



## BENEFICIATION AND PROCESSING OF NATURAL AND TECHNOGENIC RAW MATERIALS

Research paper

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## Application of polystyrene sulfonates for the depression of magnesium-containing silicates in copper-nickel ore flotation

A.A. Lavrinenko<sup>1</sup> , G. Yu. Golberg<sup>1</sup>  , I.N. Kuznetsova<sup>1</sup>  ,  
O.G. Lusinyan<sup>1</sup>  , V.A. Tverskoy<sup>2</sup>  

<sup>1</sup> Research Institute of Comprehensive Exploitation of Mineral Resources of the Russian Academy of Sciences,  
Moscow, Russian Federation

<sup>2</sup> MIREA – Russian Technological University, Lomonosov Institute of Fine Chemical Technologies,  
Moscow, Russian Federation

✉ [lavrin\\_a@mail.ru](mailto:lavrin_a@mail.ru)

### Abstract

It is very urgent to increase the efficiency of depressing magnesium-containing silicates (MS) in the course of the flotation of copper-nickel ores to reduce the content of magnesium in the concentrate, which causes a significant increase in energy consumption in pyrometallurgical processing of the concentrate. The use of polymer reagents containing sulfo groups seems to be a promising area of research. However, only lignosulfonates have been studied so far in this field. The question of the effectiveness of the depressing effect of other polymer sulfonates including polystyrene sulfonates (PSS), and their comparison with polysaccharides used in industrial conditions remains unclear. The purpose of this work is to study the depressing effect of PSS on the performance of bulk flotation of copper-nickel ores. Research objectives: to experimentally compare the effectiveness of the depressing effect of PSS and a reagent from the polysaccharide class on MS; to determine the modes of PSS use to reduce the magnesium content in the concentrate without significantly reducing the recovery of copper and nickel into the bulk concentrate; to establish the effect of molecular weight and the method of obtaining PSS samples on the effectiveness of their depressing effect. Laboratory experimental studies were carried out on the bulk flotation of copper-nickel ores from the Kola Peninsula, containing 15.7% of magnesium, 0.44% of nickel and 0.25% of copper. The effect of the following polymer anionic reagents on the flotation was studied: PSSs with molecular weight ranging from 89,000 to 208,000 g/mol; polyanionic cellulose (PAC-N) was used for comparison. To increase the effectiveness of these reagents, magnesium chloride was previously added. It was found that the lowest magnesium content in the concentrate of 14.7% was achieved using a composition of magnesium chloride and PSS against 16.7% without the depressants. It was shown that PSS provides a higher recovery of copper (by 7%) and nickel (by 8%) into the concentrate than when using PAC-N, since PSS, unlike polysaccharides, does not form chelate complexes with these metals. It was also shown that for PSS samples, the molecular weight within these limits has virtually no effect on the studied ore flotation performance. New scientific knowledge has been obtained about the effect of the consumption and properties of PSS on the flotation performance. It has been shown that the practical use of this class of reagents is advisable for the flotation of copper-nickel ores with a high magnesium content in cases where it is necessary to achieve the maximum possible decreasing the content of this element in the concentrate without significantly reducing the recovery of copper and nickel.

### Keywords

flotation, copper-nickel ore, depression of magnesium-containing silicates, polystyrene sulfonates, magnesium cations, polyanionic cellulose


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## ОБОГАЩЕНИЕ, ПЕРЕРАБОТКА МИНЕРАЛЬНОГО И ТЕХНОГЕННОГО СЫРЬЯ

Научная статья

**Применение полистиролсульфонатов для депрессии магнийсодержащих силикатов при флотации медно-никелевых руд****А.А. Лавриненко<sup>1</sup> , Г.Ю. Гольберг<sup>1</sup> , И.Н. Кузнецова<sup>1</sup> ,  
О.Г. Лусинян<sup>1</sup> , В.А. Тверской<sup>2</sup> **<sup>1</sup> Институт проблем комплексного освоения недр им. академика Н.В. Мельникова РАН,  
г. Москва, Российская Федерация<sup>2</sup> МИРЭА – Российский технологический университет, Институт тонких химических технологий  
имени М.В. Ломоносова, г. Москва, Российская Федерация [lavrin\\_a@mail.ru](mailto:lavrin_a@mail.ru)**Аннотация**

Весьма актуальной является задача повышения эффективности депрессии магнийсодержащих силикатов (МС) при флотации медно-никелевых руд для снижения содержания в концентрате магния, вызывающего существенное увеличение энергозатрат на пирометаллургическую переработку концентрата. Перспективным направлением представляется применение полимерных реагентов, содержащих сульфогруппы. Однако до настоящего времени изучено действие только лигносульфонатов. Остаётся неясным вопрос об эффективности депрессирующего действия других полимерных сульфонов, включая полистиролсульфонаты (ПСС), и их сравнении с полисахаридами, применяемыми в промышленных условиях. Цель настоящей работы: изучение депрессирующего действия ПСС на эффективность коллективной флотации медно-никелевой руды. Задачи исследований: экспериментальное сравнение эффективности депрессирующего действия ПСС и реагента из класса полисахаридов на МС; определение режимов применения ПСС, обеспечивающих снижение содержания магния в пенном продукте без существенного снижения извлечения меди и никеля в коллективный концентрат; установление влияния молекулярной массы и способа получения образцов ПСС на эффективность их депрессирующего действия. Выполнены лабораторные экспериментальные исследования по коллективной флотации медно-никелевой руды Кольского полуострова, содержащей 15,7 % магния, 0,44 % никеля и 0,25 % меди. Изучено влияние на флотацию полимерных анионоактивных реагентов: ПСС со значениями молекулярной массы от 89 000 до 208 000 г/моль; для сравнения применяли полианионную целлюлозу (ПАЦ-Н). Для повышения эффективности действия этих реагентов предварительно добавляли хлорид магния. Установлено, что наименьшее содержание магния в концентрате достигается применением композиции хлорида магния и ПСС и составляет 14,7 % против 16,7 % без депрессоров. Показано, что ПСС обеспечивает более высокое извлечение меди (на 7 %) и никеля (на 8 %) в концентрат, чем в случае применения ПАЦ-Н, так как ПСС, в отличие от полисахаридов, не образует хелатные комплексы с указанными металлами. Также показано, что для образцов ПСС значение молекулярной массы в указанных пределах практически не влияет на показатели флотации исследованной руды. Получены новые научные знания о влиянии расхода и свойств ПСС на показатели флотации и показано, что практическое применение этого класса реагентов целесообразно при флотации медно-никелевых руд с высоким содержанием магния в тех случаях, когда требуется достигнуть максимально возможного снижения содержания этого элемента в концентрате без существенного снижения извлечения меди и никеля.

**Ключевые слова**

флотация, медно-никелевая руда, депрессия магнийсодержащих силикатов, полистиролсульфонаты, катионы магния, полианионная целлюлоза

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**Introduction**

The current stage of mining industry development is characterized by the involvement of relatively lean copper-nickel ores in processing [1–4]. A significant problem in the flotation of such ores is the presence of magnesium-containing silicate minerals (MS), including talc, serpentinite, and a number

of others [5, 6]. As a result of the extraction of these silicates into the concentrate, the content of harmful impurities, especially magnesium, increases. This, in turn, has an adverse effect on the subsequent processes of pyrometallurgical processing of the concentrate. For instance, according to [7], the effect of MS on the processing of nickel sulfide concentrate con-



sists in increasing energy consumption, increasing equipment wear, and growing the amount of sulfur dioxide atmospheric emission. This makes the problem of MS depression in copper–nickel ore flotation processes rather relevant.

Lowering MS recovery into flotation concentrate is achieved by using depressants that change the surface properties of these minerals by reducing the contact angle and/or increasing the negative surface charge. As a result, a potential barrier is created between a MS particle and an air bubble, which prevents the formation of a flotation complex and its extraction into the concentrate.

To date, various methods for depression of MS, mainly talc and serpentinite, have been developed. The first one is characterized by natural hydrophobicity due to the peculiarities of the crystal structure: weakly polar Si–O bonds predominate on the basal surface, which constitutes about 90% of the total surface of this mineral [8]. Therefore, the contact angle is relatively high, from 60 to 90° [9, 10]. Unlike talc, serpentinite is more hydrophilic, but its surface charge in acidic, neutral, and alkaline media (up to pH 11–12) is positive [11]. As a result of the mutual attraction of negatively charged sulfide particles and positively charged serpentinite particles, the latter are extracted into flotation concentrate. In this regard, various methods are used for talc and serpentinite depression.

Polysaccharides including carboxymethylated starches and celluloses (CMS and CMC, respectively), have become popular as talc depressants [12, 13]. They are characterized by a strong depressing effect not only on silicates, but also on sulfide minerals [14], i.e. low selectivity. Studies carried out at the IPKON RAS have shown that a domestically produced CMC sample manufactured under the PAC–N brand name (low molecular weight polyanionic cellulose) has a higher depressing capability against MS than foreign samples of reagents of the same class [15]. It is known that the effectiveness of CMC increases when combined with liquid glass, both in acidified [16] and in neutral form [17]. The papers [18, 19] have shown the possibility of effective depression of talc by lignosulfonates with the preliminary addition of calcium cations. The mechanism of depression in this case consists in reducing the hydrophobicity of talc under the influence of strong anionic sulfonate groups. At the same time, calcium cations contribute to an increase in the adsorption capacity of talc in relation to lignosulfonates. It is noted that the adsorption of lignosulfonate on chalcopyrite is lower than that on talc; this suggests that polymer reagents containing sulfo groups are selective in their depressing effect on

talc. The effect of other polymer sulfonates on the flotation of copper–nickel ores has not yet been studied both in Russia and abroad.

The results of monomineral talc flotation showed the depressing effect of sodium polystyrene sulfonates (PSS), which is slightly weaker than that of CMC and increases when magnesium or aluminum cations are pre-added [20].

For the depression of serpentinite during the flotation of copper–nickel ores, liquid glass in particular is used [21]. Its effect is mainly to neutralize the positive surface charge of this mineral by silicate anions. It is also known about the use of graphene oxide, which can selectively aggregate serpentinite [7, 22], organic phosphates, in particular sodium phytate [6], and acid treatment [23].

An analysis of the literature sources made it possible to establish the following:

- modern methods of MS depression using polysaccharides, liquid glass, and other reagents make it possible in some cases to effectively reduce the magnesium content in the concentrate, but at the same time reduces, and in some cases significantly, the recovery of copper and nickel into the bulk flotation concentrate due to the depression of the sulfides of these metals;

- to date, the effectiveness of the depressing effect of polymer sulfonates and polysaccharides has not been compared;

- the effect of PSS on monomineral talc flotation has been studied, but it is unclear what effect PSS has on the flotation performance of copper–nickel ore containing MS, including on the concentrate yield, its magnesium content, and the recovery of copper and nickel.

**The purpose of this work** is to study the depressing effect of polystyrene sulfonates on the performance of bulk flotation of copper–nickel ore.

#### **Research objectives:**

- experimental comparison of the effectiveness of the depressing effect of PSS and a reagent from the polysaccharide class on MS;

- determining the modes of PSS use that reduce the magnesium content in the concentrate without significantly reducing the recovery of copper and nickel into the bulk concentrate;

- establishing the effect of molecular weight and the method of producing PSS samples on the effectiveness of their depressing effect.

To achieve these goals, it was planned to conduct experimental studies on the flotation of copper–nickel ores with reagent compositions to achieve the lowest magnesium content in the concentrate without significantly reducing the recovery of copper and nickel.



### Procedure of experiments

The studies were carried out with a sample of copper–nickel ore from the Kola Peninsula. The elemental composition of the ore according to X-ray fluorescence analysis was as follows: Si – 17.2, Mg – 15.8, Fe – 12.9, Al – 2.5, Ca – 2.0, S – 1.13, Ni – 0.44, Cu – 0.25, Cr – 0.20 %. X-ray phase analysis revealed the following minerals in the ore: antigorite, chlorite, amphibole, olivine, spinel minerals, pentlandite, violarite, pyrrhotite, chalcopyrite, chalcophyllite, etc.

The experiments were carried out on a laboratory flotation machine with a cell volume of 150 cm<sup>3</sup> according to a scheme that involves sequential rougher and recleaner flotation of the initial ore sample with separate supply of reagents and appropriate stirring. A sample of an aqueous suspension of the initial ore (pulp) was prepared: the weight of the sample was 45 g, pH = 9. After mixing for 60 seconds, the reagents were sequentially fed in the following order: a depressant, collectors, and a frother. The contact time of each reagent with the pulp was 60 sec with permanent stirring. The froth product was sampled every 15 seconds. After 300 seconds of rougher flotation, a recleaner flotation of the cell product was carried out, with adding the above reagents sequentially in an amount equal to 40% of the consumption in the rougher flotation. The recleaner flotation lasted 180 sec. The combined concentrate and tailings were weighted. The grades of copper, nickel, magnesium, and silicon in them were determined by X-ray fluorescence analysis. The studies were carried out using parallel experiments. Statistical analysis showed that the discrepancy between the results in a pair of the parallel experiments was approximately ±0.8% (relative).

The effectiveness of the depressing effect of the studied reagents was determined based on the yield of concentrate  $\gamma$ , the recovery of copper  $\varepsilon_{\text{Cu}}$  and nickel  $\varepsilon_{\text{Ni}}$  into the concentrate; the grades of these metals ( $\beta_{\text{Cu}}$  and  $\beta_{\text{Ni}}$ , respectively) in the concentrate, as well as the content of magnesium  $\beta_{\text{Mg}}$ ; the Hancock–Luyken criterion (HL), which takes into account the values of  $\varepsilon$ ,  $\gamma$ , as well as the grades of copper and nickel in the initial ore  $\alpha$ :

$$HL = \frac{\varepsilon - \gamma}{100 - \alpha}. \quad (1)$$

Laboratory samples of linear sodium PSS, which were not previously used in ore flotation, were used as MS polymer depressants. The properties of the studied PSS samples are presented in Table 1. For comparison, carboxymethylated cellulose PAC–N manufactured by Policell CJSC with an average viscosity molecular weight of about 116,000 g/mol and a gamma number of 90% was also used as a polymer depressant.

Potassium butyl xanthate (PBX) and dibutyl dithiophosphate (DBTP) were used as collectors. To increase the effectiveness of the depressing effect of the polymer reagents, MgCl<sub>2</sub> was added, since the Mg<sup>2+</sup> cation, according to [20], contributes to talc depression with the use of PSS.

### Findings and Discussion

In the ore flotation without depressants but with the use of PBX and DBTP, the highest copper and nickel recoveries were achieved at PBX consumption of 112 g/t and that of DBTP of 84 g/t: 89.6% and 85.5%, respectively. This reagents composition was used in further experiments.

The depressing effect of polystyrene sulfonates on MS was studied using the example of the effect of L–50 in comparison with PAC–N (Fig. 1).

In Fig. 1, one can see that the optimal consumption of L–50 depressant is 700 g/t. At this consumption, the concentrate yield decreases from 49.8% to 44.6%. At the same time, copper recovery decreases from 89.7% to 88.5%, and nickel recovery, from 86.1% to 82.8%. A further increase in the depressant consumption leads to a significant decrease in the recovery of the metals into the concentrate. For instance, at L–50 consumption of 1,400 g/t, copper recovery into the concentrate was 79%, and that of nickel, 76.6%.

The data presented in Fig. 1, *b* show that effective results were obtained at a PAC–N consumption of 420 g/t. Under this flotation regime, copper recovery into the concentrate was 81.7%, and that of nickel, 76.6%, while the grades in the concentrate increased from 0.4 to 0.74% Cu and from 0.7 to 1.22% Ni.

An analysis of the beneficiation performance when using various depressants in accordance with the Hancock–Luyken (HL) criterion showed (Fig. 2) that the maximum HL criterion for both copper and nickel is achieved at L–50 and PAC–N consumption of 700 and 420 g/t, respectively.

Table 1

Properties of the studied polystyrene sulfonates

Reagent symbol	Medium viscosity molecular weight (MW), g/mol	Chain growth regulator; concentration, mol/l
L–50	97,000	Isopropanol; 0.3
L–51	89,000	Isopropanol; 0.9
L–54	89,000	Glycine, 0.9
L–55	96,000	Glycine, 0.9
L–5	93,000	Trimethylamine; 0.008
L–6	208,000	Trimethylamine; 0.041
L–7	176,000	Trimethylamine; 0.082



Thus, the optimal consumption of the depressants was 700 g/t for L-50 and 420 g/t for PAC-N, that corresponded to relatively low metal losses in the course of flotation. These values were adopted for further research to determine the most effective modes of the use of these reagents.

According to a number of studies, for example [20], the effectiveness of the depressing effect of polymer reagents on MS increases when multicharged cations, in particular  $Mg^{2+}$ , are pre-added. Therefore, in this study, the effect of the addition of this cation on the depressing action of PSS and PAC-N was investigated.

The results of experiments using L-50 and the preliminary addition of  $MgCl_2$  at a consumption of 0 to 70 g/t showed that the lowest bulk concentrate yield was achieved at a consumption of  $MgCl_2$  of 7 g/t through reducing the floatability of rock minerals due

to hydrophilization of their surfaces. This reduces the magnesium content in the concentrate by approximately 2.0% compared to the regime without the use of the depressants.

Figs. 3 and 4 show data characterizing the ore flotation with the following compositions of the studied depressants: 1 – without depressants; 2 – L-50, 700 g/t; 3 – PAC-N, 420 g/t; 4 –  $MgCl_2$ , 7 g/t + L-50, 700 g/t; 5 –  $MgCl_2$ , 7 g/t + PAC-N, 420 g/t.

The data in Fig. 3, *a* show that the lowest values of  $\gamma$ , approximately 27% and 25%, are achieved by using PAC-N and  $MgCl_2$  in combination with PAC-N, respectively, that indicates the latter's high depressing capacity. At the same time, L-50, if used individually, even slightly increases the  $\gamma$  value that may be due to the manifestation of some flocculating ability of this reagent.

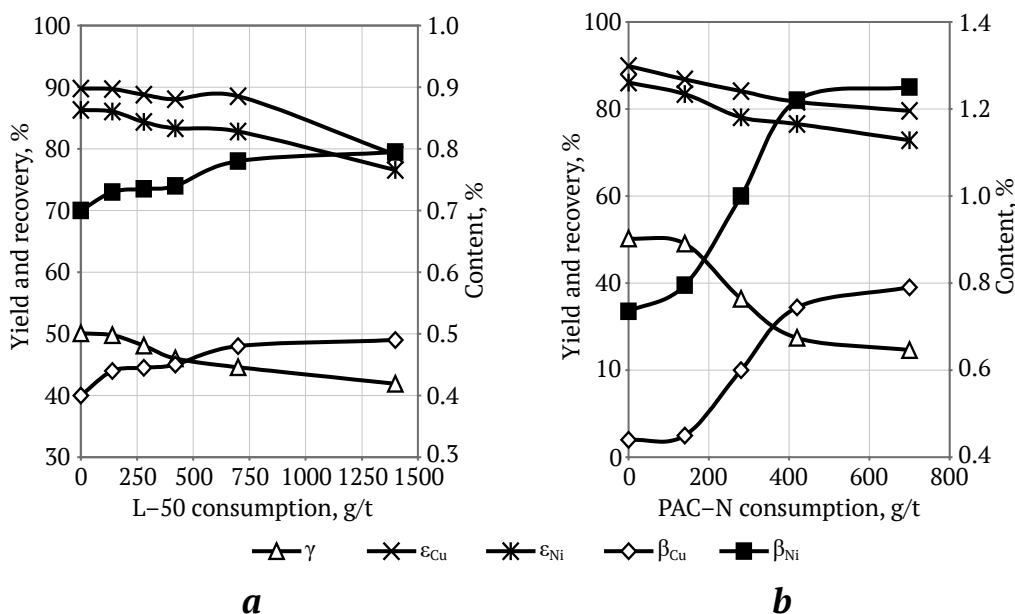


Fig. 1. The effect of depressant consumption on ore flotation: *a* – L-50; *b* – PAC-N

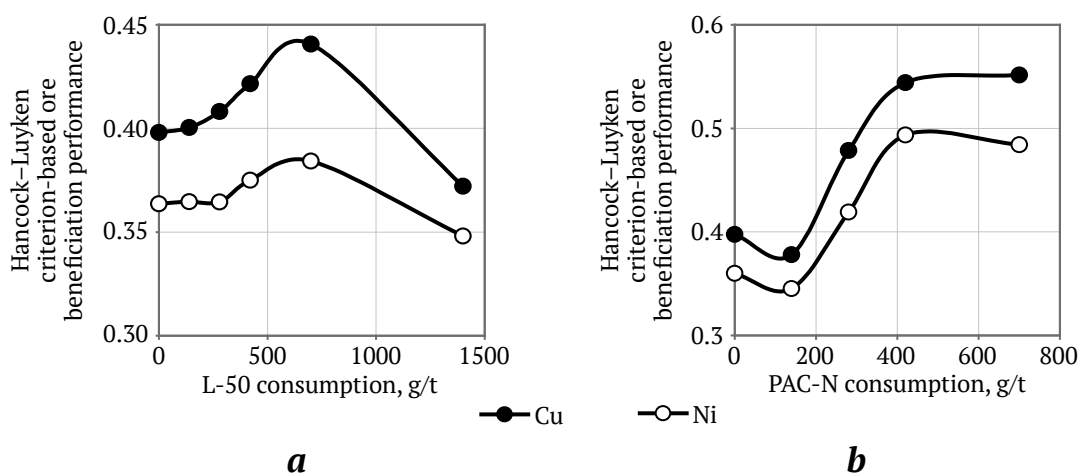
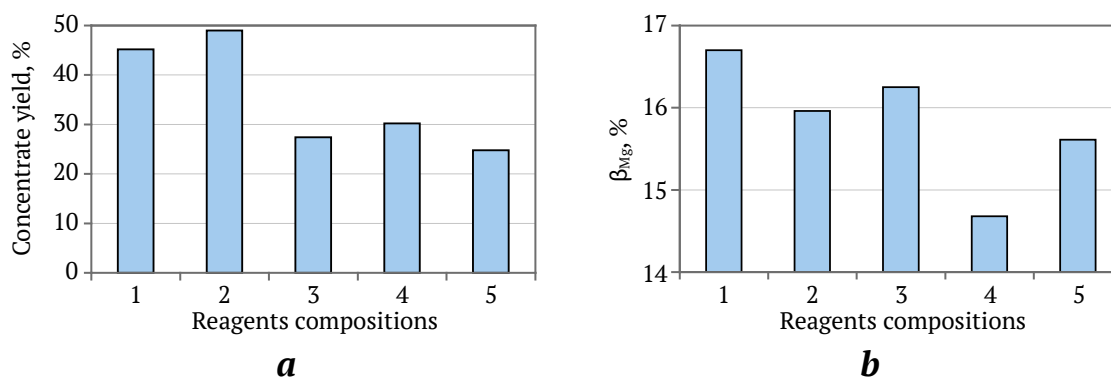
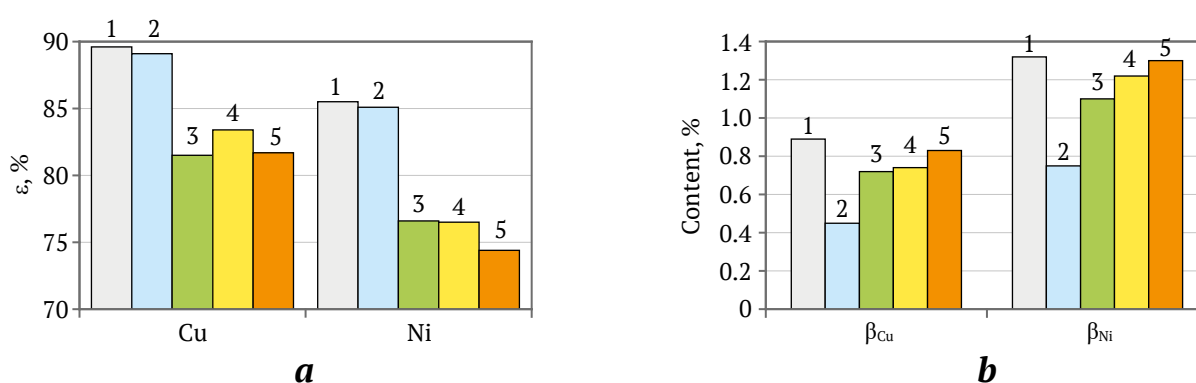


Fig. 2. The effect of depressant consumption on the ore beneficiation performance according to Hancock-Luyken criterion: *a* – L-50; *b* – PAC-N

**Fig. 3.** The effect of depressant compositions:*a* – on the concentrate yield; *b* – on the magnesium content in the concentrate**Fig. 4.** The effect of depressant compositions: *a* – on the recovery of copper and nickel into the concentrate; *b* – on the content of copper and nickel in the concentrate

In the case of preliminary addition of  $MgCl_2$ , for L-50, the  $\gamma$  value decreases from 49 to 30%, and for PAC-N, from 27 to 25%. It is obvious that the difference in  $\gamma$  values with the use of  $MgCl_2$  and a polymer reagent compared to the individual use of the latter for L-50 is 19% versus 2% for PAC-N. This is probably due to the fact that L-50 sulfo groups are more strongly attracted to the surface of minerals modified by  $Mg^{2+}$  ions than PAC-N carboxyl groups.

Fig. 3, *b* shows that composition No. 4 ( $MgCl_2$  and L-50) provides the lowest magnesium content in the concentrate: 14.7% versus 16.7% for No. 1 (without depressants) and 15.6% for No. 5 ( $MgCl_2$  and PAC-N). Overall, the magnesium content in the concentrate is reduced by about 2%.

Fig. 4, *a* shows downtrend of the recovery values  $\epsilon$  with the use of the depressants. At the same time, L-50 reduces the recovery to a lesser extent than PAC-N, as can be seen from the comparison of compositions Nos. 2, 3 and Nos. 4, 5: in the case of individual use of the depressants, L-50 reduces the recovery of copper and nickel compared to the experiment without depressants by 0.5 and 0.4%, respectively, against 8.1 and 8.9% for PAC-N at its effective consumption. When  $MgCl_2$  is first added to L-50, the recovery of cop-

per and nickel decreases by 6.2% and 9.0%, respectively, compared to the experiment without the depressants; for PAC-N, by 7.9 and 11.1%, respectively. The data in Fig. 4, *b* show that the least decrease in  $\beta$  is observed when  $MgCl_2$  and PAC-N are used.

Thus, L-50 has an effect on MS in the presence of  $MgCl_2$  only, and, at the same time, provides less effective depression as compared to PAC-N. A comparative analysis of the mechanisms of interaction between PSS and PAC-N with the MS surface, taking into account literature data, showed that for linear PSS macromolecules characterized by a smaller Kuhn segment length (4 nm versus about 20 nm), and, therefore, higher flexibility than PAC-N, some of the anionic groups are distant from the surface, or shielded, and therefore do not participate in the formation of surface charge. Unlike PSS, a PAC-N macromolecule has a wave-like, close to flat shape and is located along the mineral surface [24]. As a result, most of the anionic groups participate in the formation of surface charge. In contrast to PSS, a PAC-N macromolecule also contains hydrogen atoms capable of forming hydrogen bonds with electronegative atoms on the MS surface. This presumably determines the weaker effect of PSS on these minerals compared to CMC.

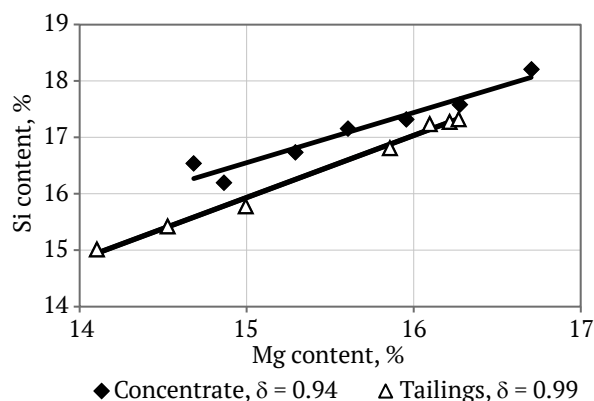


Fig. 5. Correlation between silicon and magnesium content in flotation products

At the same time, polysaccharides, in contrast to PSS, form chelated complexes with copper and nickel [25, 26], and this leads to a lower recovery of these metals into the concentrate when using PAC-N compared to L-50.

It was also found that the contents of silicon and magnesium in both concentrate and tailings are correlated with very high values of the determination coefficient  $\delta$ , as can be seen in Fig. 5; this confirms that magnesium is mainly concentrated in silicate minerals.

The attempts to use other PSS samples for MS depression, which differ from L-50 in MM values, as well as by reagents for regulating chain growth, showed very similar recovery and content values in the bulk concentrate:

- for Cu – 85.7–87.0% and 0.48–0.59%, respectively;
- for Ni – 75.2–80.4% and 0.74–0.90%, respectively.

The analysis of the dependences of  $\gamma$ , as well as  $\varepsilon$  and  $\beta$  values for copper and nickel on the MM of these PSS samples showed that the determination coefficient  $\delta$  does not exceed 0.21; this indicates that the MM value in the range from 89,000 to 208,000 g/mol has virtually no effect on the results of the ore flotation with the listed PSS samples. The reagents used to regulate chain growth during the polymerization of PSS (isopropanol, glycine, trimethylamine, see Table 1) also did not had an effect on the results.

### Practical application

Based on the experimental data obtained, the use of PSS is recommended for the flotation of copper-nickel ores with a high magnesium content in cases where it is necessary to achieve the greatest possible restriction of the content of this element in the bulk concentrate without significantly reducing the recovery of copper and nickel, especially when the use of polysaccharide depressants does not significantly re-

duce the magnesium content in the concentrate and/or there is a significant decrease in the valuable metal recovery. PSS consumption is several hundred grams per ton; it is determined experimentally for a specific ore. Before applying PSS, it is advisable to add aqueous solutions of magnesium compounds so that the consumption of  $Mg^{2+}$  ions is about 5–10 g/t. At the same time, the expected magnitude of reducing the recovery of copper and nickel into the bulk concentrate will be lower compared to the use of CMC. This will make it possible to obtain an economic effect by reducing energy consumption for the subsequent pyrometallurgical processing of the concentrate.

It also seems appropriate to conduct separate studies with linear PSS samples with a MM of more than 1 million g/mol.

### Conclusions

Based on experimental studies on bulk flotation of copper-nickel ore using sodium polystyrene sulfonate and PAC-N carboxymethyl cellulose, new scientific knowledge was obtained about the effect of the consumption and properties of polystyrene sulfonates on flotation performance.

1. It was found that in terms of reducing the concentrate yield, polystyrene sulfonate generally has a weaker depressing effect on magnesium-containing silicates than PAC-N. However, when using polystyrene sulfonate, the magnesium content in the concentrate is approximately 1% lower than when using PAC-N that allows reducing energy consumption in the course of the subsequent pyrometallurgical processing of the concentrate. Polystyrene sulfonate also provides a higher recovery of copper (up to by 7%) and nickel (up to by 8%) into the concentrate than when using PAC-N, since it does not form chelate complexes with these metals unlike polysaccharides.

2. It was found that the most effective MS depression is achieved by sequential applying magnesium chloride with a consumption of 7 g/t and polystyrene sulfonate with a consumption of 700 g/t. At the same time, the magnesium content in the concentrate is reduced by 2% compared to the flotation without depressants that justifies the use of this composition.

3. It was found that for the polystyrene sulfonate samples, the molecular weight ranging 89,000 to 208,000 g/mol, as well as the reagents used in the course of the synthesis process to regulate chain growth, have virtually no effect on the flotation results.

4. It has been shown that the practical use of PSS is advisable for the flotation of copper-nickel ores with a high magnesium content in cases where it is necessary to achieve the maximum possible decreasing the content of this element in the concentrate without significantly reducing the recovery of copper and nickel.



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### Information about the authors

**Anatoly A. Lavrinenko** – Dr. Sci. (Eng.), Chief Researcher, Head of the Laboratory, Research Institute of Comprehensive Exploitation of Mineral Resources of the Russian Academy of Sciences, Moscow, Russian Federation; ORCID [0000-0002-7955-5273](https://orcid.org/0000-0002-7955-5273); e-mail [lavrin\\_a@mail.ru](mailto:lavrin_a@mail.ru)

**Grigory Yu. Golberg** – Dr. Sci. (Eng.), Leading Researcher, Research Institute of Comprehensive Exploitation of Mineral Resources of the Russian Academy of Sciences, Moscow, Russian Federation; ORCID [0000-0002-7968-3144](https://orcid.org/0000-0002-7968-3144), Scopus ID [41761734500](https://scopus.org/authorid/41761734500); e-mail [gr\\_yu\\_g@mail.ru](mailto:gr_yu_g@mail.ru)

**Irina N. Kuznetsova** – Cand. Sci. (Eng.), Senior Researcher, Research Institute of Comprehensive Exploitation of Mineral Resources of the Russian Academy of Sciences, Moscow, Russian Federation; ORCID [0000-0002-5980-8472](https://orcid.org/0000-0002-5980-8472), Scopus ID [57201564209](https://scopus.org/authorid/57201564209); e-mail [iren-kuznetsova@mail.ru](mailto:iren-kuznetsova@mail.ru)

**Oganes G. Lusinyan** – Cand. Sci. (Eng.), Lead Engineer, Research Institute of Comprehensive Exploitation of Mineral Resources of the Russian Academy of Sciences, Moscow, Russian Federation; ORCID [0000-0002-5655-1747](https://orcid.org/0000-0002-5655-1747), Scopus ID [57201648662](https://scopus.org/authorid/57201648662); e-mail [lusinyan.oganes@yandex.ru](mailto:lusinyan.oganes@yandex.ru)

**Vladimir A. Tverskoy** – Dr. Sci. (Chem.), Professor, MIREA – Russian Technological University, Lomonosov Institute of Fine Chemical Technologies, Moscow, Russian Federation; ORCID [0000-0003-4348-8854](https://orcid.org/0000-0003-4348-8854), Scopus ID [6604012434](https://scopus.org/authorid/6604012434), ResearcherID [H-8042-2017](https://orcid.org/H-8042-2017); e-mail [tverskoj@mirea.ru](mailto:tverskoj@mirea.ru)

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