Mechanism of physisorption of collectors in activation of non-sulfide mineral flotation by metal ions

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Abstract. The authors address the problem of activation of non-sulfide minerals by metal ions. A brief analysis of modern ideas about the mechanism of activation of rutile, ilmenite, and fluorite by copper sulfate or lead nitrate is given. It is shown that modern thermodynamic ideas about the mechanism of activation incompletely agree with the accumulated experimental and practical information on flotation with the use of activators. A new mechanism of mineral flotation activation based on the physically adsorbed species of collectors is proposed. The proposed mechanism considers the kinetics of the formation of flotation contact and the influence exerted by the collector–activator associates stabilized by the collector anions.

1. Introduction
The research into the influence exerted by salts of polyvalent metals on flotation of oxides, silicates and salt-forming minerals using radioactive isotopes shows that cations of metal in many cases activate flotation at low consumption of salts. According to [1], salt consumption should "equal the amount capable to attach to mineral surface owing to the increased consumption and attachment strength of an anion collector. The higher consumption of salt suppresses flotation as the collector is bound in pulp and oleates of polyvalent metals, possessing no collecting abilities, are generated. Even in small amount, ferric chloride suppresses cassiterite" (Figure 1).

2. Non-sulfide minerals activation by metal ions: a review
Collectability of hardly dissolvable oleates of different metals in flotation of nonsulphide minerals is highlighted in [2]. The outcome of flotation by finely dispersed fresh precipitates of oleates of polyvalent metals is equivalent to flotation by initial carbonic acid.

In [3] the data on flotation of fluorite by tagged precipitates of $^{14}$C-bearing calcium tridecylate (see Table 1). The precipitates had different dispersiveness. The collector consumptions was equivalent to 300 g/t of sodium tridecylate, pine oil consumption was 40 g/t, and S : L = 1 : 14.
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Figure 1. Effect of concentration of salts of polyvalent metals on mineral recovery by sodium oleate [1].

Table 1. Calcium tridecylate precipitate flotation of fluorite [3].

| Collector                                              | Recovery, % | Adsorption of tridecylate |
|--------------------------------------------------------|-------------|---------------------------|
| Sodium tridecylate solution                            | 93.8        | 4.860 × 10^{-10} mole/cm² | 74.6 | 6.01 |
| Finely dispersed fresh precipitate of calcium tridecylate | 92.0        | 5.550                      | 85.5 | 6.30 |
| Finely dispersed precipitate of calcium tridecylate after aging for a few hours before flotation | 88.2        | 5.175                      | 78.6 | 6.10 |
| Coarsely dispersed precipitate after mixing concentrated solutions of sodium tridecylate and calcium chloride | 78.1        | 4.285                      | 66.0 | 6.30 |
| Coarsely dispersed precipitate of calcium tridecylate in mixing in smaller volume | 79.2        | 4.730                      | 72.8 | 6.61 |
| Dried precipitate of calcium tridecylate                | 11.0        | 0.93                       | 14.3 | 6.4  |

It follows from the table that precipitates are not waste of reagent but possess almost the same collectability as the reagent solution. The authors of [3] suppose that precipitates of fat acid salts exert water-repellent action due to adhesion to the mineral surface or as a result of adsorption of fat acid anions, which shifts equilibrium towards further dissolving of precipitate. This explanation of high collecting ability is assumed as unsatisfactory. First, precipitates attach to mineral surface insufficiently strongly for the flotation aggregate to survive in the turbulent flows of slurry and, second, precipitates are represented as separate micro-particles than the cover on the surface of mineral to be recovered. The micro-particles create extra chemical heterogeneity on the mineral.

Rutile flotation with salicyl hydroxamic acids is studied in [4]. The activator was lead nitrate. The authors suppose that hydroxyl lead species Pb(OH)⁺ interact with the Brønsted centers of Ti–OH and form surface compounds of Ti–O–Pb⁺ on rutile. The surface compound has facilitating effect of adsorption of C₇H₇NO₃ and floatability of rutile. Attachment of the agent is governed by chemosorption and ion–electrostatic interaction. It is emphasized that the maximum change in ζ-potential of the mineral surface at the consumption of Pb(NO₃)₂ of 2·10⁻⁴ mole/l and acid of 5·10⁻⁴ mole/l is observed in the range of pH of pH 6.3. In the same pH range, the maximum recovery of rutile is noticed. Rutile floatability with salicyl hydroxamic acid at the concentration of 5·10⁻⁴ mole/l drops when the lead nitrate concentration is raised above 2·10⁻⁴ mole/l. The authors explain the drop in floatability by
competition of hydroxyl ions and salicyl hydroxamic acid ions for making bonds with the lead on the mineral surface. This explanation also seems unconvincing for low pH of 6.3. Another cause of the drop in flotation ability with an increase in the activator consumption can be formation of lead and salicyl hydroxamic acid in slurry, which means fixation and inaccessibility of the collecting agent. The latter statement disagrees with the experimental data on high collectability of precipitates (see the table) [3]. The mechanism of stimulating rutile floatability by the Coulomb interaction between the positively charged mineral surface and salicyl hydroxamic acid anions seems incompletely realistic. In the range of low concentrations of activator, the conclusions are proved—the increased shift of $\zeta$-potential due to adsorption of lead ions correlates with the improved floatability of the mineral. In the range of the higher consumption of activator (more than $2.5 \times 10^{-4}$ mole/l), the higher shift of $\zeta$-potential and the forces of the Coulomb interaction between the collector and mineral surface brings no positive effect.

The authors connect the mineral floatability strongly with the hydrophobic behavior of its surface and pay no attention to the kinetics of formation of flotation contact between air bubble and mineral particle. For this reason, the lead nitrate is assumed as a conditioner of Ti–O–Pb$^{+}$ compounds which give positive charge to the mineral surface.

An increase in the floatability of ilmenite with lead ions is illustrated in [5]. The inactivated ilmenite micro-flotation with oleate was efficient in the pH range of 6–8. The maximum adsorption was observed at pH 4 and it was higher than adsorption in the pH range of 6–8, i.e. in the range of the maximum recovery of ilmenite. Adsorption of the collector gradually decreased with growing pH. In the optimum range of pH, the collector derivative (RCOO)$_2$H–, by the authors’ opinion, has the highest effect of the floatability of the mineral.

After addition of lead ions, both adsorption of the collector and floatability of ilmenite grew. The rate of adsorption increased from $8.6 \times 10^{-7}$ to $11.3 \times 10^{-7}$ mole/m$^2$, and the mineral recovery rose from 44.08 to 74.18%. The optimum range of pH remained the same. The authors think that lead ions increase the energy of the chemical bonding between oleate-ions and ilmenite. As a result of treatment of ilmenite with oleate, by the data of X-ray photoelectron spectroscopy, the bonding energy of Fe2p at the surface of ilmenite changed by 0.3 eV; after treatment by lead ions and oleate—by 0.4 eV. The chemical shift of other metals in the ilmenite lattice was unaltered. The authors suppose that the increase in ilmenite floatability after addition of lead is governed by the change in the energy of the chemical bonding between oleate and ferrum ions. Cations of titanium and calcium are the places of physical sorption of the collector.

In the optimum pH range of 6–8, i.e. in the range of the maximum floatability, lead-activated ilmenite changes the sign of $\zeta$-potential of the surface from positive to negative (Figure 2). The mineral floatability remains maximum, which means that flotation properties of the mineral are thanks to both physisorption and chemisorption.

![Figure 2. Recovery of ilmenite versus pH. Concentration: sodium oleate—$1 \times 10^{-5}$ M, lead nitrate—$1 \times 10^{-4}$ M [5].](image)
No explanation is given to which properties of the associates (RCOO)₂H⁻ are connected with the high floatability of the mineral. Nor do the authors disclose the cause of low floatability in the acidic range of pH.

Effect of one- and bi-valent salts (NaCl, Ca(Cl)₂) on floatability of artificial malachite with sodium oleate has been investigated in [6]. The medium pH is chosen as 9.5. It is found that an increase in the sodium chloride concentration from 1·10⁻⁶ to 1·10⁻³ M results in a gradual rise in the floatation ability of malachite treated in solution with the reagent concentration of 2·10⁻⁵ M. The curve of the malachite floatability with sodium oleate versus the concentration of Ca²⁺ ions is an extremum function. At Ca(Cl)₂ concentration higher than 3·10⁻⁵ m, the mineral floatability drops. The authors explain the gradual increase in the floatability with sodium ions by the compression of the double electric layer of bubbles and the drop in the floatability with calcium ions at the concentration higher than 3·10⁻⁵ M by their adsorption at the hydrophobizated surface of malachite and by the increase in its hydratation capacity. Formation and consolidation of calcium oleate precipitates is beyond the scope of the discussion.

Influence of ionic force of solution of adsorption of sodium oleate at the surface of apatite is studied in [7]. The topography and phase contrast of apatite crystal before and after treatment by the reagent solution are estimated. It is found that after treatment, the surface roughness grows from 25.3 to 288 nm. The authors think that calcium dioleate in the form of associates precipitates at the mineral surface and makes it better floatatable. However, the authors leave unspecified the treated surface properties that contribute to flotation. Formation of coarse associates 288 nm in size implies that these properties have no connection with the increased hydrophobic behavior of the mineral surface.

The review of the experimental studies into flotation of rutile, ilmenite, fluorite and other minerals shows that the results are explained by the mechanism of physisorption. Precipitate is represented by dispersed particles the structural units of which are the metal and collector compounds and the size is stabilized by the collector anions. These particles attach to the hydrophobic mineral surface in accord with the law of balancing of polarities of the contact media and, for this reason, cannot reduce the surface wettability. Upon the rupture of interlayer, such particles can function as a removal of kinematic constraint of the particle–bubble flotation contact. The increase in the concentration of metal and approach to stoichiometric ratio of reaction components results in enlargement of particles of the colloid system. In this case, colloids contain coarse dispersed particles with their surface activity relative to gas–water interface less than the surface activity of colloids with fine dispersed particles. The spreading rate of colloids with the coarse dispersed particles is also lower than the spreading rate of colloids with the fine dispersed particles. Precipitated on the mineral surface from the solution, such colloids fail to exert considerable influence on removal of water from the interlayer. The drop in the floatability with the increase in the flow rate of the activator [4, 5] is connected with the described phenomenon. Flotation of fluorite with the tagged precipitate of calcium tridecylate illustrated the influence of the precipitate coarseness of the mineral recovery [3].

3. Conclusions
Activation of flotation of non-sulphide ore has been discussed in the framework of thermodynamics of flotation event. Formation of precipitates of collectors with multi-valent metals and associates is understood as additional hydrophobization of mineral surface. The drop in the floatability under concentrations higher than a threshold value is explained by the hydrophilization of the recovered minerals with hydroxides irrespective of pH of the medium. It is shown that the increased floatability of minerals with the heavy metal ions can be explained in the framework of the kinetics of flotation event. The collector–metal ion precipitation removes the kinetic constrain of the bubble–particle flotation contact.

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