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Utilizing Russian polymer anion active depressants in the flotation of out-of-balance talcose copper nickel ore

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Abstract: Experimental studies were conducted on the flotation of low-sulfide copper-nickel ore containing flotation-active magnesium silicates, specifically talc, using organic polymeric anionic reagents containing carboxyl and hydroxyl groups as depressants. The following reagents, which contain carboxyl groups, were examined: carboxymethyl cellulose and carboxymethylated starch; polyacrylic acid and its derivatives; sodium humate. Copolymers of ethylene oxide with ethylenediamine and glycerol containing hydroxyl groups were also investigated. The objective of this study was to identify new efficient domestic depressants for flotation-active silicates, selectively acting in the flotation of low-sulfide copper-nickel ore, in comparison with the performance of foreign Depramin 347 depressant. The impact of depressant reagents on the surface properties of talc was determined by the values of air bubble detachment force and electrokinetic potential. It was observed that for reagents containing carboxyl groups, the depressing effectiveness decreased in the following order: carboxymethyl cellulose \rightarrow carboxymethylated starch \rightarrow polyacrylic acid \rightarrow sodium humate. This reduction was attributed to a decrease in the acidic properties of the reagents, a decline in their adsorption affinity for talc, and a decrease in the proportion of active carboxyl groups participating in the formation of the electrokinetic potential. Furthermore, a trend towards increased depressing ability was noted for carboxymethyl cellulose samples with an increasing degree of substitution. In contrast, reagents containing hydroxyl groups had virtually no depressing effect on talc. The data obtained support the use of domestic industrial samples of carboxymethyl cellulose, namely CMC 7N and PAC-N, as depressants for floating silicates, particularly talc, which is a detrimental impurity in the concentrate.

Keywords: flotation, copper-nickel sulfide ore, talc, depressants, carboxyl groups, hydroxyl groups, air bubble detachment force, electrokinetic potential, adsorption.

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Применение отечественных полимерных анионоактивных депрессоров при флотации забалансовой оталькованной медно-никелевой руды

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Аннотация: Были выполнены экспериментальные исследования по флотации малосульфидной медно-никелевой руды, содержащей флотоактивные магниевые силикаты, в частности тальк, с применением в качестве депрессоров органических полимерных анионоактивных реагентов, содержащих карбоксильные и гидроксильные группы. Исследовали следующие реагенты, содержащие карбоксильные группы: карбоксиметилированные целлюлоза и крахмал; полиакриловая кислота и ее производные; гумат

натрия. Также изучали сополимеры окиси этилена с этилендиамином и глицерином, содержащие гидроксильные группы. Цель исследования — выявление новых эффективных отечественных депрессоров флотоактивных силикатов, селективно действующих при флотации малосульфидной медно-никелевой руды, по сравнению с действием зарубежного депрессора Depramin 347. Влияние реагентов-депрессоров на поверхностные свойства талька определяли по значениям силы отрыва пузырька воздуха и электрокинетического потенциала. Установлено, что для реагентов, содержащих карбоксильные группы, депрессирующая способность убывает в следующей последовательности: карбоксиметилцеллюлоза → карбоксиметилированный крахмал → полиакриловая кислота → гумат натрия. Это обусловлено уменьшением кислотных свойств реагентов, убыванием их адсорбционного сродства к тальку и снижением доли активных карбоксильных групп, принимающих участие в формировании электрокинетического потенциала. При этом выявлена тенденция к возрастанию депрессирующей способности образцов карбоксиметилцеллюлозы с увеличением степени замещения. В то же время реагенты, содержащие гидроксильные группы, практически не оказывают депрессирующего действия на тальк. Полученные данные обосновывают применение отечественных промышленных образцов карбоксиметилцеллюлозы (КМЦ 7Н, ПАЦ-Н), в частности в качестве депрессоров талька при флотации медно-никелевой руды, что позволяет снизить содержание в концентрате талька, являющегося вредной примесью.

Ключевые слова: флотация, медно-никелевая сульфидная руда, тальк, депрессоры, карбоксильные группы, гидроксильные группы, сила отрыва пузырька воздуха, электрокинетический потенциал, адсорбция.

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Introduction

Sulfide copper-nickel ores serve as a valuable source not only for copper and approximately 90 % nickel but also for platinum group metals (PGM), gold, silver, cobalt, selenium, tellurium, and other rare and trace elements. These elements are closely associated with sulfides of base metals and sometimes with the surrounding rock. As free-milling ore reserves continue to deplete, the industrial utilization of complex raw materials with low concentrations of valuable components becomes necessary. This demands the development of new reagent flotation modes.

A significant challenge in processing both sulfide and particularly low-sulfide copper-nickel ores is the presence of hydrophobic waste rock minerals, notably magnesium silicates such as talc, chlorite, sericite, and olivine (forsterite). These minerals readily enter flotation concentrates, increasing smelting costs and reducing smelting efficiency. Hydrophilic silicates also contribute negatively. For example, complex orthopyroxene particles with a talc periphery significantly dilute concentrates in the flotation of Merensky Reef ores [1]. Hydrophilic serpentine enters the concentrate due to partial coating of sulfides by oppositely charged serpentine slurry particles, which diminishes the recovery and flotation rate of sulfides [2].

The significance of researching the processing of low-sulfide copper-nickel ores with high talc content stems from the necessity to depress the flotation of flotation-active magnesium-bearing silicate minerals.

In global practices of copper-nickel ore concentration, non-toxic natural polysaccharides such as guar gum, carboxymethyl cellulose (CMC), and occasionally dextrin, either individually or in combination, are widely employed as depressants for hydrophobic waste rock [3]. The most effective depressant for hydrophobic silicates is guar gum, although its high cost and limited availability (mostly used abroad) present challenges [4]. The depression of magnesium-containing silicates can also be achieved using more readily available and cost-effective polysaccharides, thanks to their widespread sources of production and annual reproducibility. These include starch derivatives, dextrin, and carboxymethyl starches (CMS) [5—8]. However, apart from a few derivatives like dextrin, there is limited documentation on the use of starch derivatives as depressants in sulfide minerals flotation [8].

In Russia, the depression of hydrophobic waste rock during the flotation of copper-nickel ores relies on the use of a more readily available anionic polysaccharide polymer, carboxymethyl cellulose (CMC). The most challenging issue encountered is the depression of talc, which, due to its inherent high hydrophobicity, is susceptible to degradation in an aqueous environment, resulting in the formation of fine particles. Talc also exhibits exceptionally high flotation activity, presenting significant challenges in the flotation process of complex PGM-containing copper-nickel sulfide ores [4]. The adsorption of an anionic polymer onto talc is influenced by various factors, including the characteristics of the polymer (such as type, number of ionized polar groups, degree of substitution (DS), and molar mass (MM)), as well as solution properties [5; 9-13].

Since hydrophobic interaction plays a pivotal role in the sorption of polymeric depressants onto talc, adsorption increases with the degree of polymerization of the reagent, augments the hydrophobicity of the macromolecule. However, high molecular weight polymers exhibit lower selectivity compared to their low molecular weight counterparts [5]. Polysaccharides and other polymers traditionally employed in the flotation of sulfide ores typically have molar masses (MM) in the range of 150–600 t/kmol. In recent years, polysaccharides with lower MM (100–150 t/kmol) have also proven to be effective [14].

The depressant effect of anionic polymers on talc diminishes as the pH increases. At high pH and low ionic strength of the solution, the adsorption density of anionic polymers is at its lowest. Conversely, at high ionic strength and low pH, especially in the presence of Mg, Ca, and other ions, the adsorption density increases [9—13]. The presence of divalent and trivalent cations enhances the depression of talc but also reduces the selectivity in the flotation of mineral mixtures. The degree of polymer substitution influences not only its solubility but also its ability to be adsorbed onto talc and sulfide minerals [13; 15].

The interaction mechanisms between polysaccharides and mineral surfaces encompass hydrophobic, chemical, electrostatic, and acid-base interactions, in addition to the formation of hydrogen bonds [5; 9; 15; 16]. These mechanisms contribute to the partial adsorption of polysaccharides onto sulfide minerals, thereby impeding their flotation. The interaction between polysaccharides and sulfides has received limited research attention [6]. The selectivity of their effects during flotation is contingent upon MM and DS values [16]. Few studies have explored the impact of the polymer's chemical nature on selectivity, and typically, the choice of polymer for waste rock depression is made through empirical means.

Previous studies have focused on the depressant properties of corn dextrin from Bio Polimer, Depramin 267 and 347 CMC from Akzo Nobel, and the synthetic polymer Akremon D-13 [17]. Additionally, carboxymethylated corn starches (CMS) with varying viscosities, synthesized at the Research Institute of Starch Products, have been examined [6]. The most favorable results were obtained with the Depramin 347 depressant.

This study aims to identify effective domestic depressants for silicate flotation that exhibit selectivity in the flotation of low-sulfide copper-nickel ore, in comparison to the foreign depressant Depramin 347.

Research methodology

The research focuses on investigating the depressant effect during the flotation of out-of-balance talcose copper-nickel ore and the hydrophilic properties of Russia-manufactured anionic polymers with varying degrees of substitution (DS) and viscosity (MM-related characteristics) towards talc and sulfides. This study also involves comparing these reagents with the most effective depressant identified in previous research, Depramin 347 (refer to Table 1).

Flotation experiments were conducted using out-of-balance ore, which contained the following components by weight: 0.12 % Cu, 0.2 % Ni, 0.01 % Co, 0.8 % S, 1.9 % Fe, 0.94 % Mg, 50.5 % SiO_2 , 1.1 g/t Pd, 0.2 g/t Pt, and 0.06 g/t Au. The mineral composition of the ore consisted of chalcopyrite (0.3 %), pentlandite (0.6 %), pyrrhotite (0.2 %), pyrite (0.14 %), pyroxenes (58 %), talcum powder (12 %), amphiboles (8 %), magnesite (3.75 %), plagioclases (1 %), and other constituents.

Flotation of the ore, which was ground to 84 % fineness at $-71~\mu m$, was carried out under natural pH conditions of 7. The primary flotation process began with the addition of a silicate depressant, followed by Aerophine 3416 and butyl xanthogenate collectors at a rate of 25 g/t each, and MIBK foaming agent at a rate of 20 g/t. Control flotation received 40 % of the reagents from the primary flotation flow rate. Subsequently, concentrates from both the primary and control flotations were combined.

For the flotation of a 5 g sample of talc, which was ground to $-71~\mu m,$ a 100~mL chamber was used presence of 50 mg/L MIBK.

In order to investigate the hydrophilizing effects of the depressants, we employed a method that assesses mineral wettability by measuring the detachment force of an air bubble from the mineral surface in a reagent solution.

The examination of the interactions between depressants of varying viscosity and DS with the surfaces of sulfides and talc was conducted by measuring the ζ -potential of minerals using a ZETA-check PMX 500 instrument (Germany). The cell had a volume of 50 mL, and the weight of finely ground mineral used was 0.2 g.

The depressant's effectiveness was assessed by calculating the relative reduction in Ni and Si recovery in the concentrate, expressed as a percentage:

$$\Delta = 100 \, \frac{\varepsilon_0 - \varepsilon_i}{\varepsilon_0} \, ,$$

where ε_0 represents the component extraction without

Properties of investigated reagents

Характеристика исследованных реагентов

| Description | Dynamic viscosity of 2 % solution at $t = 25$ °C, mPa·s; MM | Degree of substitution (DS) |
|--|---|-----------------------------------|
| Containing carboxyl groups (-COOH) | | |
| Carboxymethylated starch CMS BUR-1V (ZAO Polycell), 60 % active substance | about 300 (4 % solution) | 0.4 |
| Carboxymethyl cellulose CMC 7N (ZAO "Polycell"), 50 % active substance | \leq 40 (Höppler), \leq 140 (Brookfield), degree of polymerization $-$ 350 | 0.6-0.8 |
| Carboxymethyl cellulose (polyanionic cellulose) PAC-N (ZAO "Polycell"), 45 % active substance | ≤ 40 (Höppler), ≤ 170 (Brookfield), degree of polymerization − 500, MM ~ 116 000 | 0.9 |
| Carboxymethyl cellulose Depramin 347 ("Akzo Nobel"), 80 % active substance | 91 (Brookfield) | 0.54 |
| Na humate (mixture of polycondensed aromatic compounds containing side OH- and COOH-groups) | - | - |
| Macromer 30H (NPP "Macromer"), polyacrylic acid, 45 % active substance | MM ~ 12 000 | |
| Macromer 17N (NPP "Macromer"), polyacrylic acid with grafted polyoxyethylene glycol chains (PAA), 50 % active substance | MM ~ 36 000 | |
| Containing hydroxyl groups (-OH) | | |
| Laprol 3703-2-37 (NPP "Makromer") based on glycerol, block copolymer with ethylene oxide: 37 %, 100 % active substance | MM ~ 3700 | |
| Lapramol 6504 (NPP "Makromer") based on ethylenediamine, 25–30 % ethylene oxide, propylene oxide, 100 % active substance | MM ~ 6500 | |

the depressant, ε_i represents the component extraction at the *i*-th depressant flow rate.

The selectivity of the depressant's action was determined using Cohen's enrichment factor (*I*):

$$I = \varepsilon_{Ni} / \varepsilon_{Si}$$
.

Results and discussion

The results of copper-nickel ore flotation process for talc and other silicates depression using reagents, displayed in the table, are illustrated in Fig. 1. The selectivity of the reagent action is depicted in Fig. 2.

Based on the obtained data, it can be concluded that the suppressive effect of depressants on the flotation of silicates and sulfides follows this order: PAC-N \cong CMS 7N > Depramin 347 > Na humate \cong CMS BUR-1V (as shown in Figs. 1 and 2). However, CMC

with a higher degree of polymerization and DS (CMC 7N and PAC-N) exhibited lower selectivity at low flow rates. Yet, at flow rates exceeding 600 g/t, their selectivity improves to the level of Depramin 347.

Depressants containing hydroxyl groups (Laprol, Lapramol), as well as Macromer 30N with MM \sim 12000 at a flow rate of 400 g/t, had almost no impact on the flotation results of the ore under investigation (the concentrate yield decreased by approximately 1 %). However, when using Macromer 17N with an MM of 36000, the depressant's effectiveness increased. The concentrate yield decreased by 5 %, and the nickel recovery in the concentrate also decreased by 5 %.

The investigation into talc flotation with MIBK in the presence of CMC depressants revealed an escalation in the depressant's impact as the viscosity (molar mass) and DS of CMCs increased, particularly for PAC-N (as demonstrated in Fig. 3). The hierarchy of dimin-

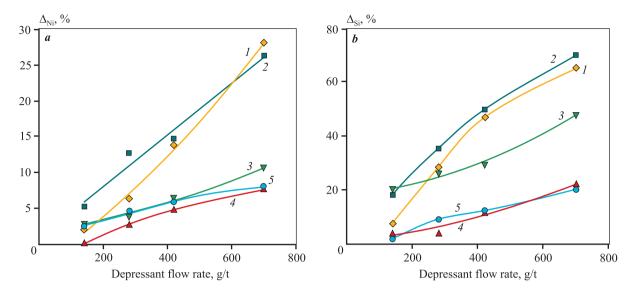


Fig. 1. Relative decrease (Δ) in Ni (a) and Si (b) recovery into concentrate during Cu–Ni ore flotation 1 - CMC 7N; 2 - PAC-N; 3 - Depramin 347; 4 - CMS BUR-1V; 5 - sodium humate

Рис. 1. Относительное снижение (Δ) извлечения Ni (a) и Si (b) в концентрат при флотации Cu—Ni руды I — KMЦ 7H; 2 — ПАЦ-H; 3 — Depramin 347; 4 — KMK БУР-1B; 5 — гумат Na

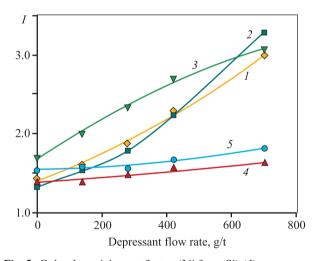
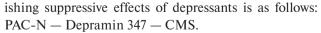


Fig. 2. Cohen's enrichment factor (Ni from Si) (*I*) I - CMC 7N; 2 - PAC-N; 3 - Depramin 347, 4 - CMS BUR-1V; 5 - sodium humate

Рис. 2. Коэффициент разделения Ni от Si по Коэну (I) I – KMЦ 7H; 2 – ПАЦ-H; 3 – Depramin 347; 4 – KMK БУР-1B; 5 – гумат Na



In order to elucidate the mechanism of action of the polysaccharides used on the primary ore minerals (pentlandite, pyrrhotite) and talc, studies were conducted to assess their hydrophobicity and surface charge following treatment with depressants.

The impact of depressant adsorption on altering the hydrophobicity of minerals, assessed through the air

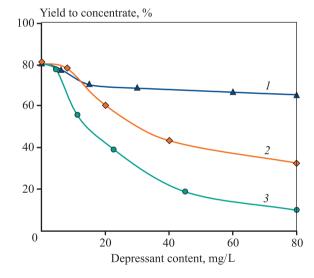


Fig. 3. The influence on talc flotation with MIBC: CMS (*1*), Depramin 347 (*2*) and PAC-N (*3*)

Рис. 3. Влияние КМК (*I*), Depramin 347 (*2*) и ПАЦ-Н (*3*) на флотацию талька с МИБК

bubble detachment force from the slurry of talc, pentlandite, and pyrrhotite, was substantiated by the results obtained from flotation experiments. Detachment force measurements were conducted in the presence of a combination of Aerophine 3416 A and butyl xanthogenate (in a 1:1 ratio) with a total concentration of 30 mg/L. The data depicted in Fig. 4 demonstrate that CMCbased depressants significantly enhance the hydrophilicity of the talc surface when compared to CMC and Na humate. The degree of hydrophilization decreases in the following order: PAC-N > Depramin 347 > Depramin 3

Measurements of the electrokinetic potential of the examined minerals revealed that CMCs with higher viscosity and DS exert a more pronounced effect on shifting the ζ -potential of talc towards negative values (as illustrated in Fig. 5). The influence of CMS and CMC on the ζ -potential of talc remains consistent across the pH range of 7 to 9 (as shown in Fig. 6). Furthermore, for pH levels greater than 7, the negative ζ -potential of talc remains essentially unaltered [18; 19]. Therefore, altering the pH within the range of 7 to 9 is unlikely to affect the adsorption of anionic CMC and CMS. These findings strongly suggest that the primary mechanism driving the adsorption of polysaccharides onto talc is hydrophobic interaction, rather than electrostatic forces.

The negative shift in the ζ -potential on pyrrhotite and chalcopyrite following interaction with anionic polysaccharides indirectly suggests the adsorption of these polymers, as shown in Figs. 7 and 8. The most signifi-

cant shift is observed on pyrrhotite, particularly in the presence of high-viscosity depressants like CMC 7N and CMS BUR-1V, and this shift intensifies as pH levels increase. A similar correlation was noted, for instance, with starch tricarboxylate as a depressant [19]. It appears that a larger quantity of these polysaccharides is adsorbed onto the pyrrhotite surface compared to chalcopyrite. This was hypothesized to be due to the presence of more metal hydroxyl layers on pyrrhotite, which facilitated greater polysaccharide adsorption [19].

The studies have demonstrated that CMC-based depressants exhibit superior efficiency, both in terms of silicate suppression and the selectivity of their action, when compared to CMS and Na humate in the flotation of talcose copper-nickel ore. As the viscosity (degree of polymerization) of CMC and its DS increase, the suppressive effect of the polymer on both silicates and sulfides intensifies, yet the selectivity in separating sulfides from silicates diminishes. Among the investigated options, CMS with average values of these characteristics prove to be the most effective for the flotation of low-sulfide Cu—Ni ore.

An analysis of the averaged relative changes in the interaction between talc and the examined depres-

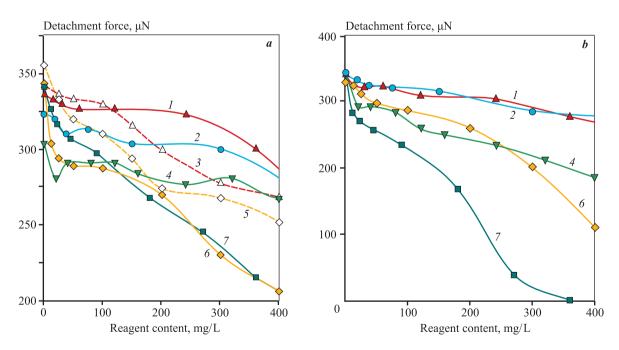


Fig. 4. Detachment force of air bubble from pentlandite (1, 2, 4, 6, 7) and pyrrhotite (3, 5) (a) and tale (b) in the presence of depressants:

1, 3 – CMS BUR-1V; 2 – sodium humate; 4 – Depramin 347; 5, 6 – CMC 7N; 7 – PAC-N

Рис. 4. Сила отрыва пузырька воздуха от пентландита (1, 2, 4, 6, 7) и пирротина (3, 5) (a), а также талька (b) в присутствии депрессоров

1, 3 — КМК БУР-1В; 2 — гумат Na; 4 — Depramin 347; 5, 6 — КМЦ 7Н; 7 — ПАЦ-Н

sants, in conjunction with the known physicochemical properties of these reagents, including values such as the acidity constant (pKa) and their maximum adsorption capacity on the talc surface (G) [20–26], reveals that the efficiency of depressants in the flotation of talcose copper-nickel ore follows a descending order: carboxymethyl cellulose \rightarrow carboxymethylated starch \rightarrow polyacrylic acid (PAA) \rightarrow sodium humate (SH)

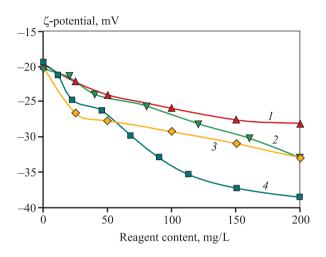


Fig. 5. Comparison of anionic depressants influence on talc zeta potential at pH=9

1 – CMS BUR-1V; 2 – Depramin 347; 3 – CMC 7N; 4 – PAC-N

Рис. 5. Сравнение влияния анионных депрессоров на ζ -потенциал талька при pH = 9

1 – КМК БУР-1В; 2 – Depramin 347; 3 – КМЦ 7Н; 4 – ПАЦ-Н

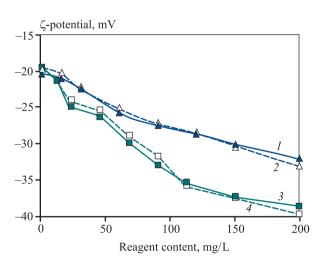


Fig. 6. pH influence on talc ζ -potential in the presence of depressants

1, 2 - CMS; 3, 4 - PAC-N 1, 3 - pH = 9; 2, 4 - pH = 7

Рис. 6. Влияние рН на ζ-потенциал талька в присутствии депрессоров

 $1, 2 - KMK; 3, 4 - \Pi A \coprod - H$ 1, 3 - pH = 9; 2, 4 - pH = 7

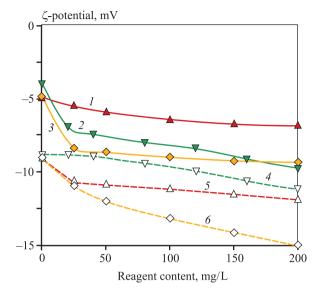


Fig. 7. Influence of depressants concentration on ζ -potential of chalcopyrite (1-3) and pyrrhotite (4-6) at pH = 7 1, 5 - CMS BUR-1V; 2, 4 - Depramin 347; 3, 6 - CMC 7N

Рис. 7. Влияние концентрации депрессоров на ζ -потенциал халькопирита (1—3) и пирротина (4—6) при рH = 7

1, 5 – KMK БУР-1В; 2, 4 – Depramin 347; 3, 6 – КМЦ 7Н

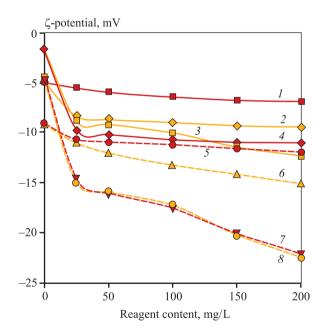


Fig. 8. Electrokinetic potential of chalcopyrite (1-4) and pyrrhotite (5-8) with CMS BUR-1V (1, 4, 5, 7) and CMC 7N (2, 3, 6, 8) at pH = 7(1, 2, 5, 6) and pH = 9(3, 4, 7, 8)

Рис. 8. Электрокинетический потенциал халькопирита (1—4) и пирротина (5—8) в присутствии КМК БУР-1В (1, 4, 5, 7) и КМЦ 7H (2, 3, 6, 8) при рH = 7 (1, 2, 5, 6) и рH = 9 (3, 4, 7, 8)

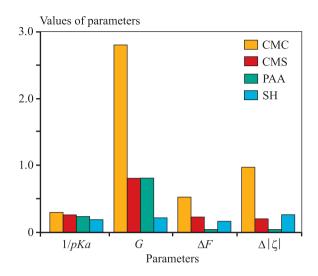


Fig. 9. Relative change of interaction parameters for polymeric reagents with talc

 Γ – adsorption value, mg/m²; ΔF – relative decrease of detachment force; $\Delta |\zeta|$ – relative increase of electrokinetic potential modulus; pKa – the indicator of acidity constant

Рис. 9. Относительное изменение параметров взаимодействия полимерных реагентов-депрессоров с тальком

 Γ — величина адсорбции, мг/м²; ΔF — относительное снижение силы отрыва, доли ед.; $\Delta |\zeta|$ — относительное увеличение модуля электрокинетического потенциала, доли ед.; pKa — показатель константы кислотности

(Fig. 9). This decrease in efficiency can be attributed to a reduction in the acidic properties of the reagents, a decline in their affinity for adsorption onto talc, and a decrease in the proportion of active carboxyl groups participating in the formation of the electrokinetic potential.

Therefore, it can be deduced from the collected data that polyanionic cellulose PAC-N and CMC 7N exhibit the highest depressant capacity when it comes to the flotation of sulfides in comparison to talc.

Based on a comprehensive set of experimental and analytical studies concerning the depressant impact of domestic samples of carboxymethylated starch (CMS BUR, CMS-363), carboxymethyl cellulose (PAC-N, CMC 7N), polyacrylic acid (PAA), and sodium humate (SH) in relation to talc (flotation-active silicates) during the flotation of talcose low-sulfide copper-nickel ore, a consistent pattern has been established regarding the diminishing depressing efficacy of the studied reagents containing carboxyl groups in relation to talc. Furthermore, a notable trend towards an increased depressant effectiveness of CMC samples with a higher degree of substitution has been observed. This holds the promise of reducing the content of undesirable impurities in the concentrate.

Conclusions

Based on an extensive series of experimental and analytical investigations regarding the depressing effects of domestically sourced polymeric anionic reagents containing carboxyl groups on talc (flotation-active silicates) during the flotation of talcose low-sulfide Cu-Ni ore, a discernible pattern emerges: their depressing effectiveness decreases in the following order-carboxymethyl cellulose \rightarrow carboxymethylated starch \rightarrow polyacrylic acid → sodium humate. This reduction can be ascribed to a decrease in parameters indicative of the reagents' affinity for talc. Remarkably, an increase in the degree of substitution within CMC molecules corresponds to an augmentation of their capacity to depress talc. These findings solidify the recommendation to employ domestic industrial samples of carboxymethyl cellulose PAC-N and CMC 7N as depressants for silicates, particularly talc, which is recognized as an undesirable impurity in the concentrate.

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O.G. Lusinyan – prepared ore samples for investigation, conducted flotation experiments and calculations, and participated in result discussion.

G.Yu. Golberg – acquired and analyzed published data, analyzed experimental data, participated and contributed to result discussions.

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