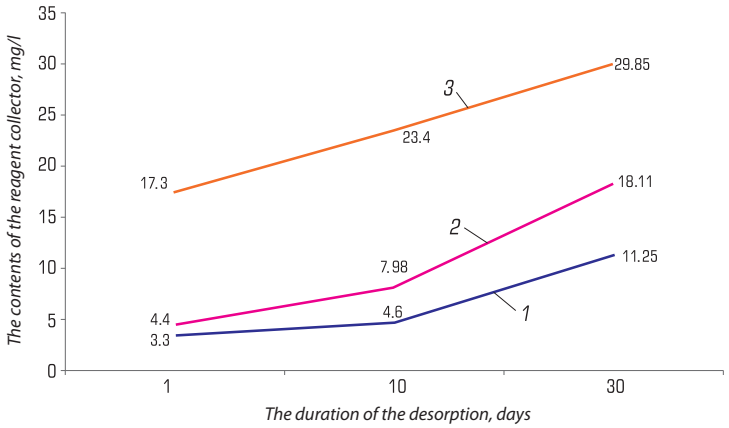

Fig. 3. The dependence of the total content in the eluate collecting agents (definitely method GLPC) from the length of their desorption from the flotation tailings tap water:
1, *2*, *3* — reagents 1, 2, 3 respectively

transformation and the scale of destruction. Wide application of surfactants inevitably results in their entering natural geosystems and, first of all, ground and surface water. Surfactants aggravate water quality and depress water self-clarification. As a consequence of wide application of different reagents in mineral flotation, the flotation tailings become multi-component organic–mineral combinations where the key role belongs to production-generated organic compounds [1].

Ecological standards to be abided by production raise the reagent regime requirements. Aside from higher efficiency, there are the requirements of maximum selectivity of mineral separation, minimum range and toxicity of reagents to be used, including toxicity for the environment. Flotation agents enter the environment with waste-tailings, both with solid and fluid phases. Water after a work cycle contains multicomponent admixtures ranging from solid fine disperse suspended matter to polyvalent metal ions and surfactants that exerted adverse effect on the environment and recycling water supply processes. Surfactants divide into agents that quickly decay in the environment and agents that do not decay and can accumulate in bodies up to unallowable concentrations. One of the negative effects of surfactants on the environment is the reduction of surface tension. Only a few surfactants are assumed as safe (alkyl polyglycosides) since their breakdown products are carbohydrates. However, when surfactants adsorb at the surface of earth/sand particles, the rate and degree of their decay drops many times. Since nearly all surfactants are capable of adsorption at particles of earth, sand and clay, the surfactants can, under normal conditions, release (desorb) heavy metal ions captured by the particles and thereby elevate the risk of entry of these substance in human body. Therefore, it is very important that production waste (pulp slurry of flotation tailings) that enter the environment (tailings ponds) have minimized content of surface active substances.

Mineral mining and processing waste are the most intensive source of a wide range of compounds most of which belong in the category of eco-toxicants.

In view of the aforesaid, this study aims at estimation of residual concentration of flotation agents-collectors in recirculated water, in fluid and solid phases of pulp slurry in hematite ore flotation tailings, as well as at the analysis of the effect exerted by temperature and time parameters on withstandability of these flotation agents.

In the capacity of collectors, the study involved cationic amine-bearing surfactants (CABS) since the requirement to control their residual composition is dictated by their high toxicity and hazard for the environment. The concentrations of flotation agents were measured using the spectrophotometric analysis (SPA) [2] (simple, inexpensive and low selective) and the selective gas-liquid partition chro-

matography (GLPC) based on the certified procedures [3, 4]. Consumption of CABS of various manufactures per 1 t of hematite ore was the same in all tests. Conventionally, CABS were denoted as 1, 2 and 3. These flotation agents were alkylamine acetates having similar compositions and structures.

The performed analysis showed different concentrations of CABS 1, 2 and 3 in water phase of pulp slurry of tailings and iron concentrate (**Fig. 1**). The water phase of iron concentrate after thickening contains smaller amount of CABS than the water phase of pulp slurry of tailings, which agrees with the data of the reverse cationic flotation.

The highest imprecision of estimating CABS concentrations was exhibited by SPA (Fig. 1). The SPA procedure [2] is meant for assessment of mass concentration of a reagent by the extraction-photometric method in the concentration range 0.25–1.25 mg/dm^3. For in-process measurements, this method is convenient, simple and informative. The ecological control requires more accurate selective methods and procedure, in particular, GLPC. Photocolorimetry and spectrophotometry yield errors and overestimated data, and are inselective. This should be taken into account in performing expert examination and in calculation of permissible wastewater discharge standards when processing plants operate in the mode with excess wastewater discharge from tailings ponds in natural water bodies.

Not less important is information on the capacity and degree of surfactant desorption from solid phase of pulp slurry in tailings ponds. The solid phase of pulp slurry of hematite ore processing tailings sorbs many surfactants, and if desorbed, these amines go to water phase of the tailings. The model laboratory experiments were carried out to analyze the process of desorption of three chosen flotation agents–collectors with eluent changed in 1, 10 and 30 days (**Figs. 2** and **3**). As follows from Figs. 2 and 3, the test flotation agents possess different ability to desorb from solid phase of tailings. The highest ability is shown by surfactant 3. Collector 1 is probably stronger bonded with the solid phase of pulp slurry and its elution rate is the lowest. Consequently, desorption of amine-bearing surfactants can take place in pulp slurry of tailings, which results in the increased concentration of the surfactants in the recirculated water.

For the purposes of preservation, aside from the data of the reagent safety charts, it is required to know withstandability of the reagent under various conditions. This information is also important for developing optimized reagent regimes and for economical use of expensive flotation agents. The laboratory testing show that the surfactants decompose in dilute solutions (**Figs. 4** and **5**), and the surfactant concentration drops almost 4 times within a month (observation period); the drop in the concentration in the first 10 days is smaller at 5 °C (Fig. 4) than at 20 °C (Fig. 5). The change of the surfactant content under varied temperature was observed

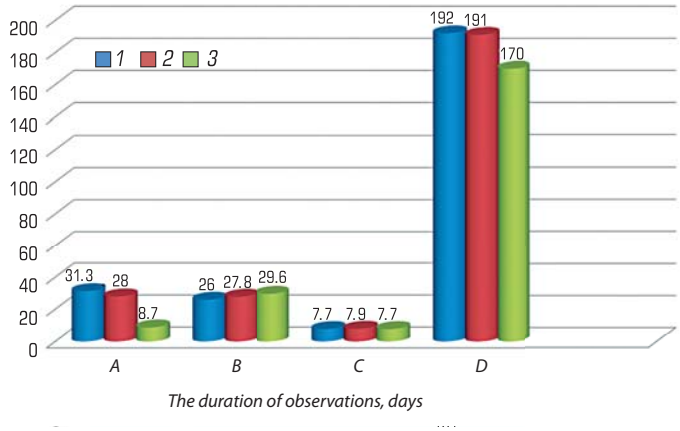

Fig. 4. Changes in the analyzed parameters in the circulating water in time when the temperature of the exposition 5 °C (*A*, *B* content (mg/l) of reagent 1, measured GLPC- and SPA-method, respectively; *C* — the pH; *D* — COD). The duration of the observation, days:
1 — 0 (initial data); *2* — 10; *3* — 30

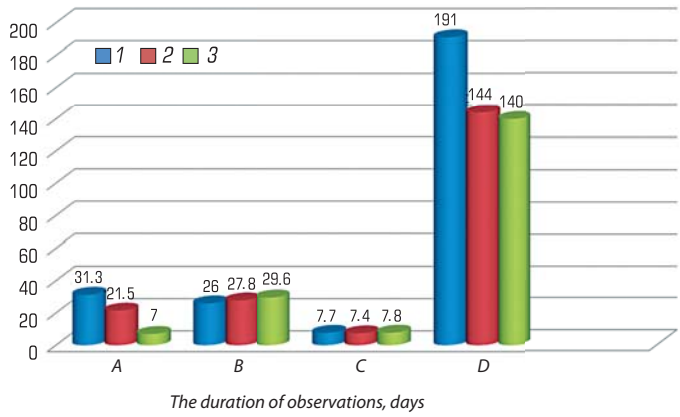

Fig. 5. Changes in the analyzed parameters in the circulating water in time when the temperature of the exposition 20 °C (*A*, *B* content (mg/l) of reagent 1, measured GLPC- and SPA-method, respectively; *C* — the pH; *D* — COD). The duration of the observation, days:
1 — 0 (initial data); *2* — 10; *3* — 30

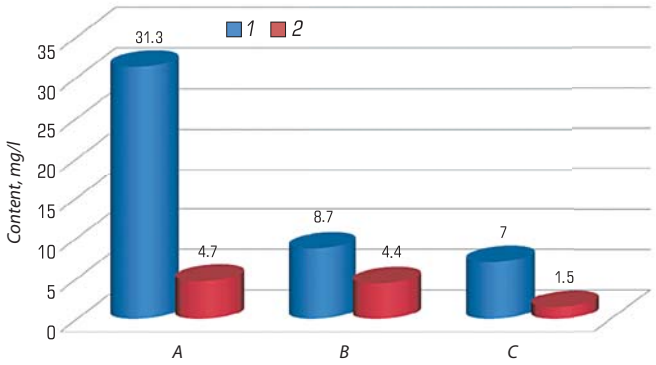

Fig. 6. The effect of temperature on the stability of reagent 1 in the circulating water (*1*) and the eluate (*2*) desorption from tailings tap water is definitely a method GLPC):
A — initial data; *B*, *C* — temperature 5 and 20 °C accordingly

both in the recirculated water (Figs. 4 and 5) and in the eluate after desorption from processing tailings (**Fig. 6**). With higher temperature, decomposition of the test surfactants intensifies.

With the non-selective SPA based on determination of amine group, it is nearly impossible to detect the change in the concentration of a surfactant or its chemical transformations in water phase (Figs. 4 and 5). The overestimated content of the surfactants with SPA can be explained by photometer-recorded complexes formed with the test surfactant and other amine groups, which are probably present in flotation water, the more so the commercial flotation agents are the mixtures of various compounds that often undergo appreciable transformation of the initial structure in aqueous environment of process media, and new compounds originate, which are not in the list of the test characteristics [5]. Therefore, the more precise estimation of CABS requires a more selective method of analysis.

The chemical transformations in the recirculated water were estimated based on the chemical oxygen demand index (COD) that decreased with time (Figs. 4 and 5).

Thus, the production ecology monitoring should use selective methods of estimation of flotation agent concentrations, including the calculation of standards for allowable wastewater discharge in surface water bodies and onto local terrain. Amine-bearing collectors undergo chemical transformations during flotation. The content of the amine-bearing collectors in the recirculated water and in the water phase in tailings ponds reduces with time. Decomposition of CABS intensifies under higher temperature.

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