Analysis of the Application of Reagent Combination in the Flotation of Non-sulfide Ore

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Abstract. A brief review of articles on the flotation of minerals using a combination of reagents is presented. It is noted that the main attention of the authors is aimed at studying the effect of the combination of collectors at the mineral-liquid interface. It was shown that one of the reagents or associates formed as a result of their joint action, possessing surface activity, can serve as a desorbed form of sorption and help reduce the induction time during the formation of a flotation complex.

1. Introduction

It has been proved by numerous investigations [1–7] that the use of combinations of reagents in flotation appears to be more promising as compared to individual reagents. Combinations of collecting reagents find application in flotation of sulfide and non-sulfide minerals. The applied combinations comprise different reagents including ionic and non-ionic, anionic and cationic collectors, and others. Three beneficial effects from the use of reagent mixtures are indicated: increased recovery, better adsorption of the main collector on the mineral surface and increased adsorption selectivity [1]. Thus, the studies were usually focused on the reagent action at the mineral-liquid interface, while insufficient attention was paid to the reagent action at the gas-liquid interface.

In [2], flotation of rhodochrosite using oleic acid and Dodecyl Benzene Sulfonate has been studied. Experiments have shown that the use of a combination of these collectors increases the performance of flotation as compared to the use of oleic acid: the commercial component recovery value was higher than 90% for flotation with a mixture of these reagents, and about 70% for flotation with oleic acid only. The authors believe that mixtures of these reagents are co-adsorbed on the mineral surface thereby contributing to enhancement of flotation properties.

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To increase the selectivity of carboxyl collectors, in [3] it has been proposed to use them in combination with amphiphilic compounds in which the molecule contains a long hydrocarbon radical and groups of a high electron density. The authors believe that the use of the main collector in combination with an additional reagent enables attaining an increased contribution of the hydrogen bond in the interaction with floated minerals as compared to the effect of using an individual carboxyl collector, which results in a greater difference in the energy of its fixation on the separated minerals, and hence to an increased separation selectivity. Owing to the interaction between the main reagent and the additional reagent (secondary reagent), the formation of associates was observed on the molecular surface that increased its hydrophobicity more strongly than the original carboxylic collector, which resulted in better flotation performance.
In [4], results have been shown obtained from experiments on flotation separation of scheelite-sulfide ores containing calciferous minerals: scheelite, calcite, apatite, fluorite. According to IR spectrometry and adsorption isotherm data, it has been found that in the scheelite's surface layer the formation of intermolecular associates bonded due to hydrogen bonding between sodium oleate and iso-dodecyl alcohol was observed, which contributed to the boundary layer of water getting thinner and the flotation process gaining efficiency. For calcite, higher iso-alcohols, on the contrary, decreased the probability of the oleate fixation in the molecular form. In the presence of iso-alcohols, selective aggregation of scheelite monomineral fraction particles was observed resulting in a recovery enhancement by three times for scheelite and 1.4–1.1 times for apatite and calcite, respectively.

In [1], the focus was also being put on the study of separation selectivity enhancement for calcic minerals (calcite, francolite, fluorite and gypsum) with the use of a collector mixture comprised of two non-ionic and anionic reagents. It has been shown that the adsorption of an ionic surface active substance (SAS) increases in the presence of a non-ionic SAS due to hydrophobic interactions of the hydrocarbon chain and a decrease of the electrostatic repulsion between ionic molecular groups that are protected from each other by molecules of the non-ionic SAS.

In [5], flotation experiments have been carried out with fluorite in a Hallimond tube. A comparison has been drawn between flotation results obtained with the use of a single reagent (sodium sarcosinate, sodium dodecanoate and dodecyl ammonium chloride) and a mixture of collectors (sodium sarcosinate with dodecyl ammonium chloride and sodium dodecanoate with dodecyl ammonium chloride). Fluorite recovery equal to 60% was attained at a sarcosinate concentration of 3*10^{-5} mol/L. The use of sarcosinate at the same concentration but in combination with dodecyl ammonium chloride (60 : 40) resulted in an increase of fluorite recovery up to 90%. For explanation of their results, the authors refer to the work of Schubert and Schneider in which the effect made by a mixture of two ionic and non-ionic collectors is explained by their co-adsorption with formation of a mixed layer that increases the adsorption density of nonpolar groups within the adsorption layer and decreases the repulsion forces of the collector's ionic groups. It eventually leads to enhancement of the association of non-ionic groups of the added reagent with ionic groups of the first reagent and contributes to a higher hydrophobicity. According to the authors, a higher degree of recovery for the use of sodium sarcosinate in combination with dodecyl ammonium chloride was caused by a synergetic effect. The distance between solidophilic groups of sarcosinate chemically attached to the mineral surface is greater because of the molecular structure. It provides enough space for additional adsorption of the second collector (amine) in the adsorption layer. As a result, the association of nonpolar groups becomes significantly improved that leads to a higher hydrophobicity.

Experiments described in [6] have been carried out with the use of such reagent combinations as sodium oleate and cetyl trimethyl ammonium bromide; sodium oleate and potassium ethyl xanthate. Tested minerals included fluorite, calcite, pyrite and gold. It was determined that the combined use of sodium oleate and cetyl trimethyl ammonium bromide in fluorite and calcite (pH 8.0) flotation results in a higher surface hydrophobicity and a greater contact angle.

The authors of [7] carried out flotation of smithsonite with a mixture of two cationic and anionic reagents: Armac C (amine salt) and sodium amyl xanthate. An optimum relationship for the collector mixture has been determined as 8:1 for pH 11 which enables 64% zinc recovery for a content of 31%. It is supposed that, after adsorption of Armac C, xanthate can be adsorbed as a co-adsorption complex or dixanthogenyl, neutral and hydrophobic dimer, due to Van der Waals forces with the hydrocarbon chain of previously adsorbed Armac C, and that may enhance the collector's power and decrease the selectivity.

2. Results and discussion
Researchers [5, 6] believe that the beneficial effect of collector reagents combinations in flotation is associated with the co-adsorption of them on the mineral surface and the increase of sorption density and hydrophobicity. It is known that sometimes a 1±3% monolayer is enough for flotation [8] and that...
the increase in flotation recovery performance is not directly related to the collector's sorption density on the mineral surface.

Using atomic force microscope (AFM) investigation, it has been found that muscovite flotation with a mixture of reagents (dodecylamine / sodium oleate) involves the formation of a dense multilayer adsorption coating with uniformly distributed volumetric connections [9].

Previously, it has been shown in [10] that it is necessary for effective flotation to fix the collecting reagent on the mineral surface both chemically and physically. The main function of the physical desorbed form of the collector's sorption is to reduce the induction time in the formation of a flotation complex. The physical desorbed form of sorption may be represented by different compounds: ion-molecular associates, molecules. The collecting capacity of the reagent's desorbed forms is determined by its surface parameters: spreading rate and surface pressure. In flotation with a combination of reagents, the function of physisorption active at the gas-liquid interface can be performed by one of the reagents or associates formed as a result of interaction between two reagents. According to [3], for example, the interaction between main and secondary reagents brings about the formation of associates considered as compounds that increase hydrophobicity. It has been shown by the authors that changes in the secondary reagent structure induced hydrophobicity changes in such associates.

According to research findings presented in [11], a change in the structure of the reagent's hydrocarbon fragment has an influence on the reagent's surface properties and such changes correlate with the reagent's flotation activity. It has been noted in [4] that the formation of intermolecular associates observed in connection with the use of sodium oleate and iso-dodecyl alcohol contributed to the boundary layer getting thinner and the flotation process gaining efficiency. Hence, it can be assumed that the function of such associates includes, besides the action at the mineral-liquid interface, the manifestation of activity at the gas-liquid interface.

In [12], experiments are described with flotation of lead-zinc ore from the Gorevsky Location. The regents used included butyl xanthate in combination with Flotec carbon reagent and octyl alcohol in various proportions. It has been found that the use of xanthate (5 g/t) and octyl alcohol (100 g/t) resulted in a metal recovery increase up to 65.7% for lead and 25.9% for zinc. Changes in the ratio of these components, namely, an increase of octyl alcohol consumption to 500 g/t, as well as the use of xanthate without an additional reagent, resulted in a decrease of metal recovery. The author believes that the use of surfactants at increased concentrations results in a decrease in the surface tension of bubbles that, in turn, causes the spreading rate of the film formed by surfactants desorbed from the mineral to the gas-liquid interface and the flotation performance values to decrease. The use of a combination consisting of xanthate collectors and Flotec allowed the recovery performance to increase up to 79.9% for lead and 66.3% for zinc. Owing to its low solubility, Flotec is fixed on the mineral surface in the form of micro-droplets and performs the function of the physical desorbed form of the reagent's sorption.

It has been noted in [13] that the synergic effect in the use of a reagent combination is manifested not only at the mineral-liquid interface, but also at the gas-liquid interface. It was shown that the combination of reagents induced a greater decrease in the surface tension of the solution than it was with the use of a single reagent. Besides, the critical concentration for micelle formation (CCM) values in the mixture were lower than for a single reagent.

According to [6], experiments to determine the surface tension showed the presence of a synergetic effect at the gas-liquid interface. For example, the introduction of cetyl trimethyl ammonium bromide into a sodium oleate solution will reduce the surface tension more strongly than the introduction of cetyl trimethyl ammonium bromide into pure water.

Thus, it can be assumed that when using a combination of collectors, an additional reagent or compounds that are formed during the interaction of the main reagent with an additional one, perform the function of the collector's physical desorbed form, i.e., fixed on the mineral surface preliminarily hydrophobizated by the reagent, they move to the gas-liquid interface and, spreading over it, contribute to the removal of the liquid layer between the mineral particle and the air bubble.
3. Conclusions
In this work, a number of works by domestic and international researchers has been studied, which review the results of experiments on flotation of various ores using a combination of reagents. It is shown that further study of the mechanism of combined reagent action can be promising in consideration of the previously proposed and studied mechanism of the physical desorbed form of the reagent's sorption active at the gas-liquid interface.

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