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Research article

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Joint use of sodium silicate and polysaccharides in the flotation of talcose copper-nickel ores

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Abstract: The paper considers the combined effect of polysaccharides (carboxymethyl cellulose and carboxymethyl starch) with sodium silicate in the flotation of talcose copper-nickel ore. The analysis of the flotation results and the assessment of hydrophobicity and surface charge of minerals showed that the composition of carboxymethylated polysaccharides and sodium silicate hydrophilizes the talc surface more effectively than each of the reagents separately. Moreover, sodium silicate alone hardly depresses the talc surface at all. The depression of flotation-active silicates is effective when polysaccharide and sodium silicate are sequentially supplied. Under these conditions, sodium silicate makes a significant contribution to increasing the negative charge on the talc particles surface. The effect is more pronounced for compositions with starch, characterized by a lower degree of substitution compared to cellulose. It results in a significantly reduced recovery of flotation-active magnesium-containing silicates and a slight decrease in sulfide recovery. To determine the features of the mechanism of talc and sulfide minerals depression in flotation, we performed calculations using the extended DLVO theory based on the obtained values of the zeta potential and force of detachment. We established that sulfide minerals have no potential barrier preventing their interaction with an air bubble, regardless of the compositions of the studied depressants used. We propose the following interaction mechanism: when sodium silicate is supplied first, the talc basal surface is very insignificantly hydrophilized as $\text{SiO}(\text{OH})_3^-$ ions are not easy to fix. On the contrary, when the carboxymethylated polysaccharide is supplied first, significant hydrophilization of the talc surface with carboxyl groups occurs due to the hydrophobic interaction between the corresponding regions of the macromolecule and the talc basal surface.

Keywords: flotation, hydrophobicity, zeta potential, talc, sodium silicate, carboxymethyl cellulose, carboxymethyl starch, copper-nickel ore.

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Совместное применение жидкого стекла и полисахаридов при флотации оталькованных медно-никелевых руд

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Аннотация: Рассмотрено совместное действие полисахаридов (карбоксиметилированной целлюлозы и карбоксиметилированного крахмала) с жидким стеклом при флотации оталькованной медно-никелевой руды. На основании анализа результатов фло-

тации, оценки гидрофобности и поверхностного заряда минералов показано, что композиция карбоксиметилированных полисахаридов и жидкого стекла гидрофилизует поверхность талька более эффективно, чем каждый из реагентов по отдельности. При этом одно жидкое стекло почти не депрессирует поверхность талька. Эффективная депрессия флотоактивных силикатов достигается при последовательной подаче полисахарида и жидкого стекла. В этих условиях жидкое стекло вносит существенный вклад в увеличение отрицательного заряда поверхности частиц талька. Эффект проявляется в большей мере для композиции с крахмалом, имеющим более низкую степень замещения по сравнению с целлюлозой. В результате существенно падает извлечение флотоактивных магнийсодержащих силикатов при небольшом снижении извлечения сульфидов. С целью определения особенностей механизма депрессии талька и сульфидных минералов при флотации на основании полученных данных по значениям электрокинетического потенциала и силы отрыва были выполнены расчеты по расширенной теории ДЛФО. Установлено, что для сульфидных минералов потенциальный барьер их взаимодействия с пузырьком воздуха отсутствует при применении любых композиций исследованных депрессоров. Предложен следующий механизм взаимодействия: в случае, если в первую очередь подается жидкое стекло, то гидрофилизация базальной поверхности талька весьма незначительна по причине затруднения закрепления ионов $\text{SiO}(\text{OH})_3^-$; напротив, когда сначала вводится карбоксиметилированный полисахарид, происходит существенная гидрофилизация поверхности талька карбоксильными группами вследствие гидрофобного взаимодействия между соответствующими участками макромолекулы и базальной поверхности талька.

Ключевые слова: флотация, гидрофобность, электрокинетический потенциал, тальк, жидкое стекло, карбоксиметилированная целлюлоза, карбоксиметилированный крахмал, медно-никелевая руда.

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Introduction

Efficient depression of rock minerals is crucial in the flotation of copper nickel ores since naturally hydrophobic talc and other flotation-active magnesium-containing silicates may easily be recovered into the flotation concentrate, increasing the costs of further pyrometallurgical processing. Plant-based polysaccharides are widely used for talc depression [1]. Earlier research focused on various talc depressants, including the most effective one — carboxymethyl cellulose (CMC) [2]. The main difficulty in applying polysaccharides is their selectivity. With an increased molecular weight of the reagent, depressing ability improves, but the sulfides recovery in the concentrate deteriorates [3–7]. Therefore, it is important to look for ways to boost selectivity and reduce recovery of magnesium-containing silicates in the concentrate when using depressants of flotation-active rock minerals.

An analysis of literature data on the use of reagent complexes and their mechanism of action in the flotation of talcose copper-nickel ores proved the viability of using compositions of sodium silicate (SS) with carboxymethylated polysaccharides [8–12]. According to [13], the sequential supply of acidified sodium silicate (SS) and CMC enhances the efficiency of flotation separation of chalcopryrite and talc due to the hydrophilization of talc basal surfaces by polymeric silicic acid formed during SS acidification. Thus, in the flotation with a CMC concentration of 500 mg/L,

the recovery of chalcopryrite and talc in the concentrate amounted to 16 % and 45 % respectively, against 95 % and 90 % without a depressant. Moreover, the addition of acidified SS only during the flotation had practically no impact on the recovery of these minerals in the concentrate.

However, researchers in [14] note that the addition of sodium silicate acidified with oxalic or hydrochloric acids reduces the floatability of silicates. At the same time, the sequential supply of these depressants with an SS concentration of 250 mg/L and a CMC concentration of 300 mg/L ensured, respectively, 28 % and 43 % recovery of talc and chalcopryrite in the concentrate. The paper [15] showed that in the talc flotation with the pH medium increasing from 8.6 to 10.5 and the non-acidified SS concentration surging from 0 to 300 mg/l, the recovery of talc in the concentrate rises from 70 % to 78 %. However, with a further increase in pH and SS consumption, it drops, which, in our opinion, can be attributed to the enhanced concentration of double-charged anions $\text{SiO}_2(\text{OH})_2^{2-}$ at pH above 10.5. It is also indicated that the use of CMC in combination with SS causes a reduction of roughly 7 % in the talc recovery in the concentrate. At the same time, it remains unclear how the order of feeding non-acidified SS and polysaccharides affects the surface properties of talc, sulfide minerals, and, in general, the results of talcose copper-nickel ore flotation.

Many researchers [12; 15; 16 et al.] attribute the depressing effect of sodium silicate to the hindrance of the collector's sorption on the mineral surface. Non-acidified SS is known to have a depressing effect on quartz in a weakly alkaline medium as $\text{SiO}(\text{OH})_3^-$ ions are fixed on its surface [17]. It also affects flotation-active forsterite (forming a chemical compound with magnesium [18]) and serpentine in a strongly alkaline medium, as the positive surface charge of these minerals is compensated by $\text{SiO}_2(\text{OH})_2^{2-}$ anions [19]. Thus, SS impacts silicate minerals through different mechanisms of depression.

The literature data on the properties of SS solutions (e.g., [20]) indicate that the molecular form H_4SiO_4 predominates in a slightly alkaline medium at $\text{pH} = 7.0 \div 9.4$, with single-charged anions $\text{SiO}(\text{OH})_3^-$ are also present in relatively small amounts. Considering that about 90 % of the surface of talc particles is represented by basal areas characterized by very high hydrophobicity due to relatively low-polarity Si—O bonds prevailing [21], there are reasons to believe that the adsorption value of $\text{Si}(\text{OH})_4$ and $\text{SiO}(\text{OH})_3^-$ in a weakly alkaline medium is relatively small. This is probably why these compounds do not contribute to talc hydrophilization or an increase in the absolute value of the negative ζ -potential of the surface. The findings of [15] also support this assumption.

The purpose of this work is to determine, using the example of flotation of out-of-balance copper-nickel ore, the conditions under which compositions of non-acidified sodium silicate and polysaccharide depressants have a potent depressing effect on flotation-active silicates.

The objective of the research was to find out how depressants should be applied to reduce the concentrate yield while maintaining acceptable copper and nickel recovery.

Materials and methods

The research aims to study the depressing effect of depressant compositions on talc and other flotation-active silicates in the flotation of talcose copper-nickel ore.

For flotation experiments, we used the ore comprising the following major elements, %:

Cu	0.12
Ni	0.2
Co	0.01
S	0.8
Fe	1.9
Mg	0.94
SiO_2	50.5

Its mineral composition includes the following elements, wt.%:

Chalcopyrite	0.3
Pentlandite	0.6
Pyrrhotite	0.2
Pyrite	0.14
Pyroxene	58
Talc	12
Amphiboles	8
Magnesite	3.75
Plagioclases	1

By the content of valuable components, the ore is classified as out-of-balance.

The scheme shown in Fig. 1 was used to conduct flotation of the ore crushed to a size of 84 % grade $-71 \mu\text{m}$, at $\text{pH} = 7$ (generated by the flotation medium). In the main flotation, the silicate depressant was fed first, to be followed by the collector — butyl xanthogenate 50 g/t. Methylisobutylcarbinol (MIBC), with consumption of 20 g/t, was used as a foaming agent. Reagent consumption in the control flotation amounted to 40 % of that in the main flotation. The concentrates from the main and control flotations were then combined. The following reagents were used as talc depressants:

- sodium silicate;
- carboxymethyl starch CMS-BUR (JSC NPO “Polycell”, Russia), with 0.4 degree of substitution of hydroxyl groups by carboxyl ones and 60 % content of the active substance;
- carboxymethyl cellulose (polyanionic cellulose) PAC-N (JSC NPO “Polycell”) with a 0.9 degree of substitution at 45 % of active substance.

Depressants concentrations and consumption were recalculated taking into account the content of the active ingredient in the reagent.

The changes in the minerals hydrophobicity caused by depressants were evaluated by determining the force of air bubble detachment from the mineral surface using a torsion balances. Sections of natural samples of pyrrhotite, pentlandite, and talc were measured [22]. NaOH was used to provide a $\text{pH} = 7$ solution.

The zeta potential of the minerals was determined using a ZETA-check PMX 500 device (“Particle Metrix”, USA). A 0.2 g sample of finely ground mineral was placed in a 50 ml cell. The measurement principle is based on the evaluation of the flow potential.

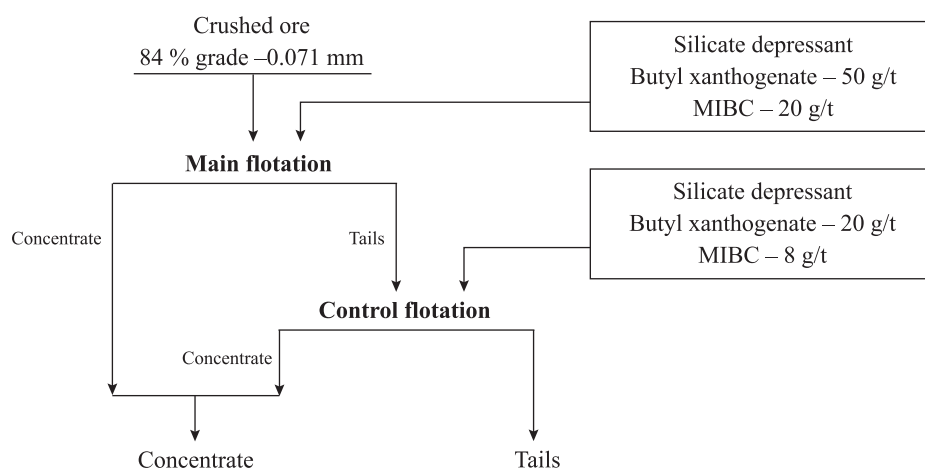


Fig. 1. Scheme of flotation experiments

Рис. 1. Схема флотационных опытов

Results and discussion

Figure 2 shows the findings of flotation studies of copper-nickel ore with sodium silicate, carboxymethyl starch, and carboxymethyl cellulose, as well as combinations of SS + CMS-BUR and SS + PAC-N. Based on the analysis, we came to the following conclusions: sodium silicate does not significantly depress rock minerals; the concentrate yield decreased by 10 % from 52.9 % to 42.8 %, at an SS consumption of 5.6 kg/t. The PAC-N reagent demonstrates better depressing properties compared to CMS-BUR. At the same consumption of 700 g/t, the use of CMS-BUR reduced the concentrate yield from 52.9 % to 40.9 %, PAC-N reduced it to 22.6 %. The combinations of depressants in the compositions of SS + CMS-BUR and SS + PAC-N showed stronger depressant properties compared to each reagent separately. When the combination of SS + CMS-BUR is used, the order of feeding the depressant is important. When SS is introduced first, followed by CMS-BUR, the concentrate yield drops to 27.9 %. However, if SS is fed after starch, the yield plummets to 18.8 % (see Fig. 2, *a*). Therefore, it is recommended to feed SS after CMS-BUR. The combined use of PAC-N and SS also enhances the depressing effect in the flotation (see Fig. 2, *b*), but the order of feeding reagents does not significantly affect the result. With an SS consumption of 5.6 kg/t and PAC-N consumption of 700 g/t, the concentrate yield decreases from 52.9 % to 15.9 %. For the composition CMS-BUR + SS, the minimum required depressant consumption is 280 g/t of starch and 1.4 kg/t of SS, and its further increase does not affect depression (see Fig. 2, *a*). When PAC-N + SS is used, the concen-

trate yield gradually declines with increasing reagent consumption (see Fig. 2, *b*). 1.4 kg/t of SS; further increases do not affect depression (see Fig. 2, *a*). When PAC-N + SS is used, the concentrate yield gradually declines with increasing reagent consumption (see Fig. 2, *b*).

Figure 3 shows the results of copper and nickel recovery into the concentrate using compositions of SS + CMS-BUR and SS + PAC-N depressants. With an SS consumption of 5.6 kg/t and polysaccharide consumption of 700 g/t, CMS-BUR showed slightly better selectivity for nickel: nickel recovery was 58.6 %, while with PAC-N, this value was 54.4 %.

The results of measurements of the air bubble detachment force from the talc surface showed that the combined use of depressants (Fig. 4, *a*, curves 4 and 5) increases the hydrophilization of the mineral surface compared to each depressant used individually. For pentlandite and pyrrhotite (Fig. 4, *b* and *c*), the compositions reduce the hydrophobicity of sulfides, but to a lesser extent than for talc. Thus, for talc with the maximum concentration of each depressant (600 mg/L), the detachment force drops from 300 μ N to 50 μ N, while for sulfides under the same conditions, it decreases by 50–60 μ N to 280–290 μ N. It was found that the different order of feeding depressants barely affects the force of air bubble detachment from the mineral surface.

The zeta ζ -potential of talc shifts more in the presence of different depressants (Fig. 5, *a*) when sodium silicate is added. With its content of 250 mg/L, the value of ζ -potential is –48 mV, while with the same concentration of CMS-BUR and PAC-N, it is about –35 mV. The effect of SS addition to polysaccharides is most pro-

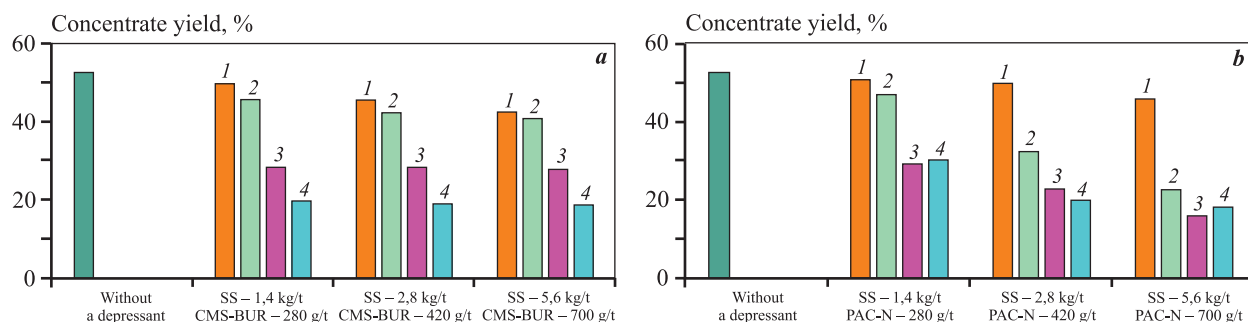


Fig. 2. Impact of the composition of depressants CMC-BUR with SS (a) and PAC-N with SS (b) on the concentrate yield in the flotation of copper nickel ore

a: 1 – SS, 2 – CMS-BUR, 3 – SS + CMS-BUR, 4 – CMS-BUR + SS

b: 1 – SS, 2 – PAC-N, 3 – SS + PAC-N, 4 – PAC-N + SS

Рис. 2. Влияние сочетания депрессоров КМК-БУР с ЖС (a) и ПАЦ-Н с ЖС (b) на выход концентрата при флотации медно-никелевой руды

a: 1 – ЖС, 2 – КМК-БУР, 3 – ЖС + КМК-БУР, 4 – КМК-БУР + ЖС

b: 1 – ЖС, 2 – ПАЦ-Н, 3 – ЖС + ПАЦ-Н, 4 – ПАЦ-Н + ЖС

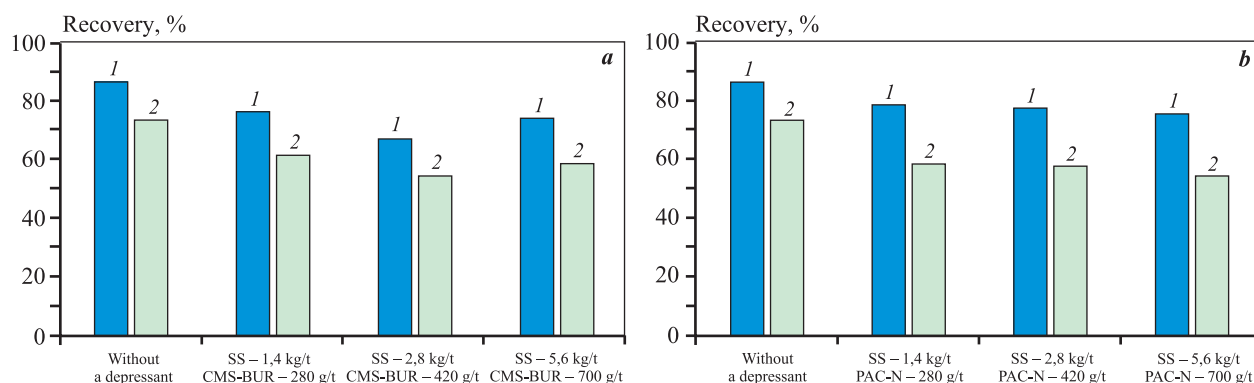


Fig. 3. Impact of the composition of depressants CMS-BUR + SS (a) and PAC-N + SS (b) on the recovery of Cu (1) and Ni (2) in the flotation of copper nickel ore

Рис. 3. Влияние композиции депрессоров КМК-БУР + ЖС (a) и ПАЦ-Н + ЖС (b) на извлечение Cu (1) и Ni (2) при флотации медно-никелевой руды

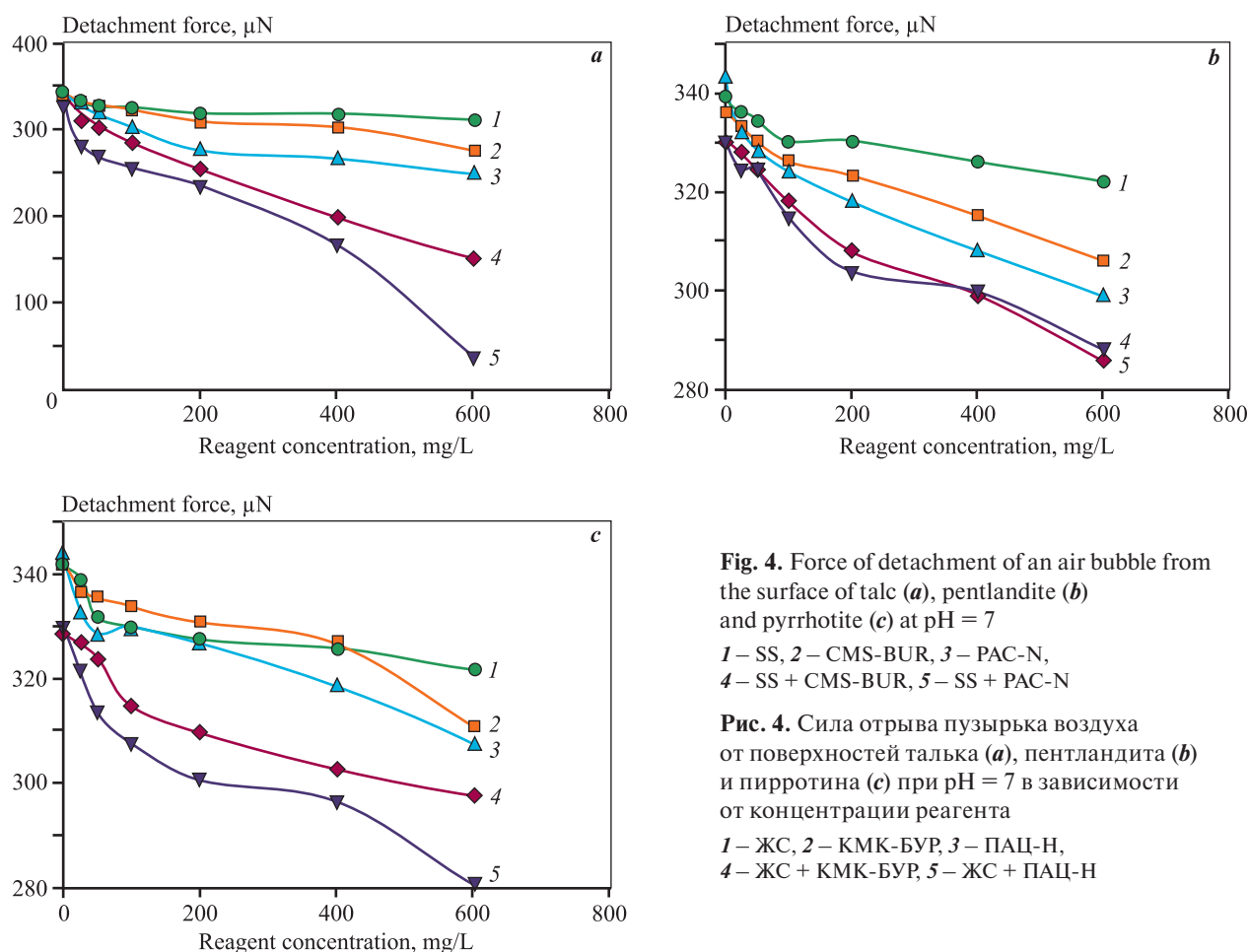
nounced with its content of 100 mg/L. When the concentration of polysaccharide was increased to 250 mg/L, the value of ζ -potential was close to that in the presence of one SS.

For chalcopyrite, the shift of ζ -potential was almost the same regardless of the depressant (Fig. 5, b). The value of zeta potential of chalcopyrite without reagents is -4 mV, while in the presence of CMS-BUR and PAC-N, the concentration of each being 250 mg/L, it reaches -8.5 mV, and when SS is added, this value amounts to about -10 mV. The combination of depressants, with 100 mg/L SS concentration and 250 mg/L polysaccharide concentration, shifts the potential to -10 mV.

The zeta potential of pyrrhotite without reagents reaches -8.8 mV (Fig. 5, c), and it shifts more when sodium silicate is added. The combination of depressants shifts the potential toward negative values by 1–2 mV up to 11 mV.

Thus, when depressants affect talc at a concentration of 250 mg/L, the zeta potential shifts from the initial value by 16–28 mV to the values of -36 ... -48 mV depending on the depressant. For sulfides (pyrrhotite and chalcopyrite) ζ -potential is -8 ... -10 mV with a shift from the initial one by 1–2 mV towards negative values.

To determine the features of the mechanism of talc and sulfide minerals depression in the flotation based



on the obtained values of the zeta potential and detachment force, we made calculations using the extended DLVO theory, taking into account the components of the potential energy of interaction between a mineral particle and an air bubble: electrostatic (U_E with the “+” sign), molecular (U_M with the “–” sign) and hydrophobic (U_H with the “–” sign). The calculation method based on this theory for talc depression is described in [23]. According to [24], if the curve showing dependence of the total potential energy (U) of the particle interaction with a bubble on the distance between the surfaces of these objects (h) has a barrier with a height of minimum $10 kT$ (where $k = 1.38 \cdot 10^{-23}$ J/K — Boltzmann constant; T — absolute temperature, K), the interaction of these objects is hampered. When the barrier is lower or non-existent, the interaction is unimpeded.

Considering the literature data, the following parameter values included in the equation of the extended DLVO theory were used in the calculations:

— ionic strength of the dispersion medium — 0.04 mol/L ;

— Hamaker constants for talc particles and air bubbles are $1.7 \cdot 10^{-20}$ and $3.7 \cdot 10^{-20}$ J, respectively;

— the surface potential (ϕ) of air bubbles in the aqueous medium at pH = 7, according to various data, ranges from -0.037 to -0.265 V.

Figures 6 and 7 features the calculated curves of U dependence on h at pH = 7. The presented data demonstrates that in the absence of reagents the calculated curve is entirely in the region of negative U values, since talc particles, due to their natural hydrophobicity, freely interact with air bubbles. In the presence of individual reagents, including SS, CMS-BUR and PAC-N, maxima emerge on the curves corresponding to the value of $h \sim 2\text{--}3 \text{ nm}$. They are located above the curve for the reagentless mode, but still entirely within the region of negative values, even when the consumption of investigated reagents is at its maximum.

Figure 6 also shows that curve 4 corresponding to SS is located above curves 2 and 3 for PAC-N and CMS-BUR. We attribute this to the fact that some part of carboxyl groups does not participate in forming the

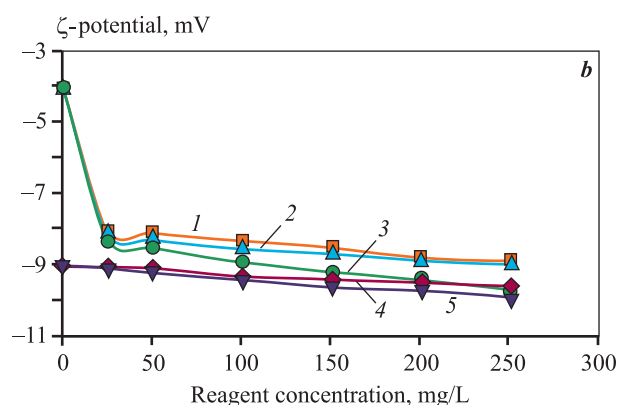
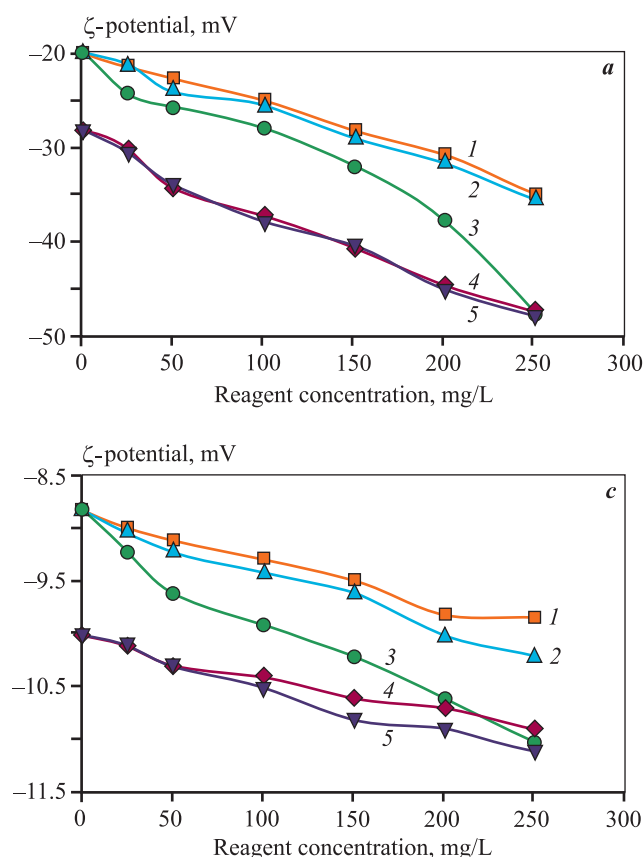


Fig. 5. ζ -potential of talc (a), chalcopyrite (b) and pyrrhotite (c) with different depressants at pH = 7

1 – CMS-BUR, 2 – PAC-N, 3 – SS, 4 – SS (100 mg/l) + CMS-BUR, 5 – SS (100 mg/l) + PAC-N

Рис. 5. ζ -потенциал талька (a), халькопирита (b) и пирротина (c) с разными депрессорами при pH = 7 в зависимости от концентрации реагента

1 – КМК-БУР, 2 – ПАЦ-Н, 3 – ЖС, 4 – ЖС (100 мг/л) + КМК-БУР, 5 – ЖС (100 мг/л) + ПАЦ-Н

negative charge of the talc surface due to steric hindrances and incomplete dissociation. At the same time, silicic acid ions are characterized by a denser arrangement on the talc surface, which causes a greater negative charge and, consequently, a greater value of the electrostatic component.

Figure 7 shows that the use of PAC-N composition with SS creates a potential barrier of interaction between the particle and the bubble with an ordinate of about 10 kT. This is presumably due to the fact that PAC-H hydrophilizes the talc surface with carboxyl groups. This, in turn, creates favorable conditions for additional hydrophilization of talc by $\text{SiO}(\text{OH})_3^-$ ions and increase in the negative charge of the surface. At the same time, compared to the mode without reagent supply at the point corresponding to the maximum height of the potential barrier ($h = 1.7$ nm), the value of U_E is 4.5 times higher, and that of U_H is 1.4 times lower. This gives reasons to suggest that the electrostatic component makes the most significant contribution to the barrier formation due to the increased number of negatively charged groups on the talc surface. This effect is the greatest for PAC-H, for which the degree of substitution is 0.9. At the same time, CMS-BUR, characterized by a much lower degree of substitution

(0.4), cannot create a potential barrier under the same conditions.

Also, the calculations revealed that for sulfide minerals, there was no potential barrier in their interaction with an air bubble no matter what compositions of investigated depressants were used.

Based on the above, the following mechanism of talc depression by the compositions of polysaccharides and SS seems feasible. If SS is fed first, the hydrophilization of the basal surface of talc is insignificant as $\text{SiO}(\text{OH})_3^-$ ions are not easy to fix. On the contrary, when the carboxymethylated polysaccharide is fed first, according to the detachment force measurement data, the talc surface is substantially hydrophilized by the carboxyl groups due to hydrophobic interactions between the corresponding sites of the macromolecule and the talc basal surface. This, in turn, creates favorable conditions for additional hydrophilization of talc by $\text{SiO}(\text{OH})_3^-$ ions, and their contribution to the increase in the negative charge of the surface is more noticeable for the CMC-BUR reagent with a 0.4 degree of substitution compared to PAC-N, for which this parameter is 0.9.

Thus, the depressant reagents decrease the hydrophobic component and increase the electrostatic one due to their negative charge.

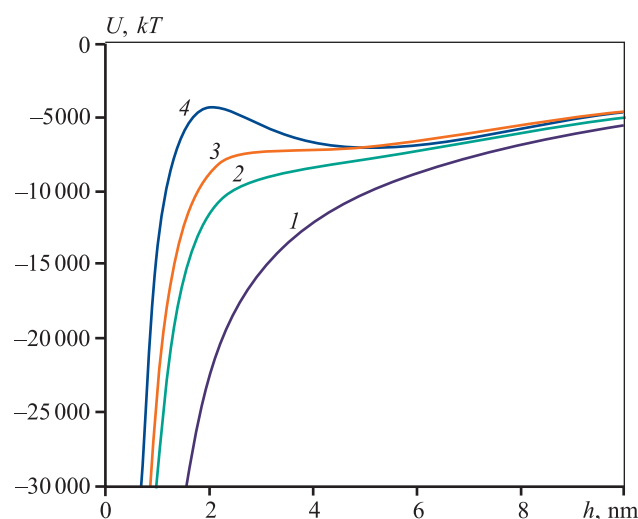


Fig. 6. Potential curves illustrating the interaction of air bubbles and talc particles with individual depressants in the quantity of 250 mg/L each at pH = 7

1 – without reagents, 2 – CMS-BUR, 3 – PAC-N, 4 – SS

Рис. 6. Потенциальные кривые взаимодействия пузырьков воздуха и частиц талька с индивидуальными депрессорами в количестве 250 мг/л каждого при pH = 7

1 – без реагентов, 2 – КМК-БУР, 3 – ПАЦ-Н, 4 – ЖС

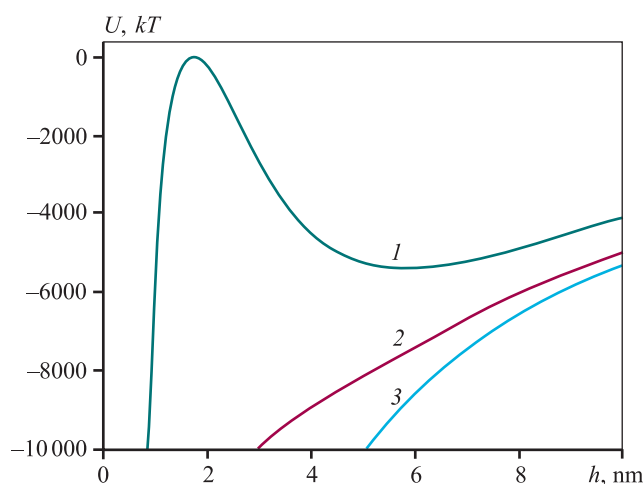


Fig. 7. Potential curves illustrating the interaction of air bubbles, talc particles (1, 2) and pyrrhotite (3) with depressant compositions

1 – PAC-N + SS, 2 – CMS-BUR + SS, 3 – PAC-N + SS
Concentrations: SS – 100 mg/L, CMS-BUR – 250 mg/L, PAC-N – 250 mg/L

Рис. 7. Потенциальные кривые взаимодействия пузырьков воздуха и частиц талька (1, 2) и пирротина (3) с композициями депрессоров
1 – ПАЦ-Н + ЖС, 2 – КМК-БУР + ЖС, 3 – ПАЦ-Н + ЖС
Концентрации ЖС – 100 мг/л, КМК-БУР – 250 мг/л, ПАЦ-Н – 250 мг/л

Conclusion

The investigation of the flotation of talcose copper-nickel ore, along with the assessment of the hydrophobicity and surface charge of minerals, revealed that the combination of carboxymethylated polysaccharides and sodium silicate hydrophilizes the talc surface more effectively than each of the reagents separately. However, sodium silicate alone hardly depresses the talc surface at all. The depression of flotation-active silicates is effective when polysaccharide and sodium silicate are sequentially supplied. Under these conditions, SS contributes significantly to the increase in the negative charge on the talc particle surfaces. This effect is more pronounced for compositions with starch characterized by a lower degree of substitution compared to cellulose.

The combined use of carboxymethylated polysaccharide and sodium silicate considerably reduces the yield of concentrate due to the depression of flotation-active magnesium-containing silicates, with a slight decrease in the recovery of sulfides. This subsequently creates conditions for enhancing the efficiency of the concentrate's pyrometallurgical processing.

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