
METALLURGY OF NONFERROUS METALS

Investigation into the Influence of Sodium Lignosulfonate, Anionic Surfactants, and Their Mixtures on the Copper Cementation Rate by Zinc

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Abstract—This article is devoted to the influence of sodium lignosulfonate (SL), anionic surfactants (sodium dodecylsulfate (SDS), sodium dodecylbenzene sulfonate (SDBS)), and their mixtures on the copper cementation rate by zinc. The results demonstrated a copper cementation rate decreasing at LS and SDBS concentrations increasing. Excessive zinc consumption was also detected on copper-ion cementation due to LS and SDBS anion adsorption onto positively charged zinc cathodic areas and copper particles. This led to a decrease in the growth rate of nuclei of copper particles and energy consumption for the formation of new nucleation centers, as well as the creation of conditions for reducing the overvoltage of hydrogen evolution. At the same time, an increase in temperature led to zinc consumption decreasing in the presence of LS. The reagents under investigation could be ranked according to their degree of negative influence on copper cementation increasing in the following order: SDS < SDBS < LS. Testing LS and SDS mixtures showed their irregular influence on the copper cementation rate at different temperatures. In experiments with LS and SDBS mixtures, a linear decrease in the copper-ion cementation rate upon an increase in SDBS concentration and simultaneous zinc-consumption enhancement was fixed. Due to the negative influence of the investigated reagents, we offered a purification method from organic impurities through the use of multilayered aluminosilicates modified by cationic surfactants. The results indicate the high effectiveness of removing organic impurities from solutions, which allowed us to increase the cementation rate in the presence of the LS and SDBS mixture by 50% while, at the same time, decreasing zinc consumption.

Keywords: cementation, copper, zinc, sodium lignosulfonate, sodium dodecylsulfate, sodium dodecylbenzenesulfonate

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INTRODUCTION

In hydrometallurgy, organic reagents and surfactants are often used, for example, in electrolysis, to create dense foam on the bath surface [1, 2] or to obtain powders of a given size [3–7]. In the autoclave processing of sulfide zinc raw materials, surfactants are also often used to reduce the wettability of minerals by molten sulfur formed during leaching [8–10]. A number of papers [11–13] indicate deterioration in the performance of hydrolytic purification from iron and cementation purification from copper, nickel, and cobalt from solutions after autoclave leaching in the presence of high amounts of lignosulfonates.

Studies have shown that the cementation process is very sensitive to the presence of surfactants and organic impurities [11–14]: the extraction of metals from solutions decreases and the particle size of

cementate decreases [15–17], which is associated with an increase in hydrogen evolution and passivation of the cementator surface. However, individual studies indicate a positive effect of some organic compounds (nettle extract and sodium diethyldithiocarbamate) on the cementation rate of copper with zinc and a decrease in the zinc consumption, including to the evolution of hydrogen [18–20]. Therefore, a preliminary assessment of the effect of organic reagents used in leaching on the subsequent stages of the process plays an important role in predicting the feasibility of using reagents.

Our earlier studies have shown the possibility of reducing the consumption of lignosulfonates due to the additional introduction of anionic surfactants [21, 22]. This paper is devoted to studying the effect of sodium lignosulfonate, anionic surfactants, and their

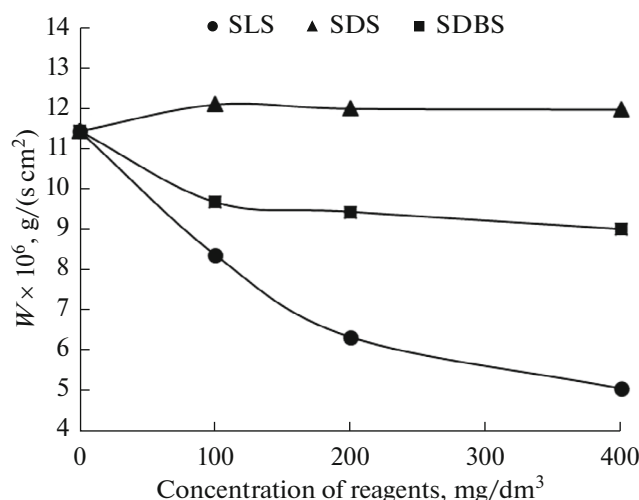


Fig. 1. Influence of the concentration of reagents on the cementation rate of copper ions ($t = 45^\circ\text{C}$). (●) SLS, (▲) SDS, and (■) SDBS.

mixtures on the indicators of cementation purification of solutions from copper.

EXPERIMENTAL TECHNIQUE

Experiments on the cementation of copper were carried out using the technique of a rotating disk made of zinc of Ts1 grade, which was glued into a polyamide shell. In the course of the experiments, temperature ($t = 25\text{--}65^\circ\text{C}$), duration ($\tau = 60\text{--}900 \text{ s}$), the concentration of sodium lignosulfonate (SLS) produced by Solikamskbumprom JSC, sodium dodecyl sulfate (SDS), and sodium dodecylbenzenesulfonate (SDBS) and their mixtures ($50\text{--}400 \text{ mg/dm}^3$) were varied. The disk rotation speed remained unchanged and was 800 rpm, the initial copper concentration was 0.54 g/dm^3 , and the solution pH was 5.0. After cementation, the solutions were analyzed for copper and zinc content on an Analytic Jena novAA 300 atomic absorption spectrophotometer.

The specific reduced rate of cementation of copper ($W, \text{ g/(s cm}^2\text{)}$) was calculated using the formula

$$W = \frac{(C_{0\text{Cu}} - C_{\tau\text{Cu}})V}{\tau S}, \quad (1)$$

where V is the volume of the solution, dm^3 ; $C_{0\text{Cu}}$ and $C_{\tau\text{Cu}}$ are initial and current copper concentration, g/dm^3 ; τ is duration of the experiment, s; and $S = 3.14 \text{ cm}^2$ is disk area.

The specific dissolution rate of zinc ($v, \text{ g/(s cm}^2\text{)}$) was determined to establish its excess consumption during the cementation of copper. The following equation was used:

$$v = \frac{C_{\tau\text{Zn}}V}{\tau S}. \quad (2)$$

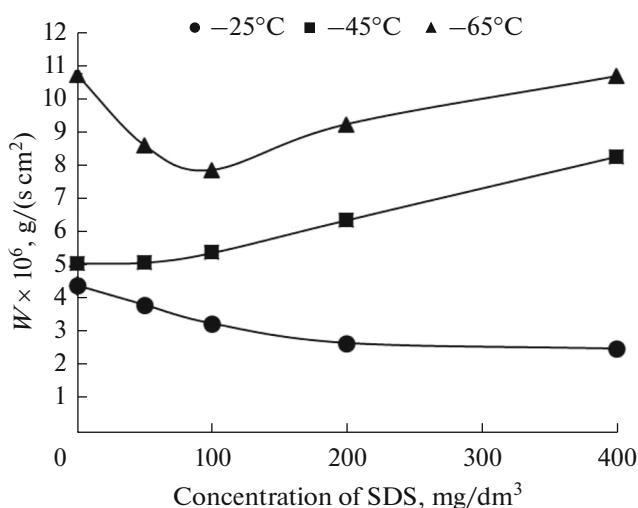


Fig. 2. Influence of a mixture of SLS + SDS on the cementation rate of copper ions at different temperatures ($C_{\text{SLS}} = 400 \text{ mg/dm}^3$). (●) 25, (■) 45, and (▲) 65°C .

The size of the cementate particles was assessed micrometrically using a Micromed 3 microscope. The sample was preliminarily diluted with technical alcohol ≈ 10 times and applied to a glass slide. A video eyepiece was used to take pictures of the particles. The resulting images were processed using an ImageJ specialized software, and the average particle size was determined.

The adsorptive removal of organic impurities was carried out using a highly dispersed layered aluminosilicate modified with a cationic surfactant (hereinafter, MAS) [23] (the content of the cationic surfactant was 5%). The MAS consumption was maintained at 0.5 g/dm^3 and the sorption time was 10 min.

RESULTS AND DISCUSSION

Preliminary experiments on the cementation of copper ions in the presence of individual reagents (Fig. 1) showed a significant negative effect of SLS on the process, with the addition of which its rate decreased by 30–55%. With the introduction of 100 mg/dm^3 of SDBS, the cementation rate of copper ions decreased 15%, and a further increase in its concentration to 400 mg/dm^3 led to a smooth decrease in W by another 6%. The addition of SDS had no effect on the cementation rate at $t = 45^\circ\text{C}$, but at 65°C it decreased 11%. Thus, the studied surfactants can be ranked according to the degree of increase in the negative effect they have on the cementation of copper ions in the following order: $\text{SDS} < \text{SDBS} < \text{SLS}$.

Testing a mixture of SLS + SDS showed its non-uniform effect on the cementation rate at various temperatures (Fig. 2). Thus, at room temperature, the values of W decrease almost linearly from 4.4×10^{-6} to

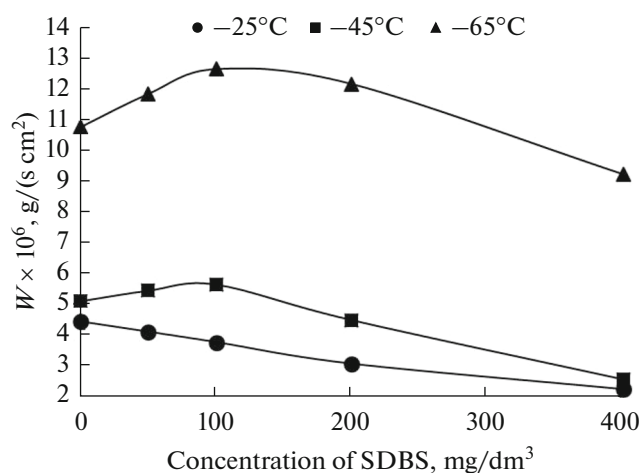


Fig. 3. Influence of a mixture of SLS + SDBS on the cementation rate of copper ions at different temperatures ($C_{\text{SLS}} = 400 \text{ mg/dm}^3$). (●) 25, (■) 45, and (▲) 65°C.

$2.5 \times 10^{-6} \text{ g/(s cm}^2\text{)}$ at $C_{\text{SLS}} = 400 \text{ mg/dm}^3$. An increase in t up to 45°C leads to a linear increase in the cementation rate of copper ions with an increase in the concentration of SDS in the mixture up to $8.3 \times 10^{-6} \text{ g/(s cm}^2\text{)}$. This may be due to the physical

desorption of SLS from the surface of the zinc disk during heating. The minimum on the curve at $t = 65^\circ\text{C}$ (100 mg/dm^3) may be due to a decrease in the over-voltage of hydrogen evolution upon the addition of SLS to SDS with increasing temperature.

When testing a mixture of SLS + SDBS (Fig. 3) at room temperature, a linear decrease in the cementation rate of copper ions was recorded with an increase in the concentration of SDBS by 54% (at $C_{\text{SDBS}} = 400 \text{ mg/dm}^3$). In the range of $C_{\text{SDBS}} = 100\text{--}400 \text{ mg/dm}^3$ at $t = 45$ and 65°C , a linear decrease in the value of W is recorded. However, at concentrations of SDBS up to 100 mg/dm^3 in a mixture with 400 mg/dm^3 SLS, an insignificant increase in the cementation rate is observed from 5.1×10^{-6} to $5.6 \times 10^{-6} \text{ g/(s cm}^2\text{)}$ at $t = 45^\circ\text{C}$ and from 10.8×10^{-6} to $12.6 \times 10^{-6} \text{ g/(s cm}^2\text{)}$ at 65°C .

Table 1 shows the results of calculations of the consumption of the metal-cementing agent for the reduction of copper ions relative to the stoichiometric molar consumption of zinc. The data indicate an excessive consumption of zinc (Zn/Cu) during cementation in the presence of SLS, and its values decrease with an increase in temperature from 1.33 (at $t = 45^\circ\text{C}$) to 1.15 (at 65°C) due to the desorption of SLS from the

Table 1. Zinc consumption for the cementation of copper ions in the presence of reagents

Reagent	$C_{\text{surfactant}}, \text{mg/dm}^3$	$t, ^\circ\text{C}$	$W \times 10^6, \text{g/(s cm}^2\text{)}$	$v \times 10^6, \text{g/(s cm}^2\text{)}$	Zn/Cu
Without surfactant	—	25	84.48	89.05	1.03
		45	114.56	126.75	1.09
		65	158.08	180.05	1.12
SLS	100	25	64.64	91.65	1.40
		45	83.84	113.75	1.33
		65	106.88	124.15	1.15
SDS	100	25	80.64	75.4	0.92
		45	121.6	117	0.95
		65	152.96	161.2	1.04
SDBS	100	25	109.44	118.95	1.07
		45	97.28	113.1	1.15
		65	145.92	165.1	1.12
SLS	400	25	44.16	58.5	1.30
		45	51.2	64.35	1.24
		65	107.52	133.9	1.22
SLS + SDS	400 + 100	25	32.64	36.4	1.10
		45	54.4	69.55	1.26
		65	78.72	117	1.46
SLS + SDBS	400 + 100	25	37.76	41.6	1.08
		45	56.32	66.95	1.17
		65	126.72	161.85	1.26

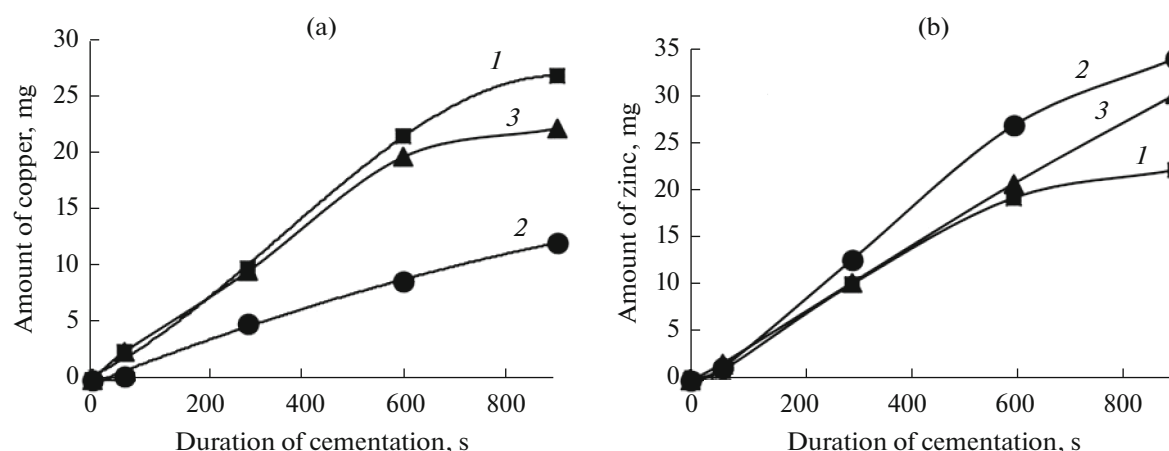


Fig. 4. Influence of solution purification with modified aluminosilicate on the kinetics of metallic copper isolation (a) and zinc dissolution (b) in the cementation process. $t = 65^{\circ}\text{C}$, $C_{0\text{Cu}} = 0.5 \text{ g/dm}^3$, and $V = 0.1 \text{ dm}^3$. (1) Solution without adding reagents; (2) solution before purification from reagents containing, mg/dm^3 , 400SLS + 400SDBS; and (3) solution after purification.

surface of the cementing agent. The SDBS reagent insignificantly increased the consumption of the cementing agent with increasing temperature. In addition, the average size of cementate particles in the presence of organic impurities decreased from $105 \mu\text{m}$ without surfactants to $\approx 90 \mu\text{m}$ upon their introduction (Table 2). In the presence of SLS mixtures with anionic surfactants, an increase in the consumption of the cementing agent with increasing temperature is noted, which may be associated with a decrease in the

overvoltage of hydrogen evolution due to heating and due to the adsorption of surfactants on positively charged cathode sites, including on the surface of freshly deposited copper. The latter assumption is confirmed by a decrease in the average particle size of cementate particles to $70\text{--}85 \mu\text{m}$, which indicates the consumption of energy of the system for the creation of new nucleation centers, the growth of which is suppressed by the adsorption of organic impurities.

In view of the negative effect of mixtures of SLS with anionic surfactants, an assessment was made of the possibility of purifying solutions using aluminosilicate modified with a cationic surfactant (MAS). The mechanism of action of this sorbent is the physical adsorption of anions by the positively charged surface of the MAS. The experimental results indicate (Fig. 4) an increase in the degree of copper extraction by $\approx 50\%$ after purification from the mixture of SLS + SDBS reagents. In this case, the cementation rate increased from 4.4×10^{-6} to $10.3 \times 10^{-6} \text{ g/(s cm}^2\text{)}$, and without additives it was $11.3 \times 10^{-6} \text{ g/(s cm}^2\text{)}$. Zinc consumption (Zn/Cu) also decreased from 2.8 to 1.04 after purification.

CONCLUSIONS

The use of lignosulfonates and their mixtures with anionic surfactants at the stage of autoclave leaching can lead to a decrease in the rate of copper extraction and an increase in the consumption of the cementing agent due to a decrease in the overvoltage of hydrogen evolution. It is shown that the studied surfactants can be ranked according to the degree of increase in their negative effect on the cementation of copper ions in the following order: $\text{SDS} < \text{SDBS} < \text{SLS}$. The com-

Table 2. Results of the analysis of the particle size of the cement sludge

Reagent	$C_{\text{@ПAB}}$, mg/dm^3	Cp. particle size, μm
Without surfactant	0	105.58
SLS	200	99.83
SDS	200	88.40
SDBS	200	90.81
50 mg/dm^3 LS + SDS	200	90.96
200 mg/dm^3 LS + SDS	200	87.54
400 mg/dm^3 LS + SDS	200	80.45
50 mg/dm^3 LS + SDBS	200	67.71
200 mg/dm^3 LS + SDBS	200	68.30
400 mg/dm^3 LS + SDBS	200	69.69

$C_{0\text{Cu}} = 0.5 \text{ g/dm}^3$, $\tau = 900 \text{ s}$, and $t = 45^{\circ}\text{C}$.

bined addition of SLS and SDBS leads to a decrease in the cementation rate of copper ions with an increase in the concentration of SDBSN. When using a mixture of SLS + SDS, a linear decrease in the rate at room temperature and its increase at $t = 45^{\circ}\text{C}$ and an increase in the consumption of SDS were observed.

A method for minimizing the effect of surfactants through the use of a modified highly layered aluminosilicate (MAS) has been proposed. The proposed method for removing organic impurities from solutions may be relevant for the traditional technology of processing zinc concentrates, where lignosulfonates are used in small amounts in zinc electroextraction.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- Alfantazi, A.M. and Dreisinger, D.B., Foaming behavior of surfactants for acid mist control in zinc electrolysis processes, *Hydrometallurgy*, 2003, vol. 69, nos. 1–3, pp. 57–72.
[https://doi.org/10.1016/S0304-386X\(03\)00002-1](https://doi.org/10.1016/S0304-386X(03)00002-1)
- Freire, N.H.J., Majuste, D., Angora, M.A., and Ciminelli, V.S.T., The effect of organic impurities and additive on nickel electrowinning and product quality, *Hydrometallurgy*, 2017, vol. 169, pp. 112–123.
<https://doi.org/10.1016/j.hydromet.2016.12.009>
- Dang, D.M.T., Dang, C.M., and Fribourg-Blanc, E., Investigation of the influence of different surfactants on controlling the size of silver nanoparticles, *Int. J. Nanotechnol.*, 2015, vol. 12, nos. 5–7, pp. 505–514.
<https://doi.org/10.1504/IJNT.2015.067908>
- Yue, S.X., Su, Y.C., Luo, Z.B., Yu, Q.S., Tursun, R., and Zhang, J., Influence of surfactant interaction on ultrafine copper powder electrodeposition, *Materialwiss. Werkstofftech.*, 2019, vol. 50, no. 7, pp. 856–863.
<https://doi.org/10.1002/mawe.201800103>
- Demeev, B.B., Dauletbay, A., and Nauryzbaev, M.K., The effect of organic surface-active additives upon the kinetics of electrodeposition of ultrafine copper powder, *Chem. Eng. Trans.*, 2016, vol. 47, pp. 211–216.
<https://doi.org/10.3303/CET1647036>
- Li, Q., Zhao, Y., and Zhang, C., Influence of cetyltrimethylammonium bromide and sodium lauryl sulfate on production of zinc powders by alkaline electrowinning, *Russ. J. Non-Ferrous Met.*, 2014, vol. 55, no. 1, pp. 65–72.
<https://doi.org/10.3103/S1067821214010131>
- Salem, J.K., Hammad, T.M., Almoqayyed, S., and Hejazy, N.K., Influence of cationic surfactant and temperature on the growth of ZnO nanoparticles, *Tenside, Surfactants, Deterg.*, 2018, vol. 55, no. 3, pp. 188–195.
<https://doi.org/10.3139/113.110563>
- Owusu, G., Dreisinger, D.B., and Peters, E., Interfacial effects of surface-active agents under zinc pressure leach conditions, *Metall. Mater. Trans. B*, 1995, vol. 26, no. 1, pp. 5–12.
<https://doi.org/10.1007/BF02648972>
- Owusu, G. and Dreisinger, D.B., Interfacial properties determinations in liquid sulfur, aqueous zinc sulfate and zinc sulfide systems, *Hydrometallurgy*, 1996, vol. 43, nos. 1–3, pp. 207–218.
- Owusu, G., Peters, E., and Dreisinger, D.B., Surface tensions and contact angles due to lignin sulphonates in the system: Liquid sulphur, aqueous zinc sulphate and zinc sulphide, *Can. J. Chem. Eng.*, 1992, vol. 70, no. 1, pp. 173–180.
<https://doi.org/10.1002/cjce.5450700125>
- Karavasteva, M., The effect of certain surfactants on the cementation of copper by suspended zinc particles, *Hydrometallurgy*, 1996, vol. 43, nos. 1–3, pp. 379–385.
- Karavasteva, M., The influence of copper on the effect of certain surfactants during the cementation of cadmium by suspended zinc particles, *Hydrometallurgy*, 1998, vol. 48, no. 3, pp. 361–366.
- Karavasteva, M., The effect of certain surfactants on the cementation of nickel from zinc sulphate solutions by suspended zinc particles in the presence of copper, *Can. Metall. Q.*, 1999, vol. 38, no. 3, pp. 207–210.
[https://doi.org/10.1016/S0008-4433\(99\)00008-7](https://doi.org/10.1016/S0008-4433(99)00008-7)
- Karavasteva, M., The effect of certain surfactants on the cementation of cobalt from zinc sulphate solutions by suspended zinc particles in the presence of copper or antimony, *Can. Metall. Q.*, 2001, vol. 40, no. 2, pp. 179–184.
<https://doi.org/10.1179/000844301794388416>
- Granata, G., Tsendorj, U., Liu, W., and Tokoro, C., Direct recovery of copper nanoparticles from leach pad drainage by surfactant-assisted cementation with iron powder, *Colloids Surf., A*, 2019, vol. 580, p. 123719.
<https://doi.org/10.1016/j.colsurfa.2019.123719>
- Begletsova, N., Selifonova, E., Chumakov, A., Al-Alwani, A., Zakharevich, A., Chernova, R., and Glukhovskoy, E., Chemical synthesis of copper nanoparticles in aqueous solutions in the presence of anionic surfactant sodium dodecyl sulfate, *Colloids Surf., A*, 2018, vol. 552, pp. 75–80.
<https://doi.org/10.1016/j.colsurfa.2018.05.023>
- Cheng, X., Zhang, X., Yin, H., Wang, A., and Xu, Y., Modifier effects on chemical reduction synthesis of nanostructured copper, *Appl. Surf. Sci.*, 2006, vol. 253, pp. 2727–2732.
<https://doi.org/10.1016/j.apsusc.2006.05.125>
- Zaabar, A., Aitout, R., Amoura, D., Maizia, R., Makhloufi, L., and Saidani, B., Effect of nettle plant extract on the overconsumption diminution of zinc as sacrificial metal during cementation of copper, *Miner. Eng.*, 2019, vol. 142, article no. 105933.
<https://doi.org/10.1016/j.mineng.2019.105933>
- Zaabar, A., Aitout, R., Makhloufi, L., Alilat, K., Maziz, S., and Saidani, B., Effect of nettle plant extract

- on the cementation of copper onto zinc in acidic sulfate solutions, *Hydrometallurgy*, 2013, vol. 136, pp. 58–64. <https://doi.org/10.1016/j.hydromet.2013.03.004>
20. El-Saharty, A.A., El-Nammamy, N.H., and El-Araby, H.A., Sodium diethyldithiocarbamate as accelerator of the rate of copper cementation, *Egypt. J. Aquat. Res.*, 2015, vol. 41, pp. 289–293. <https://doi.org/10.1016/j.ejar.2015.08.002>
21. Kolmachikhina, E.B., Ryzhkova, E.A., Dmitrieva, D.V., Sviridov, V.V., and Naboychenko, S.S., Lignosulfonate, anionic surfactants and their mixtures influence on water solutions surface tension and zinc concentrate pressure leaching, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2019, vol. 525, no. 1, p. 012023. <https://doi.org/10.1088/1757-899X/525/1/012023>
22. Khazieva, E.B., Sviridov, V.V., Menshchikov, V.A., and Naboychenko, S.S., Influence of surface-active substances on sulfur state during the autoclave leaching of zinc concentrates, *Tsvetn. Met. (Moscow, Russ. Fed.)*, 2017, no. 2, pp. 46–50.
23. Ordinartsev, D.P., Sviridov, A.V., and Sviridov, V.V., Extracting vanadium, molybdenum, and tungsten from acidic solutions via adsorption on modified montmorillonite, *Russ. J. Phys. Chem. A*, 2018, vol. 92, no. 10, pp. 2060–2064. <https://doi.org/10.1134/S0036024418100229>

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