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Study of the chemical composition of dichloromethane extract *Tamarix hispida*

In this article, first time there was observed dichloromethane extract from the aerial part of the *Tamarix hispida* (*Tamaricaceae*) harvested in the Almaty region of the Republic of Kazakhstan. The extraction of the previously dried and crushed vegetable raw material was carried out with dichloromethane in a Soxhlet apparatus. The extract was investigated by gas chromatography with mass spectrometry module under the following conditions: SHP-5MS gas chromatography column (30 m × 250 mm × 0.25 mm) temperature at 40 °C for 5 minutes. As the carrier gas we used helium at a flow rate of 1 ml/min; with temperature programming up to 250 °C and a temperature change of 50 °C/min. Sample 0.2 µl was taken for assay. The compounds were identified by mass spectra and retention times, using the NIST library and Wiley GC/MS. As a result 25 compounds were identified in the dichloromethane extract which the highest contents were: piceol; methyl 3-(acetoxo)-20-hydroxy-12-en-28-oate; 6,10,14-trimethyl-2-pentadecanone; 2-hydroxy-1,1,10-trimethyl-6,9-epidioxycyclodecalin, respectively. The presence of halogen-organic compounds: heptadecyl ester of 3-chloropropionic acid, 2-chlorophenylethyl ester of fumaric acid and 1,54-dibromo tetrapentacotane were detected in the extract. Halogen-containing compounds were firstly detected in the genus *Tamarix*.

Keywords: dichloromethane extract, *Tamaricaceae*, *Tamarix hispida*, aerial mass, halogenorganic compounds, dichloromethane, chromatography-mass spectrometry, Soxhlet method.

Tamarix are decorative bushes or trees, mostly evergreen, with pink or white flowers. They are relatively long-lived plants that can tolerate a wide range of environmental conditions and withstand abiotic stresses, such as high temperatures, salt and drought. *Tamarix* withstands saline soils, regulating the balance of salt through the release of secret salts through the deciduous glands and consuming large amounts of water from underground sources [1, 2].

Tamarix is widespread in Central Asia, India, Pakistan, and Southern Europe in the Caucasus, the Crimea and even in some regions of North America. Plant *Tamarix hispida* Willd. belongs to the genus *Tamarix* family *Tamaricaceae*. In folk medicine the plant is used for treating rheumatism, syphilis, infertility, and as an astringent for gastrointestinal diseases and bleeding [3]. *Tamarix hispida* Willd. is characterized by the diversity of the composition of natural metabolites, which have a wide range of biological effects. Currently there are studies on biologically active substances of polyphenolic nature (tannins, flavonoids and their glycosides, phenolic acids) [3–6]. In the aspect we investigated the data on the study of the lipophilic extract having the most interest.

Continuing the study of the chemical composition we studied the dichloromethane extract obtained from the aerial part of *Tamarix hispida* Willd. raw plant materials harvested in the Almaty region during the flowering phase in 2016.

The extraction of the previously dried and crush vegetable raw material was carried out by dichloromethane in a Soxhlet apparatus. The extract was examined by gas chromatography using a gas chromatograph with an Agilent Technologies 7000 GS / MS mass-selective detector under the following conditions: a SHP-5MS column (30 m × 250 mm × 0.25 mm) was used, the gas velocity of the helium carrier was

1 ml/min. The gas chromatography column temperature at 40 °C for 5 minutes; with temperature programming up to 250 °C with a temperature change rate of 5 °C/min. For assay 0,2 µl sample was taken.

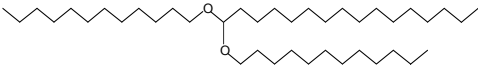
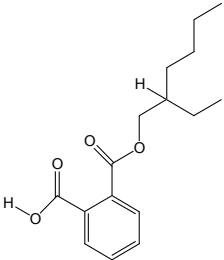
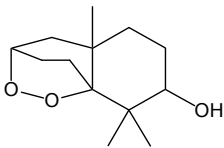
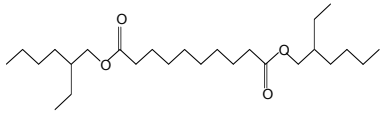
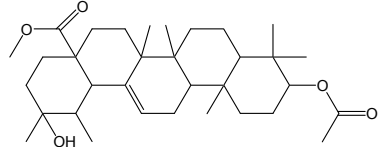
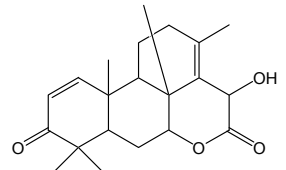
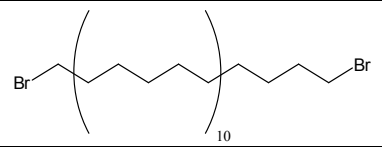
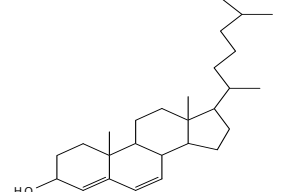
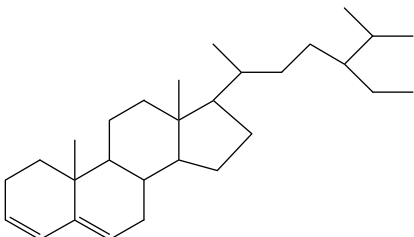
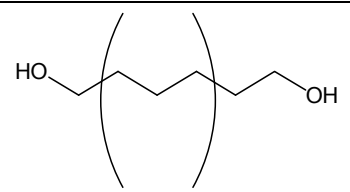
The components were identified by mass spectra and retention times, using the NIST library and Wiley GC / MS. The results are shown in Table.

Table

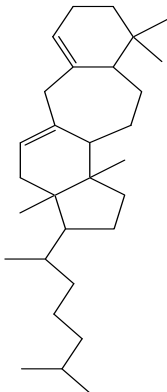
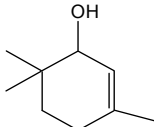
Component composition of the dichloromethane extract of the aerial mass *Tamarix hispida* Willd.

No.	Compound	Structure	M, g/mol	RT, min	W, %
1	2	3	4	5	6
1	4'-Hydroxy acetophenone (Piceol) $C_8H_8O_2$		136	3.61	36.91
2	Fumaric acid 2-chlorophenylethyl ester $C_{12}H_{11}ClO_4$		254	24.38	1.33
3	3,7,11,15-Tetramethyl-2-hexadecen-1-ol $C_{20}H_{40}O$		296	26.74	2.30
4	6,10,14-Trimethyl -2-pentadecanone $C_{18}H_{36}O$		268	33.56	7.82
5	1,2-Epoxyoctadecane $C_{18}H_{36}O$		268	34.51	1.31
6	3-Chloropropionic acid, heptadecyl ether $C_{20}H_{39}ClO_2$		346	35.35	2.75
7	2-Hydroxy-1,1,10-trimethyl- 6,9-epidioxydecalin $C_{13}H_{22}O_3$		226	42.04	0.56
8	3,7,11,15-Tetramethyl-1-hexadecyn-3-ol $C_{20}H_{38}O$		294	42.41	0.46
9	(8Z) -14-Methyl-8-hexadecenal $C_{17}H_{32}O$		252	42.52	0.59
10	Izopropyl 9-octadecenoate $C_{21}H_{40}O_2$		324	43.19	1.30
11	4,7,7-Trimethylbicyclo[4.1.0]hepta- 3-ol $C_{10}H_{18}O$		154	44.08	0.96
12	(2E)-5-hydroxy-3,4,4-trimethyl- 2-hexenoic acid $C_9H_{16}O_3$		172	45.13	0.48

Continuation of Table

1	2	3	4	5	6
13	Ethyleneglycol monododecyl ether $C_{40}H_{82}O_2$		594	47.22	1.85
14	Monoethylhexylphthalate $C_{16}H_{22}O_4$		278	48.06	0.39
15	2-Hydroxy-1,1,10-trimethyl-6,9-epidioxycalinal $C_{13}H_{22}O_3$		226	48.73	7.04
16	Decanedioic acid bis(2-ethylhexyl) ester $C_{26}H_{50}O_4$		426	49.55	0.63
17	Methyl 3-(acetyloxy)-20-hydroxyurs-12-en-28-oate $C_{33}H_{52}O_5$		528	51.38	22.26
18	15-Hydroxy-4-methylpicrasa-1,13-diene-3,16-dione $C_{21}H_{28}O_4$		344	52.24	1.71
19	1,54-Dibromo-tetrapentacontane $C_{54}H_{108}Br_2$		914	52.91	1.16
20	4,6-Cholestadien-3β-ol $C_{27}H_{44}O$		384	54.96	1.25
21	Stigmastan-3,5-diene $C_{29}H_{48}$		396	55.20	0.96
22	1,30-Triacontanediol $C_{30}H_{62}O_2$		454	55.53	0.89

Continuation of Table

1	2	3	4	5	6
23	3-(5,5-dimethyl-hexyl)-3a,10,10,12b-tetramethyl-1,2,3,3a,4,6,8,9,10,10a,11,12,12a,12b-tetradecahydro-benzo[4,5]cyclohepta[1,2-E]indene $C_{30}H_{50}$		410	57.77	2.54
24	3,6,6-Trimethyl-2-cyclohexen-1-ol $C_9H_{16}O$		140	60.32	2.60

Note. W is the content of the components; RT is the retention time; M is molar mass.

In the dichloromethane extract, 25 compounds were identified, of which the most abundant were: piceol (36.91 %); methyl 3-(acetyloxy)-20-hydroxyurs-12-en-28-oate (22.26 %); 6,10,14-trimethyl-2-pentadecanone (7.82 %); 2-hydroxy-1,1,10-trimethyl-6,9-epidioxydecalin (7.04 %), respectively.

In the extract halogen-organic compounds were detected in small amounts: 3-chloropropionic acid, 2.75 % heptadecyl ester, 2 fumaric acid 2-chlorophenylethylester (1.33 %) and 1,54-Dibromo tetrapentacotane (1.16 %). Halogen-organic compounds were first identified in the genus *Tamarix*.

From the literature data it is known that halogenated derivatives are rarely found in plants, but to date, chlorine and bromine containing mono-, di-, tri-, sesquiterpenoids, iridoids, alkaloids, phenolic compounds, fatty acids and other compounds isolated from plant material are known [6, 7].

It should be noted that previously we isolated some terpenoids, steroids and limiting alcohols from the native species of *Tamarix* plants, and some terpenoids were identified and characterized by physicochemical data [6–9]. The chemical composition of the dichloromethane extract from *Tamarix hispida* was firstly analyzed by gas chromatography.

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***Tamarix hispida* өсімдігінің дихлорметандық экстрактының химиялық құрамы**

Мақалада алғаш рет Қазақстанның Алматы аймағынан жиналған *Tamarix hispida* Willd. (*Tamaricaceae*) өсімдігінің жер үсті бөлігінен алынған дихлорметан экстрактының химиялық құрамы қарастырылған. Алдын ала кептіріліп, ұнтақталған өсімдік шикізатының экстракциясы Сокслет аппаратында дихлорметан ерітіндісімен жүргізілді. Алынған экстракт газды хроматография және масс-спектрометрия әдісімен келесі шарт бойынша зерттелді: 40 °C температурада 5 мин аралығында SHP-5MS (30 м × 250 мм × 0.25 мм) газхроматографиялық бағанасында ұсталынды; тасушы газ — гелий ағынының жылдамдығы 1 мл/мин; бағдарламалау температурасы 250 °C дейін және температураның өзгеруі 5 °C/мин. Сынама көлемі 0,2 мкл. NIST және Wiley GC/MS кітапханасын қолдана отырып, масс-спектрі және ұстау уақыты бойынша сәйкестендірілді. Дихлорметан экстрактысында 25 қосылыс анықталды, оның ішінде сәйкесінше пинеол; метил 3-(ацетокси)-20-гидроксиурс-12-ен-28-оат; 6,10,14-триметил-2-пентадеканон, 2-гидрокси-1,1,10-триметил-6,9-эпидиоксидакалин көп мөлшерде байқалды. Зерттелген экстрактада галогенорганикалық қосылыстар аз мөлшерде кездеседі: 3-хлорпропион қышқылының гептадецил эфирі, фумар қышқылының 2-хлорфенилэтил эфирі және тетрапентаконтанның 1,54-дибромы. Алғаш рет *Tamarix* өсімдік түрінде галоген туындылары табылды.

Кілт сөздер: дихлорметан экстракт, *Tamaricaceae*, *Tamarix hispida*, өсімдігінің жер үсті бөлігінен, галогенорганикалық қосылыстар, хромато-масс-спектрометрия, Сокслет әдісі.

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Исследование химического состава дихлорметанового экстракта *Tamarix hispida*

В статье впервые рассмотрен химический состав дихлорметанового экстракта, полученного из надземной массы растения *Tamarix hispida* Willd. (*Tamaricaceae*), заготовленного в Алматинском регионе Республики Казахстан. Экстракцию предварительно высушенного и измельченного растительного сырья проводили дихлорметаном в аппарате Сокслета. Полученный экстракт исследовали методом газовой хроматографии с масс-спектрометрией при следующих условиях: газохроматографическую колонку SHP-5MS (30 м × 250 мм × 0.25 мм) выдерживали при температуре 40 °C в течение 5 мин; газ-носитель — гелий со скоростью потока 1 мл/мин; с программированием температуры до 250 °C и скоростью изменения температуры 5 °C/мин. Объем аликвоты 0,2 мкл. Соединения идентифицировали по масс-спектрам и времени удерживания, с использованием библиотеки NIST и Wiley GC/MS. В дихлорметановом экстракте идентифицировали 25 соединений, из которых в наибольшем количестве составили: пинеол; метил 3-(ацетокси)-20-гидроксиурс-12-ен-28-оат; 6,10,14-триметил-2-пентадеканон; 2-гидрокси-1,1,10-триметил-6,9-эпидиоксидакалин соответственно. В исследуемом экстракте выявили присутствие галогенорганических соединений в небольших количествах: гептадециловый эфир 3-хлорпропионовой кислоты, 2-хлорфенилэтиловый эфир фумаровой кислоты и 1,54-дибром тетрапентаконтан. Галогенопроизводные соединения впервые обнаружены в растениях рода *Tamarix*.

Ключевые слова: дихлорметановый экстракт, *Tamaricaceae*, *Tamarix hispida*, надземная масса, галогенорганические соединения, дихлорметан, хромато-масс-спектрометрия, метод Сокслета.

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Scale inhibitor testing of new organophosphoric compounds

A new generation of organophosphorous scale inhibitors has been developed. Inhibitors are intended to prevent the deposition of sulphate and carbonate salts in surface and downhole equipment during oil production, treatment and transportation. The I type inhibitor (aminophosphonic acid) was synthesized through the Moedritzer-Irani reaction of the condensation of 4,4'-(propane-2,2-diylbis(4,1-phenylene))bis(oxy)dianiline (A diamine) with formaldehyde and phosphorous acid, the II type inhibitor by phosphorylation of glycolized PET flex-(bis-hydroxyethyl terephthalate) with polyphosphoric acid. The structure of the developed organophosphorus compounds was confirmed by IR spectroscopy. High inhibitory efficacy of the first and second types of reagents for the deposition of carbonate and calcium sulphates was revealed. The morphology of the solid sediments of mineral salts was studied by scanning electron microscopy (SEM). It is revealed that the inhibition of crystal formation occurs at the stage of nucleation. Embedding in the surface of crystal nucleus, the inhibitors prevent formation of crystalline phase in a solution and crystal growth.

Keywords: organophosphoric compounds, aminophosphonic acid, phosphoric acid ester, scaling inhibitors, synthesis, reaction of Moedritzer-Irani, glycolize, testing.

Introduction

Oil production in Kazakhstan has been steadily increasing over the last several years, while the average water cut of oil wells has been increasing, for some fields, water cut exceeds 90 % [1]. As a result of increased water cutting of the extracted products, the inorganic salt scale precipitation on the surface of pumping equipment, infield equipment, in production columns, in oil collection and treatment systems increases that result in a failure of expensive equipment, capital expenditures on equipment repair, and decline in oil production [2].

The efficiency of suppression of scale inhibitors is comprehensive, taking into account physical and chemical processes, the composition of produced water, development of wells, etc. Preferred method of combating scale buildup is inhibitor protection that refers to preventative methods [3].

Inorganic compounds, different classes of organic compounds can be scale inhibitors, but the compounds based on derivatives of phosphonic and phosphoric acids have received the greatest distribution, as these compounds are capable of forming complex compounds with salt-forming cations and preventing their interaction with salt-forming anions [4].

In this paper, we present the results of a comparative evaluation of the effectiveness of protection against the deposition of sulphate and carbonate salts by new organophosphoric compounds of 2 types — aminophosphonic acid and phosphoric ester of bis-hydroxyethyl terephthalate.

Experimental

Reagents and materials. Phosphonic acid 98+% (Alfa Aesar, Karlsruhe, Germany); formaldehyde, aqueous 37 % solution (Sigma-Aldrich); 4,4'-(propane-2,2-diylbis(4,1-phenylene))bis(oxy)dianiline (diamine A) the product purity is 99.9 % by ¹H NMR spectroscopy; bis-hydroxyethylterephthalate obtained by the glycolysis reaction with ethylene glycol of a secondary PET flex, the structure of the product was confirmed by FTIR spectroscopy; polyphosphoric acid 115 % (Sigma-Aldrich); sodium chloride, State Standard 233–77; hexavalent magnesium chloride State Standard 4209–77; sodium bicarbonate State Standard; calcium chloride, dehydrated State Standard 6–09–47–11–81; ethylenediaminetetraphosphonic acid (EDTA); filtering paper; distilled water; laboratory scales in accordance with State Standard 24104–01.

Synthesis of organophosphates. Aminophosphonic acid was obtained by condensation of diamine A, formaldehyde and phosphorous acid through the Moedritzer–Irani reaction. The synthesis technique is described in the paper [5].

The phosphoric ester was obtained by phosphorylation of bis-hydroxyethylterephthalate with polyphosphoric acid. The synthesis technique is described in the paper [6]. The structure of synthesized organophosphates was confirmed by IR spectral analysis using Agilent Carry 660 IR spectrometer and Bruker Tensor II Fourier IR.

Static tests for scale inhibition [7]. The evaluation of the effectiveness of the scale inhibitor aminophosphonic acid against calcium carbonate and calcium sulphate deposits under static conditions was carried out according to previously described methods. The static laboratory method consists of precipitating CaCO_3 and CaSO_4 from water, i.e. heating with or without the presence of a scale inhibitor. In our work we used imitates of formation water of the chloride-calcium and sulphate-calcium type. The salt composition that simulates carbonate deposits is $\text{Ca}^{2+} = 1100 \text{ mg/L}$, $\text{Mg}^{2+} = 380 \text{ mg/L}$, $\text{Na}^+ = 7500 \text{ mg/L}$, $\text{HCO}_3^- = 976 \text{ mg/L}$, $\text{Cl}^- = 14023 \text{ mg/L}$. Two solutions are required to imitate scale formation. Solution 1 contains 3046 mg/L calcium chloride and hexavalent magnesium chloride 3177 mg/L, while solution 2 is sodium chloride 18084 mg/L and sodium bicarbonate 1344 mg/L.

The effectiveness of scale inhibition was determined for concentrations of 10, 30, 50, 70, 100, 150 or 200 ppm of solution 1 in 50 mL. This was mixed with 50 mL of solution 2. Lids were placed on the flasks, and the temperature was fixed at 75 °C for 5 hours. Then the samples were filtered and the calcium ion content determined. 10 mL of filtrate were placed in the conical flasks and 40 mL of distilled water, 2.5 mL of 20 % sodium hydroxide solution and 10–15 mg of a mixture of murexide and sodium chloride were added. Secondly, the salt composition simulating sulphate (gypsum) deposits is $\text{Ca}^{2+} = 4911 \text{ mg/L}$, $\text{Mg}^{2+} = 148 \text{ mg/L}$, $\text{Na}^+ = 11623 \text{ mg/L}$, $\text{SO}_4^{2-} = 8792 \text{ mg/L}$, $\text{Cl}^- = 20291 \text{ mg/L}$. To prepare the imitation of scale formation in this case, two further solutions are needed. Solution 3 is calcium chloride 1360 mg/L, while solution 4 contains sodium chloride 18800 mg/L, hexahydrate magnesium chloride 1240 mg/L and sodium sulphate 13000 mg/L. The same procedure was carried out with solutions 3 and 4 as for solutions 1 and 2. The content of calcium ions in each case is calculated by the formula:

$$X = \frac{V_t \times N_t \times 20.04 \times 1000}{10}, \quad (1)$$

where V_t — volume of EDTA- Na_2 , which went to titration, mL; N_t — molar concentration of equivalent solution of EDTA- Na_2 , mol/L equivalent; 10 — volume taken for titration; 20,04 — molar mass of the equivalent of calcium ion, g/mol.

For comparison, the experiment is conducted in parallel without the addition of scale inhibitor. The effectiveness of the scale inhibitor (%) is determined by the formula:

$$E = \frac{C_p - C_x}{C_0 - C_x} \times 100 \%, \quad (2)$$

where C_x — content of calcium ions in a sample that does not contain an inhibitor, mg/L; C_p — content of calcium ions in the sample containing the inhibitor, after thermostating, mg/L; C_0 — content of calcium ions in the initial solution, mg/L.

Results and discussion

Well-known foreign technologies for controlling scale precipitation of mineral salts on the surface of process equipment at petrochemical complexes are based on the treatment of water with inorganic phosphate derivatives [8]. In water treatment systems for inorganic phosphates, there are environmental limitations in the concentration due to the fact that phosphates promote excessive growth of algae, oxygen deficiency and extinction of fish [9].

One of the safe water treatment technologies is the use of organic phosphates, such as phosphoric esters, phosphonic acids. Organic phosphates contain less phosphorus, are biodegradable, have low toxicity, are not inferior in efficiency to inorganic phosphates. For their properties, these compounds are classified as complexons, their complexing properties are realized due to the presence of hydrogen atoms of phosphonic groups [10]. According to [10], the mechanism of scaling inhibition by organophosphates can be explained by the formation of complex compounds with crystal nucleus of mineral salts. Inhibition occurs due to adsorption of organophosphates on the surface of growing crystals of mineral salts, which excludes the possibility of formation of a crystalline phase in a solution. The scheme for the complex formation of the phosphoric ester with calcium ions is shown in Figure 1.

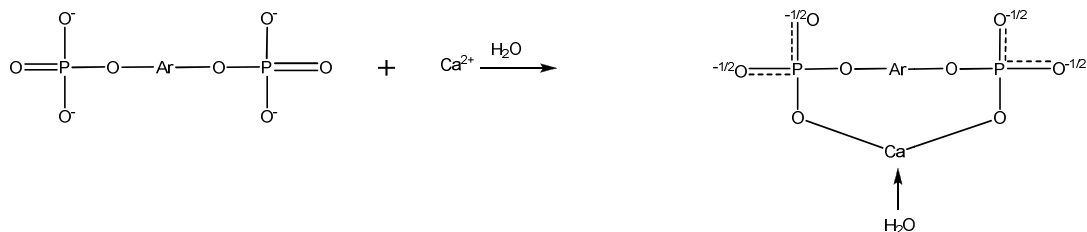


Figure 1. Scheme of complexation of the phosphoric acid ester with calcium ions

The new organophosphonates that we developed were identified and characterized [5, 6]. In order to confirm the structure, their IR spectral analysis was carried out. Figures 2 and 3 shows the IR spectra of aminophosphonic acid and phosphoric acid monoester of bis-hydroxyethylterephthalate, respectively.

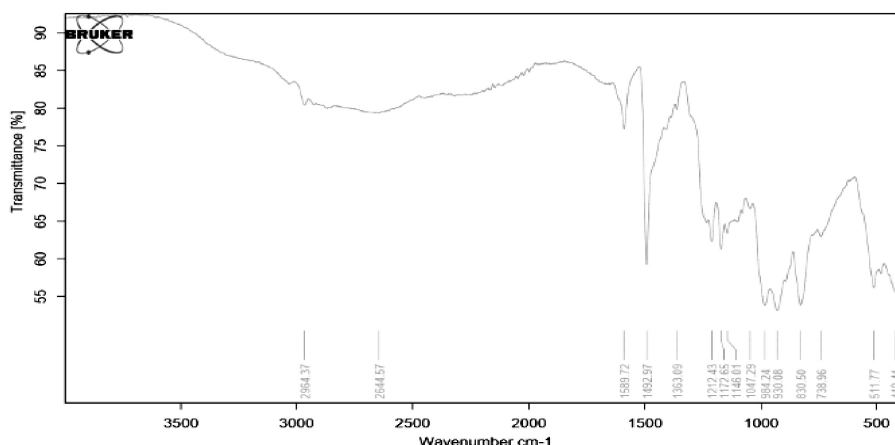


Figure 2. IR spectrum of aminophosphonic acid

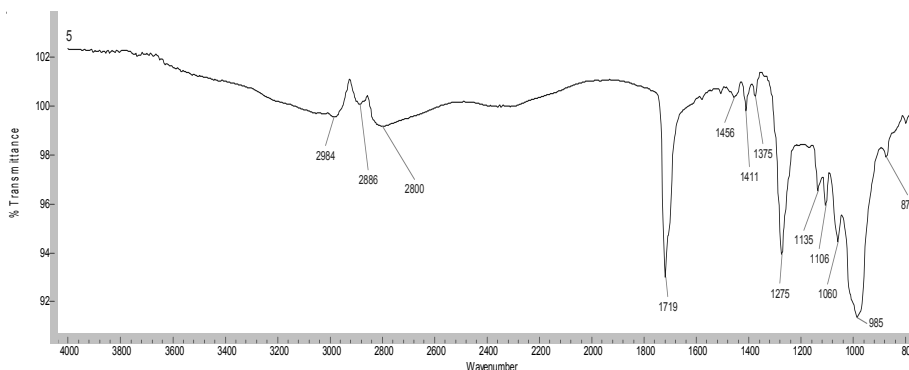
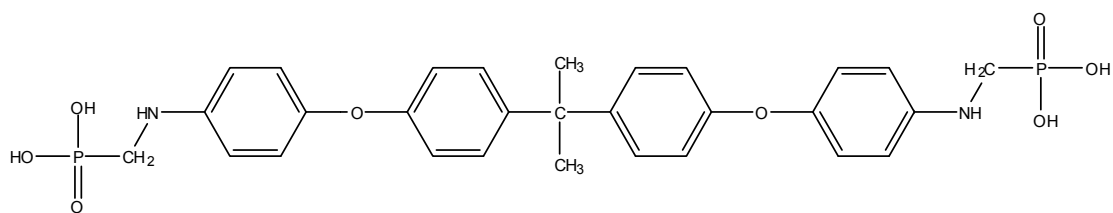


Figure 3. IR spectrum of phosphoric acid ester

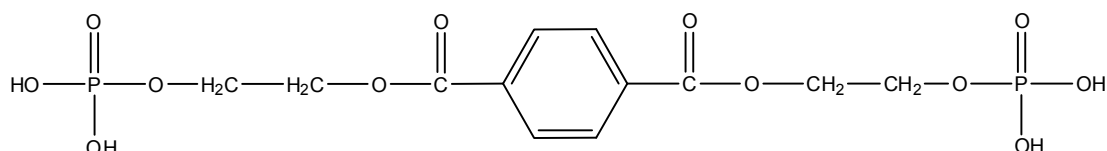
The IR spectrum showed absorption bands in the 2964 cm^{-1} region attributable to stretching vibrations in the $-\text{CH}_3$ and $-\text{CH}_2$ groups. The absorption band at 1590 cm^{-1} indicates the stretching vibrations of the $\text{C}=\text{C}$ double bonds in the aromatic ring. The stretching vibrations at 1363 cm^{-1} correspond to the $\text{C}-\text{N}$ bonds. The absorption band at 1173 cm^{-1} shows the stretching vibrations of the $\text{P}=\text{O}$ group. The 738 cm^{-1} band describes the stretching vibrations of the $\text{P}-\text{C}$ bond.

In the IR spectrum of the phosphoric ester of bis-hydroxyethylterephthalate, an absorption band is observed in the region of 1719 cm^{-1} , which can be attributed to the stretching vibrations of the carbonyl group of the compound ester. The $2966, 2881\text{ cm}^{-1}$ bands are attributed to the vibrations of the CH bonds in the CH_2 groups; in the region of 1504 cm^{-1} , they are referred to vibrations in the aromatic ring, in the 2800 cm^{-1} region to the $\text{P}-\text{OH}$ deformation oscillations. Fluctuations in the region of 985 cm^{-1} can be attributed to the deformation in the $\text{P}-\text{OC}$ group, in the 1106 cm^{-1} region — to the stretching vibrations in $\text{P}=\text{O}$.

Based on the data of IR spectroscopic studies, the expected chemical structure of the organophosphates was obtained (Fig. 4).



Propane-2,2 phenylene-diylbis bis(4,1)-phenylene)bis(4,1-bis(azadienyl)bis(methylene)diphosphonic acid (a)



Bis(2-(phosphonoxy)ethyl)terephthalate (b)

Figure 4. Alleged chemical structure of organophosphates: phosphoric acid ester of bis-hydroxyethyl terephthalate (a) and aminophosphonic acid (b) [5, 6]

In order to identify the scale inhibition ability, organophosphonic compounds have been tested on different models of produced water. The tests were carried out in model solutions at a temperature of 75 °C and an inhibitor concentration from 10 to 200 ppm. The results of the inhibition studies are shown in Figures 5 and 6. As the figures show, the new reagents exhibit a sufficiently high inhibitory activity with respect to the CaCO_3 and CaSO_4 deposits. At the same time, it can be noted that the inhibition efficiency on CaCO_3 deposits was higher for aminophosphonic acid. The maximum protection at a concentration of 200 ppm of this reagent was 94 %, and for the phosphoric ester at the same concentration was 85 %. However, the inhibition efficiency on CaSO_4 deposits (Fig. 6) is much higher for phosphoric ester, the maximum efficiency was 100 % and reached at a concentration of 30 ppm, the maximum inhibition degree for aminophosphonic acid was 97 % at a concentration of 200 ppm.

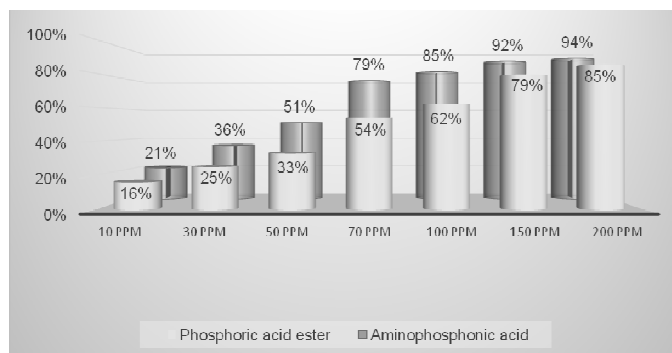


Figure 5. Effectiveness of inhibitors on CaCO_3 deposits

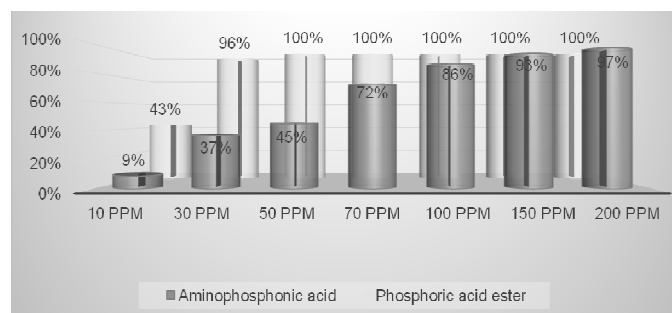


Figure 6. Effectiveness of inhibitors on CaSO_4 deposits

The reason for the different efficiency of the inhibitors was elucidated in the study of scale samples by scanning electron microscopy using a JEOL JSM-6490LV instrument. The authors [11] note that CaCO_3 has the property of polymorphism, the precipitates have the same chemical composition, but they have different crystalline structures — calcite, aragonite and vaterite. Aragonite, unlike vaterite, has a more stable crystalline form [12]. The vaterite under normal conditions (25 °C, atmospheric pressure) eventually transforms into a more stable form of calcite, and at temperatures (70–80 °C) first transforms into aragonite, and then into calcite. Compared to calcite, aragonite and vaterite are soluble in water. This is due to the fact that aragonite and vaterite have a lower value of free surface energy as compared to calcite, which reduces their adhesion on the surface of the equipment, due to the interaction between the crystals [13]. Moreover, it was reported in [14–17] that under certain conditions occurrence of two more forms of calcium carbonate is possible: calcium carbonate monohydrate and calcium carbonate hexahydrate.

Figures 7, 8 and 9 shows micrographs of precipitation of mineral salts before and after treatment with inhibitors.

As can be seen on Figure 7, the difference in the formation of crystals is obvious. Crystals formed without an inhibitor are in the form of calcite. The phase composition of the precipitate obtained in the presence of aminophosphonate is characterized by a higher content of aragonite and vaterite. For the phosphoric ester, there are preferably more crystals in the form of vaterite. Also, from Fig. 6 for aminophosphonic acid and phosphoric ester, it follows that these compounds have complexing properties and are able to be embedded in the surface of the crystallization nucleus, as a result of which crystal growth ceases.

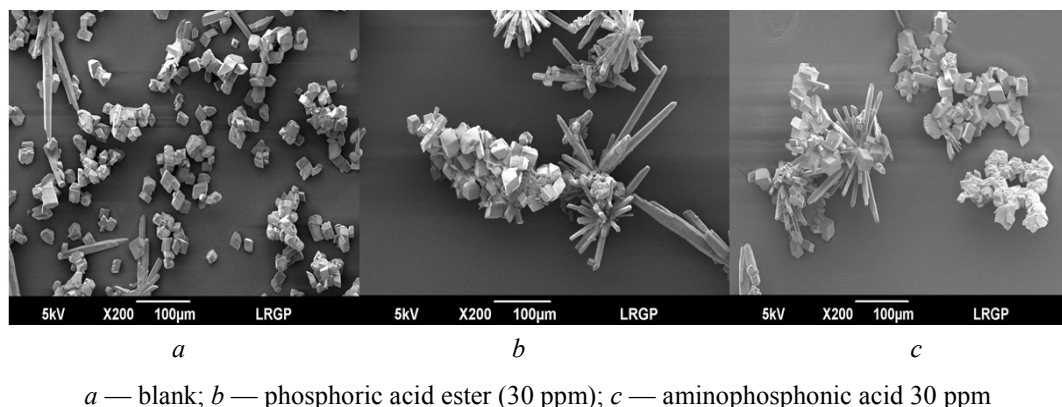


Figure 7. Micrographs of carbonate sediments without an inhibitor and with scaling inhibitors

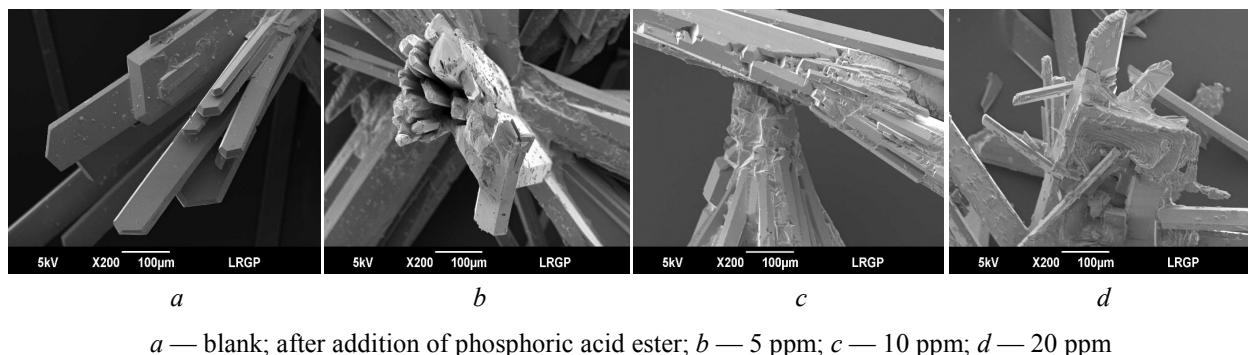
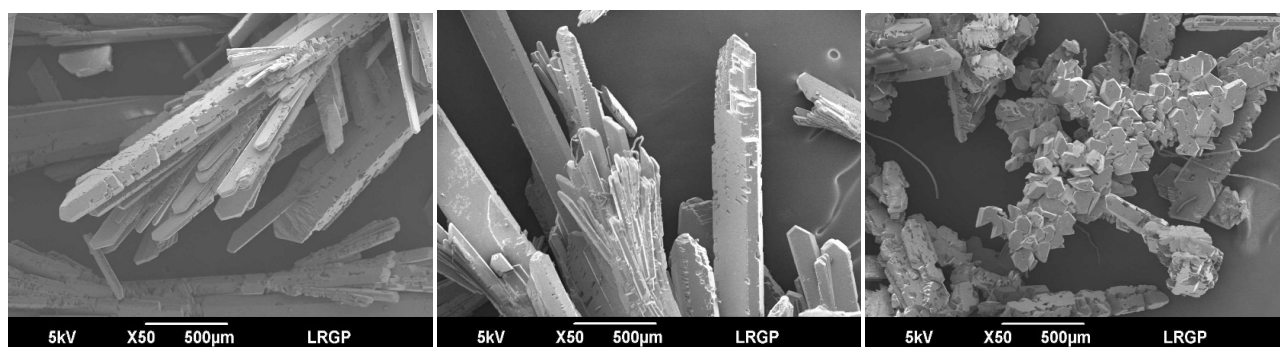


Figure 8. Microphotographs of sulfate sediments

Figure 8*a* shows that the structure of deposits of sulphate sediments without an inhibitor has structures in the form of smooth needles. When phosphoric ester inhibitors were added, the destruction of gypsum deposits started (Figure 8*b*, 8*c*, 8*d*). Complete destruction of the deposit was achieved at a concentration of 30 ppm. A similar effect was observed for aminophosphonic acid (Fig. 9), but in this case the concentration of the reagent was higher than that of the phosphoric ester (Fig. 9 *a*, *b*, *c*). The beginning of destruction of sulphate sediments was observed at a concentration of 10 ppm. Complete destruction was noted at 200 ppm.



a — 10 ppm;

b — 100 ppm;

c — 150 ppm

Figure 9. Microphotographs of sulfate sediments without inhibitor

Thus, it was shown that inhibitors have not only high inhibitory properties with respect to carbonate and calcium sulphate deposition, but are also capable of altering the morphology of crystals, which favorably affects the destruction of already fallen salt crystals and their removal with process fluid.

The inhibitors are highly effective for total deposits of carbonate salts (94 and 85 %) and sulphates (97 and 100 %) at a concentration of 200 ppm.

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Тұз шөгінділерінің ингибиторлары ретіндегі жаңа фосфорлы органикалық қосылыстардың сынақтары

Мұнай өндіру, дайындау және тасымалдау барысында қолданылатын жер бетіндегі және ұңғымадағы қондырғыларды сульфатты және карбонатты тұздардың шөгінділерінен қорғайтын, жаңа буындағы фосфорлы органикалық тұз шөгінділерінің ингибиторы жасап шығарылды. Бірінші түрлі ингибитор (аминфосфон қышқылы) Моедритцер-Ирани реакциясы арқылы 4,4'-(пропан-2,2-диилбис(4,1-фенилен)бис(окси)дианилиннің (диамин А) формальдегидпен және фосфорқышқылымен конденсациялау арқылы синтезделді, екіншісі — гликолизденген ПЭТ флексін — полифосфор қышқылының бисгидроксиэтилтерефталатын фосфорлау арқылы. Жасалған фосфорлы органикалық қосылыстарының құрылымы ИК-спектроскопия әдісімен расталған. Сканерлеуші электронды микроскопия арқылы (РЭМ) минералды тұздардың қатты тұнбаларының морфологиясы зерттелді. Кристалл түзілуінің тежелуі ядро түзілу сатысында орын алатыны анықталды. Кристалл ядроларының бетіне кірістірілуі арқылы ингибиторлар ерітіндідегі кристалдық фазаның түзілуін және кристалдардың өсуін болдырмайды.

Кілт сөздер: фосфорлы органикалық қосылыстар, аминфосфон қышқылы, фосфор қышқылының күрделі эфирі, тұз шөгінділері ингибиторлары, синтез, Моедритцер-Ирани реакциясы, гликолиз, тестілеу.

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Испытания новых органофосфорных соединений в качестве ингибиторов солеотложений

Разработаны органофосфорные ингибиторы солеотложений нового поколения, предназначенные для предотвращения отложений сульфатных и карбонатных солей в наземном и скважинном оборудовании при нефтедобыче, подготовке и транспорте нефти. Ингибитор первого типа (аминофосфоновая кислота) был синтезирован по реакции Моедритцера-Ирани конденсацией 4,4'-(пропан-2,2-диил-бис(4,1-фенилен)-бис(окси)дианилина (диамина А) с формальдегидом и фосфористой кислотой, второго — фосфорилированием гликолизированного ПЭТ флекса — бис-гидрокси-этилтерефталата полифосфорной кислотой. Структура разработанных органофосфорных соединений подтверждена методом ИК-спектроскопии. Растровой электронной микроскопией (РЭМ) изучена морфология твердых осадков минеральных солей. Выявлено, что ингибирование кристаллообразования происходит на стадии зародышеобразования. Встраиваясь в поверхность зародышей кристалла, ингибиторы препятствуют образованию кристаллической фазы в растворе и росту кристаллов.

Ключевые слова: органофосфорные соединения, аминофосфоновая кислота, сложный эфир фосфорной кислоты, ингибиторы солеотложения, синтез, реакция Моедритцера-Ирани, гликолиз, тестирование.

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Synthesis and study of antioxidant activity of hydrazone and thiosemicarbazidebased on N-morpholinoacetic acid hydrazide

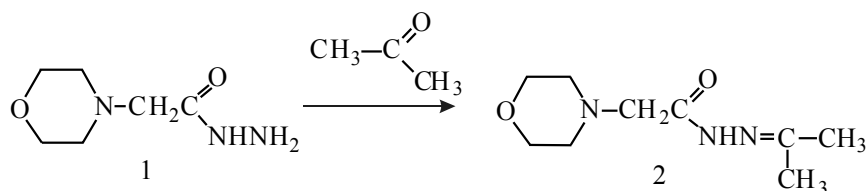
Data on the synthesis and study of the effect of 2-morpholino-N-(propane-2-ylidene) acetohydrazide and 2-(2-morpholinoacetyl)-N-phenylhydrazinocarbothioamide hydrochloride on the electroreduction of oxygen (EV O₂) in various concentrations were presented. The structures of synthesized compounds were studied by IR and ¹H NMR spectroscopy methods. Cathode voltammetry on a mercury-film electrode was used as a method for estimating the antioxidant activity of samples. In this approach, the determination of antioxidant activity reflected the number of active forms of oxygen neutralized by the antioxidant in a certain time. The change in the current of the O₂ OV in its absolute value indicated that the samples under study reacted with oxygen and its active radicals in the test solution. The degree of change in the current of the O₂ OV was an indicator of the activity of the sample under study. A similar voltammogram was obtained for the substance under study. A decrease in the cathodic current of E2 O₂ is observed, which indicates that they exhibit antioxidant activity with respect to this process. In addition, there was a shift in the potential of the cathode current of the O₂O₂ to the positive potential region. All of the above implies the existence of an EU mechanism (electrochemical — chemical stage), which includes the subsequent chemical reaction of the interaction of antioxidants with active oxygen radicals. It is shown that the aqueous solution of the studied morpholine derivatives exhibits antioxidant activity.

Keywords: 2-morpholino-N-(propane-2-ylidene)acetohydrozide, 2-(2-morpholinoacetyl)-N-phenylhydrazinocarbothioamide¹H NMR spectrum, IR spectrum, antioxidative activity, cathodic voltammetry method, voltammograms, thiosemicarbazide.

It is known that a metabolic transformation of substances in the human body generates free toxic oxygen radicals [1, 2]. They are formed during reactions of lipid peroxidation, metabolism of various drugs or due to impact of external factors (the action of ultraviolet radiation, ionizing radiation). Once they are formed in the body, radicals interact with cell structures, ultimately resulting to cell membranes shock, thus accompanying the development of pathological processes of many diseases. Normally the regulation of the products of activated oxygen metabolites and free radicals in human organs and tissues is performed by vitamins, pigments, hormones, and enzymes. Despite the high efficiency of the antioxidant system, it is not always able to protect the body against the development of oxidative stress. In this regard, one of the priorities is to produce preparation having antioxidant properties with the purpose of use in the prevention and treatment of diseases. In this perspective the synthesis based on hydrazine containing morpholine derivatives are of considerable interest since morpholine-containing fragment is a structural element of numerous natural and synthetic bioactive substances. It should be noted that practically all morpholine derivatives have a broad spectrum of biological activity such as an anti-pyretic, anti-inflammatory, antimicrobial, anti-bacterial, anti-tuberculosis, and anti-cancer one. In order to continue the targeted research to find new opportunities on obtaining new bioactive derivatives with antioxidant effect, N-morpholylaceticacid hydrazide was selected as a synthon.

This work provides the synthesis and study of antioxidative activity of 2-morpholino-N-(propane-2-ylidene)acetohydrazide and 2-(2-morpholinoacetyl)-N-phenylhydrazinocarbothioamide in regard to oxygen radicals by cathodic voltammetry method.

It is known [3, 4], that hydrazones are widely used in synthetic chemistry due to their simple production method and diverse biological activity. The most common method of hydrazones synthesis is the condensation of hydrazines from carbonyl compounds [5]. Thus, we synthesized 2-morpholino-N-(propane-2-ylidene)acetohydrazide (2) obtained with condensing of N-morpholylaceticacidhydrazide (1) with acetone. Product 2 appeared to be a well crystallizing white substance that is soluble in many organic solvents with the yield of 79 %.

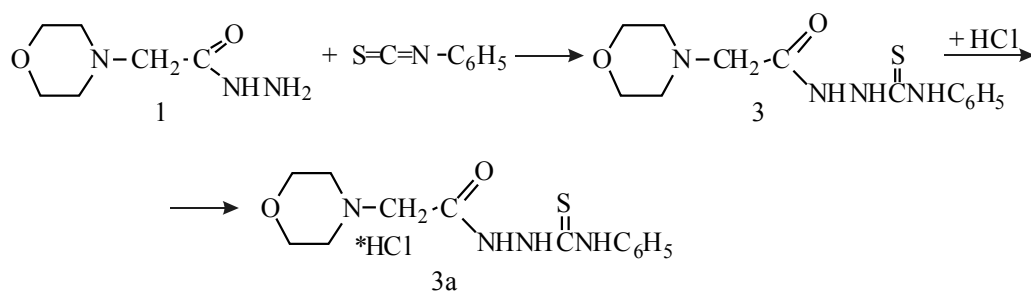


The IR spectrum of compound 2 have troughs at 3185–3255 cm⁻¹ that correspond to stretching vibrations of N–H group, and troughs at 1675–1690 cm⁻¹ correspond to stretching vibrations of C=O groups of hydrazone.

In the ¹H NMR spectrum of 2-morpholino-N-(propane-2-ylidene)acetohydrazide (2) signals of methylene protons of morpholine fragment are represented as two triplets centered in 2.52 and 3.39 ppm. Methylene protons of NCH₂-fragments appear at the 3.52 ppm as the narrow singlet. There are two intensive singlets of two methyl groups at 1.75 ppm and 1.95 ppm in the strong field. Singlet in region of 6.21 ppm belongs to N–H proton.

It should be noted that the sulfur-containing functional group in some medicines can be the main element determining the bioactivity, while in others it can just have a certain influence on the pharmacological effect. The biological effect of sulfur-containing compounds first used as drugs appeared due to their antibacterial properties. In this regard, the particular interest is in thiosemicarbazides and their derivatives.

In continuation of research on the synthesis of new biologically active compounds, particularly thiosemicarbazide 3, N-morpholinylacetic acid hydrazide (1), we studied reaction of its condensation with phenylisothiocyanate in alcohol medium at equimolar ratios of the reactants. The reaction proceeds in quiet mild conditions for the synthesis in good yield of the desired product (90 %). Synthesized thiosemicarbazide derivative 3 is a white crystalline powder, soluble in polar organic solvents. In order to obtain water-soluble form of 2-(2-morpholinoacetyl)-N-phenylhydrazinocarbothioamide (3) hydrochloride 3a was derived.

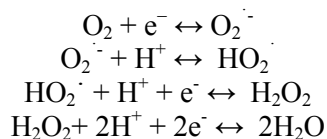


There are absorption bands in the IR spectrum of compound 3 at 1140–1240 cm⁻¹, which is characteristic for the NH–CS group of the thiosemicarbazide fragment and amide group C(O)NH at 1690–1675 cm⁻¹ as well as NH group at 3390–3360 cm⁻¹.

Protons of the phenyl ring are presented in the ¹H NMR spectrum of N-morpholinylacetic acid N-phenylthiosemicarbazide (3) along with the methylene protons signals of the morpholine fragment (2.45 ppm and 3.61 ppm) and NCH₂ fragment (3.07 ppm) in a weak field 7.15–7.34 ppm. Amide and thioamide NH protons are appearing in weak fields in the form of three singlets in the region of 9.85 ppm, 9.80 ppm and 7.98 ppm.

It is known that free radicals are an important part of the pathogenesis of many diseases [1]. Therefore, using voltammetric analyzer at various concentrations in aqueous solution is an important chapter in studying pharmacological activity of 2-morpholino-N-(propane-2-ylidene)acetohydrazide (2) and hydrochloride of 2-(2-methylmorpholinoacetyl)-N-phenylhydrazinocarbothioamide (3a).

The activity of the samples was determined by using cathodic voltammetry, particularly the electrochemical reduction of oxygen (O₂ EV). Model reaction of O₂ EV proceeds by a mechanism similar to oxygen reduction in body cells and tissues:



In this case, the first wave of O₂ EV (reduction of oxygen to hydrogen peroxide) with formation of active oxygen species: O₂, HO²⁻ is under consideration. It is assumed that substances react with oxygen and its active radicals on the indicative electrode surface, which is reflected in changes of O₂ EV cathode current.

The activity of the studied substance with respect to O₂ EV was determined by the following procedure: O₂ EV voltammograms were recorded in the absence of studied substance (background curve). In the absence of extraneous peaks background solution was considered as pure. Then, studied substance with known concentration was added in a cell (for 10 mL supporting electrolyte volume) and cathodic O₂ EV voltammograms were obtained in the same conditions. The measurements were repeated at least 3 times over the defined period of time and value of O₂ EV current limit was estimated each time.

O₂ EV Slope by its absolute value indicates that the studied samples react with oxygen and its active radicals in the test solution. Degree of O₂ EV current change is an indicator of the activity of the test sample.

For the same type of the substance voltammogram is obtained and cathode current decrease is observed in the O₂ EV, which indicates the exertion of antioxidant activity relating to this process. In addition, there was a shift in potential cathode current of O₂ EV to the positive potentials area. All aforesaid requires a ES mechanism (electrochemical — chemical steps), which comprises the subsequent chemical reaction of the antioxidants with active oxygen radicals.

Antioxidant activity of 2-morpholino-N-(propane-2-ylidene)acetohydrazide(2) and 2-(2-morpholinoacetyl)-N-phenylhydrazino carbothioamide (3a) with different concentrations are shown in the Table.

Table

Antioxidant activity of the compounds (2 and 3a) with different concentrations

Substance concentration, g/mL	Average value mole/L	
	Compound 2	Compound 3a
0.00001	0.1432	0.1512
0.0001	0.2355	0.3039
0.001	0.4153	0.4624

The obtained data (Table) demonstrates that hydrochloride of 2-(2-methylmorpholinoacetyl)-N-phenylhydrozinocarbothioamide (3a) expresses the highest antioxidant activity at the maximal analyzed concentration. In the same time moderate growth of antioxidant activity of 2-morpholino-N-(propane-2-ylidene)acetohydrazide (2) is observed as well. It is shown that even at the lowest concentration studied substance reacts with oxygen and its active forms, deactivating them in the solution. Antioxidant activity in this case can be considered as a useful feature that extends the potential range of uses of the researched compounds.

Thus, hydrazone and thiosemicarbazide synthesis was performed on the base of N-morpholinyl acetic acid hydrazide and the influence on the electrochemical reduction of oxygen (O₂EV) at different concentrations was investigated by cathodic voltammetry using the mercury coated electrode. In this approach, determination of antioxidant activity reflects the amount of reactive oxygen species antioxidant neutralizes over time. It is demonstrated that an aqueous solution of researched compounds exhibits antioxidant activity against oxygen radicals.

Experimental

¹H-NMR spectrum was recorded on the Bruker 400 spectrometer at 400 MHz in DMSO-*d*₆ solution relative to the internal standard TMS. Melting point was determined on a Boetius instrument. Progress of the reaction and purity of the obtained compound was monitored by thin layer chromatography on the Silufol UV-254 plates in the system of isopropanol – benzene – 25 % ammonia solution 10:5:2. The plates were displayed with iodine vapors. Hydrazide of N-morpholinoacetic acid was prepared as described in [6].

2-Morpholino-N-(propane-2-ylidene)acetohydrazide (2). 10 mL of acetone is added to the 1.59 g (0.01 mol) of N-hydrazide of morpholine acetic acid. The mixture is heated for 10 minutes to dissolve hydrazide. The mixture is kept at room temperature until fine-grained sediment precipitates. Completion of the reaction is detected with TLC. Re-crystallization from petroleum ether gives 1.57 g (79 %) of a white powdery substance with m. p. 95–97 °C. ¹H-NMR (DMSO-*d*₆), δ, ppm.: 2.52 t (4H, N(CH₂)₂, J_{HH} 4.66), 3.39 s (2H, NCH₂), 3.56 t (4H, O(CH₂)₂, J_{HH} 4.65), 6.21 s (1H, NHN), 1.75 s (3H, CH₃), 1.95 s (3H, CH₃).

N-Phenylthiosemicarbazide of N-morpholinylacetic acid (3). 1.59 g (0.01 mole) of N-morpholinylacetic acidhydrazide is dissolved in 5 mL of ethanol, then 1.48 g (0.011 mole) of phenylthiocyanate is added by drops. Mixture is mixed during 30 min at 50–60 °C. Completion of the reaction is detected with TLC. Solu-

tion is cooled, precipitated fine-grained sediment is filtered and rinsed with small amount of petroleum ether. After re-crystallization from benzene 2.64 g (90 %) of compound 3 with m.p. 147–150 °C was obtained. ^1H NMR spectrum (500 MHz, DMSO- d_6 , δ , ppm, J/Hz): 2.45 t (4H, $\text{N}(\text{CH}_2)_2$, $J = 4.3$), 3.07 b.r.s (2H, $\text{N}-\text{CH}_2$), 3.61 t (4H, $\text{O}(\text{CH}_2)_2$, $J_{\text{HH}} 4.6$), 7.15–7.34 m (5H, Ar), 9.85 s [1H, $\text{NH}(\text{C}=\text{S})$], 7.98 s (1H, NH), 9.80 s [1H, $\text{NH}(\text{C}=\text{O})$].

Hydrochloride of N-morpholinylacetic acid N-phenylthiosemicarbazide (3a). Saturated with gaseous HCl benzene solution is added to the obtained product 3 dissolved in benzene. Presipitated fine-grained white powder is filtered and rinsed with absolute benzene several times.

Reagent preparation. Stock solutions of researched substances at a concentration of 0.1 g/ml are prepared as follows: using analytical balance 0.5 g sample was weighed and dissolved in 5 ml of distilled water. Further, 0.01 g/ml and 0.001 g/ml solutions are prepared with followed dilutions with distilled water in 10 ml vials. Aliquots of 0.1 ml volume were taken for studies obtaining appropriate working concentrations of test solutions presented in the table.

The voltammetric analysis method used in this work is expressive, with high sensitivity (10^{-10}) and broad analytical capabilities. The developed technique is unique, reproducible, and does not require long-term sample preparation.

Experiment methodology of antioxidant activity determination included obtaining and analysis of the voltammograms of cathodic O_2 EV using voltammetric analyzer connected to the computer [7]. Direct current mode of cathodic voltammetry was used, potential sweep speed $W = 40$ mV/s, the working range of potentialis in range from 0.0 to 1V, solution stirring time is 20 seconds, settling time is 10 seconds. Electrochemical cell was a glass beaker containing an indicator of mercury coated electrode, silver chloride reference electrode and a silver chloride auxiliary electrode immersed into supporting electrolyte solution. Phosphate buffer solution was chosen as supporting electrolyte in a volume of 10 mL and with pH 6.86, which is close to the physiological value.

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N-морфолинилсірке қышқыл гидразиді негізінде гидразондар мен тиосемикарбазидтердің синтезі мен тотығуға қарсы белсенділікті анықтау

Мақалада 2-морфолино-N-(пропан-2-илиден)ацетогидразидпен 2-(2-морфолиноацетил)-N- фенилгидразинакарботиоамид гидрохлоридінің синтездері бойынша мәліметтер мен әртүрлі концентрацияда (ЭВ O_2) оттектің электрлі қайта қалпына келтіру үрдісіне әсері келтірілген. Синтезделген қосылыстардың құрылымы ИҚ- мен ЯМР ^1H -спектроскопия әдістерімен зерттелген. Тотығуға қарсы белсенділіктің бағалау тәсілі ретінде сынапты-кабыршықты электродта катодты вольтамперометрия қолданылған. Тотығуға қарсы белсенділікті анықтау тәсілінде белгілі бір уақытта тотығуға қарсы бейтараптандырылған оттегінің белсенді түрлерінің мөлшері келтірілген. ЭВ O_2 тоғының өзінің

абсолютті мәнінің өзгеруі зерттелінген косылыстардың белгілі бір ерітіндіде белсенді радикалдармен және оттегімен әрекеттескенін кұаландырады. ЭВ O_2 тоғының өзгеру дәрежесі зерттелінетін заттың белсенділігінің көрсеткіші болып табылады. Зерттелінетін зат үшін біртүпті вольтамперограмма алынды, ЭВ O_2 катодты тоғының азаюы байқалған. Бұл осы үрдіс бойынша тотығуға қарсы белсенділіктің пайда болуын дәлелдейді. Сонымен қатар ЭВ O_2 катодты тоғының потенциалының оң аймаққа ығысуы белгілі. Жоғарыда айтылғандардың барлығы ЕК (электрохимиялық — химиялық кезеңдер) тотығуға қарсы белсенді оттекті радикалдармен химиялық әрекеттесу реакциясына түсетін механизмнің барын болжайды. Зерттелінген морфолин туындыларының сулы ерітінділері тотығуға қарсы белсенділікке ие екендігі көрсетілді.

Кілт сөздер: 2-морфолино-N-(пропан-2-илиден)ацетогидразид, 2-(2-морфолиноацетил)-N-фенилгидразинокарботиоамид, 1H ЯМР-спектрі, ИК-спектрі, тотығуға қарсы белсенділік, катодтық вольтамперометрия әдісі, вольтамперограмма, тиосемикарбазид.

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Синтез и изучение антиоксидантной активности гидразонов и тиосемикарбазидов на основе гидразида N-морфолиноуксусной кислоты

В статье приведены данные по синтезу и изучению влияния 2-морфолино-N-(пропан-2-илиден)-ацетогидразида и гидрохлорида 2-(2-морфолиноацетил)-N-фенилгидразинокарботиоамида на процесс электровосстановления кислорода (ЭВ O_2) в различных концентрациях. Исследовано строение синтезированных соединений методами ИК- и ЯМР 1H -спектроскопии. В качестве метода оценки антиоксидантной активности образцов применена катодная вольтамперометрия на ртутно-пленочном электроде. В данном подходе определение антиоксидантной активности отражало количество активных форм кислорода нейтрализованных антиоксидантом за определенное время. Изменение тока ЭВ O_2 по своему абсолютному значению свидетельствует о том, что исследуемые образцы реагируют с кислородом и его активными радикалами в исследуемом растворе. Степень изменения тока ЭВ O_2 являлась показателем активности исследуемого образца. Для исследуемого вещества получена однотипная вольтамперограмма, наблюдалось уменьшение катодного тока ЭВ O_2 , что свидетельствует о проявлении ими антиоксидантной активности по отношению к данному процессу. Кроме того, наблюдался сдвиг потенциала катодного тока ЭВ O_2 в положительную область потенциалов. Все сказанное выше предполагает наличие механизма ЕС (электрохимическая — химическая стадии), который включает последующую химическую реакцию взаимодействия антиоксидантов с активными кислородными радикалами. Показано, что водный раствор изученных производных морфолина проявляет антиоксидантную активность.

Ключевые слова: 2-морфолино-N-(пропан-2-илиден)ацетогидразид, 2-(2-морфолиноацетил)-N-фенилгидразинокарботиоамид, 1H ЯМР-спектр, ИК-спектр, антиокислительная активность, метод катодной вольтамперометрии, вольтамперограмма, тиосемикарбазид.

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Novel polyesters based on nitrogen-containing heterocycles: synthesis and research

The article presents the results of studies carried out at assembling two branches of science such as the chemistry of heterocyclic compounds and the chemistry of step-growth polymerization. 2,4-Dimethyl-3,5-diethoxycarbonylpyrrole (Knorr pyrrole) was synthesized by a series of successive transformations. 2,4-Dimethylpyrrole-3,5-dicarboxylic acid was obtained by Knorr pyrrole hydrolysis, optimal conditions for reaction were chosen. The process was shown to be completed within an hour and a half in an alcohol-alkaline medium. A new polyester based on 2,4-dimethylpyrrole-3,5-dicarboxylic acid and ethylene glycol was synthesized by a polyesterification reaction. The physicochemical characteristics of the polymer obtained were established. Light-scattering method was used to determine the mass-average molar mass of the polyester, which turned out to be equal to 5263. The good convergence of the data calculated and the reproducibility of the experiment for determining the turbidity of dilute polymer solutions by turbidimetric method indicates the reliability of the results. Analysis of the structure and physical and chemical properties of the polymer synthesized suggests that a polyester based on 2,4-dimethylpyrrole-3,5-dicarboxylic acid and ethylene glycol can be used as a component of alkyd resins potentially possessing biological activity.

Keywords: Knorr pyrrole, 2,4-dimethylpyrrole-3,5-dicarboxylic acid, polyesterification, polyester, turbidimetry.

The chemistry of heterocyclic compounds is of particular interest for scientists as these compounds have other atoms of the elements of the periodic system in addition to the carbon and hydrogen atoms in their structure [1]. This is due to the special properties of the corresponding compounds. These properties include fungicidal, acaricidal ones, different types of pharmacological activity, and new optical properties of heterocyclic compounds, the application of which is possible in all spheres of human activities.

The presence of heteroatoms in molecules such as nitrogen particularly leads to a decrease in toxicity and an increase in the high physiological activity of organic compounds. Their heterocyclic derivatives show more effective biologically active properties in comparison with aliphatic ones [2].

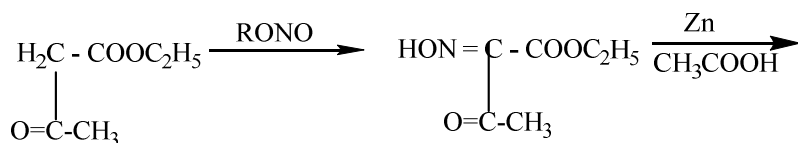
Compounds referring to pyrroles — five-membered nitrogen containing cyclic molecules — constantly attract the researchers' attention despite the fact that Knorr synthesis is known from the end of XIX century.

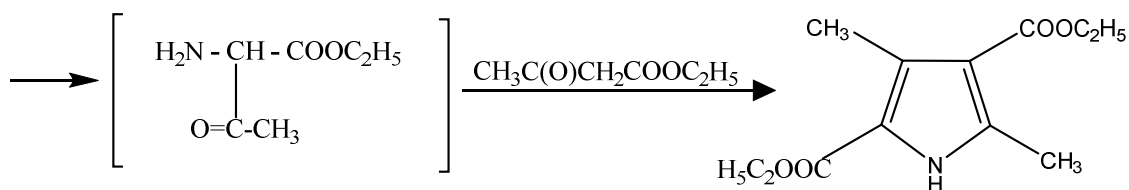
Pyrroles and their derivatives are structurally important heterocycles used in pharmaceuticals, natural products, catalysts, pesticides, dyes and conducting polymers [3]. Synthesizing polysubstituted pyrroles is often challenging and current methods, like the Paal-Knorr reaction, often results in low atom economy in which two oxygen atoms are lost per pyrrole ring produced and/or two water molecules are released as a by-product.

Multifunctional derivatives of Knorr pyrrole are interesting for organic synthesis and as potential monomers as well.

The aim of present work is synthesis of disubstituted acyl derivatives of Knorr pyrrole for their introduction in polyesterification for obtaining N-containing polyesters which can potentially possess valuable properties.

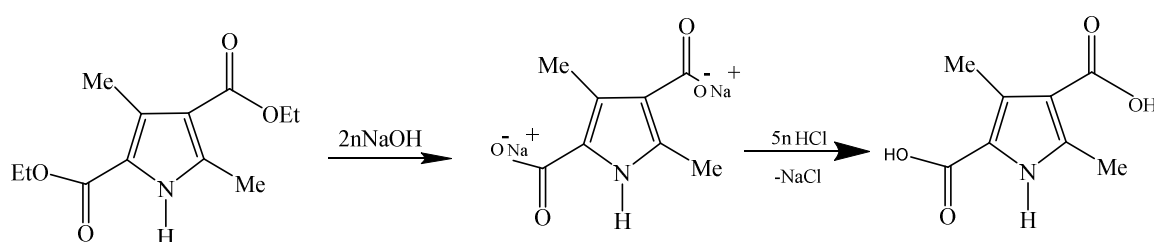
For obtaining starting material for step-growth polymerization firstly we synthesized 2,4-dimethyl-3,5-diethoxycarbonylpyrrole (Knorr pyrrole) by series of transformations. The synthetic protocol proceeds according to the following scheme:





The reaction was monitored by means of the thin layer chromatography.

To continue investigations we carried out hydrolysis of ester groups of 2,4-dimethyl-3,5-diethoxycarbonylpyrrole. The hydrolysis reaction is known to irreversible one in the alkaline medium and is effective for the synthesis of the corresponding acids. Therefore we hydrolyzed Knorr pyrrole in the presence of base such as sodium hydroxide. Necessary conditions were chosen, aqueous-alcohol medium was applied for completely dissolving Knorr pyrrole. Then calculated amount of sodium hydroxide was added. The reaction was completed during one and half hour. The reactive mixture was treated by concentrated hydrochloric acid for isolation of heterocyclic dicarboxylic acid.

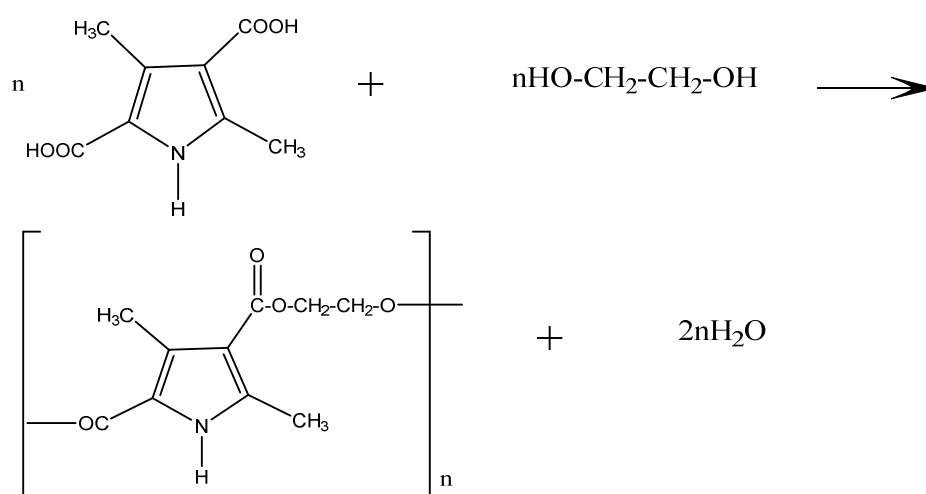


The acid obtained was completely purified by treatment of aqueous alcohol solution. Synthesized 2,4-dimethylpyrrole-3,5-dicarboxylic acid is white powder, insoluble in water, melting point is equal to 205 °C.

Dicarboxylic acids are known to be monomers for step-growth polymerization to obtain various polyesters, polyamides, polyurethanes and their modified derivatives [4, 5].

So according to research objective we carried out polyesterification of 2,4-dimethylpyrrole-3,5-dicarboxylic acid and ethylene glycol at equimolar ratio of parent materials. The process was self-catalyzed and for synthesis of high molar mass polyester it is necessary to remove water, i.e. by-product of reaction, for shifting equilibrium to obtain final polymeric product.

The process was lasted for two hours and the reaction termination was determined by the amount of water eliminated in the Dean-Stark vessel and on the basis of the IR spectrum of the product obtained. We assume that synthesis of polyester proceeds according to the following scheme.



Next step of investigation was studying of properties characteristic for obtained polyester based on 2,4-dimethylpyrrole-3,5-dicarboxylic acid and ethylene glycol.

To estimate the mass-average molar mass of the polyester the Debye method (light scattering) was used [6]. Determination of turbidity of polymer solutions was carried out turbidimetrically using a 2100 AN HACH nephelometer at $\lambda = 5460 \text{ \AA}$. This method is the most reliable and convenient one of the few direct methods for determining the polymers molar mass and covering an exceptionally wide range of molar masses. In addition it is a direct method for measuring the size of macromolecules in solution used for approbation and calibration of other indirect methods, in particular, hydrodynamic ones [6].

The concentration of the initial solution for determining the polymer molar mass in the wavelength region $10^5\text{--}10^7$ is of the order of $2 \cdot 10^{-3} \text{ g/cm}^3$ (0.2 g/dl). For preparing the solution a sample of polyester of 0.1 g (accurate to 0.0001) was placed in a pre-weighed measuring flask ($\sim 50 \text{ ml}$) with ground glass stopper. Further the sample was dissolved in an increasing volume of thoroughly purified and repeatedly distilled solvent, finished to the graduating mark and weighed. The concentration of the solution C_1 (g/cm^3) was calculated by the formula (1):

$$C_1 = \frac{m_p}{m_s} \rho, \quad (1)$$

where m_p — is polymer mass, g; ρ — is solvent density, g/cm^3 ; m_s — is solvent mass, g.

Then 30 ml of the prepared solution was transferred to a cuvette of the instrument, the turbidity of the solution in NEPH units and the refractive index were determined up to full reproducibility. A series of solutions was prepared from the available solution by successively diluting an aliquot ($\sim 30 \text{ ml}$) of each previous solution to 50 ml in a volumetric flask, turbidity and refractive indices were determined. The concentration of the subsequent solutions was calculated according to the formula (1).

In continuation of the research the division scale of nephelometer (β) was determined according to formula (2):

$$\beta = \frac{R'_{90}}{\tau \left(\frac{n}{n_1} \right)^2}. \quad (2)$$

Further the reduced intensity of polymer solutions (R'_{90}) was calculated by substituting the values in the formula (3):

$$R'_{90} = \beta (NEPH_{\text{solution}} - NEPH_{\text{solvent}}). \quad (3)$$

The constant value (H) was calculated by means of formula (4):

$$H = \frac{32(3,14)^3 n_0^2 (\Delta n / \Delta C)^2}{3\lambda^4 N_A}. \quad (4)$$

The obtained data for measurements and calculations are presented in the Table.

Table

Results of turbidimetric measurements and calculations

$C \cdot 10^{-3}, \text{ g/cm}^3$	τ_{NEPH}	$\beta_{NEPH}, 10^{-6}$	$R'_{90}, 10^{-6}$	$H_{NEPH}, 10^{-3}$	$HC/R_{90}, 10^{-3}$	n_{20}^d
2.0644	20.70	22.79	0.4582	217.969	0.0009	1.3782
1.0322	14.10		0.3077		0.0007	1.3779
0.5161	10.10		0.2165		0.0005	1.3770
0.2580	6.98		0.1455		0.0003	1.3770
0.1290	5.72		0.1169		0.0002	1.3765
0.0645	3.90		0.0752		0.0001	1.3760

Based on the calculated values, a plot of the dependence $\frac{HC}{R'_{90}} = f(C)$ was made (see Fig.).

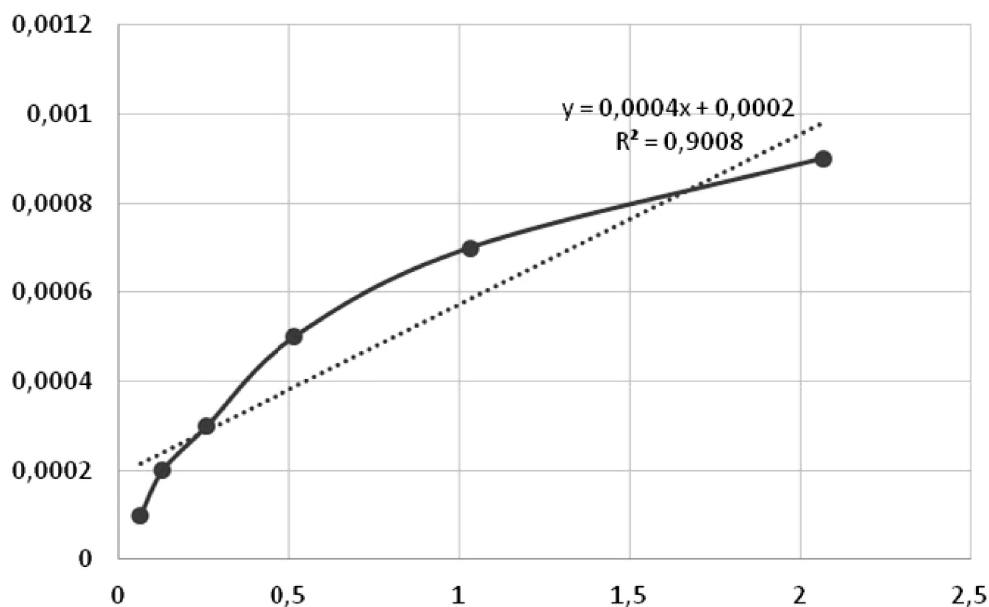


Figure. Dependence of $\frac{HC}{R'_{90}}$ on concentration of polymer ($C, 10^{-3}, \text{g/cm}^3$)

Extrapolating the resulting straight line to C leading to 0, we obtained a segment corresponding to limiting meaning of $\frac{HC}{R'_{90}} = \frac{1}{M_w}$. According to the plot datum the value $\frac{1}{M_w}$ is equal to 0.00019, so mass-average molar mass of the polyester obtained is equal to 5263. Determination of polyester solubility shows that it is soluble in organic solvents and partially soluble in aqueous alcohol mixture.

So we conclude that novel polyester based on Knorr pyrrole derivative such as 2,4-dimethylpyrrole-3,5-dicarboxylic acid and well-known monomer such as ethylene glycol was obtained by step-growth polymerization. Molar mass of polymer synthesized was determined by light-scattering method. The presence of five-membered heterocycle containing nitrogen, ester and methylene groups let us assume that such polyesters can exhibit biological activity and other valuable properties.

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Азотқұрамды гетероциклдердің негізіндегі жаңа күрделі полиэфирлер: синтезі және зерттелуі

Мақалада екі ғылымның — гетероциклді қосылыстар химиясы мен поликонденсациялық процестер химиясының — қиылысуындағы зерттеу нәтижелері келтірілген. 2,4-Диметил-3,5-диэтоксикарбонилпиррол (Кнорр пирролы) ілеспелі айналулар қатарымен синтезделді. 2,4-диметилпиррол-3,5-дикарбон қышқылы Кнорр пирролын гидролиздеу арқылы алынды. Процес спирт-сілтілі ортада біржарым сағаттың ішінде толығымен аяқталатыны көрсетілді. Жаңа күрделі эфир 2,4-диметилпиррол-3,5-дикарбон қышқылы мен этиленгликольдің негізінде полиэтерификациялау реакциясы арқылы синтезделді. Алынған полимерлердің физикалық-химиялық сипаттамалары анықталды. Күрделі эфирдің ортамассалық молекулалық массасы жарықшашу әдісі арқылы анықталып, 5263 тең екені көрсетілді. Есептеу мәліметтері мен турбидиметрлік әдіспен сұйытылған полимер ерітінділерін бұлдырлығын анықтау бойынша тәжірибе мәліметтерінің сәйкестігі нәтижелердің нақтылығын көрсетті. Синтезделген полимердің физикалық-химиялық қасиеттері мен құрылымын сараптау 2,4-диметилпиррол-3,5-дикарбон қышқылы мен этиленгликольдің негізіндегі күрделі полиэфирдің биологиялық белсенділікке ие алкидті шайырлардың компоненті ретінде қолдануының мүмкіндігін тұжырымдады.

Кілт сөздер: Кнорр пирролы, 2,4-диметилпиррол-3,5-дикарбон қышқылы, полиэтерификациялау, күрделі полиэфир, турбидиметрлік.

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Новые сложные полиэфиры на основе азотсодержащих гетероциклов: синтез и исследование

В статье представлены результаты исследований, выполненных на стыке двух наук — химии гетероциклических соединений и химии поликонденсационных процессов. 2,4-Диметил-3,5-диэтоксикарбонилпиррол (пиррол Кнорра) был синтезирован рядом последовательных превращений. Гидролизом пиррола Кнорра была получена 2,4-диметилпиррол-3,5-дикарбоновая кислота, подобраны оптимальные условия проведения реакции. Показано, что процесс полностью завершается в течение полутора часов в спиртово-щелочной среде. Новый сложный полиэфир на основе 2,4-диметилпиррол-3,5-дикарбоновой кислоты и этиленгликоля был синтезирован реакцией полиэтерификации. Были установлены физико-химические характеристики полученного полимера. Методом светорассеяния была определена среднемассовая молекулярная масса сложного полиэфира, которая оказалась равной 5263. Хорошая сходимость расчетных данных и воспроизводимость эксперимента по определению мутности разбавленных растворов полимера турбидиметрическим методом указывают на достоверность результатов. Анализ структуры и физико-химических свойств синтезированного полимера предполагает, что сложный полиэфир на основе 2,4-диметилпиррол-3,5-дикарбоновой кислоты и этиленгликоля может быть использован в качестве компонента алкидных смол, потенциально обладающих биологической активностью.

Ключевые слова: пиррол Кнорра, 2,4-диметилпиррол-3,5-дикарбоновая кислота, полиэтерификация, сложный полиэфир, турбидиметрия.

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The influence of nanostructured carbon additives to the functional electrode characteristics of lithium-ion batteries

This research is devoted to the study of the effect of nanostructured carbon additives on the functional characteristics of a positive electrode based on vanadium oxide for lithium-ion batteries. It has been shown that the use of carbon nanotubes and graphene oxide instead of traditional carbon black significantly increases the specific characteristics of the electrode. Also the improvement of the specific characteristics of the positive electrode in lithium-ion batteries when using graphene and carbon nanotubes instead of carbon black was proved. This effect is explained by an increase in the speed of movement of lithium ion inside the material, due to the higher conductivity of nanotubes and graphene, and a more compact contact of crystals. It is due to higher electronic conductivity of carbon nanotubes and graphene compared to conventional carbon black. In addition, the intercalation of quasi-one-dimensional (nanotubes) and quasi-two-dimensional (graphene) structures into the electrode makes possible to ensure a more compact contact of active substance particles with a current collector. This helps to reduce the mass fraction of the conductive additive in the electrode structure and increase its specific parameters. It is shown that the use of graphene and carbon nanotubes as conductive additives instead of conventional carbon black may increase significantly the specific characteristics of positive electrodes in lithium-ion batteries.

Keywords: nanostructured carbon additive, electrode, carbon soot, speed of Li-ion, Li-ion battery, carbon nanotubes, graphene oxide, vanadium oxide.

Currently, lithium-ion batteries are the most commonly used chemical energy sources. Considering the evolution of modern electronic devices there are clear trend to minimization and increased functionality. This leads to a significant increase in energy consumption which, in return, requires the creation of more efficient and compact energy sources.

Specific energy lithium-ion battery is determined by specific characteristics of electrode materials and first of all by the cathode material characteristics as it accounts for approximately 40 % of the mass of all active components. In addition, the battery contains inactive components such as current collectors, separators, box, etc., which are necessary for the functioning of the battery.

Therefore, the problem of increasing energy efficiency of modern energy storage devices with restrictions imposed on the battery form-factor, on the one hand is related to the problem of obtaining and investigating new active electrode materials. On the other hand, it is important to search for new engineering solutions that allow reducing the mass of inactive components, and thereby contributing to an increase in the specific energy of the battery.

Among the most promising cathode materials the highlight vanadium pentoxide (V_2O_5), of which the specific capacity reaches 400 mAh/g [1], that is 2–2.5 times exceeds the specific values of traditional positive electrode materials ($LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$). Vanadium oxide, like traditional cathode materials, has low electron conductivity. Therefore, when forming a positive electrode, it is necessary to use a conduc-

tive additive that would ensure the transport kinetics of lithium ions during the intercalation/deintercalation into vanadium oxide structure. Typically, in commercial batteries, various carbon blacks are used as such an additive (for example, TimcalSuperC45). Publications of recent years indicate that the use of various carbon nanostructures, such as graphene and nanotubes, as conductive additives, can significantly improve the specific parameters of the electrodes of lithium-ion batteries [2–5].

This effect is due to the higher electronic conductivity of carbon nanotubes and graphene compared to conventional soot. In addition, the introduction of quasi-one-dimensional (nanotubes) and quasi-two-dimensional (graphene) structures into the electrode makes it possible to ensure a more intimate contact of active substance particles with a current collector. This helps to reduce the mass fraction of the conductive additive in the electrode structure and increase its specific parameters.

The purpose of this work was to study the effect of various nanostructured carbon additives on the specific characteristics of a positive electrode based on vanadium oxide for lithium-ion batteries.

The procedure for preparing the electrode included several stages. At first stage, a cathode paste consisting of a hydrothermally synthesized vanadium oxide powder [1], a conductive additive and a polymer binder, was needed. As conductive additives, carbon nanotubes (Oxal, RF), reduced graphene oxide obtained by the modified Hammers method, or carbon black TimcalSuper C45 were used. Polyvinylidene fluoride, hsv-900 (kynar), was used as a polymer binder. Dry components were added with N-methylpyrrolidone, and then the solution was mechanically stirred for 6 hours at 60 °C. The portion of dry substances in the solution was 60–80 mg/ml. The mass loading of each of their dry components was determined by the ratio of 88.5 % (vanadium oxide powder): 1.5 % (conductive carbonaceous additive): 10 % (polymer binder).

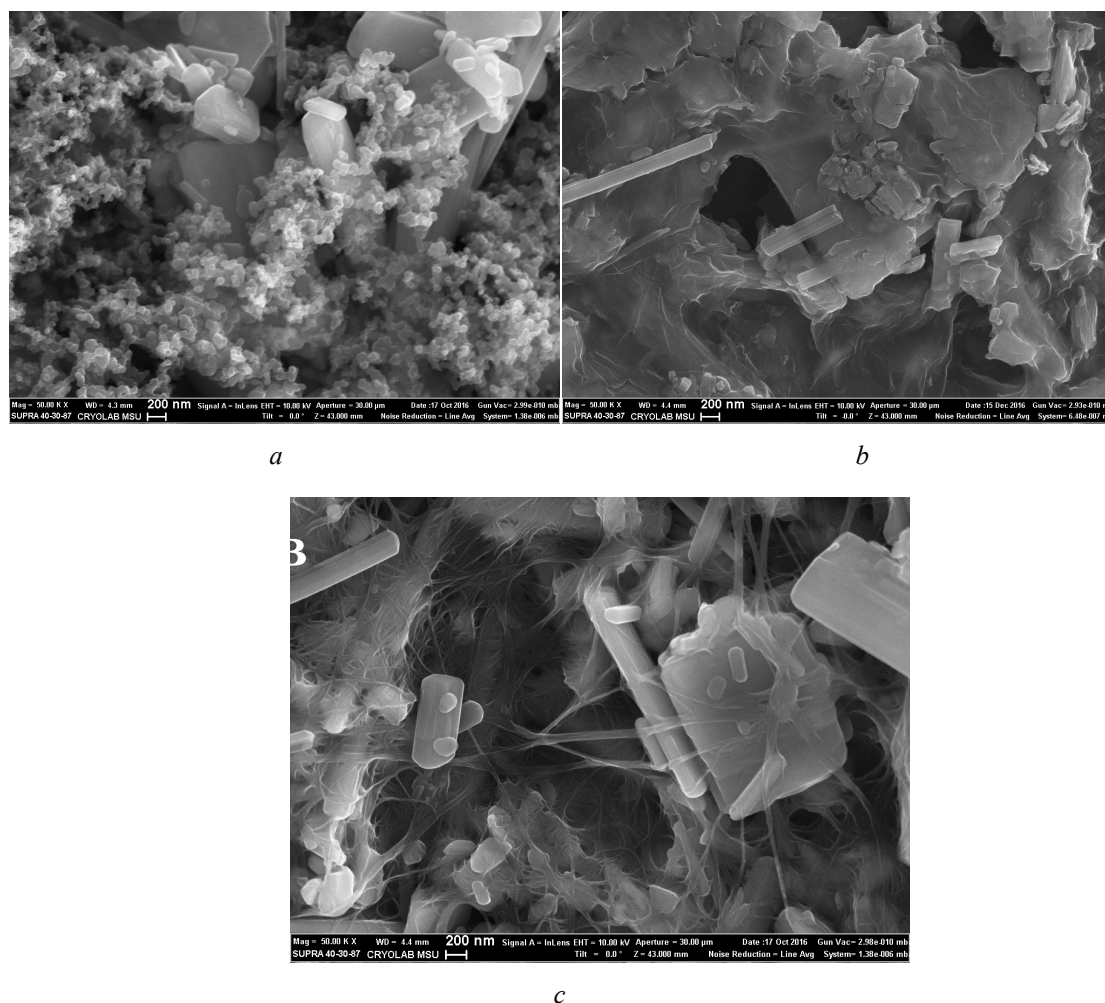


Figure 1. Micrographs of vanadium oxide electrodes with the addition of carbon black C45 (*a*), reduced graphene oxide (*b*) and carbon nanotubes (*c*)

After stirring, the solution was applied using an airbrush onto aluminum foil 20 μm thick. Further, the sample was dried and electrodes with a diameter of 1.5 mm were formed from it. Electrochemical testing of the electrodes was carried out in standard 2032 cells. Metallic lithium was used as a negative electrode. The cells were assembled in a glove box in an argon medium with a moisture/oxygen level of not more than 0.1/1 ppm.

As a separator, polypropylene film Celgard 2500 was used. As an electrolyte, 1M LiClO_4 solution was used in a mixture of propylene carbonate with 1, 2-dimethoxyethane (PC:DME) with a ratio of 7:3 by volume. Galvan static cell cycling was performed on an 8-channel MTI-BST8-MA power supply analyzer in a voltage range of 2–4 V. The charge/discharge current of the cell was set at a rate of 10 mA per gram of cathode coating.

Figure 1 presents microphotographs of the surface of electrodes with different carbon additives. It can be seen that the particles of all carbon additives are uniformly distributed over the surface of the electrodes. In this case, if the soot particles form separate agglomerates (Fig. 1a), the flakes of the reduced graphene oxide (Fig. 1b) and the carbon nanotubes evenly cover the vanadium oxide crystals. Presumably, due to the morphology and large surface area, the two-dimensional flexible graphene sheet like particles and the long fibers formed by the nanotubes should have a larger contact area with the active substance particles as opposed to the spherical soot particles, thereby providing the best electronic transport in the cathode material. In addition, in view of the ability of the reduced graphite oxide and carbon nanotubes to form good coatings, an increase in the adhesion of the paste to the aluminum foil is contemplated.

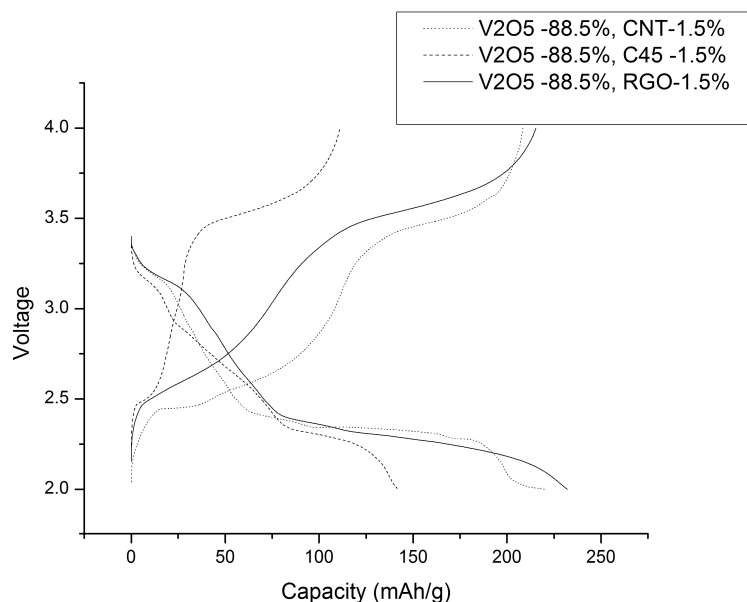


Figure 2. Galvan static Discharges/Charging Curves of Cells with a Positive Electrode Based on Vanadium Oxide and Various Conducting Additives (1.5 wt.%): Carbon nanotubes, reduced graphene oxide, and commercial TimcalSuper C45. The current is 10 mA/g

Figure 2 shows galvan static discharges/charge curves of electrodes with the same percentage of three different conductive additives and the same amount of vanadium oxide. All curves are represented by a series of plateaus in the 2–4 V regions, which are characteristic for phase transitions inside vanadium oxide crystals during intercalation/deintercalation of lithium ions. This indicates that all the carbon structures used in the experiments provide transport of lithium ions into vanadium oxide crystals. However, specific capacitance of the carbon-based electrode was approximately 150 mAh/g, which is significantly lower than the specific electrode indexes, based on reduced graphene oxide and carbon nanotubes. So the specific capacitance of these electrodes was about 225–240 mAh/g.

Thus, it is clearly shown that the use of graphene and carbon nanotubes as conductive additives instead of traditional soot allows increasing significantly the specific characteristics of positive electrodes in lithium-ion batteries. Such an effect can be explained by an increase in the transport kinetics of lithium ions within the active material due to higher conductivity of nanotubes and graphene and more dense contact with crystals.

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Литий-иондық аккумуляторлардың электродтарының функционалды сипаттамаларына наноқұрылымды көміртегі қоспалардың әсері

Мақала литий-иондық аккумуляторлар үшін ванадий тотығы негізіндегі оң зарядты электродының функционалды сипаттамаларына наноқұрылымды көміртекті қоспалардың әсерін зерттеуге арналған. Көміртекті нанотүтікшелерді және қарапайым көміртек күйесінің орнына тотықсызданған графен тотығын қолдану электродтың меншікті сипаттамаларын жоғарлататыны көрсетілген және графен мен көміртекті нанотүтікшелерді қолдану литий-иондық батареялардағы оң зарядты электродтың ерекше сипаттамаларын жақсартатыны дәлелденген. Бұл эффект материал ішіндегі литий-ионның қозғалу жылдамдығының өсуімен түсіндіріледі, және бұл нанотүтікшелер мен графеннің жоғары өткізгіштігін және кристалдармен тығыз түйісуін қамтамасыз етеді. Осындай эффект дәстүрлі күйенің орнына көміртекті нанотүтікшелер мен графеннің электрондық өткізгіштігінің аса жоғары болуымен жүзеге асырылады. Сонымен қоса электродқа квазибірлешемді (нанотүтікше) және квазиекілешемді (графен) жүйелерді енгізу белсенді зат бөлшектерінің тоқ алғышпен тығыз байланысын қамтамасыз етеді. Бұл электрод жүйесіндегі өткізгіш қоспаның массалық үлесінің төмендеуіне және оның меншікті көрсеткіштерінің артуына әкеледі. Литий-иондық аккумуляторларда қарапайым күйенің орнына графен мен көміртекті нанотүтікшелерді өткізгіштік қоспалар ретінде қолдану оң зарядты электродтардың меншікті сипаттамаларының артуына себеп болады.

Кілт сөздер: наноқұрылымды көміртек қоспасы, электрод, көміртекті күйе, литий-ионның жылдамдығы, литий-иондық батареялар, көміртекті нанотүтікшелер, графен оксиді, ванадий тотығы.

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Влияние наноструктурированных углеродных добавок на функциональные характеристики электродов литий-ионных аккумуляторов

Статья посвящена изучению влияния наноструктурированных углеродных добавок на функциональные характеристики положительного электрода на основе оксида ванадия для литий-ионных аккумуляторов. Было показано, что использование углеродных нанотрубок и восстановленного оксида графена вместо традиционной углеродной сажи значительно повышает удельные характеристики электрода, а также доказано улучшение специфических характеристик положительного электрода в литий-ионных батареях при использовании графена и углеродных нанотрубок вместо обычной сажи. Этот эффект объясняется увеличением скорости передвижения литий-иона внутри материала, обусловленным более высокой проводимостью нанотрубок и графена и более плотным контактом кристаллов. Кроме того, внедрение в электрод квазиодномерных (нанотрубки) и квазидвухмерных (графен) структур позволяет обеспечить более плотный контакт частиц активного вещества с токосъемником. Это способствует снижению массовой доли проводящей добавки в структуре электрода и повышению его удельных показателей. Показано, что использование графена и углеродных нанотрубок в качестве проводящих добавок вместо традиционной сажи позволяет существенно повысить удельные характеристики положительных электродов в литий-ионных аккумуляторах.

Ключевые слова: наноструктурированные углеродные добавки, электрод, углеродная сажа, скорость ионов лития, литий-ионные батареи, углеродные нанотрубки, оксид графена, оксид ванадия.

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Electrochemical behavior of zirconium

In recent years, alternating current has been widely used in various fields of chemical and electrochemical technology. When a symmetric alternating current passes through an electrochemical cell, in principle there should be no visible changes, since the product restored to the cathode half-period should be oxidized back to the anodic half-period. However, depending on the conditions of electrolysis, electrode material, etc. a purposeful course of the electrochemical process is possible. From the point of view of developing methods for the production of pure metal and its various compounds widely used in modern industry, a study on the electrochemical behavior of zirconium is of theoretical and practical interest. The paper shows the distinctive peculiarities of electrochemical processes occurring on a zirconium electrode during electrolysis by an industrial alternating current. Optimal conditions for zirconium dissolution were determined when studying the influence of current density on zirconium and titanium electrodes, the concentration and temperature of the electrolyte, the duration of electrolysis and the frequency of alternating current. The elimination of the passivation process of the zirconium electrode and the increase of the rate of the metal dissolution were shown while the polarization of zirconium by an alternating current in combination with a titanium electrode.

Keywords: electrolysis, zirconium, industrial alternating current, current density, a frequency of alternating current.

Introduction

At present, the electrochemical behavior of metals under alternating current polarization is comprehensively investigated. However, there is no information on obtaining salt of refractory metals, such as zirconium in the literature. As can be seen from preliminary studies, one of the most promising methods for the preparation of zirconium compounds is the dissolution of metallic zirconium wastes by electrochemical means when polarized by alternating current in aqueous solutions.

Electrochemical properties of refractory metals have their own characteristics. Their anodic ionization proceeds by forming a nonmetallic solid phase. In the anodic polarization of refractory metals such as titanium, zirconium, tungsten passes in a passive, transpassive state, or some become metal-ion through the formation of a surface film when the anodic potential in the electrolyte increases [1–6].

Such properties of these metals are due to the electronic and external structure of atoms.

Studies of recent years on the study of electrode processes under the influence of alternating current have shown that under certain conditions some electrochemical reactions proceed with a sufficiently high rate with the formation of the target products [7]. In this regard, a comprehensive study of the electrochemical behavior of zirconium under polarization by alternating current of 50 Hz is perspective.

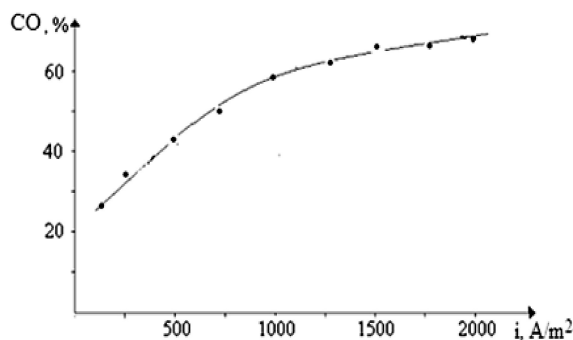
Experimental

The aim of this work was to study the electrochemical behavior of zirconium under polarization by alternating current in nitric acid solution, the effect of various electrolysis parameters and obtaining its salt — zirconium nitrate.

The studies were carried out in a 50 ml glass electrochemical cell; the electrode spaces were not separated. Zirconium plate of 2.5×2.5 size and a titanium wire (grade VT-01) were used as electrodes. The source of the sinusoidal alternating current was power supply V-24 (in simplified form, it is a step-down transformer with a smooth voltage regulation), which had AC terminals. Before the experiment, the electrodes were thoroughly cleaned and rinsed with distilled water. It should be noted that after electrolysis the loss of electrode mass was determined and the current output (CO) of zirconium was calculated for the anode half-period.

The effect of various parameters on the electrolysis process, in particular, the current density at electrodes, the concentration and temperature of electrolyte and the frequency of the current were studied.

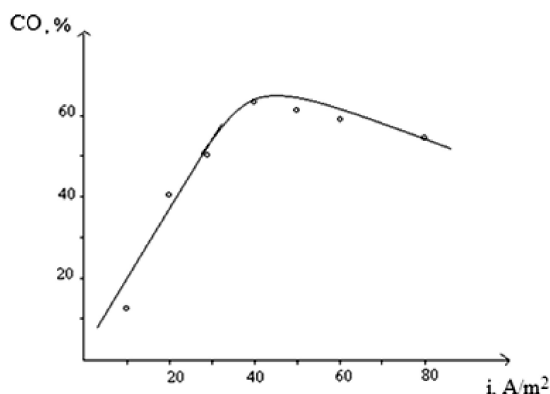
The influence of the current density on the zirconium electrode in the interval of 100–2000 A/m² was studied. As the results of the study showed, the current output increases from 26 % to 65 % with increasing current density (Fig. 1).



$C_{\text{HNO}_3} = 0.5\text{M}$; $\tau = 0.5$ hour; $t = 20$ °C; $\nu = 50$ Hz

Figure 1. Effect of current density on the zirconium electrode on the current output of zirconium dissolution in nitric acid solution

When investigating the effect of the alternating current density on a titanium electrode on the current output (CO) of zirconium dissolution in the range of 10–80 kA/m² in nitric acid solution 0.5M at a current density on a zirconium electrode of 2000 A/m², the dependence has a curve form passing through the maximum (Fig. 2). The results of the experiments showed that when the current density on the titanium electrode is increased up to 40 kA/m², the value of the CO of the zirconium dissolution increases, reaching 65 %. Since the current density is higher than 40 kA/m², the CO decreases, since it seems that more friable oxide films which have low semiconductor properties are formed at higher current densities on the titanium electrode. When zirconium is polarized by alternating current in the anodic half-period, zirconium ions (IV) are formed.



$C_{\text{HNO}_3} = 0.5\text{M}$; $\tau = 0.5$ hour; $t = 20$ °C; $\nu = 50$ Hz

Figure 2. Influence of the alternating current density on a titanium electrode on the current output of the zirconium dissolution in nitric acid solution

As is known, the use of alternating current accelerates the zirconium dissolution process. In the polarization of zirconium by alternating current in nitric acid solution, zirconium ions (IV) form salt by interacting with nitrate ions.

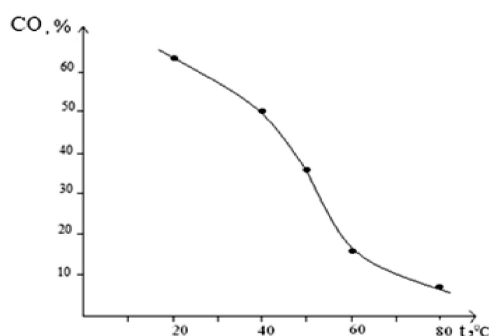
An increase of the concentration of nitric acid from 0.25 to 1.0M leads to an increase in the current output and a further increase of the concentration to 3.0M leads to a decrease in the current output of dissolution of the electrode under the study (see Table). The CO of the zirconium dissolution in nitric acid concentration of 5 mol/l is 41 %. An increase in the concentration of nitric acid leads to a decrease in electrical conductivity, which in turn reduces the CO. In addition, intense oxygen evolution is observed and the surface of the zirconium electrode is passivated with an increase of nitrate ions in the anode half-period.

Table

Influence of the nitric acid concentration on the current output of the zirconium dissolution
 $(i_{Zr} = 2000 \text{ A/m}^2; i_{Ti} = 40 \text{ kA/m}^2; \tau = 30 \text{ min}; t = 20^\circ \text{C}; \nu = 50 \text{ Hz})$

$C, \text{ M}$	0.25	0.5	1.0	1.5	2.0	2.5	3.0
$\text{CO}, \%$	37	63	82	78	74	72	70

The calculated reaction order is 1.24. It means that the reaction of the zirconium dissolution is first-order. The known regularities in the course of chemical reactions involve an increase in the rate of the reaction, however in our experiments it has been established that as the temperature rises (Fig. 3), a decrease in the current output on the dissolution of the zirconium electrode is observed. If the CO is 63 % at $t = 20^\circ \text{C}$, then it is 10 % at 80°C . As the temperature rises, the mobility of ions decreases, which leads to a decrease in the current output. Optimal conditions for electrolysis: $C_{\text{HNO}_3} = 0.5 \text{ M}$, $i_{Zr} = 2000 \text{ A/m}^2$; $\tau = 0.5 \text{ hour}$.

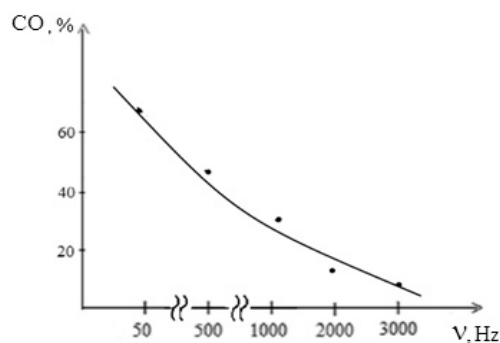


$i_{Zr} = 2000 \text{ A/m}^2; i_{Ti} = 40 \text{ kA/m}^2; \tau = 0.5 \text{ hour}; C_{\text{HNO}_3} = 0.5 \text{ M}; \nu = 50 \text{ Hz}$

Figure 3. Influence of the electrolyte temperature on the current output of the zirconium dissolution in nitric acid solution

The dependence of the current output of the zirconium dissolution under the polarization by alternating current on the duration of electrolysis shows that with an increase in the time from 0.25 to 1.5 hours, the CO decreases. If the CO is 62 % at 0.25 h, then at 1.5 h it reaches 20 %. The decrease in the CO in prolonged experiments is due to the formation of an oxide on the surface of the electrode, resulting in partial screening of the electrode and inhibition of the dissolution process.

One of the main parameters of electrolysis is the frequency of alternating current. In this regard, the influence of the frequency of alternating current on the zirconium dissolution in nitric acid solution was studied (Fig. 4). It was found that the highest value of the CO on the zirconium dissolution is observed at a frequency of 50 Hz. An increase in the frequency of alternating current from 50 to 3000 Hz at a current density on zirconium electrode 2000 A/m^2 and titanium electrode kA/m^2 leads to a decrease in the current output of the zirconium dissolution from 64 % to 5 %.



$i_{Zr} = 2000 \text{ A/m}^2; i_{Ti} = 40 \text{ kA/m}^2; \tau = 0.5 \text{ hour}; C_{\text{HNO}_3} = 0.5 \text{ M}; t = 20^\circ \text{C}$

Figure 4. Influence of the alternating current frequency on the current output of the zirconium dissolution in nitric acid solution

Apparently, at a high current frequency, the required duration of the anode half-period is not ensured for the dissolution reaction to proceed. This decrease is also associated with a decrease in the magnitude of the average amplitude of the alternating current with increasing frequency, which leads to a decrease in the polarization of electrodes. At this point, hydrogen ions are involved in the electrode process. In the cathode half-period, hydrogen ions are reduced to an active atomic state and in the anodic half-period they are back oxidized to hydrogen ions.

Conclusions

Thus, for the first time, we have studied the electrochemical behavior of zirconium under polarization by alternating current. The effect of various parameters of the electrolysis of the current density, the concentration and temperature of the electrolyte, the duration of electrolysis and the frequency of the alternating current on the current output zirconium dissolution have been studied. Optimal conditions for the zirconium dissolution have been determined. It was established that zirconium nitrate is formed when zirconium is polarized by the alternating current, which allows to develop optimal methods for obtaining zirconium nitrate.

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Цирконийдің электрохимиялық қасиеті

Соңғы жылдары айнымалы ток әртүрлі химиялық және электрохимиялық технология салаларында кеңінен қолдануда. Симметриялы айнымалы тоқты электрохимиялық ұяшықтан өткізген кезде негізінен ешқандай өзгерістер орын алмауы керек, себебі катодты жартылай периодта тотықсызданған өнім анодты жартылай периодта кері тотығуы тиіс. Алайда электролиз жағдайына электрод материалына және тағы басқа жағдайларға байланысты мақсатты электрхимиялық процесс жүруі мүмкін. Теориялық және практикалық тұрғыдан цирконийдің электрохимиялық қасиеттерін зерттеу қазіргі заманғы өнеркәсіпте кеңінен қолданатын таза металл және оның қосылыстарын алуда қызығушылық туындайды. Мақалада айнымалы токпен поляризацияланған цирконий электродында жүретін электрохимиялық үрдістердің ерекшеліктері көрсетілген. Цирконий және титан электродтарындағы ток тығыздығының, электролит концентрациясы мен температурасының, электролиз ұзақтығының және айнымалы ток жиілігінің әсерлерін зерттегенде айнымалы токпен поляризацияланған цирконийдің еруінің оңтайлы жағдайлары анықталды. Титан электродымен жұптасқанда цирконий электродында пассивтену процесі жойылып, металдың еру жылдамдығы артатындығы белгілі болды.

Кілт сөздер: электролиз, цирконий, өндірістік айнымалы ток, ток тығыздығы, айнымалы ток жиілігі, электрхимиялық процесс.

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Электрохимическое поведение циркония

В последние годы переменный ток находит все более широкое применение в различных областях химической и электрохимической технологии. При пропускании через электрохимическую ячейку симметричного переменного тока в принципе никаких видимых изменений произойти не должно, так как восстановленный в катодный полупериод продукт должен обратно окисляться в анодный полупериод. Однако, в зависимости от условий электролиза, материала электрода и т.д., возможно целенаправленное протекание электрохимического процесса. Исследование электрохимического поведения циркония представляет и теоретический, и практический интерес, с точки зрения разработки методов получения чистого металла и различных его соединений, широко применяемых в современной промышленности. В работе показаны отличительные особенности электрохимических процессов, протекающих на циркониевом электроде при электролизе промышленным переменным током. Определены оптимальные условия растворения циркония при исследовании влияния плотности тока на циркониевом и титановом электродах, концентрации и температуры электролита, продолжительности электролиза и частоты переменного тока. Показано, что при поляризации переменным током циркония в паре с титановым электродом устраняется процесс пассивации циркониевого электрода, и скорость растворения металла возрастает.

Ключевые слова: электролиз, цирконий, промышленный переменный ток, плотность тока, частота переменного тока, электрохимический процесс.

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Physicochemical regularities of the sorption of amino acids on the surface of hydroxylapatite

Biogenic and pathogenic mineral formations contain calcium phosphates. It is known that hydroxylapatite is the main mineral component of bone tissue, tooth enamel, and dentin. The basis of the processes of mineralization is proposed to be in the adsorption interaction of free amino acids and associated protein molecules with inorganic components in body fluids and emerging phases. However, the mechanism of their interaction is not fully understood. In this paper the adsorption of amino acids on the surface of hydroxylapatite has been studied. The synthesis of calcium phosphates from solution has been carried out. According to the results of XRD and IR spectroscopy it has been established that precipitation is represented by the phase of hydroxylapatite. The adsorption of amino acids in a wide range of variation of their concentrations and the pH of the solution has been investigated. It has been established that adsorption of amino acids on the surface of hydroxylapatite reaches saturation. The effect of pH on the maximum adsorption of amino acids on hydroxylapatite has been considered. It has been established that adsorption of amino acids is described by the Langmuir model. The result of IR spectroscopy confirmed adsorption. It has been determined by the sign of the surface charge of the solid phase of hydroxylapatite. The values of the Gibbs energy have been calculated. It has been revealed that the interaction of amino acids with the surface of the hydroxylapatite is characterized by physical adsorption.

Keywords: hydroxylapatite, adsorption, amino acid, dissolution, surface charge, solution, Langmuir model, Freundlich model.

Introduction

Calcium phosphates are part of biogenic and pathogenic mineral formations. Biogenic formations are part of different organs and have different functions; they are genetically determined, their place in the body is strictly defined. Pathogenic mineral formations occur in the disruption of the functioning of the whole organism or its separate organs. It is known that hydroxylapatite is the main mineral component of bone tissue, tooth enamel and dentin. The hydroxylapatite plays an important role in many physiological processes in the human body [1–4].

In the papers [5–13] the researchers described that calcium phosphates had an excellent biological activity and had been widely used in bone reconstruction or orthopedic supplements, as the primary inorganic material the composition of the hard tissues of the body.

Interaction of organic and mineral components is important in such processes of biogenic crystallization, as the formation of mammals bone matrix, as well as the emergence and growth of pathogenic entities.

Hydroxylapatite (HA) and dicalcium phosphate dihydrate (DCPD) $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ are of greatest interest from number of the biocompatible low-temperature calcium phosphates. In nature DCPD expressed in the mineral brushite is the most soluble of biocompatible calcium phosphates, whereas HA is less soluble [14]. In [9] it is examined the differences in stability of calcium phosphates, and also indicated the CA/P ratio, to confirm the differences between the calcium phosphates.

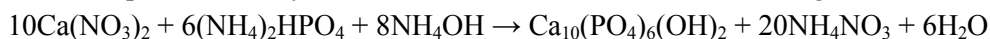
There are a number of assumptions, according to which the basis of the processes of mineralization, is in the adsorption interaction of free amino acids and associated protein molecules with inorganic components in body fluids and emerging phases [15, 16]. The mechanism of their interaction is not fully understood.

In this regard, recent studies aimed at studying the regularities of adsorption of amino acids on the inorganic component of physiognomic and pathogenic neoplasms.

The aim of this work is investigation of peculiarities of adsorption of amino acids on the hydroxylapatite by varying the pH of the solution.

Materials and methods

The synthesis of hydroxylapatite. It is carried out by deposition from aqueous solution at room temperature by the method of spontaneous crystallization in accordance with the following reaction:



The precipitate is obtained by mixing dilute solutions of calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ in the ratio of 1.67:1, and aqueous solution of ammonia NH_4OH at room temperature (22–25 °C). When the synthesis was carried out, to a 500 ml solution containing $\text{Ca}(\text{NO}_3)_2$, 5 ml of conc. NH_4OH solution, 500 ml of a solution $(\text{NH}_4)_2\text{HPO}_4$ with a concentration of (50 mmol/l) are rapidly poured. The total volume of the mixture is 1000 ml. After mixing the solutions, the pH of the system is corrected to 12.00 ± 0.05 with solutions of NaOH (20 %) and/or HNO_3 (1:1).

After the heterogeneous system settling for two days, the solution was filtered using a water-jet pump, Bunsen flask and a Buchner funnel (using two filters, a blue ribbon). After filtration, the filter cake was washed with water ($V=50$ ml), dried in a drying box at a temperature of ~ 100 °C until complete removal of water. The dried precipitate is ground in a porcelain mortar into a powder, transferred into a special marked container and weighed on an analytical balance.

It is the determination of the sign of the charge of the particles of the sols of hydroxylapatite by the method of capillary analysis. When a piece of filter paper is immersed in water, thin wall paper is charged negatively. These allow determining the sign of the charge of the colloidal particles. Negatively charged particles rise through the capillaries.

We used the direct potentiometric method for pH measurements. The measurements were carried out in a glass beaker, which pre-processes. The measurement error is ± 0.01 pH units.

Determination of the concentration of calcium ions in the experiment performed by direct potentiometry using ion-selective electrode and calibration schedule determined by the value of $[\text{Ca}^{2+}]$.

Determination of phosphate ions was carried out by the molybdenum blue method (State Standard 18309–72) on the KFK-2 device, using the red filter ($\lambda_{\text{ef}} = 690$ nm) and cuvettes with a layer thickness of 2 cm. The determination is repeated three times and the average values of optical densities to build a calibration curve: $D = f\{C(\text{PO}_4^{3-})\}$, calculate the regression equation.

Error determinations are found within 2–4 Rel. %. X-ray diffraction (XRD) is used to study the mineral (phase) composition of synthesized solid phases of hydroxylapatite. A diffractogram was obtained by the «method of powder» for stationary x-ray apparatus DRON-3 [17, 18]. Phase identification was performed using ASTM international indexes and tables [18]. The sensitivity of the XRD method for these measurements is 3 %.

The infrared spectroscopy method was used for more information on the composition of the samples obtained. IR spectrum was obtained on the FSM 2201 spectrophotometer. Mathematical processing of the data was carried out using statistical software Statistica 10 and Static2 from the StatSoft statistical package. The sensitivity of the method of IR-spectroscopy for the measurement data was < 5 %.

The method of area measurement was used to analyze the specific surface of synthetic calcium phosphates. Analysis of the specific surface of the samples according to the BET method (SBET-N2) was carried out using techniques of single-point standard gas adsorption equilibrium at an absolute pressure in the adsorption unit Sorbtometr, IK SB RAS (OSC SB RAS, Omsk). The limit of permissible relative error of measurement of the specific surface in the mode of multiple measurements is not more than 5 %.

The adsorption experiment. 0.5 g of hydroxylapatite sample was placed in a flask and the solution of amino acids was poured. The concentration of amino acids was varied as follows: 2, 4, 6, 8, 10, 15, 20, 25, 30 mmol/l and pH range $5.00\text{--}8.00 \pm 0.05$ (except 6.50) in increments of 0.50. Shaking is carried out for 30 minutes, then it was left for 48 hours. After the specified time the content of the flasks was filtered and there was determined the content of amino acids in the filtrate by the method of transfer of amino acids in a solu-

ble copper salt and subsequent photometric determination, the pH after adsorption was measured, the mass of precipitation was determined.

Determination of the concentration of amino acids in the experiment was assessed by the photometric determination of amino acids. The essence of the method for determination of the concentration of amino acids used in the analysis is based on the conversion of amino acids into soluble copper salts and their subsequent photometric determination. KFK-2 photoelectric colorimeter was used for measurements. Determination of optical density of standard solutions is carried out in the wavelength interval that includes the value of 670 nm. A calibration curve was built for measurements. Determining the unknown concentration of amino acids was performed using a calibration chart.

Results and discussion

1. The results of the synthesis of crystals of hydroxylapatite. The methods of XRD and IR spectroscopy were established that the precipitation obtained after 48 hours of crystallization, represented by the phase of hydroxylapatite (Fig. 1), belonging to the hexagonal crystal structure (2Θ corresponds to 31.8, 32.9, 39.9). The crystallite size was calculated of equal to $D = 13$ nm [19], which is consistent with the data [2].

The IR spectrum of the samples contained the whole spectrum of the bands characteristic for hydroxylapatite (Fig. 2) and have a complex structure. The presence of absorption at 1113, 1019, 958 cm^{-1} and 604, 573, 469 cm^{-1} correspond to vibrations of a group PO_4^{3-} as well as trough at 3576, 3400 cm^{-1} that are characteristic for OH- stretching vibrations of molecules of structurally bound water. One can also notice that the spectrum contains absorption bands of CO_3^{2-} with the peaks at 1460, 1420 and 865 cm^{-1} . In addition, a broad band in the region of 2700–3700 cm^{-1} and peak at 3540 cm^{-1} can be attributed to the stretching vibrations of H-O-H and OH^- , respectively.

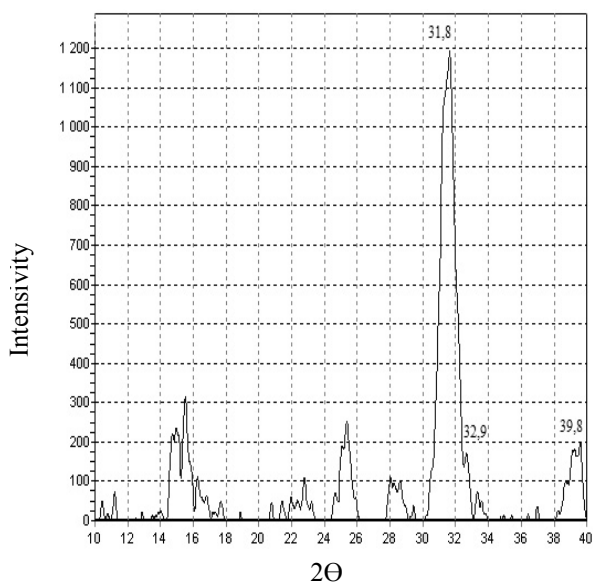


Figure 1. The diffraction pattern of the synthesized sample of hydroxylapatite at $\text{pH} = 5.50 \pm 0.05$ (48 hours)

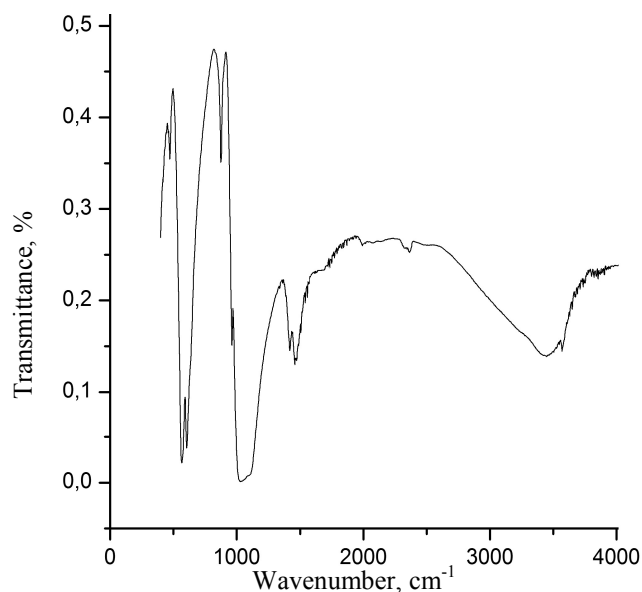
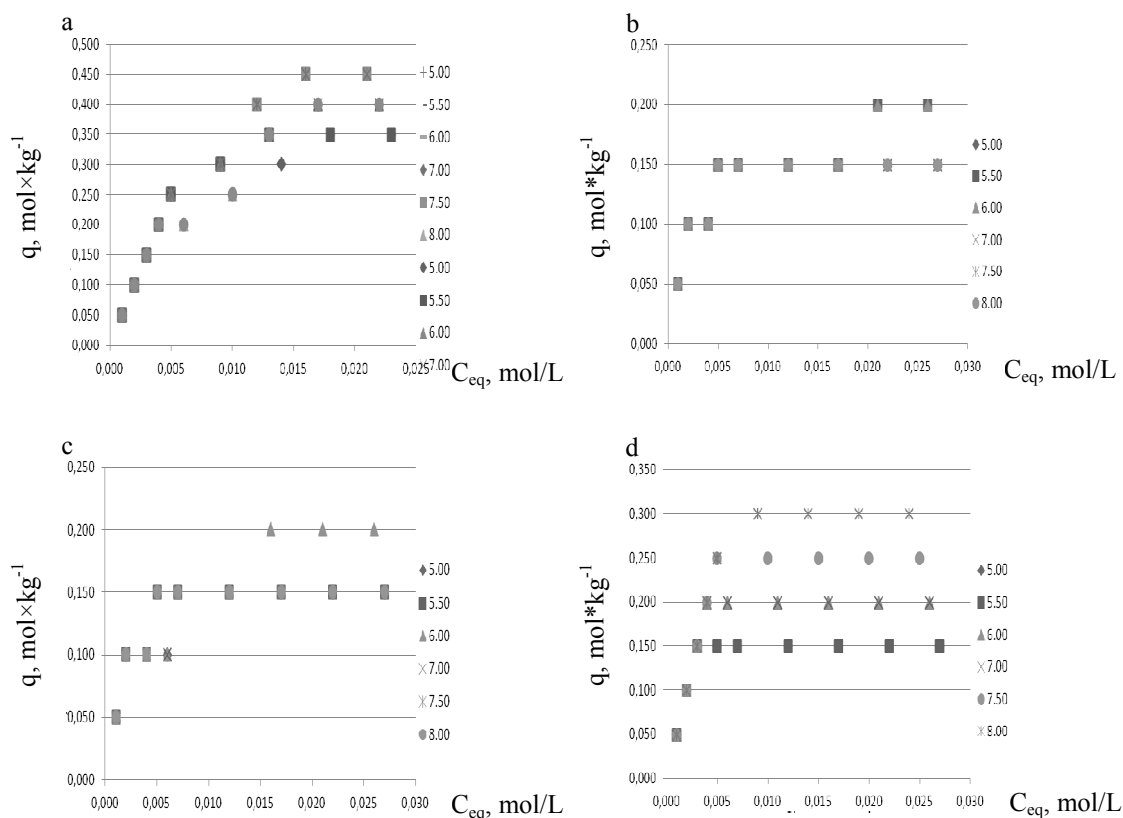


Figure 2. The IR spectrum of the sample of hydroxylapatite synthesized at $\text{pH} = 5.50 \pm 0.05$ (48 hours)

The specific surface of hydroxylapatite was calculated by the method of BET, and its value was 72.0 m^2/g . Analysis of the supernatant liquid and calculation of the Ca/P ratio showed that the Ca/P in the synthesized hydroxylapatite was equal to 1.67 that corresponded to the ideal HA.

2. The results of adsorption experiment. As a result of the adsorption experiment, isotherms of adsorption of amino acids to hydroxylapatite were obtained (Fig. 3). Referring to the curves, it can be concluded that the adsorption reaches saturation. This allows for $C_{\text{am}} = 0.030 \text{ mol} \times \text{L}^{-1}$ to compare the values of adsorption while varying the pH of the solution to finding the values of maximum adsorption (Table 1).



a — glycine; *b* — arginine; *c* — alanine; *d* — aspartic acid

Figure 3. Isotherms of adsorption of amino acids on hydroxylapatite

Table 1

The maximum adsorption of amino acids at varying pH, q , mol×kg⁻¹

Amino acid	pH					
	5.00	5.50	6.00	7.00	7.50	8.00
Glycine	0.400	0.350	0.400	0.400	0.450	0.400
Alanine	0.150	0.150	0.200	0.150	0.150	0.150
Aspartic acid	0.150	0.150	0.200	0.200	0.250	0.300
Glutamic acid	0.300	0.250	0.250	0.200	0.200	0.200
Arginine	0.200	0.200	0.200	0.150	0.150	0.150

The pH values, at which the maximum adsorption of amino acids on the surface of hydroxylapatite occurs, are shown in the table 1. These amino acids are in charged ionic forms at given pH values of the solution. To determine the equation describing the adsorption, the experimental data were processed from the position of the Langmuir theory (1) and the Freundlich theory (2) (Table 2):

$$q = \frac{q_m K_L C}{1 + K_L C}, \quad (1)$$

where q_m — is the limiting amount of adsorption, mol×kg⁻¹; K_L — is the adsorption equilibrium constant; C — is equilibrium concentration of adsorbate, mol×L⁻¹.

$$q = K_F C^n, \quad (2)$$

where K_F — is coefficient of proportionality; n — is exponent, $n < 1$.

Table 2

**Equations described by the models of Freundlich and Langmuir,
for adsorption of amino acids on hydroxylapatite by varying the pH of the solution**

Amino acid	$q_{\max}$, $\text{mol} \times \text{kg}^{-1}$	$\text{pH}_{\max}$	Equation model of		R^2	
			Langmuir	Freundlich	Langmuir	Freundlich
Glycine	0.450	7.50	$q = 0.749 \times \frac{46.49 \times C}{1 + 46.49 \times C}$	$q = 9.158 \times C^{0.722}$	0.960	0.958
Alanine	0.200	6.00	$q = 0.239 \times \frac{11.40 \times C}{1 + 11.40 \times C}$	$q = 0.938 \times C^{0.401}$	0.958	0.899
Aspartic acid	0.300	8.00	$q = 0.368 \times \frac{33.47 \times C}{1 + 33.47 \times C}$	$q = 2.965 \times C^{0.534}$	0.969	0.831
Glutamic acid	0.300	5.00	$q = 0.368 \times \frac{33.15 \times C}{1 + 33.15 \times C}$	$q = 2.966 \times C^{0.534}$	0.969	0.831
Arginine	0.200	5.00– 6.00	$q = 0.216 \times \frac{13.08 \times C}{1 + 13.08 \times C}$	$q = 0.782 \times C^{0.361}$	0.957	0.846

The obtained values of q_m are adequate, as all practical values of q are less than q_m . As can be seen from Table 2, adsorption of amino acids has a good correlation in the linear coordinates of the model of Langmuir.

It was further used to calculate the change of Gibbs energy according to the formula (3) (Table 3):

$$\Delta G = -RT \times \ln K, \quad (3)$$

where R — is the universal gas constant, $R = 8.314 \text{ kJ}/(\text{Kmol} \times \text{K})$; K — is the constant of adsorption equilibrium.

Table 3

The value of the Gibbs free energy for adsorption of amino acids, $-\Delta G$, $\text{kJ} \times \text{mol}^{-1}$

Amino acid	pH					
	5.00	5.50	6.00	7.00	7.50	8.00
Glycine	8.94	8.87	9.08	9.08	9.51	8.80
Alanine	6.47	7.42	6.03	6.47	7.42	7.42
Aspartic acid	8.53	8.53	8.50	8.50	8.56	8.70
Glutamic acid	8.67	8.53	8.53	8.46	8.46	8.46
Arginine	6.37	6.37	6.37	7.42	7.42	7.42

The values of the Gibbs energy were calculated and there was revealed that the interaction of amino acids with the surface of the hydroxylapatite was characterized by physical adsorption due to forces of electrostatic interaction of positively and negatively charged centers, as well as due to the formation of hydrogen bonds.

Analysis of the surface charge of the solid phase of hydroxylapatite at $\text{pH} = 5.00, 6.50, 8.00 \pm 0.05$ has shown that its surface is positively charged under the given pH values of the solution. It can be seen that after adsorption ($C_{\text{aa}} = 4 \text{ mmol/l}$), glycine addition does not change the sign of the surface charge, because it is possible to incorporate glycine into the hydroxylapatite structure. With the addition of alanine, there is also no surface recharge, since physical adsorption binds its positive and negative groups at the ends, and as a result, the uncharged side group does not affect the charge of the surface. When adsorption of arginine is also binding its end groups, but at these pH values it is in the form of positively charged zwitterions, and as a result, outside the surface is its charged positively side group, which does not change the charge of the surface. However, with the addition of aspartic and glutamic acids, it can be seen that the surface is recharging, they are at the given pH values of the solution in the form of negatively charged zwitterions. Because of this, adsorption on the surface has a negatively charged side group that forms a layer on the surface, which as a result changes the charge of the surface of the hydroxylapatite (Table 4).

Table 4

The sign of the charge hydroxylapatite in the presence of amino acids of a similar concentration

Amino acid	pH		
	5.00	6.50	8.00
Without amino acid	+	+	+
Glycine	+	+	+
Alanine	+	+	+
Aspartic acid	–	–	–
Glutamic acid	–	–	–
Arginine	+	+	+

The result of IR spectroscopy confirmed adsorption. On the IR spectrum of the sample after the adsorption experiment (Fig. 4), the vibration band at 1650 cm^{-1} should be considered as the total, reflecting the vibrations of C=O, N–H, O–H bonds in amino acid and OH-ions in hydroxylapatite. Also, the appearance of specific absorption bands associated with the vibrations of N–H and C–N bonds, which appear in the $3500\text{--}3300$, $1650\text{--}1500$, $1360\text{--}1000\text{ cm}^{-1}$ regions, is registered, which confirms the possibility of adsorption of amino acids on hydroxylapatite.

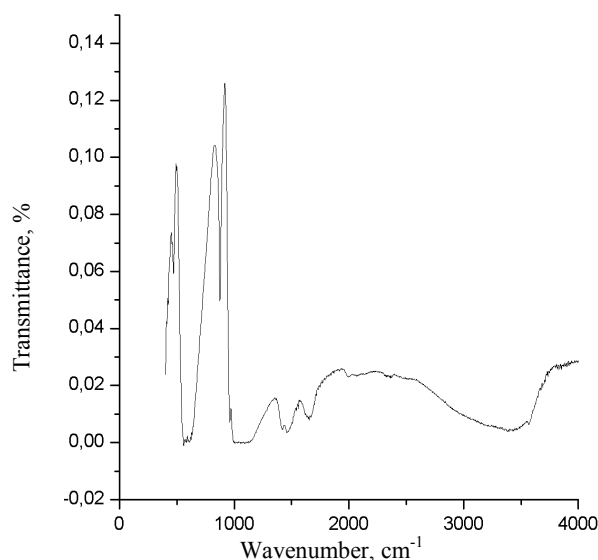


Figure 4. The IR spectrum of the sample after the adsorption experiment (48 hours)

Previously we have found that glycine, aspartic and glutamic acids adsorption is described by Freundlich model. For alanine and arginine adsorption is described by the model of Langmuir [20, 21].

Conclusions

1. It was carried out the synthesis of hydroxylapatite, the structure of which was confirmed by XRD and IR spectroscopy. The values of the sign of the surface charge of hydroxylapatite were found to be positive. τ
2. The processes of adsorption of amino acids on the hydroxylapatite were investigated. There was identified that the values of pH of maximum adsorption were as follows: glycine at $\text{pH} = 7.50 \pm 0.05$, the alanine at $\text{pH} = 6.00 \pm 0.05$, aspartic acid at $\text{pH} = 8.00 \pm 0.05$, glutamic acid at $\text{pH} = 5.00 \pm 0.05$, arginine at $\text{pH} = 5.00\text{--}6.00 \pm 0.05$.
3. Adsorption of amino acids was described by the Langmuir model.
4. The values of the Gibbs energy were calculated. There was revealed that the interaction of amino acids with the surface of the hydroxylapatite was characterized by physical adsorption.

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Гидроксилapatит бетінде аминқышқылдар сорбциясының физика-химиялық заңдылықтары

Кальций фосфаттары физиогендік және патогендік минералды түзілімдердің бір бөлігі болып табылады. Гидроксилapatит сүйектің, тіс эмалі және дентиннің негізгі минералды компоненті болып табылатыны белгілі. Органикалық және минералды компоненттердің өзара әрекеті биогенді кристалдану үрдістерінде сүтқоректілердің сүйек матрицасын қалыптастыру, сондай-ақ патогенді түзілістердің нуклеациясын және өсуін қамтамасыз етуде үлкен маңызға ие. Мұнда минералдану процестерінің негізінде биофлуидтердің бейорганикалық компоненттері мен қалыптастырушы фазалары бар ақуыз молекулаларына байланыстырылған бос аминқышқылдардың және ақуыз молекулаларының адсорбциялық өзара әрекеттесуінің бірнеше болжамдары бар. Алайда олардың өзара әрекеттесулерінің тетігі толық зерттелмеген. Мақалада гидроксилapatит бетінде аминқышқылдардың адсорбциясы зерттелді. Кальций фосфатын ерітіндіден синтездеу жүргізілді. РФА және ИҚ спектроскопиясының нәтижелеріне сүйене отырып, тұнба гидроксилapatит фазасы арқылы анықталған. ВЭТ әдісімен гидроксилapatиттың бетінің ауданы 72,0 м²/г болатыны анықталды. Аминқышқылдардың адсорбциясы олардың концентрациялары мен ерітінділер рН-нің кең ауқымында

зерттелген. Гидроксилапатит бетіндегі аминқышқылдардың адсорбциясы қанықтылық қажет ететіндігі анықталды. Аминқышқылдардың максималды адсорбциясына гидроксилапатит бетіндегі ерітіндінің pH-ның әсері қарастырылды. Аминқышқылдардың гидроксилапатит бетіндегі адсорбциясы Ленгмюр үлгісімен сипатталғаны зерттелді. ИҚ-спектроскопия нәтижелері адсорбция фактісін растау үшін берілген. Гидроксилапатиттің қатты фазасының бетіндегі зарядтың белгісі анықталды. Гидроксилапатит бетінің зарядының белгісі оң болғаны расталды. Гиббс энергиясының мәндерін есептеу жүргізілді және аминқышқылдардың гидроксилапатит пен өзара әрекеттестігі физикалық адсорбциямен сипатталатыны дәлелденді.

Кілт сөздер: гидроксилапатит, адсорбция, аминқышқылы, ерігіштігі, бетінің заряды, ерітінді, Ленгмюр моделі, Фрейндлих моделі.

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Физико-химические закономерности сорбции аминокислот на поверхности гидроксилапатита

Фосфаты кальция входят в состав физиогенных и патогенных минеральных образований. Известно, что гидроксилапатит является основной минеральной составляющей костной ткани, зубной эмали и дентина. Взаимодействие органической и минеральной составляющих имеет большое значение в таких процессах биогенной кристаллизации, как формирование костного матрикса млекопитающих, а также зарождение и рост патогенных образований. Существует ряд предположений, согласно которым в основе процессов минерализации лежит адсорбционное взаимодействие свободных аминокислот и связанных белковых молекул с неорганическими компонентами биожидкостей и формирующихся фаз. Однако механизм их взаимодействия до конца не изучен. В работе изучена адсорбция аминокислот на поверхности гидроксилапатита. Осуществлен синтез фосфатов кальция из раствора. По результатам РФА и ИК-спектроскопии установлено, что осадки представлены фазой гидроксилапатита. С помощью метода БЭТ рассчитали удельную поверхность гидроксилапатита, равную 72,0 м²/г. Исследована адсорбция аминокислот в широком интервале варьирования их концентраций и pH раствора. Доказано, что адсорбция аминокислот на поверхности гидроксилапатита достигает насыщения. Рассмотрено влияние pH раствора на значение максимальной адсорбции аминокислот на поверхности гидроксилапатита. Доказано, что адсорбция аминокислот на поверхности гидроксилапатита описывается моделью Ленгмюра. Результаты ИК-спектроскопии приведены для подтверждения факта адсорбции. Проведено определение знака заряда поверхности твердой фазы гидроксилапатита. Получено, что значение знака заряда поверхности гидроксилапатита положительное. Осуществлен расчет значений энергии Гиббса и выявлено, что взаимодействие аминокислот с поверхностью гидроксилапатита характеризуется физической адсорбцией.

Ключевые слова: гидроксилапатит, адсорбция, аминокислота, растворение, поверхностный заряд, раствор, модель Ленгмюра, модель Фрейндлиха.

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*F.M. Dostoevsky Omsk State University, Russia
(E-mail: golovanoa2000@mail.ru)***Physicochemical regularities of the sorption of amino acids on the surface of brushite**

Calcium phosphates are part of biogenic and pathogenic mineral formations. Brushite occurs mainly in conjunction with other calcium phosphates in the composition of pathogenic mineral formations in the body of animals and humans. There are a number of assumptions, according to which the basis of the processes of mineralization is the adsorption interaction of free amino acids and associated protein molecules with inorganic components of biological liquids. However, the mechanism of their interaction is not fully understood. In this paper the adsorption of amino acids was studied on the surface of brushite. Brushite was synthesized in the system of $\text{Ca}(\text{NO}_3)_2 \cdot (\text{NH}_4)_2\text{HPO}_4$ with equal concentrations. According to the results of XRD and IR spectroscopy it was established that precipitation was represented by the phase of brushite. It was implemented dynamic dissolution of the solid phase of brushite when the pH was varying. Equations of the kinetic graphs were obtained. It was investigated the adsorption of amino acids in a wide range of variation in their concentrations and the pH of the solution. It was considered the effect of pH on the maximum adsorption of amino acids on brushite. The results of IR spectroscopy confirmed adsorption. The solid phase of brushite was determined by the sign of the surface charge. The values of the sign of the surface charge of brushite were found to be positive. The values of the Gibbs free energy were calculated. There was revealed that the interaction of amino acids with the surface of the brushite was characterized by physical adsorption.

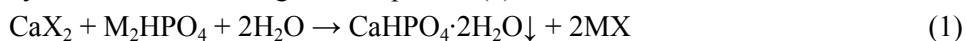
Keywords: brushite, adsorption, amino acid, dissolution, surface charge, solution, model of Langmuir, model of Freundlich.

Introduction

Biogenic and pathogenic mineral formations contain calcium phosphates. Biogenic formations are part of different organs and have different functions; they are genetically determined, their place in the body is strictly defined. Pathogenic mineral formations occur in the disruption of the functioning of the whole organism or its separate organs. It is known that in the early stages of the formation of pathogenic aggregates crystallize calcium hydrogen phosphate dihydrate, an analog of natural mineral brushite [1–3]. In the body of animals and humans brushite occurs mainly in conjunction with other calcium phosphates in the composition of pathogenic mineral formations, different places (teeth, salivary, kidney, and other stones) [4]. In the papers [5–11] the researchers describe that calcium phosphates have an excellent biological activity and have been widely used in bone reconstruction or orthopedic supplements, as the primary inorganic material of the composition of the hard tissues of the body. Interaction of organic and mineral components is important in such processes of biogenic crystallization, as the formation of bone matrix of mammals, as well as the emergence and growth of pathogenic entities. In one of the classifications, they are divided into two groups: low temperature ones and high temperature ones [12, 13]. Hydroxylapatite (HA) and calcium hydrogen phosphate dihydrate (DCPD) $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ are of greatest interest from number of the biocompatible low-temperature calcium phosphates. DCPD in nature expressed in the mineral brushite is the most soluble of biocompatible calcium phosphates, HA is less soluble. At 60–100 °C brushite gradually turns into CaHPO_4 (DCPA) dicalcium phosphate. In [14] it is discussed the stability of calcium phosphates and the Ca/P ratio. There are some assumptions, according to which the basis of the processes of mineralization lies in the adsorption interaction of free amino acids and associated protein molecules with inorganic components of biological liquids [2]. The mechanism of their interaction is not fully understood. In this regard, recent studies aimed at studying the regularities of adsorption of amino acids on the inorganic component of pathogenic neoplasms. The purpose of this work is the study of the peculiarities of adsorption of amino acids on brushite by varying the pH of the solution.

Materials and methods

The synthesis of brushite. It is carried out by deposition from aqueous solution at room temperature by the method of spontaneous crystallization according to the equation (1):



The precipitate is obtained by mixing dilute solutions of calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ with equal concentrations at room temperature (22–25 °C). When synthesis is carrying out a solution of $\text{Ca}(\text{NO}_3)_2$ was poured quickly to 250 ml of a solution containing $(\text{NH}_4)_2\text{HPO}_4$ with equal concentrations (50 mmol/L). The total volume of the mixture is 500 ml. After mixing the solutions, the pH of the system was adjusted to a value of 5.50 ± 0.05 by using solutions of NaOH (20 %) and/or HNO_3 (1:1).

After the heterogeneous system settling for two days, the solution was filtered under the vacuum using a water jet pump. Some part of the supernatant liquid was selected for chemical analysis, measure the pH of the equilibrium solution. The filter cake was washed with water ($V = 50$ ml) after filtration and dried in a drying cabinet at a temperature of ~ 80 °C to constant weight for the complete removal of free water, and then at room temperature (in a desiccators). The dried precipitate was transferred into a labeled container and weighed on an analytical balance.

It is determination of the sign of the charge of the particles of the sols of brushite by the method of capillary analysis. When a piece of filter paper immersed in water, thin wall paper was charged negatively. These allow determining the sign of the charge of the colloidal particles. Negatively charged particles rise through the capillaries.

It is the dynamic dissolution. A portion of the sample brushite a mass of 0.1000 g is taken on an analytical balance in a dry time glass. The study of the dissolution process is carried out at constant stirring of the solution. Using dedicated time intervals to note the amount of pCa. At the end of the measurement indissoluble precipitate was filtered off through a folded filter, dried in a drying box at a temperature of ~ 80 °C to complete removal of chemically unbound water. The dried precipitate is transferred into a labeled container and weighed on an analytical balance.

We used the direct potentiometric method for pH measurements. The measurements were carried out in a glass beaker, which pre-processes. The measurement error is ± 0.01 pH units.

Determination of the concentration of calcium ions in the experiment was performed by direct potentiometry using an ion-selective electrode and calibration schedule determined by the value of $[\text{Ca}^{2+}]$.

Determination of phosphate ions was carried out by the molybdenum blue method (State Standard 18309–72 on the KFK-2 device using the red filter ($\lambda_{\text{ref}} = 690$ nm). The determination is repeated three times and the average values of optical densities were found to build a calibration curve: $D = f\{C(\text{PO}_4^{3-})\}$, calculate the regression equation. Error definitions are found within 2–4 Rel. %.

It is X-ray diffraction (XRD). It is used to study the mineral (phase) composition of synthesized aqueous solid phases brushite. The diffractograms were obtained by the «method of powder» for stationary DRON-3 X-ray apparatus [15]. Phase identification was performed using ASTM international indexes and tables [16]. The sensitivity of the XRD method for these measurements is 3 %.

The method of infrared spectroscopy was used for more information on the composition of the samples obtained. IR spectrum was obtained on the FSM 2201 spectrophotometer. Mathematical processing of the data was carried out using statistical software Statistica 10 and Static2 from the statistical package Stat Soft. The sensitivity of the method of IR-spectroscopy for the measurement data was < 5 %.

It is the method of area measurement of the specific surface of synthetic calcium phosphates. Analysis of the specific surface of the samples according to the BET method (SBET-N2) was carried out using techniques of single-point standard gas adsorption equilibrium at an absolute pressure in the adsorption unit Sorbtometr, IK SB RAS (OSC SB RAS, Omsk). The limit of permissible relative error of measurement of the specific surface in the mode of multiple measurements is not more than 5 %.

The adsorption experiment. 0.5 g of Brushite sample was placed in a flask and the solution of amino acids was poured. The concentration of amino acids: 2, 4, 6, 8, 10, 15, 20, 25, and 30 mmol/L and pH range $5.00 - 8.00 \pm 0.05$ (except 6.50) in increments of 0.50 were varied. Shaking was carried out for 30 minutes, and then it was left for 48 hours. After the specified time the content of the flasks was filtered and there was determined the content of amino acids in the filtrate by the method of transfer of amino acids in a soluble copper salt and subsequent photometric determination, measurement of the pH after adsorption, determination of the mass of precipitation.

Determination of the concentration of amino acids in the experiment was assessed by photometric determination of amino acids. The essence of the method including determination of the concentration of amino acids used in the analysis is based on the conversion of amino acids into soluble copper salts and their subsequent photometric determination. KFK-2 photoelectric colorimeter was used for measurements. Determination of optical density of standard solutions is carried out in the wavelength interval that includes the

value of 670 nm. A calibration curve was built for measurements. Determining the unknown concentration of amino acids was performed using a calibration chart.

Results and discussion

1. The results of the synthesis of brushite crystals

The methods of XRD and IR spectroscopy establish that the precipitation obtained after 48 hours of crystallization was represented by the brushite phase (Fig. 1), belonging to the monoclinic crystal system (2θ corresponds to 11.172, 29.411, and 35.419). The crystallite size was calculated to be equal to $D = 48.06 \mu\text{m}$ [17], which was consistent with the data [3].

The IR spectrum of the samples contained the whole range of the bands characteristic for brushite (Fig. 2) and have a complex structure. It was noticed the presence of absorption bands of the stretching ($1135, 1060, 986 \text{ cm}^{-1}$) and bending ($653, 578, 527 \text{ cm}^{-1}$) vibrations of a group HPO_4^{2-} as well as bands characteristic for vibrations of the water $3531, 3484, 1646 \text{ cm}^{-1}$. The specific surface of brushite was calculated by the method of BET and its value was $9.0 \text{ m}^2/\text{g}$. Analysis of the supernatant liquid and calculation of the Ca/P ratio showed that the Ca/P of the synthesized brushite was equal to 1.02, for a perfect brushite this value was $\text{Ca/P} = 1.00$.

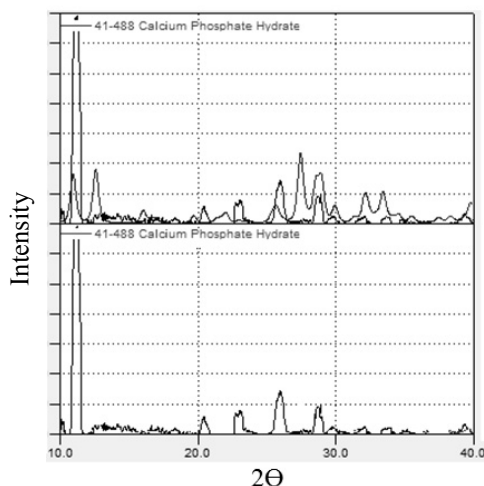


Figure 1. The diffraction pattern of the synthesized brushite sample at $\text{pH} = 5.50 \pm 0.05$ (48 hours)

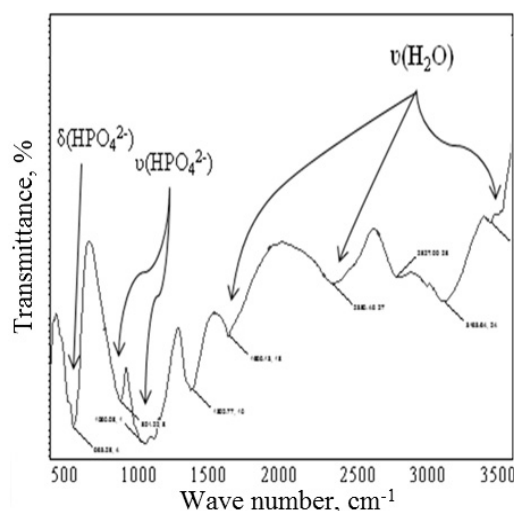


Figure 2. The IR spectrum of the brushite sample synthesized at $\text{pH} = 5.50 \pm 0.05$ (48 hours)

2. The results of the study of the properties of brushite

The method of dynamic dissolution is used to converse synthesized samples of brushite from the solid phase to the liquid phase, while varying the pH.

The exponential dependence of the pCa from time to time is obtained, which corresponds to the reaction of the first order when the rate of change of the number of «active centers of dissolution» ($C(t)$) to dissolve the material is proportional to their number at the moment (1):

$$\frac{dC(t)}{dt} = -kC(t), \quad (1)$$

where the coefficient k does not depend on time.

At this stage of dissolving, the rate of change of concentration decreases with time (2):

$$\frac{dC(t)}{dt} = C_m b \exp(-bt). \quad (2)$$

Therefore, the initial dissolution rate can be considered as a quantitative measure determined as the tangent of the slope of a linear plot a straight line constructed in the coordinates of the $\text{pCa} = f(t)$ [2].

According to the obtained data, the dependence was constructed (Fig. 3). The kinetic curves were processed and the data are summarized in the Table 1.

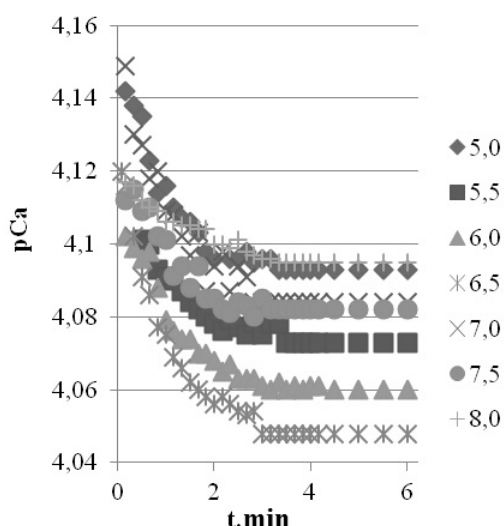


Figure 3. Kinetic curves of dissolution precipitation brushite in aqueous solution at different pH value

Table 1

Parameters of brushite dissolution depending on the variation of pH in an aqueous solution

pH	Equation	R ²	K, s ⁻¹	V, mol*(l* min) ⁻¹
5.00	$pCa = 4.093 + 0.0425 \cdot \exp(-0.016t)$	0.9632	0.016	0.960
5.50	$pCa = 4.073 + 0.0425 \cdot \exp(-0.014t)$	0.9620	0.014	0.840
6.00	$pCa = 4.060 + 0.0464 \cdot \exp(-0.012t)$	0.9795	0.012	0.720
6.50	$pCa = 4.048 + 0.0707 \cdot \exp(-0.011t)$	0.9506	0.011	0.660
7.00	$pCa = 4.084 + 0.0627 \cdot \exp(-0.009t)$	0.9880	0.009	0.540
7.50	$pCa = 4.082 + 0.0371 \cdot \exp(-0.005t)$	0.9756	0.005	0.300
8.00	$pCa = 4.095 + 0.0233 \cdot \exp(-0.003t)$	0.9488	0.003	0.180

As seen that there is an inverse correlation between dissolution rate and pH of the solution, namely lowering the pH of the solution increases the dissolution rate. The calculation of the masses of the samples after dissolution allowed us to determine their loss (Table 2).

Table 2

Mass loss of brushite samples when dissolved

pH	5.00	5.50	6.00	6.50	7.00	7.50	8.00
Δm , %	27.0	22.6	18.0	17.2	16.8	13.0	8.7

The results obtained agree well with the experimental data on the velocity of dissolution, and the maximum dissolution rate of the solid phase corresponds to the greatest loss. This fact was proved by determination of the composition of the samples after dissolution using XRD. Diffraction pattern shows that the phase composition of the phases has not changed.

The surface charge of the brushite solid phase by the method of capillary analysis at pH = 5.00, 6.50, 8.00 $\pm$ 0.05 shows that the surface is charged positively.

3. The results of adsorption experiment

As a result of the adsorption experiment, isotherms of adsorption of amino acids to brushite were obtained (Fig. 4). Referring to the curves, it can be concluded that the adsorption reaches saturation. This allows for $Ca = 0.030 \text{ mol} \times L^{-1}$ to compare the values of adsorption while varying the pH of the solution to finding the values of maximum adsorption (Table 3).

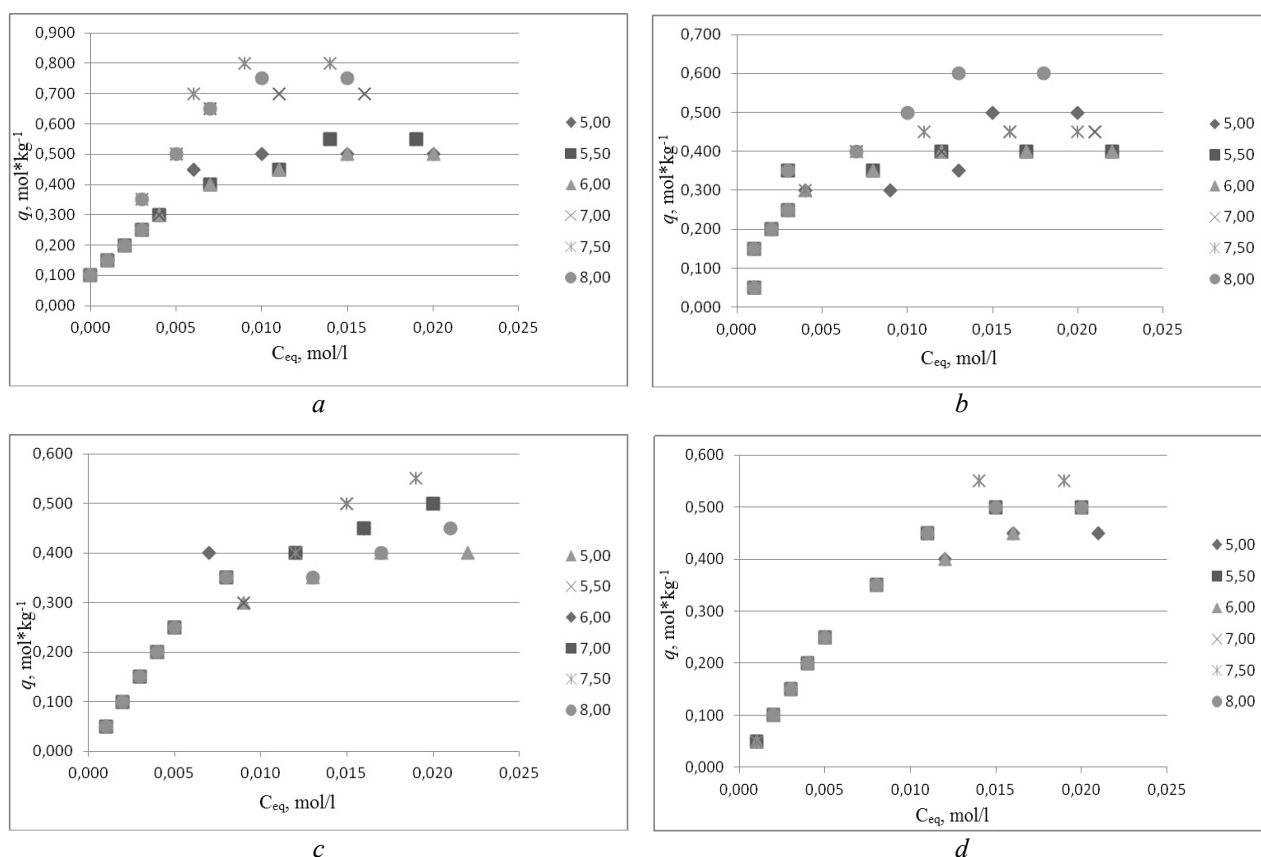


Figure 4. Isotherms of adsorption of amino acids on brushite

Table 3

The maximum adsorption of amino acids at varying pH, q , $\text{mol} \times \text{kg}^{-1}$

Amino acid	pH					
	5.00	5.50	6.00	7.00	7.50	8.00
Glycine	0.500	0.550	0.500	0.700	0.800	0.750
Alanine	0.400	0.500	0.450	0.500	0.550	0.450
Aspartic acid	0.450	0.500	0.500	0.500	0.550	0.500
Glutamic acid	0.750	0.750	0.800	0.700	0.850	0.800
Arginine	0.500	0.400	0.400	0.450	0.450	0.600

Maximum adsorption is characteristic for glycine, alanine, aspartic and glutamic acids at $\text{pH} = 7.50 \pm 0.05$, and for arginine at $\text{pH} = 8.00 \pm 0.05$. At given pH values of the solution, these amino acids are in charged ionic forms.

To determine the equation describing the adsorption, the experimental data were processed from the position of the Langmuir theory (3) and the Freundlich theory (4) (Table 4):

$$q = \frac{q_m \cdot K_L \cdot C}{1 + K_L \cdot C}, \quad (3)$$

where q_m — is the limiting amount of adsorption, $\text{mol} \times \text{kg}^{-1}$; K_L — is the adsorption equilibrium constant; C — is equilibrium concentration of adsorbate, $\text{mol} \times \text{L}^{-1}$.

$$q = K_F \cdot C^{\frac{1}{n}}, \quad (4)$$

where K_F — is coefficient of proportionality; n — is exponent, $n < 1$.

Table 4

**Equations described by the models of Freundlich and Langmuir,
for adsorption of amino acids on brushite by varying the pH of the solution**

Amino acid	$q_{\max}$, $\text{mol} \times \text{kg}^{-1}$	$\text{pH}_{\max}$	Equation model of		R^2	
			Langmuir	Freundlich	Langmuir	Freundlich
Glycine	0.800	7.50	$q = 1.128 \times \frac{221.1 \times C}{1 + 221.1 \times C}$	$q = 19.42 \times C^{0.704}$	0.6551	0.8993
Alanine	0.550	7.50	$q = 1.133 \times \frac{65.10 \times C}{1 + 65.10 \times C}$	$q = 8.580 \times C^{0.681}$	0.9834	0.9809
Aspartic acid	0.550	7.50	$q = 1.348 \times \frac{77.00 \times C}{1 + 77.00 \times C}$	$q = 11.81 \times C^{0.738}$	0.8803	0.9732
Glutamic acid	0.850	7.50	$q = 0.952 \times \frac{396.6 \times C}{1 + 396.6 \times C}$	$q = 5.830 \times C^{0.576}$	0.8639	0.9368
Arginine	0.550	8.00	$q = 0.946 \times \frac{99.50 \times C}{1 + 99.50 \times C}$	$q = 11.12 \times C^{0.671}$	0.8267	0.8005

The obtained values of q_m are adequate, as all practical values of q are less than q_m . As can be seen from Table 4, adsorption of glycine, aspartic and glutamic acids has a good correlation in a linear model of Freundlich to a greater extent, however alanine and arginine, on the contrary, have a good correlation in the linear coordinates of the model of Langmuir.

It was further used to calculate the change of Gibbs energy according to the formula (5) (Table 5):

$$\Delta G = -RT \cdot \ln K, \quad (5)$$

where R — is the universal gas constant, $R = 8.314 \text{ kJ}/(\text{Kmol} \times \text{K})$; K — is the constant of adsorption equilibrium.

Table 5

The value of the Gibbs free energy for adsorption of amino acids, $-\Delta G$, $\text{kJ} \times \text{mol}^{-1}$

Amino acid	pH					
	5.00	5.50	6.00	7.00	7.50	8.00
Glycine	12.39	11.84	11.87	12.73	13.38	13.14
Alanine	9.077	9.924	9.682	9.855	10.35	9.347
Aspartic acid	9.617	10.17	9.855	10.17	10.76	10.17
Glutamic acid	12.55	12.75	14.79	12.42	14.82	14.38
Arginine	10.25	10.44	10.31	10.62	10.64	11.40

As seen that the values of the Gibbs free energy correspond to the values of the maximum adsorption. The values of Gibbs free energy suggest that adsorption is, in fact, the physical adsorption.

Analysis of the surface charge of the solid phase of brushite after adsorption ($C_{\text{aa}} = 4 \text{ mmol/L}$) at $\text{pH} = 5.00, 6.50, 8.00 \pm 0.05$ has shown that adding even small amounts of aspartic acid and glutamic acid, which are at the pH values of the solution in the form of negatively charged zwitterions, leads to the recharging of the surface. This can be explained by the process of adsorption of amino acids on the surface of brushite. When you add arginine at these conditions, which is in the form of positively charged zwitterions, recharge of the surface occurs. Adsorption of glycine and alanine does not result in recharge of the surface on the whole interval of pH of the solution, although under these conditions, they are consistent in three forms: a positively charged ion, neutral, zwitterion and negatively charged ion (Table 6).

Table 6

The sign of the charge brushite in the presence of amino acids of a similar concentration

Amino acid	pH		
	5.00	6.50	8.00
Glycine	+	+	+
Alanine	+	+	+
Aspartic acid	—	—	—
Glutamic acid	—	—	—
Arginine	+	+	+

The results of IR spectroscopy confirm adsorption. The IR spectrum of the sample after the adsorption experiment (Fig. 5) have the bands in the region 2800 to 3000 cm^{-1} corresponding to the vibrations of C–H bonds in methylene groups of the organic component. Vibrations at 1650 cm^{-1} should be considered as an aggregate reflecting the fluctuation relations of C=O, N–H, O–H in the molecules of amino acids and OH^- ions in the composition of brushite.

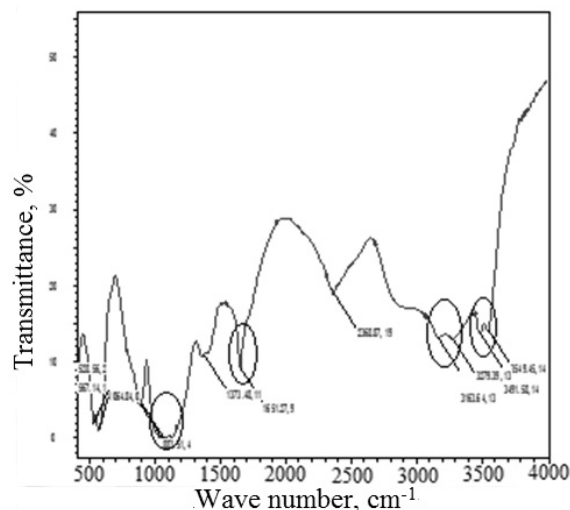


Figure 5. The IR spectrum of the sample after the adsorption experiment (48 hours)

Also, it was recorded the appearance of specific absorption bands related to vibrations of N–C and H–N bonds that occur in the regions 3500–3300, 1650–1500, 1360–1000 cm^{-1} , which confirm the possibility of adsorption of amino acids on brushite.

Conclusions

1. It has been carried out the synthesis of brushite, the structure of which is confirmed by XRD and IR spectroscopy. The dynamic dissolution in aqueous solution with different pH value has been studied. It has been obtained that the values of the sign of the surface charge of brushite are positive.

2. The adsorption of amino acids on brushite has been investigated and it is shown that maximum adsorption occurs at $\text{pH} = 7.50 \pm 0.05$ for glycine, alanine, aspartic and glutamic acid, and for arginine at $\text{pH} = 8.00 \pm 0.05$.

3. Adsorption of glycine, aspartic and glutamic acids are outlined by the model of Freundlich, while for alanine and arginine adsorption is described by the model of Langmuir. The calculated values of the Gibbs free energy of adsorption are consistent with the values of the maximum adsorption.

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Брушит бетінде аминқышқылдар сорбциясының физика-химиялық заңдылықтары

Кальций фосфаттары (КФ) физиогенді және патогенді минералды түзілімдердің құрамына кіреді. Адам және жануарлар ағзасында брушит негізінен басқа КФ бірге патогенді минералды түзілімдердің құрамында болады. Органикалық және минералды құраушыларының әрекеттесулері, сүйек кешендерінің қалыптасуы, патогенді түзілулердің тууы мен өсуі сияқты биогенді кристалдану үрдістерінде өте маңызды. Минералдану үрдістерінің негізінде бос және байланысқан амин қышқылдарының ақуыз молекулаларына биосұйықтардың бейорганикалық компоненттерімен әрекеттесуі жатыр деген бірнеше болжамдар бар. Бірақ олардың әрекеттесу механизмі әлі толық зерттелген жоқ. Жұмыста брушит бетінде аминқышқылдарының адсорбциясы зерттелген. Брушиттің синтезі $\text{Ca}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{HPO}_4$ жүйесінде эквимолды концентрацияларымен бөлме температурасында (22–25 °C) жүргізілді. РФА және ИК-спектроскопия әдістерінің көмегімен тұнбалар брушит фазасымен құрылғаны анықталды. БЭТ әдісімен брушиттің 9,0 м²/г сыйымды беті есептелді. Брушит қатты фазасының динамикалық еруі рН әртүрлі мәндерінде жүргізілді. Кинетикалық қисықтар теңдеулері алынды. Ерітіндінің рН төмендегенде брушит қатты фазасының еру жылдамдығы артатыны анықталды. Амин қышқылдарының адсорбциясы олардың концентрациялары мен ерітінді рН кең аумағында зерттелді. Ерітіндінің рН брушиттегі амин қышқылдарының максималды адсорбциялануына әсері қарастырылды. ИК-спектроскопия нәтижелері адсорбция фактысын дәлелдеу үшін берілген. Брушит қатты фазасы бетінің заряды анықталды. Брушит беті зарядының мәні оң екені анықталды. Гиббс бос энергиясының мәндері есептеліп, амин қышқылдарының брушит бетімен әрекеттесуі физикалық адсорбциямен сипатталатыны анықталды.

Кілт сөздер: брушит, адсорбция, амин қышқылы, ерігіштігі, бетінің заряды, ерітінді, Ленгмюр моделі, Фрейндлих моделі.

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Физико-химические закономерности сорбции аминокислот на поверхности брушита

Фосфаты кальция (ФК) входят в состав физиогенных и патогенных минеральных образований. В организме животных и человека брушит встречается главным образом совместно с другими ФК в составе патогенных минеральных образований. Взаимодействие органической и минеральной составляющих имеет важное значение в таких процессах биогенной кристаллизации, как формирование костного матрикса млекопитающих, а также зарождение и рост патогенных образований. Существует ряд предположений, согласно которым в основе процессов минерализации лежит адсорбционное взаимодействие свободных аминокислот и связанных в белковые молекулы с неорганическими компонентами биожидкостей. Однако механизм их взаимодействия до конца не изучен. В работе изучена

адсорбция аминокислот на поверхности брушита. Проведен синтез брушита в системе $\text{Ca}(\text{NO}_3)_2 \cdot (\text{NH}_4)_2\text{HPO}_4$ с эквимольными концентрациями при комнатной температуре (22–25 °C). По результатам РФА и ИК-спектроскопии установлено, что осадки представлены фазой брушита. Методом БЭТ рассчитали удельную поверхность брушита, равную 9,0 м²/г. Осуществлено динамическое растворение твердой фазы брушита при варьировании pH. Получены уравнения кинетических кривых. Показано, что с понижением pH раствора растет скорость растворения твердой фазы брушита. Исследована адсорбция аминокислот в широком интервале варьирования их концентраций и pH раствора. Рассмотрено влияние pH раствора на значение максимальной адсорбции аминокислот на брушите. Результаты ИК-спектроскопии приведены для подтверждения факта адсорбции. Проведено определение знака заряда поверхности твердой фазы брушита. Получено, что значение знака заряда поверхности брушита положительное. Осуществлен расчет значений свободной энергии Гиббса и выявлено, что взаимодействие аминокислот с поверхностью брушита характеризуется физической адсорбцией.

Ключевые слова: брушит, адсорбция, аминокислота, растворение, поверхностный заряд, раствор, модель Ленгмюра, модель Фрейндлиха.

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Destruction of cyanide and thiocyanate ions by bacterial and chemical methods

This article deals with the destruction of cyanide and thiocyanate ions by bacterial and chemical methods. Adsorption with granulated activated carbon and oxidation with sodium pyrosulfite in the presence of a copper sulfate catalyst were used as methods of chemical destruction. The bacterial method of destruction was carried out using the bacterial consortium *Agrobacterium tumefaciens* AC-1, *Agrobacterium tumefaciens* AC-2 and *Pseudomonas sp.* AC-3. The control solutions were placed under identical conditions without the addition of any reagent. Sodium pyrosulfite was effective reagent at removing cyanide ions with 97 % efficiency in 1–1.5 hours, while the bacterial consortium was the most productive against thiocyanate ions, resulting 99 % removal at 120 hours. Thus, the significant amount of cyanide ions has been removed chemically in the first stage, to reduce the effect of high cyanide concentrations on the bacterial process. In the second stage, the cyanide ions have been removed until the MPC levels. In addition, thiocyanate ions were neutralized completely. Model experiments with technological solutions from the gold mining plant were carried out. According to the results of the studies, the respective degrees of bacterial destruction of CN⁻ and SCN⁻ are 99 % and 99.9 %. The residual concentration of CN⁻ and SCN⁻ ions in the treated solution was ≤ 0.1 mg/l and ≤ 4 mg/l, respectively. These amounts correspond to the maximum permissible concentrations approved in the Republic of Kazakhstan and CIS countries.

Keywords: cyanide, thiocyanate, destruction, removal efficiency, degradation, sodium pyrosulfite, granulated activated carbon, bacterial consortium.

Introduction

Environmental protection has a big priority not only in the Republic of Kazakhstan, but also at international level. One of the biggest sources of contamination of the environment is a waste from the mining and processing industries. Disposal of cyanide- and thiocyanate containing residues after manufacturing is a big concern for the current waste management companies worldwide [1].

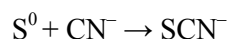
There are sufficient number of techniques for the treatment of waste water with the high content of cyanide- and thiocyanate ions, mainly, they are chemical approaches like hydrogen peroxide treatment [2], adsorption with activated carbon [3], alkaline chlorination [4], iron sulfide and zinc sulfate treatment, ozonation, UV and electrochemical neutralization [5, 6]. Most of them showed an ability to remove cyanide from the liquid phase, but with low efficiency. In addition to the high cost, they might cause secondary toxic compounds.

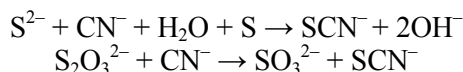
Methods

Quantitative accounting of microorganisms was carried out with the use of methods of serial dilutions [7], Goryaev's counting chamber and «Zeiss Standart 25» microscope with phase contrast device [8]. The pH and redox potential (Eh) were determined through the use of universal analyzer «Mettler Toledo Seven Multi S47-K». Thiocyanate concentrations were determined photometrically with appropriate complex [9], while the determination of cyanides was conducted use of photometry with pyridine and barbituric acid [10] and by titration with silver nitrate [11]. The determination of the metal concentration was carried out using the Kvant-2AT atomic absorption spectrometer with atomization in a graphite furnace [11].

Results

High concentrations of cyanide and thiocyanate ions are commonly observed in industrial water after cyanide leaching of gold-containing sulfide ores or concentrates. The formation of thiocyanate occurs during gold cyanidation as a product of the reaction between cyanide ions and sulfur compounds (including elemental sulfur) [12]:





Depending on the sulfur content and the number of turnover cycles, the concentration of thiocyanates in sewage or circulating waters can range from several milligrams to several grams per liter. Various model solutions containing CN^- ions with a concentration of 300 mg/l and SCN^- ions of 2500 mg/l were prepared for experiments. Adsorption with activated carbon and oxidation with sodium pyrosulfite in the presence of a copper sulfate catalyst were used as the methods of chemical destruction. The bacterial method of destruction was carried out by a consortium of bacteria *Agrobacterium tumefaciens* AC-1, *Agrobacterium tumefaciens* AC-2, *Pseudomonas sp.* AC-3. As a control in the above experiments, the control solution was prepared under identical conditions without adding any reagents.

Granular activated carbon (GAC) with a particle size of 2–4 mm and a density of 0.4 g/ml was used as an adsorbent. Chemical treatment of cyanide and thiocyanate was carried out with sodium pyrosulfite in an amount of 5 g/g for CN^- and 7 g/g for SCN^- in the presence of a copper sulfate catalyst at pH 9.0–10.0.

Bacterial degradation was carried out by a consortium of bacteria at temperature 30 °C. pH of the medium was maintained with a solution of sodium hydroxide at a level of 9.0–9.5. The experiments were carried out on an orbital shaker at 200 rpm. The results of the experiments are shown in Table 1 and Figures 1, 2.

Table 1

The results on the effectiveness of using chemical and bacterial methods at cyanide and thiocyanate ions removing

Characteristics	Duration, hours	Control		Bacterial consortium		GAC		$\text{Na}_2\text{S}_2\text{O}_5$	
		CN^-	SCN^-	CN^-	SCN^-	CN^-	SCN^-	CN^-	SCN^-
C_{ini} , mg/l	0	300	2500	300	2500	300	2500	300	2500
C_{res} , mg/l	12	279	2488	240	2188	171	2075	24	2463
	24	270	2481	225	1750	69	1925	18	2450
	36	262,5	2475	150	1563	45	1800	15	2433
	48	247,5	2469	112,5	1250	30	1700	15	2395
	96	217,5	2444	57	125	24	1300	12	2305
	120	202,5	2425	57	25	24	1200	9	2275
The removal efficiency, %		32,5	3	81	99	92	52	97	9

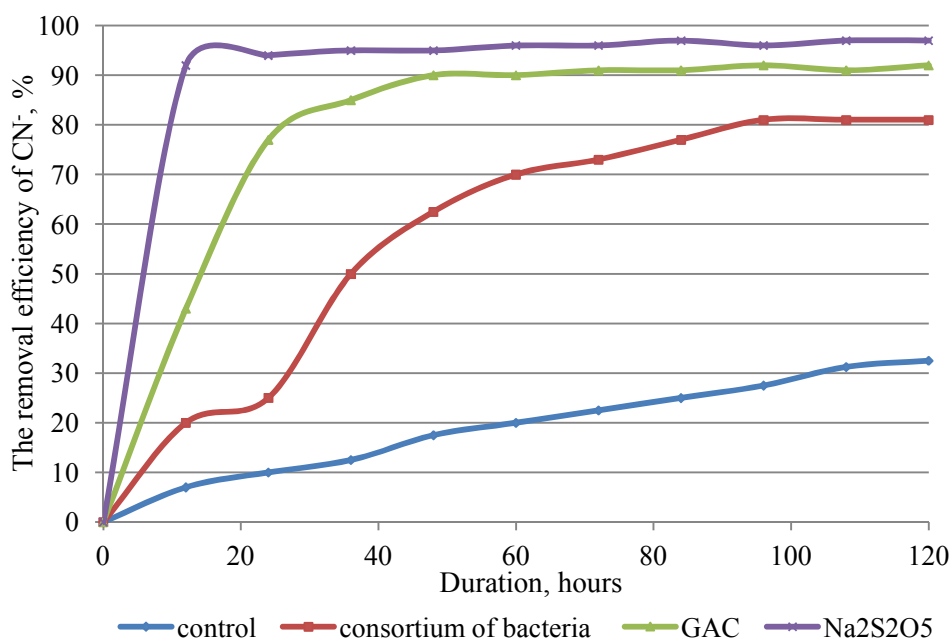


Figure 1. The removal efficiency of cyanides with chemical and bacterial methods

Table 1 and Figure 1 shows that the most effective removal of cyanide ions has been observed when $\text{Na}_2\text{S}_2\text{O}_5$ was used. The removal of CN^- was 97 % in 1–1.5 hours. When the granular activated carbon was used, the removal of cyanide ions was also intensive and achieved 90 % in 46 hours, while destruction occurred slower with the use of bacterial consortium, achieving 81 % in 96 hours. Probably, this result is related to the inhibition of bacterial growth due to the increased concentration of cyanide ions [13].

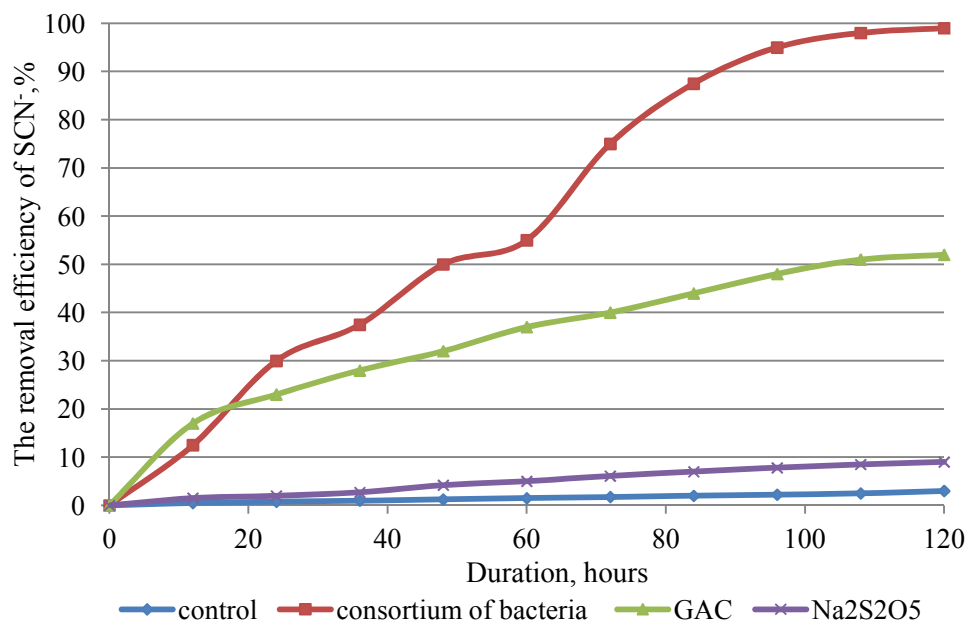


Figure 2. The effectiveness of chemical and bacterial methods at thiocyanate removal

The consortium of bacteria was able to remove 99 % of the thiocyanate ions in 120 hours, showing the highest efficiency. However, other reagents have shown less activity at the same time with 52 % and 9 % for GAC and $\text{Na}_2\text{S}_2\text{O}_5$, respectively. In the control solutions, the decrease in the concentration of cyanide and thiocyanate ions occurred under the influence of atmospheric oxygen (Table 1 and Fig. 2).

Thus, sodium pyrosulfite was the most efficient reagent at removing cyanide ions with 97 % efficiency in 1–1.5 hours, while bacterial consortium was the most productive against thiocyanate ions, resulting 99 % removal at 120 hours.

In this regard, a two-stage combined technology for the removal of cyanide and thiocyanate was developed. At the first stage, In order to reduce the effect of high concentrations of cyanide on the bacterial process, a significant amount of cyanide ions is removed chemically. The second stage is the removal of the cyanide ions until the MPC levels, also full neutralization of the thiocyanate ions.

The results of previous experiments have shown that the most optimal method is combining of the chemical (sodium pyrosulfite treatment) and bacterial methods. In other words, conversion of the cyanides to the less toxic thiocyanates with subsequent bacterial degradation is a solution to the problem of wastewater treatment.

Samples of technological solutions from the Aksu gold extraction plant (Aqmola region, Kazakhstan) were selected for model experiments. The mineral ores and concentrates of the plant are treated with cyanide solutions. Table 2 shows the chemical analysis of the samples taken.

Table 2

The results of general chemical analysis of the solution from the Aksu gold extraction plant

Sample	Analyte								
	CN^-	SCN^-	Cu	Fe	Zn	Mg	As	Ni	Sb
Industrial solution, mg/l	221	3570	15	730	7	2	1,7	3	3

In the first stage, cyanides and metal cyanide complexes were oxidized with sodium pyrosulfite (5 g/g), in the presence of copper ions at pH 9.0–10.0.

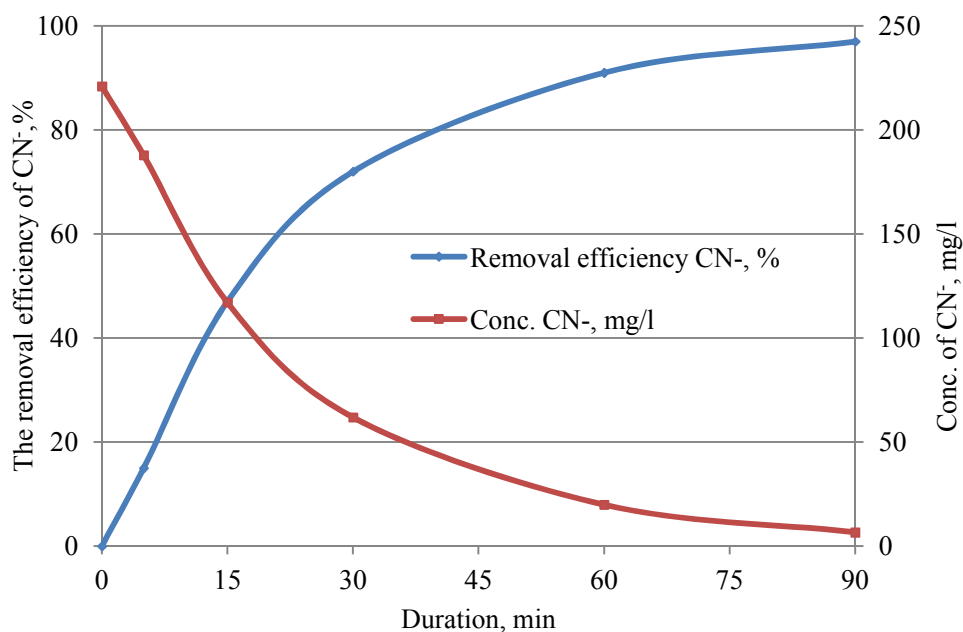


Figure 3. Effectiveness of CN^- removal with sodium pyrosulfite

The obtained data (Fig. 3) show that the neutralization degree is 97 % in 90 minutes, the residual CN^- concentration was 6.6 mg/l, whereas the concentration of thiocyanate ions increased due to the oxidation of cyanide ions, which amounted to 3785 mg/l.

In the second stage, the processing solution was passed through a bioreactor for destruction of the residual content of cyanide and thiocyanate by bacterial consortium immobilized on a zeolite. The results of the experiments are shown in Figures 4, 5.

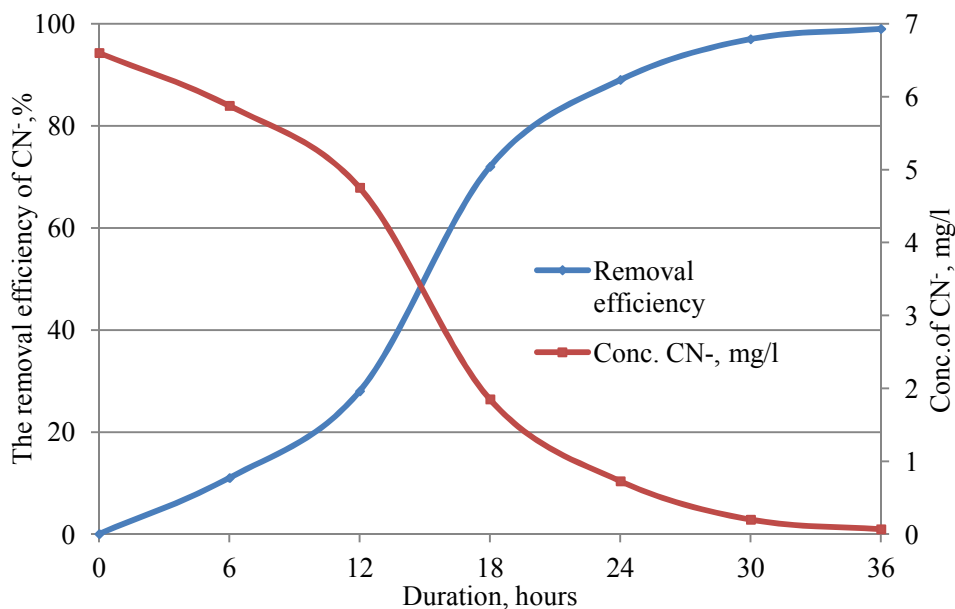


Figure 4. Effectiveness of CN^- removal with bacterial consortium *Agrobacterium tumefaciens* AC-1, *Agrobacterium tumefaciens* AC-2, *Pseudomonas sp.* AC-3

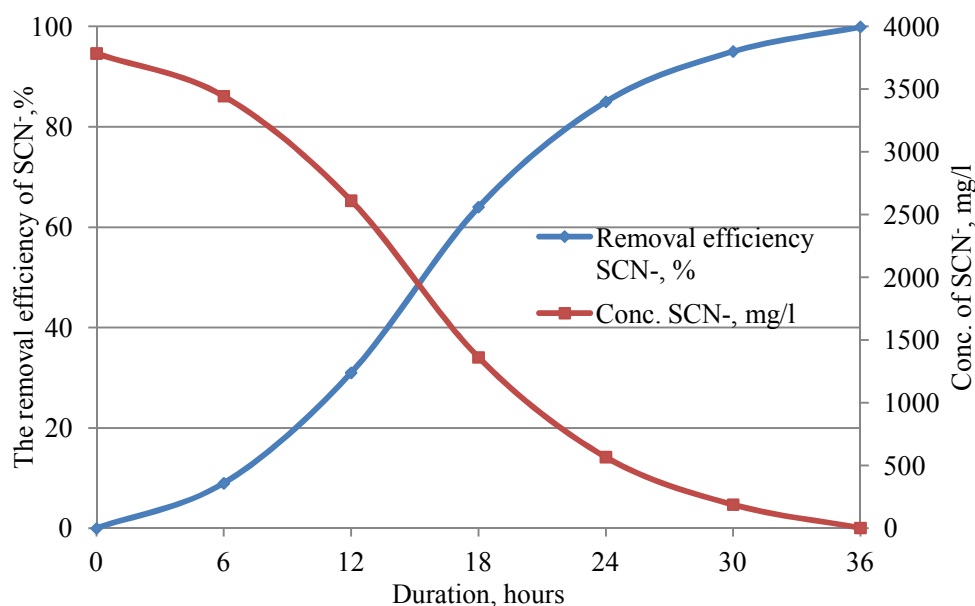


Figure 5. Effectiveness of SCN^- removal with bacterial consortium *Agrobacterium tumefaciens* AC-1, *Agrobacterium tumefaciens* AC-2, *Pseudomonas sp.* AC-3

Based on the results of the experiments, the degree of bacterial destruction of CN^- and SCN^- are 99 % and 99.9 %, respectively. Moreover, respective residual concentrations of CN^- and SCN^- ions in the treated solution were ≤ 0.1 mg/l and ≤ 4 mg/l, which corresponds to the maximum permissible concentrations approved in the Republic of Kazakhstan and CIS countries.

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Бактериялық-химиялы тәсілмен цианид- және тиоцианат-иондар деструкциясы

Мақалада бактериялық және химиялық әдістермен цианид және тиоцианат-иондар деструкция мәселелері қарастырылған. Химиялық деструкция әдістері ретінде мыс сульфаты катализаторында натрий пиросульфатпен тотықтыру және белсендірілген көмірмен адсорбциялау қолданылды. Деструкцияның бактериялық тәсілі *Agrobacterium tumefaciens* AC-1, *Agrobacterium tumefaciens* AC-2 және *Pseudomonassp* AC-3 бактериялар консорциумымен жүргізілді. Тәжірибелерді қадағалау мақсатымен бірдей шарттарда реагент қосылуынсыз модельдік ерітінділер дайындалды. Цианид иондар алып шығару үшін ең тиімді тәсіл натрий пиросульфит ықпалында байқалды: 97 % 1–1,5 сағ; *Agrobacterium tumefaciens* AC-1, *Agrobacterium tumefaciens* AC-2 және *Pseudomonassp* AC-3 бактериялар консорциумы тиоцианат-иондар алып шығару үшін: 120 сағ — 99 %. Сонымен, бірінші кезеңде бактериялық процеске бөгет болуы мүмкін цианидтің жоғары концентрациясын химиялық әдіспен төмендетті. Екінші кезеңде цианид иондар ШРК деңгейіне дейін азайып, тиоцианат-иондардың толық залалсыздандырылуы жүргізілді. Алтын шығару фабриканың технологиялық ерітінділерімен модельді эксперименттер жасалды. Зерттеу нәтижелері бойынша бактериялар консорциумымен CN^- және SCN^- бұзылу дәрежесі 99 және 99,9 % сәйкес. Өңделген ерітіндідегі CN^- және SCN^- -иондарының қалдық концентрациялары $\leq 0,1$ мг/л және ≤ 4 мг/л сәйкес болды. Бұл Қазақстан Республикасы мен ТМД елдерінде қабылданған шекті рұқсат етілген концентрация ретінде қабылданған деңгейге сай келді.

Кілт сөздер: цианид, тиоцианат, деструкция, алып шығару тиімділігі, азу, натрий пиросульфиті, түйіршіктелген белсендірілген көмір, бактериялар консорциумы.

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Деструкция цианид- и тиоцианат-ионов бактериально-химическим способом

В статье рассмотрены вопросы деструкции цианид- и тиоцианат-ионов бактериальными и химическими методами. В качестве методов химической деструкции были использованы адсорбция гранулированным активированным углем и окисление пиросульфитом натрия в присутствии катализатора сульфата меди. Бактериальный способ деструкции проведен консорциумом бактерий *Agrobacterium tumefaciens* AC-1, *Agrobacterium tumefaciens* AC-2 и *Pseudomonassp* AC-3. Для контроля ставили модельные растворы при идентичных условиях без добавления какого-либо реагента. Наиболее эффективное удаление цианид-ионов наблюдалось при воздействии пиросульфитом натрия: 97 % за 1–1,5 ч; для удаления тиоцианат-ионов консорциум бактерий *Agrobacterium tumefaciens* AC-1, *Agrobacterium tumefaciens* AC-2 и *Pseudomonassp* AC-3: за 120 ч — 99 %. Таким образом, на первой стадии удаляется значительное содержание цианид-ионов химическим способом для снижения воздействия высоких концентраций цианида на бактериальный процесс. На второй стадии происходит удаление цианид-ионов до ПДК, а также полное обезвреживание тиоцианат-ионов. Проведены модельные эксперименты с технологическими растворами золотоизвлекательной фабрики. По результатам исследований степень разрушения CN^- и SCN^- -ионов консорциумом бактерий составляет 99 и 99,9 % соответственно. Остаточная концентрация CN^- и SCN^- -ионов в обработанном растворе составила $\leq 0,1$ мг/л и ≤ 4 мг/л соответственно, что отвечает предельно допустимой концентрации утвержденных в Республике Казахстан и странах СНГ.

Ключевые слова: цианид, тиоцианат, деструкция, эффективность удаления, деградация веществ, пиросульфит натрия, гранулированный активированный уголь, консорциум бактерий.

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Research of brown iron lisakovsky raw materials solid phase metallization process

The research results of the process of lisakovsky gravitational magnetic concentrate (LGMC) solid-phase metallization using the highly reactive solid carbon reducing agent «direksil» are given in the article. There were set rational parameters of solid-phase reduction process of LGMC in the mine furnace providing the extent of its metallization of 20.4–88.6 %. It was determined the temperature range of solid-phase direct reduction of iron of 1150–1200 °C providing the maximum rate and extent of iron oxides metallization, at the same time passing over emergence of the liquid phase — fusion. Use of «direksil» as a reducing agent allows raising metallization extent of LGMC in more than 3 times in comparison with furnace coke. In the article there are given diffraction patterns (X-ray patterns) of the metallized samples of LGMC characterizing phase structure and crystal structure of the obtained restoration products depending on the type of reducing agent. The physical condition of the metallization products obtained in the mode of solid-phase restoration allows using all known methods of separation of the metallized concentrate from the dead rock. The most preferable option of such separation includes methods of magnetic separation in view of contrast formed after the system metallization. Separation of magnetic and non-magnetic products after metallization is an obligatory element of the technological scheme of LGMC metallization since the total content of iron in initial concentrate does not exceed 49 %. At that depending on metallization extent the magnetic fraction can be used as a furnace charge component when smelting the conversion iron in the blast furnace (metallization extent is less than 40 %) or steelmaking in the electric furnace (metallization extent is more than 80 %).

Keywords: brown iron, LGMC, solid-phase metallization, metallization extent, carbon reducing agent, direksil, phase structure, metallized concentrate.

Many research works and publications are devoted to studies of the iron restoration process from the lisakovsky gravitational and magnetic concentrate (LGMC) during a number of decades [1–6]. In particular the scientists of Zh. Abishev Chemical and Metallurgical Institute are engaged in solution of the problem of beneficiation and refinement (dephosphorization) of LGMC [3–6] for many years. In the works [2–6] there are concerned the results of reducing roasting of LGMC with use of gaseous, solid and liquid reducers. Authors [2] established that restoration rate of concentrate's layer was limited by external diffusion at designed temperature and gas composition. And, as the studies have shown, the external diffusive resistance for a concentrate is much less than internal diffusive resistance, for example, for the iron nugget concentrate, and is regulated by change of gas consumption, due to which the metallization rate increases significantly. This advantage of the concentrate over the layer of lumpy materials can be used for solution of problems of direct metallization of iron ore concentrates, in particular, in vertical porous tanks. But the main obstacle in the way for realization of such process is susceptibility of usual iron ore concentrates to adhesion and swelling during restoration. However, according to authors [2], as for metallization of LGMC, the process proceeds without adhesion of particles even at 1000 °C. Lisakovsky concentrates in the whole interval of reduction degree from 0 to 1 do not conglutinate both at low and high (1000 °C) temperatures, they do not inflate and, on the

contrary, considerably shrink. These features of them are favorable to solution of tasks on solid-phase metallization, with expansion of temperature limits of reduction in order to achieve the high rate of interaction. To overcome the difficulties connected with low burdening materials' bed porosity it is necessary to create such conditions for metallization of ore raw materials at which the rate of the process would not be limited by diffusive resistance. It is possible to solve this important problem when using reducer with the high reactive capacity and applying the special technology on preparation of burden constituents.

The problem of the real researches consisted in determination of temperature limits of solid-phase direct reduction of iron with a view to provide the maximum rate and extent of metallization of iron oxides, at the same time passing over emergence of the liquid phase — fusion. For solution of that we have conducted a series of experiments on studying the influence of temperature condition on metallization of the isakovsky gravitational and magnetic concentrate in the heat-treatment furnace (mine furnace). Test activity on direct restoration was carried out at 1000–1250 °C temperatures. The furnace coke (Arselor Mittal Temirtau) and new highly reactive reducer «direksil» were used as reducing agents. Carbonaceous reducing agent «direksil» was obtained from the enriched nonlinkering coal by the method of high-speed thermal-oxidative carbonization. Development and exploitation of the production technology of direksil were carried out under the direction of professor, laureate of state prize of RK V.A. Kim (Zh. Abishev Chemical and Metallurgical Institute) [7].

Ash technical specifications and chemical composition of the carbonaceous reducers used in the experiments carried out by us are given in the Tables 1 and 2. Weight ratios of LGMC to the reducing agent were 1:0.25. Preparation of furnace charge for metallization was carried out by two ways, namely,

- LGMC and reducing agent (furnace coke or direksil) were placed in the melting pot by layers;
- LGMC and reducing agent (furnace coke or direksil) were carefully mixed and placed in the melting pot.

Table 1

Technical specifications of carbonaceous reducing agents

Reducing agent	Technical structure, %				
	W ^p	A	V ^d	S ^d	P ^d
Direksil	1.0–2.0	1.0–5.0	3.6–15.0	0.20–0.40	0.01–0.04
Furnace coke of ArselorMittal Temirtau	2.0–15.0	13.8	1.5	0.50	0.045

Table 2

Chemical composition of reducing agents' ash

Reducing agent	Content, %			
	SiO ₂	Al ₂ O ₃	MgO+CaO	Fe ₂ O ₃
Direksil	48.06	18.62	4.78	7.32
Furnace coke of ArselorMittal Temirtau	48.50	20.0	8.7	16.6

The analysis of experiment results on metallization of LGMC with the use of furnace coke shows that at long isothermal holding the set temperature of emergence of the liquid phase is 1150 °C. In such a way it was observed emergence of the liquid phase — fusion (fayalite) in restoration products in the experiments carried out at the temperature of 1150 °C. Pictures of the metallized samples obtained as a result of reducing roasting of LGMC with the use of the furnace coke as a reducing agent at long isothermal holding of 60 and 90 minutes at 1150 °C are given in the Figure 1. As you can see on the fracture of the samples the fusion zone with increase in hold time up to 90 minutes covers almost total volume of the metallized product (sample b).

With reduction of isothermal time of LGMC mixture and solid reducing agent the temperature range of solid-phase restoration extends towards the greater temperature considerably. So at the time of isothermal holding of pilot samples within 5–15 minutes the noticeable emergence of the liquid phase was not observed at 1150 °C and even at 1200 °C. Noted feature of mixture behavior of LGMC and solid reducing agent is indicative of the basic possibility of realization of solid-phase restoration of LGMC at short-term holding of furnace charge within 10–15 minutes with achievement of the set extent of metallization of ≤40 % as well as ≥80 %. At the same time the subsequent separation of a ferriferous part from dead rock can be carried out by methods of magnetic separation of products of solid-phase metallization.

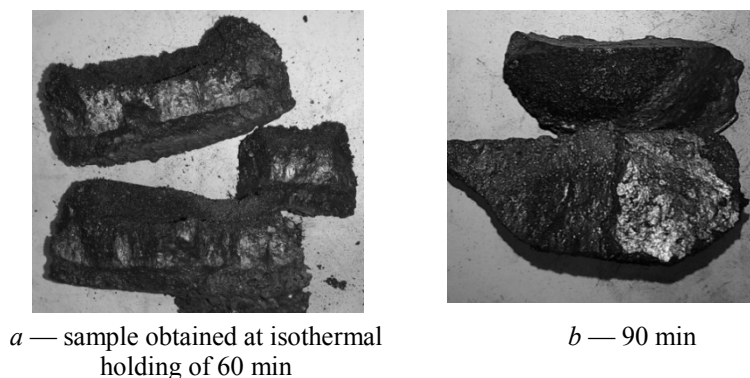


Figure 1. Metallized samples obtained at reducing roasting of LGMC using furnace coke

The concentrate which is formed at metallization extent of $\leq 40\%$ containing up to 72 % of iron can be used at domain melting of conversion iron. It opens a prospect of the wider involvement of brown iron ores into traditional two-stage steel production the balance reserves of which in Kazakhstan are estimated in billions of tons.

According to requirements to a metallized concentrate the criteria of its suitability as a furnace charge component for steel smelting in electric furnaces is metallization extent of more than 80 % at the minimum content of dead rock [8]. Results of the experiments carried out in the range of temperatures of 1150–1250 °C showed that it was necessary to apply the highly reactive reducing agent in the form of direksil for achievement of metallization extent of LGMC of $\geq 80\%$. At that in the temperature range of 1200–1250 °C the set metallization extent of LGMC (80 % and more) is provided at mixture holding within 8–10 minutes.

In compliance with a research problem at traditional ways of metallization of LGMC connected with long isothermal holding, as a rule, exceeding 60–90 minutes there were set the technological parameters of solid-phase restoration in which metallization temperature should not exceed 1100 °C. For obvious demonstration of influence of reducing agent type on metallization process of LGMC the results of the experiments carried out at 1100 °C and hold time of 90 minutes are given below. The furnace coke and direksil are considered as the solid reducing agents (see Table 1). Conditions of furnace charge preparation are described below:

- Experiment No. 1 — LGMC and furnace coke were divided into 5 parts and placed in the melting pot by layers.
- Experiment No. 2 — LGMC and direksil were divided into 5 parts and placed in the melting pot by layers.
- Experiment No. 3 — LGMC and direksil were mixed and placed in the melting pot.
- Experiment No. 4 — LGMC and furnace coke were mixed and placed in the melting pot.

The pictures of the metallized product samples of LGMC obtained as a result of solid-phase reduction with different reducing agents are given in the Figure 2.

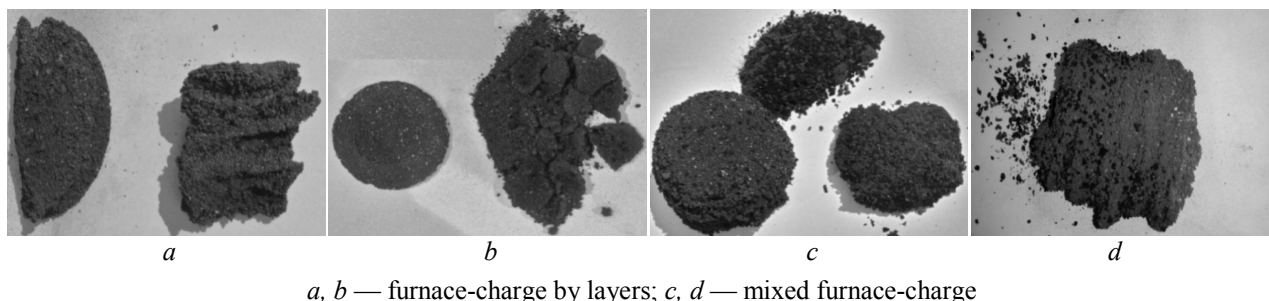


Figure 2. Pictures of metallized product samples of LGMC

Products of reducing roasting are represented by weakly caked-on particles, which crumble by easy pressing. Thus, the physical condition of the metallization products obtained in the mode of solid-phase restoration allows using all known methods of separation of the metallized concentrate from the dead rock. And the most preferable option of such separation includes methods of magnetic separation in view of contrast

formed after the system metallization. Separation of magnetic and non-magnetic products after metallization is an obligatory element of the technological scheme of LGMC metallization since the total content of iron in initial concentrate does not exceed 49 %. At that depending on metallization extent the magnetic fraction can be used as a furnace charge component when smelting the conversion iron in the blast furnace (metallization extent is less than 40 %) or steelmaking in the electric furnace (metallization extent is more than 80 %).

Samples *a* and *b* were obtained when loading furnace charge by layers, and samples *c* and *d* — as a result of carrying out metallization by furnace charge mixing. Direksil was used as a reducing agent in samples *b*, *d*; *a* and *c* were obtained with the use of furnace coke. For assessment of reduction degree of iron oxides on height of the metallized sample the test for the chemical analysis was selected by layers. Non-magnetic component of the metallized samples was separated by means of magnetic separation without crushing of the products obtained. The chemical composition of the magnetic part of the metallization products of LGMC is given in the Table 3. According to the results of analysis of the chemical composition of the magnetic component of metallized LGMC content of the total iron in the metallized products with application of direksil is higher than in samples with use of furnace coke for 5–7 abs. %.

Table 3

Chemical composition of metallized products

Exp. No.	Name	Content, %						
		Fe _{total}	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S
1	LGMC with furnace coke by layers							
	1 (upper)	67.01	10.74	6.22	n/o	0.72	0.92	0.137
	2	67.40	10.81	6.18	0.87	n/o	0.98	0.134
	3	67.66	10.18	6.18	0.35	n/o	0.96	0.077
	4	67.66	8.99	6.37	0.52	n/o	0.99	0.077
2	LGMC with direksil by layers							
	1 (upper)	68.59	14.41	6.06	n/o	0.65	0.99	0.067
	2	77.22	10.50	7.04	0.52	n/o / o	1.1	0.057
	3	76.43	11.50	6.72	0.52	2.90	1.1	0.057
	4	76.69	11.22	7.19	n/o	2.90	1.1	0.057
3	LGMC with furnace coke by mixing							
	1 (upper)	71.26	7.84	6.40	n/o	0.99	0.97	0.173
	2	71.52	7.78	6.33	n/o	0.82	1.0	0.105
	3	70.32	8.04	6.29	n/o	0.82	1.0	0.115
	4	68.86	8.51	6.16	n/o	0.82	0.94	0.192
4	LGMC with direksil by mixing							
	1 (upper)	80.31	7.44	6.85	n/o	0.82	1.12	0.077
	2	77.91	8.31	6.68	n/o	0.98	1.08	0.096
	3	72.59	8.70	6.61	n/o	0.65	1.02	0.077
	4	70.72	8.31	6.29	n/o	0.82	0.99	0.096

In Figures 3 and 4 there are given diffraction patterns (X-ray patterns) of the metallized samples of LGMC characterizing phase structure and crystal structure of the obtained restoration products depending on the type of reducing agent. It should be noted that the content of silicon dioxide in the samples obtained by mixing the furnace charge before metallization process conduction is less for 3–5 % than in the samples obtained when loading furnace charge by layers that is coordinated with data of X-ray phase analysis (Fig. 3, 4).

As a result of solid-phase restoration in all experiments we have obtained a metallized concentrate in the form of weakly caked-on particles, which crumble by easy pressing. Extent of metallization is calculated according to the chemical analysis taking into account results of X-ray phase analysis. Exponents of metallization of the obtained products depending on conditions of furnace charge preparation for recovery roasting and the applied reducer are given in the Table 4.

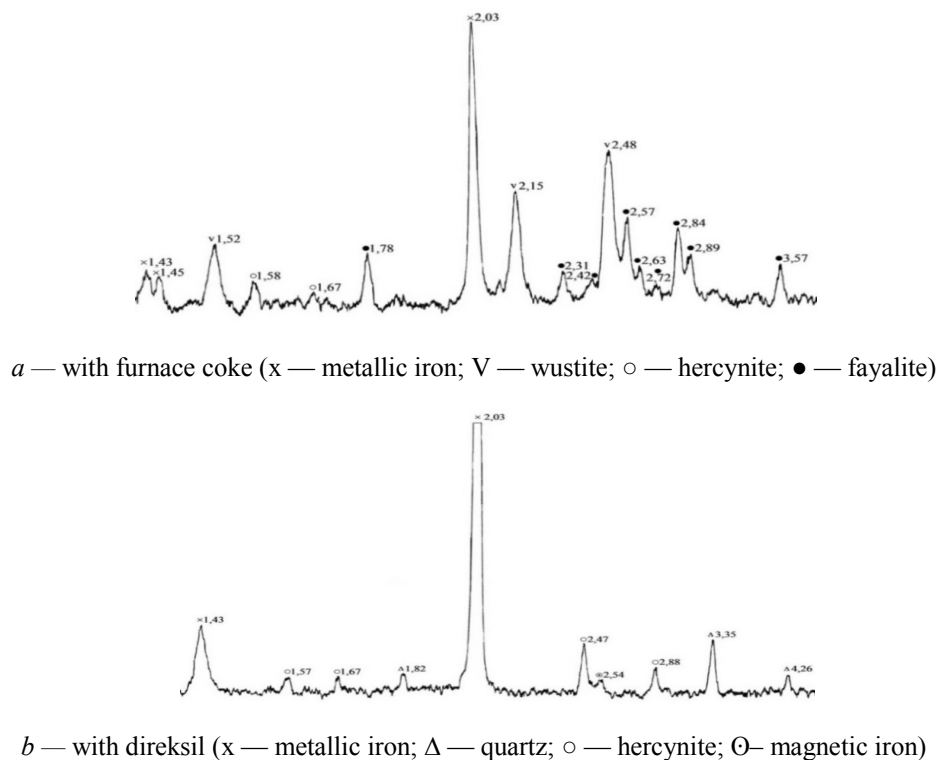


Figure 3. Diffraction pattern of the metallized product samples obtained when loading the furnace charge by layers with application of furnace coke (*a*) and direksil (*b*) as a reducing agent

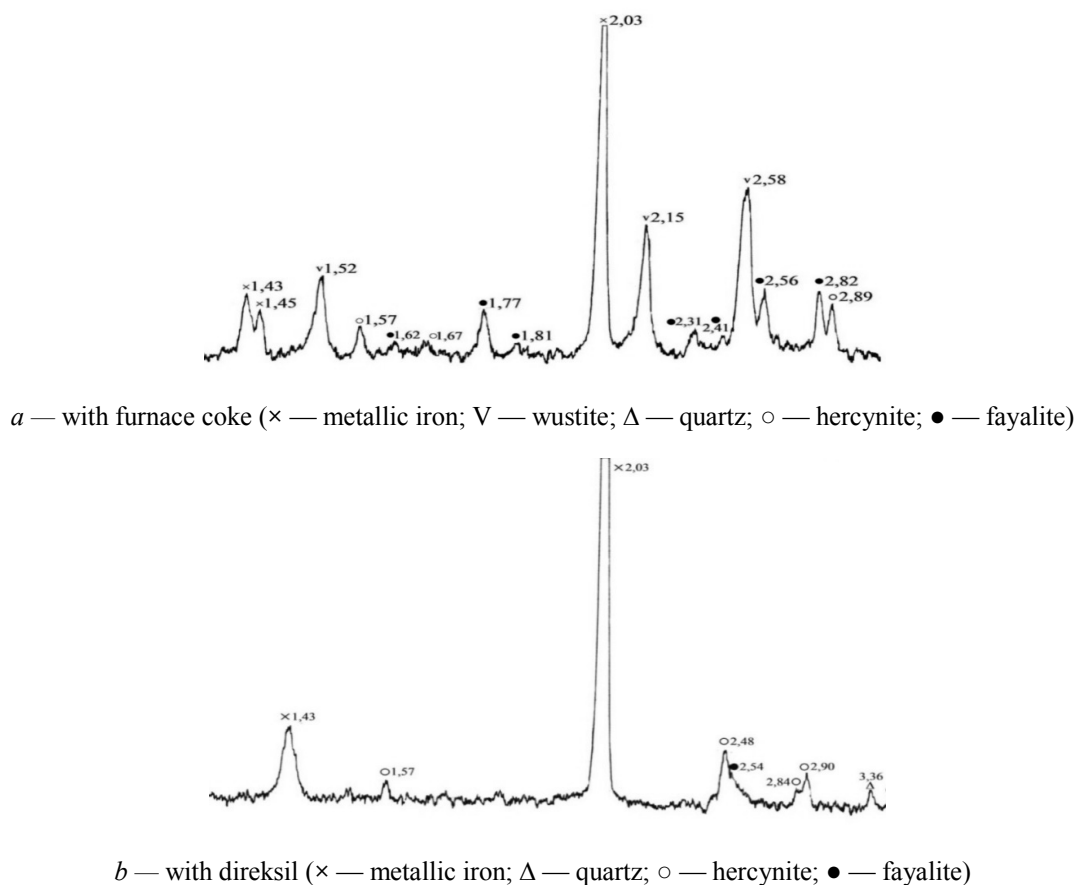


Figure 4. Diffraction pattern of the metallized product samples obtained when mixing the furnace charge with application of furnace coke (*a*) and direksil (*b*) as a reducing agent

Table 4

Metallization degree of roasted product of LGMC

Exp. No.	Name	T, °C	τ , min	Fe _{total} , %	Fe _{met} , %	α_{met} , %
1	LGMC with furnace coke by layers	1100	90			
	1 (upper)			67.01	17.13	25.26
	2			67.40	47.74	29.19
	3			67.66	16.60	24.53
	4			67.66	13.77	20.35
2	LGMC with direksil by layers	—	—			
	1 (upper)			68.59	36.03	52.53
	2			77.22	67.55	87.47
	3			76.43	67.75	88.64
	4			76.69	67.78	88.40
3	LGMC with furnace coke by mixing	—	—			
	1 (upper)			71.76	27.98	39.26
	2			71.52	27.95	39.07
	3			70.32	23.31	33.15
	4			68.86	18.05	26.21
4	LGMC with direksil by mixing	—	—			
	1 (upper)			80.31	68.41	85.18
	2			77.91	66.68	85.50
	3			72.59	36.39	50.13
	4			70.72	34.32	48.52

According to the chemical analysis (Table 4) the greatest extent of metallization of 85–88 % at the total iron content of 72–77 % was reached in the experiments No. 2 and No. 4, when using direksil as a reducing agent, activity of which is much higher than those of traditionally applied reducers, in particular, of furnace coke. At that the metallization extent in the experiment No. 2 (with direksil) is 3 times higher than in the experiment No. 1 (with furnace coke). Diffraction patterns of the metallized productsamples given in Figures 3 and 4 also confirm advantage of using direksil as a reducing agent. Characteristic peaks of metal iron are much more intensive, and presence of fayalite and hercynite, which are formed in the course of the iron oxides recovery, is insignificant (Fig. 3, *b* and 4, *b*) in comparison with phase structure of the metallized product obtained with the use of furnace coke (Fig. 3, *a* and 4, *a*). The average chemical composition of the metallized samples is as follows Fe_{total} — 77.91; SiO₂ — 8.31; Al₂O₃ — 6.68; MgO — 0.98; P — 1.08. Basicity (Al₂O₃+MgO)/SiO₂ is equal to 0.9.

Thus, as a result of conducting studies of the metallization modes of brown iron lisakovsky concentrate there are set the rational parameters of direct solid-phase restoration of LGMC in the laboratory mine furnace providing extent of its metallization of 20.38–88.64 %. It is more preferable to usedireksilas a reducing agent, highly active solid reducer from Shubarkol coal allowing raising extent of metallization of LGMC in more than 3 times in comparison with furnace coke. Optimum temperature of solid-phase metallization process of LGMC at long holding should not exceed 1100 °C. With reduction of time of isothermal holding of LGMC mixture with solid reducer the solid-phase metallization is provided at more high temperatures of roasting reaching up to 1150–1200 °C. The specified feature allows using the new technical solutions for achievement of the set metallization extents of LGMC obtaining the final products for multiple purposes.

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Қоңыр темірлі лисаков шикізатының қатты фазалық металдану үрдісін зерттеу

«Дирексил» жоғары реакционды қатты көміртекті тотықсыздандырғышты қолдану арқылы лисаков гравитациялық магнитті концентратын (ЛГМК) металдандыру үрдісіне зерттеу жүргізілді. 20,4–88,6 металдану дәрежесін қамтамасыз ететін ЛГМК-ның қатты фазалық тотықсыздану үрдісінің ұтымды көрсеткіштері орнатылды. Жоғары жылдамдық пен темір тотығының металдану деңгейін қамтамасыз етіп, сұйық фаза — балқыманың қалыптасуынан айналып өтетін қатты фазалы темірдің тікелей қалыптасуының 1150–1200 °C-дағы температура диапазоны анықталды. «Дирексилды» тотықсыздандырғыш ретінде пайдалану ЛГМК-ның металдану деңгейін домна коксымен салыстырғанда 3 еседен көп арттыруға мүмкіндік береді. Қалыпқа келтірушінің түріне байланысты алынған қалыпқа келтіруші өнімдердің кристалдық құрылымы мен фазалық құрамын сипаттайтын металданған ЛГМК түрлерінің дифрактограммалары (рентгенограммалары) келтірілген. Қатты фазалық қалыпқа келтіру тәртібінде алынған металданған өнімдердің физикалық күйі бос түрлерден металданған концентратты бөлуде барлық белгілі әдістерді пайдалануға мүмкіндік береді. Жүйелердің металдануынан кейін қалыптасатын қарама-қайшылығындай магнитті сепарация амалдары мұндай бөлулерде ең қолайлы нұсқа болып табылады. Металдандырудан кейін өнімдерді магнитті және магнитсіз бөлу ЛГМК металдандырудың технологиялық сызбасының міндетті элементі болып табылады, себебі шығыс концентратында жалпы темір құрамы 49 % аспайды. Сонымен қатар металдандыру деңгейіне байланысты магнитті фракция доменді пеште қолданбалы шойынды қорытудағы (металдандыру деңгейі 40 %-дан кем емес) немесе электр пеште болатты балқытудағы (металдандыру деңгейі 80 %-дай) шихта компоненті сияқты пайдаланылуы мүмкін.

Кілт сөздер: қоңыр темір кендері, ЛГМК, қатты фазалық металдандыру, металдандыру деңгейі, көміртекті тотықсыздандырғыш, «Дирексил», фазалық құрамы, металдандырылған концентрат.

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Исследование процесса твердофазной металлизации бурожелезнякового лисаковского сырья

В статье приведены результаты исследования процесса твердофазной металлизации лисаковского гравитационного магнитного концентрата (ЛГМК) с применением высокорекреакционного твердого углеводородного восстановителя «Дирексил». Установлены рациональные параметры процесса твердофазного восстановления ЛГМК в шахтной печи, обеспечивающие степень его металлизации 20,4–88,6 %. Определен температурный диапазон твердофазного прямого восстановления железа 1150–1200 °C, обеспечивающий максимальную скорость и степень металлизации оксидов железа, минуя при этом появление жидкой фазы — расплава. Использование «Дирексила» в качестве восстановителя позволяет повысить степень металлизации ЛГМК в более чем 3 раза по сравнению с доменным коксом. Приведены дифрактограммы (рентгенограммы) металлизированных образцов ЛГМК, характеризующие фазовый состав и кристаллическую структуру полученных продуктов восстановления в зависимости от вида восстановителя. Физическое состояние продуктов металлизации, полученных в режиме твердофазного восстановления, позволяет использовать все известные методы разделения металлизированного

концентрата от пустой породы. Причем наиболее предпочтительным вариантом подобного разделения являются приемы магнитной сепарации в виду контрастности образующейся после металлизации системы. Разделение магнитного и немагнитного продуктов после металлизации является обязательным элементом технологической схемы металлизации ЛГМК, так как суммарное содержание железа в исходном концентрате не превышает 49 %. При этом, в зависимости от степени металлизации, магнитная фракция может быть использована как компонент шихты при выплавке передельного чугуна в доменной печи (степень металлизации менее 40 %) или же выплавке стали в электрической печи (степень металлизации более 80 %).

Ключевые слова: бурожелезные руды, ЛГМК, твердофазная металлизация, степень металлизации, углеродный восстановитель, «Дирексил», фазовый состав, металлизированный концентрат.

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Development of the technological process of processing chromium-containing technogenic materials

The article is devoted to the development of the technological process for the processing chromium containing technogenic materials, which includes their roasting in the presence of sodium carbonate and the subsequent leaching of chromium from the sinter with water. Using the method of stochastic determined design of the experiment, a five-factor mathematical model of extracting chromium into a cake was obtained. It is determined that in order to achieve the minimum recovery of chromium in the cake and, accordingly, the most complete isolation of the given metal into the solution, it is necessary to conduct batch roasting under the following conditions: $t_{\text{roast}} = 960^\circ\text{C}$, $\tau_{\text{roast}} = 3\text{h}$, $N = 60\%$, and leaching at $\tau_{\text{leach}} = 2\text{h}$ and $t_{\text{leach}} = 60^\circ\text{C}$. The chemistry of the passing processes is shown. It is shown the usefulness of the obtained mathematical equation for making predictions that are more accurate when introducing the values of the arguments within the given limits of their variation into the given equation and less accurate at a considerable distance from these limits. Calculation in the indicated calcination conditions shows that the recovery of chromium in the solution increases with increasing firing temperature, time of its maintenance and consumption of Na_2CO_3 .

Keywords: chromite, stochastic determined design of the experiment, chromium leaching, sodium carbonate, sodium chromate, industrial chromium containing wastes, chromite calcination, firing of chromium-containing batch.

Products with substandard chromium content and the wastes such as dust, slimes and cakes are formed in the production of chromium, its chemical compounds and alloys with various metals [1–3]. Involvement of these wastes in the process of conversion is an important and urgent task [4–7].

A commercial product containing wt. %: 20.7 Cr; 6.31 Fe; 34.38 MgO ; 0.6 CaO ; 20.9 SiO_2 ; 2.86 Al_2O_3 was selected as an object of research. The experiments were carried out according to the scheme such as roasting of industrial products in the presence of sodium carbonate, leaching of chromium with water from the cake (the ratio of L:S in all experiments was 4:1). The method of stochastic-determined design of experiment in the modified version was used [8]. In the six-factor plan of the experiment the following factors such as the roasting temperature (t_{roast} , $^\circ\text{C}$), roasting time (τ_{roast} , h), consumption of sodium carbonate taken with respect to the weight of the commercial product (N , %), time (τ_{leach} , h) and temperature (t_{leach} , $^\circ\text{C}$) of leaching were varied. The position for one factor in the experiment's plan remained unoccupied, which is the vacant factor (Table 1).

Table 1

Plan of the experiment, results of the experiments ($\beta_{\text{c.ex.}}$, $\beta_{\text{c/b.ex.}}$, $\text{Cr}_{\text{c.ex.}}$, $\varepsilon_{\text{c.ex.}}$) and calculations ($\beta_{\text{s.t.}}$, $\beta_{\text{c/b.t.}}$, $\text{Cr}_{\text{c.t.}}$, $\varepsilon_{\text{c.t.}}$). R is correlation coefficient and t_R is its significance

	$t_{\text{roast.}}$ $^\circ\text{C}$	$\tau_{\text{roast.}}$ h	N , %	$\tau_{\text{l.}}$ h	$\tau_{\text{b.}}$ $^\circ\text{C}$	x_6	$\beta_{\text{s.ex.}}$ %	$\beta_{\text{s.t.}}$ %	$\beta_{\text{c/b.ex.}}$ %	$\beta_{\text{c/b.t.}}$ %	$\text{Cr}_{\text{c.ex.}}$ %	$\text{Cr}_{\text{cake.t.}}$ %	$\varepsilon_{\text{c.ex.}}$ %	$\varepsilon_{\text{c.t.}}$ %
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	560	1	20	1	20	1	94.33	94.67	70.22	68.20	21.94	24.08	89.03	94.2
2	560	1.5	30	1.5	40	2	95.98	96.75	64.61	68.98	23.02	22.68	93.41	96.45
3	560	2	40	2	60	3	95.36	95.96	65.71	67.84	19.67	20.78	87.15	93.44
4	560	2.5	50	2.5	80	4	93.80	93.63	64.11	66.37	17.98	18.58	83.38	87.91
5	560	3	60	3	95	5	91.79	90.42	60.12	65.60	20.33	16.05	94.28	80.68
6	660	1	30	2	80	5	92.84	93.76	76.92	74.73	18.71	17.35	90.38	79.81
7	660	1.5	40	2.5	95	1	92.04	92.99	71.43	65.28	18.15	19.5	87.68	84.21
8	660	2	50	3	20	2	90.43	90.73	64.21	60.48	15.55	16.78	72.11	71.98
9	660	2.5	60	1	40	3	88.42	87.62	62.51	66.31	17.4	14.75	84.06	74.57
10	660	3	20	1.5	60	4	88.88	87.52	83.31	87.92	19.26	18.93	93.04	95.28
11	760	1	40	3	40	4	89.55	90.64	62.96	68.89	15.92	12.77	67.68	57.93
12	760	1.5	50	1	60	5	87.78	88.43	56.11	63.30	16.29	15.21	66.1	68.19

Continuation of Table 1

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
13	760	2	60	1.5	80	1	85.73	85.4	70.3	63.72	14.81	14.45	80.13	70.07
14	760	2.5	20	2	95	2	86.11	85.31	73.33	76.93	19.08	20.7	81.11	90.98
15	760	3	30	2.5	20	3	87.80	87.18	73.85	74.41	15.2	14.22	70.5	64.8
16	860	1	50	1.5	95	3	85.77	86.57	53.33	62.08	12.78	12.01	49.39	52.68
17	860	1.5	60	2	20	4	83.58	83.6	50.21	56.12	11.62	12.05	44.91	51.23
18	860	2	20	2.5	40	5	83.85	83.51	63.33	71.31	22.47	17.6	82.49	71.37
19	860	2.5	30	3	60	1	85.44	85.34	58.46	69.05	10.07	14.48	39.97	61.13
20	860	3	40	1	80	2	85.06	84.64	74.28	68.86	10.5	12.65	52.75	57.27
21	960	1	60	2.5	60	2	81.95	82.11	60.12	57.53	7.75	9.001	35.94	39.15
22	960	1.5	20	3	80	3	82.03	82.02	66.67	61.17	19.37	17.14	74.86	59.54
23	960	2	30	1	95	4	83.48	83.82	52.31	56.34	18.6	16.57	61.1	56.97
24	960	2.5	40	1.5	20	5	83.05	83.14	57.14	57.45	15.5	12.02	59.9	45.19
25	960	3	50	2	40	1	81.75	81.12	64.31	64.90	8.5	9.131	39.42	41.68
R							0.9846		0.7270		0.8044		0.8429	
t_R							610.8173		29.3006		43.3080		57.3464	

The batch for roasting was prepared by mixing the sample of commercial product, which was the same in all experiments, and sodium carbonate according to its consumption. Thus, the mass of the batch was variable depending on the consumption of Na_2CO_3 .

During the mathematical processing of the experimental data, the yield of the sinter (β_{sinter} , %), the yield of cake calculated with respect to the mass of the sinter ($\beta_{\text{cake/sinter}}$, %), the yield of cake, found with respect to the mass of the initial batch (β_{batch} , %), chromium content in the sinter ($\text{Cr}_{\text{sinter}}$, %), in the cake (Cr_{cake} , %) and in the batch (Cr_{batch} , %), chromium recovery in the cake (ϵ_{cake} , %) and in the solution (ϵ_{sol} , %) were determined. The relationship between these variables is determined by the following relationships:

$$b_{\text{sinter}} = \frac{m_{\text{sinter}} \times 100}{m_{\text{batch}}}; \quad (1)$$

$$\beta_{\text{cake/sinter}} = \frac{m_{\text{cake}} \cdot 100}{m_{\text{sinter}}}; \quad (2)$$

$$\beta_{\text{cake/batch}} = \frac{m_{\text{cake}} \cdot 100}{m_{\text{batch}}}, \quad (3)$$

where m_{sinter} , m_{batch} , m_{cake} — are the mass of the sinter, batch and cake, respectively. Using the formulas (1)–(3), we find:

$$\beta_{\text{cake/batch}} = \frac{\beta_{\text{sinter}} \cdot \beta_{\text{cake/sinter}}}{100}. \quad (4)$$

The recovery of chromium into the sinter is equal to 100 %, which is calculated by the formula:

$$\epsilon_{\text{sinter}} = \frac{\beta_{\text{sinter}} \cdot \text{Cr}_{\text{sinter}}}{\text{Cr}_{\text{batch}}} = 100. \quad (5)$$

The extraction of chromium into a cake is determined by:

$$\epsilon_{\text{cake}} = \frac{\beta_{\text{cake/sinter}} \cdot \text{Cr}_{\text{cake}}}{\text{Cr}_{\text{sinter}}}. \quad (6)$$

According to (5) the chromium content in the sinter $\text{Cr}_{\text{sinter}}$ is:

$$\text{Cr}_{\text{sinter}} = \frac{100 \cdot \text{Cr}_{\text{batch}}}{\beta_{\text{sinter}}}. \quad (7)$$

Substituting this expression to (6), we find:

$$\epsilon_{\text{cake}} = \frac{\beta_{\text{cake/sinter}} \cdot \beta_{\text{sinter}} \cdot \text{Cr}_{\text{cake}}}{100 \cdot \text{Cr}_{\text{batch}}} \quad (8)$$

or, taking into account (4):

$$\epsilon_{\text{cake}} = \frac{\beta_{\text{cake/batch}} \cdot \text{Cr}_{\text{cake}}}{\text{Cr}_{\text{batch}}}. \quad (9)$$

The extraction of chromium to the solution is:

$$\varepsilon_p = 100 - \varepsilon_k. \quad (10)$$

Thus, the functions under consideration are related to each other and are interdependent, which is reflected on the form of the partial functions obtained in the process of their graphic representation. So, $\beta_{cake/batch}$ depends on β_{sinter} and $\beta_{cake/sinter}$ (4), and the extraction of chromium in the cake (8) is determined by the mutual influence of the four dependent variables such as $\beta_{cake/sinter}$, β_{sinter} , Cr_{cake} and Cr_{batch} .

Table 2

Partial dependencies

Function's name	No.	Equation in logarithmic form
Yield of sinter, β_{sinter}	1	$\ln\beta_{sinter1} = 6.0942 - 2.4873 \cdot 10^{-1} \ln t_{roast.}$
	2	$\ln\beta_{sinter2} = 4.4708 - 2.6092 \cdot 10^{-2} \ln \tau_{roast.}$
	3	$\ln\beta_{sinter3} = 3.8181 - 7.1847 \cdot 10^{-3} N + 0.254 \ln N$
Yield of cake form mass of the batch, $\beta_{cake/batch}$	1	$\ln\beta_{cake/batch1} = -9.6171 - 3.7299 \cdot 10^{-3} t_{roast.} + 2.5116 \ln t_{roast.}$
	2	$\ln\beta_{cake/batch2} = 3.8216 + 0.3401 \tau_{roast.} - 0.5418 \ln \tau_{roast.}$
	3	$\ln\beta_{cake/batch3} = 4.6975 - 0.1475 \ln N$
	4	$\ln\beta_{cake/batch4} = 4.3054 - 0.1691 \tau_{leach.} + 0.3149 \ln \tau_{leach.}$
	5	$\ln\beta_{cake/batch5} = 3.4662 - 4.7599 \cdot 10^{-3} t_{leach.} + 0.25013 \ln t_{leach.}$
	6	$\ln\beta_{cake/batch6} = 4.1637$
Content of chromium in the cake, Cr_{cake}	1	$\ln Cr_{cake1} = 8.872 - 0.9239 \ln t_{roast.}$
	2	$\ln Cr_{cake2} = 3.457 - 0.7835 \tau_{roast.}$
	3	$\ln Cr_{cake3} = 4.1022 - 0.3709 \ln N$
	4	$\ln Cr_{cake4} = 2.6816 + 0.1096 \tau_{leach.} - 0.251 \ln \tau_{leach.}$
	5	$\ln Cr_{cake5} = 3.2934 + 5.8036 \cdot 10^{-3} t_{leach.} - 0.2232 \ln t_{leach.}$
	6	$\ln Cr_{cake6} = 2.7602$
Extraction of chromium into a cake, ε_{cake}	1	$\ln \varepsilon_{cake1} = -3.4544 - 3.7299 \cdot 10^{-3} t_{roast.} + 1.5877 \ln t_{roast.}$
	2	$\ln \varepsilon_{cake2} = 4.5667 - 0.4434 \tau_{roast.} + 0.8582 \ln \tau_{roast.}$
	3	$\ln \varepsilon_{cake3} = 5.8029 + 7.1788 \cdot 10^{-3} N - 0.5184 \ln N$
	4	$\ln \varepsilon_{cake4} = 4.2935 - 5.95 \cdot 10^{-2} \tau_{leach.} + 6.39 \cdot 10^{-2} \ln \tau_{leach.}$
	5	$\ln \varepsilon_{cake5} = 4.0466 + 1.0437 \cdot 10^{-3} t_{leach.} + 2.69 \cdot 10^{-2} \ln t_{leach.}$
	6	$\ln \varepsilon_{cake6} = 4.2143$

Note. the partial dependencies $\ln \varepsilon_{cake,i} = f(x_i)$, where i is the number of the dependence, are obtained by substituting the arithmetic mean values $x_{i,mean}$ and $(\ln x_i)_{mean}$ to (16), excluding those mean values that are the argument of the sought expression.

In order to simplify the procedure for finding the required equations, all the particular and multifactor dependencies will be represented as functions of the logarithms of the controllable indicators. The dotted partial dependences (presented after the potentiation in Fig. 1–4) are described mathematically (see Table 2) and then we reduce these formulas according to [9] to generalized equations.

$$\ln \beta_{sinter} = 5.002 - 0.2487 \ln t_{roast.} - 2.6092 \cdot 10^{-2} \ln \tau_{roast.} - 7.1847 \cdot 10^{-3} N + 0.254 \ln N. \quad (11)$$

$$\ln \beta_{cake/batch} = -9.9813 - 3.7299 \cdot 10^{-3} t_{roast.} + 2.5116 \ln t_{roast.} + 0.3401 \tau_{roast.} - 0.5418 \ln \tau_{roast.} - 0.1475 \ln N - 0.1691 \tau_{leach.} + 0.3149 \ln \tau_{leach.} - 4.7599 \cdot 10^{-3} t_{leach.} + 0.2501 \ln t_{leach.}. \quad (12)$$

$$\ln Cr_{cake} = 11.3654 - 0.9239 \ln t_{roast.} - 0.7835 \tau_{roast.} + 1.4 \ln \tau_{roast.} - 0.3709 \ln N + 0.1096 \tau_{leach.} - 0.251 \ln \tau_{leach.} + 5.8036 \cdot 10^{-3} t_{leach.} - 0.2232 \ln t_{leach.}. \quad (13)$$

For the convenience of the following operations, we describe the dependence of the chromium content in the batch on the consumption of Na_2CO_3 by an equation of the form:

$$\ln Cr_{batch} = 2.9859 - 7.1788 \cdot 10^{-3} N. \quad (14)$$

After logarithm (9), we find:

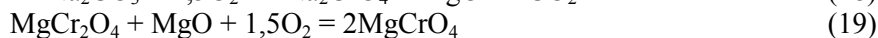
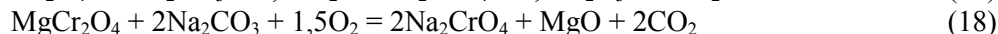
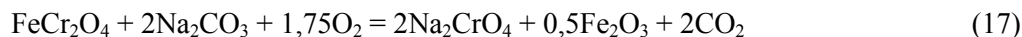
$$\ln \varepsilon_{cake} = \ln \beta_{cake/batch} + \ln Cr_{cake} - \ln Cr_{batch}. \quad (15)$$

Further, substituting expressions (12)–(14) in (15) we obtain:

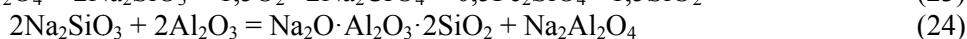
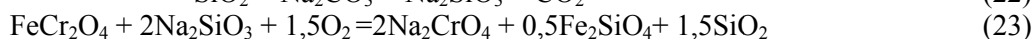
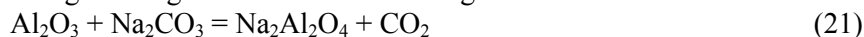
$$\ln \varepsilon_{cake} = -1.6018 - 3.7299 \cdot 10^{-3} t_{roast.} + 1.5877 \ln t_{roast.} - 0.4434 \tau_{roast.} + 0.8582 \ln \tau_{roast.} + 7.1788 \cdot 10^{-3} N - 0.5184 \ln N - 0.0595 \tau_{leach.} + 0.0639 \ln \tau_{leach.} + 1.0437 \cdot 10^{-3} t_{leach.} + 0.0269 \ln t_{leach.}. \quad (16)$$

In the present commercial product, chromium is present mainly in the form of chromospinelide, which are $MgCr_2O_4$, $FeCr_2O_4$, $Fe(Al, Cr)_2O_4$, $(MgFe)(Al, Cr, Fe)_2O_4$.

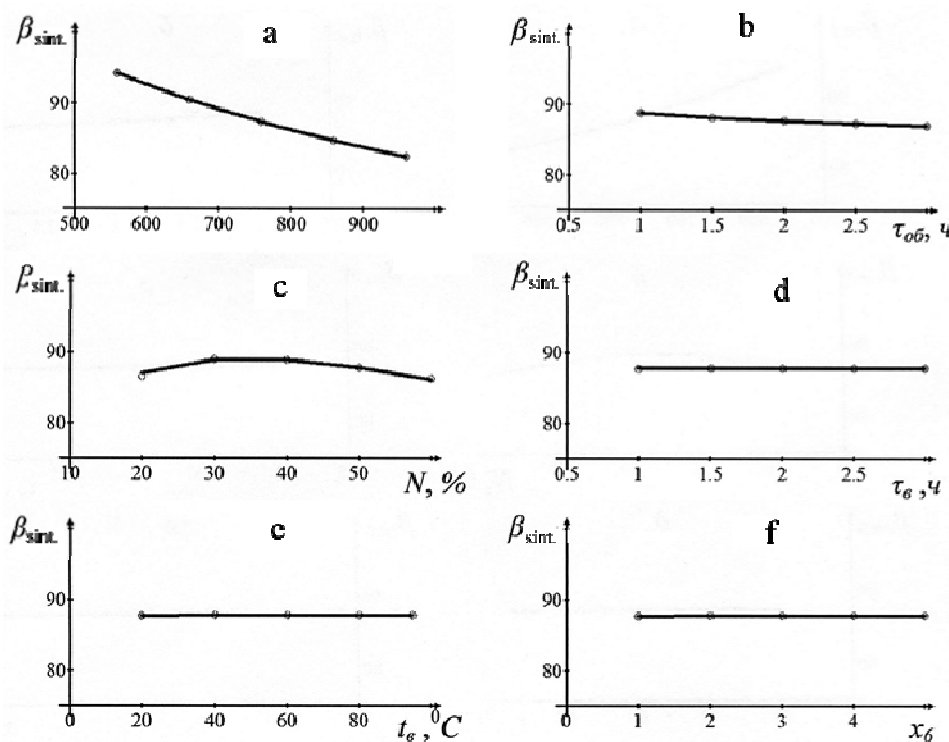
As a rule, when writing the reaction equations that occur during the roasting of batch that contains chromospinelides, the behavior of the oxides composing this batch is considered [9]. These reactions have the form:



The list of reactions that occur during roasting of chromium-containing materials includes:

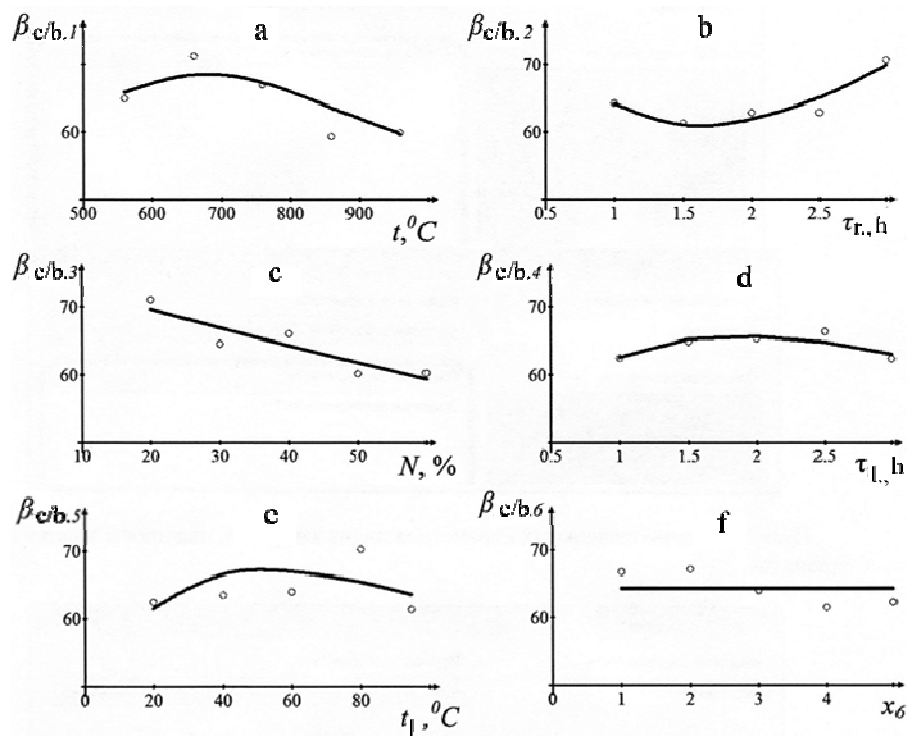


A noticeable interaction of magnesium and iron chromites with sodium carbonate (17)–(18) takes place already at a temperature of 600 °C. As the temperature rises, the degree of interaction of these components increases. Reactions (19)–(20) occur at relatively low temperatures. Reactions (21)–(22) begin at a temperature of 710–720 °C. The form of the obtained partial dependences (Fig. 1–4) is determined by the degree of completion of the reactions listed. Thus, the decreasing dependence of the yield of the sinter on temperature reflects the process of loss of the mass of the batch due to the transition to the gaseous phase of carbon dioxide. The roasting time affects the process to a lesser extent. The presence of an extremum in the dependence of the yield of the sinter on the consumption of sodium carbonate is the result of a purely mathematical effect: the mass of the sinter increases with increasing consumption of Na_2CO_3 . This law is described by a power function. The weight of the batch also increases, but is directly proportional to this parameter. As a result, the dependence of the yield of the sinter, which is a quotient of the fission mass divided by the weight of the batch (1), is obtained with an extremum.



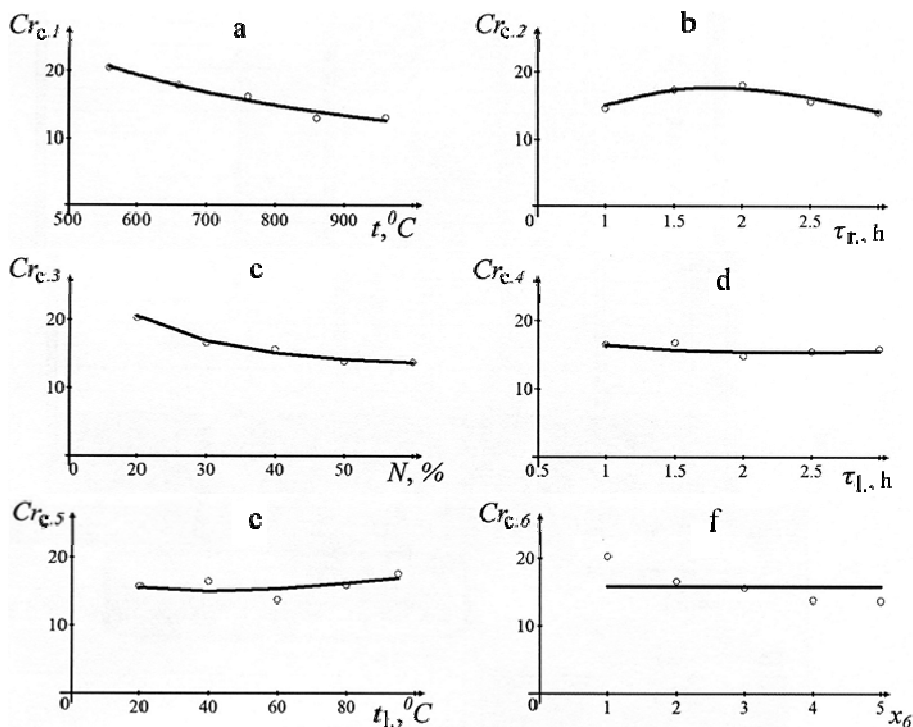
a — from the roasting temperature (t_{roast} , °C); b — from the roasting time (τ_{roast} , h);
c — from the consumption of Na_2CO_3 (N , %); d — from leaching time (τ_{leaching} , h);
e — from the leaching temperature (t_{leaching} , °C); f — from the vacant factor (x_6)

Figure 1. Partial dependences of the yield of the sinter (β_{sinter} , %)



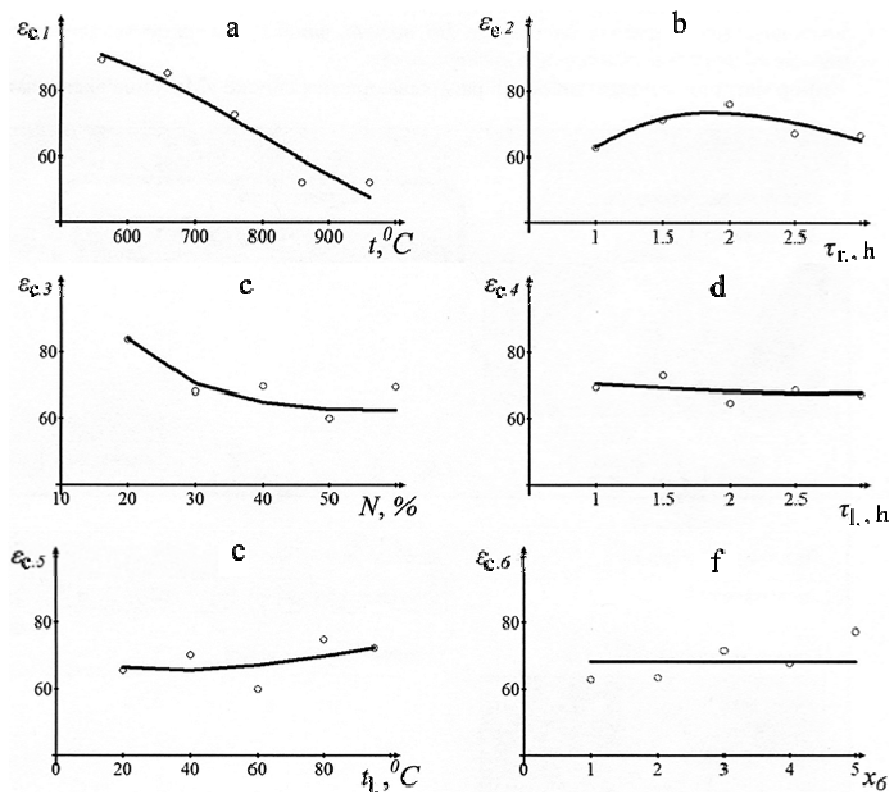
a — from the roasting temperature (t_{roast} , °C); b — from the roasting time (τ_{roast} , h);
c — from the consumption of Na_2CO_3 (N , %); d — from leaching time ($\tau_{leaching}$, h);
e — from the leaching temperature ($t_{leaching}$, °C); f — from the vacant factor (x_6)

Figure 2. Partial dependencies of cake output ($\beta_{cake/batch}$, %)



a — from the roasting temperature (t_{roast} , °C); b — from the roasting time (τ_{roast} , h);
c — from the consumption of Na_2CO_3 (N , %); d — from leaching time ($\tau_{leaching}$, h);
e — from the leaching temperature ($t_{leaching}$, °C); f — from the vacant factor (x_6)

Figure 3. Partial dependencies of the chromium content in the cake (Cr_{cake} , %)



a — from the roasting temperature (t_{roast} , °C); b — from the roasting time (τ_{roast} , h);
c — from the consumption of Na_2CO_3 (N , %); d — from leaching time (τ_{leach} , h);
e — from the leaching temperature (t_{leach} , °C); f — from the vacant factor (x_6)

Figure 4. Partial dependencies of chromium extraction in the cake (ε_{cake} , %)

The dependence of the cake yield on the roasting temperature (Fig. 2a) has an ascending and descending branch. The increase in the cake yield in the range of 560–700 °C is due to the transition to the solution of that portion of Na_2CO_3 , which did not react at low calcination temperatures. This part of Na_2CO_3 decreases with a temperature change from 560 to 700 °C. Accordingly, the yield of cake increases. An increase in the cake yield in this temperature range is also associated with the passage of reactions (19)–(20). The downward branch of the present dependence characterizes the increase in the fraction of soluble compounds as the roasting temperature rises.

It is known [9] that formation of MgCrO_4 is possible at relatively low temperatures (700–800 °C) according to the reactions (19)–(20), as well as iron silicate (23) and nepheline (24). It is likely that an increase in the cake yield with the largest roasting time of 3 h is due to the formation of these compounds. A change in the consumption of Na_2CO_3 in interval 20–60 % leads to a decrease in $\beta_{cake/batch}$ due to the increase in the amount of soluble compounds in the sinter. The leaching time and the temperature of this process have practically no effect on the yield of cake.

The content of chromium in the cake and its extraction into the latter (Fig. 3, 4) are determined by the simultaneous occurrence of the above reactions and those changes in the interdependent technological parameters (the yield of cake and sinter, the content of chromium in the cake), which are due to these reactions. With increasing of roasting temperature, the chromium content in the cake Cr_{cake} and its extraction into a product ε_{cake} decrease monotonically. The same effect occurs when the consumption of Na_2CO_3 increases. The dependences of Cr_{cake} and ε_{cake} on the roasting time characterize the processes of passing the reactions of formation of sparingly soluble compounds in the interval of 1–2 h (the chromium content in the cake and the extraction of chromium in it increase) and the increase in the fraction of soluble compounds during roasting for a time longer than 2 h. The leaching conditions practically do not affect the monitored indicators.

Analysis of the partial dependences obtained (Fig. 4) shows that in order to achieve the minimum recovery of chromium in a cake and, accordingly, the most complete extraction of metal into a solution, roast-

ing should be carried out under the following conditions such as $t_{roast.} = 960\text{ }^{\circ}\text{C}$, $\tau_{roast.} = 3\text{ h}$, $N = 60\%$, and leaching — at $\tau_{leach.} = 2\text{ h}$ and $t_{leach.} = 60\text{ }^{\circ}\text{C}$.

According to the calculation from (16), the recovery of chromium into the cake under these conditions is 42.06 %, and in the solution 57.94 %. An increase in the latter index can be achieved if the above-mentioned limits of the change in the roasting conditions are exceeded, that is, when the temperature is raised to 1100–1200 $^{\circ}\text{C}$ — the time of this operation is up to 4–5 h, — and the sodium carbonate consumption is to 70–80 %. Since the leaching parameters have the least effect on the results of the experiments, it is advisable to leave the above values unchanged, namely $\tau_{leach.} = 2\text{ h}$, $t_{leach.} = 60\text{ }^{\circ}\text{C}$. The calculation for these calcination conditions shows (Table 3) that the recovery of chromium in the solution increases with an increase in the roasting temperature, the time it takes, and the consumption of Na_2CO_3 . At the same time, as far as the limit values of factors set in the plan (Table 1) are removed, the accuracy of forecasts decreases.

Table 3

**Extraction of chromium into the cake (ϵ_{cake}) and solution (ϵ_{sol}).
The calculation data for (16), (10) — $\epsilon_{cake,t}$, $\epsilon_{sol,t}$ and experimental data — $\epsilon_{cake.ex}$, $\epsilon_{sol.ex}$.**

No.	$t_{roast.},\text{ }^{\circ}\text{C}$	$t_{roast.},\text{ h}$	$N, \%$	$\epsilon_{cake,t}$	$\epsilon_{cake.ex}$	$\epsilon_{sol,t}$	$\epsilon_{sol.ex}$
1	960	3	60	42.06	39.42	57.94	60.58
2	1000	4	70	31.50	30.81	68.50	69.19
3	1100	4	70	25.24	23.46	74.76	76.54
4	1200	4	70	19.95	15.48	80.05	84.52
5	1200	5	80	15.55	8.32	84.45	91.68

Thus, using the method of stochastic-determinated design of experiment in a modified version, a five-factor mathematical model of chromium extraction into a cake was obtained. In the derivation of this model, there was used a method that includes the preliminary finding of two multifactorial equations which describing the influence on the output of cake ($\beta_{cake/batch}$) and the content of chromium in it (Cr_{cake}) from the specified factors (roasting temperature and time of this operation, consumption of Na_2CO_3 , temperature and leaching time of chromium from the cake), with the subsequent substitution of these equations into a formula linking ϵ_{cake} , $\beta_{cake/batch}$, Cr_{cake} , Cr_{batch} . The suitability of the desired equation for making predictions that are more accurate when introducing into a given equation the values of the arguments within the given limits of their variation and less accurate at a considerable distance from these limits is shown.

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Хромқұрамды техногендік материалдарды өңдеудің технологиялық үрдісін дайындау

Мақала натрий карбонаты қатысында күйдіру және әрі қарай күйіктен хромды сумен сілтілендіруден тұратын хромқұрамды техногендік материалдарды өңдеудің технологиялық үрдісін дайындауға арналған. Тәжірибені ықтималды-детерминді жоспарлау әдісін қолдану арқылы хромды кекке бөліп алудың бесфакторлы математикалық үлгісі алынды. Хромды кекке аз мөлшерде өтуіне қолжеткізу және сәйкесінше аталған металды толығымен ерітіндіге көшіру үшін шихтаны күйдіруді келесі жағдайларда жүргізу анықталды: $t_{\text{күй}} = 960^\circ\text{C}$, $\tau_{\text{күй}} = 3$ сағ, $N = 60\%$, ал сілтілендіру $\tau_c = 2$ сағ және $t_c = 60^\circ\text{C}$. Жүретін үрдістердің химизмі келтірілді. Алынған математикалық теңдеудің берілген өзгеру шегіндегі аргументтердің мәнін теңдеуге енгізуге барысында және осы шектен алыстату барысында нақты мәндерді алуға болатындығын болжауға болатындығын көрсетеді. Аталған жағдайда есептеу ерітіндідегі хромның қалпына келу уақытын арттыру, атмосфераның температурасын жоғарылату, оны ұстау және Na_2CO_3 тұтынуы өсіп отырғандығын көрсетті.

Клт сөздер: хромит, ықтималдықпен анықталған эксперименттерді жоспарлау, хромды шаймалау, натрий карбонаты, натрий хроматы, өндірістік хром бар қалдықтар, хромитті кальцинациялау, хромды күйдіру үрдісі.

Н.А. Каргина, В.Н. Фомин

Разработка технологического процесса переработки хромсодержащих техногенных материалов

Статья посвящена разработке технологического процесса переработки хромсодержащих техногенных материалов, которая включает их обжиг в присутствии карбоната натрия и последующее выщелачивание водой хрома из спека. С применением метода вероятностно-детерминированного планирования эксперимента получена пятифакторная математическая модель извлечения хрома в кек. Определено, что для достижения наименьшего извлечения хрома в кек и соответственно наиболее полного выделения данного металла в раствор обжиг шихты следует вести в условиях: $t_{\text{об}} = 960^\circ\text{C}$, $\tau_{\text{об}} = 3$ ч, $N = 60\%$, а выщелачивание — при $\tau_v = 2$ ч и $t_v = 60^\circ\text{C}$. Представлен химизм происходящих процессов. Показана пригодность полученного математического уравнения для составления прогнозов, более точных при введении в данное уравнение значений аргументов, находящихся в заданных пределах их изменения, и менее точных при значительном удалении от этих пределов. Расчет в указанных условиях обжига показывает, что извлечение хрома в раствор возрастает при увеличении температуры обжига, времени его ведения и расхода Na_2CO_3 .

Ключевые слова: хромит, вероятностно-детерминированное планирование эксперимента, выщелачивание хрома, карбонат натрия, хромат натрия, промышленные хромосодержащие отходы, кальцинация хромита, обжиг хромосодержащей шихты.

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Investigation of the process of precipitation of arsenic from copper electrolyte with manganese oxide (IV)

The work is aimed at researching the process of depositing arsenic from copper electrolyte with manganese oxide (IV) using the method of stochastic determinated design of experiments on four levels. The chosen factors are: the frequency of dispensing of the precipitant; the ratio of precipitant to arsenic; the temperature of process; concentration of sulfuric acid; duration of experiment. Analysis of the partial dependencies of arsenic deposition showed that the increase in the amount of precipitant and the duration of the experiment had a significant influence on the course of the process. IR spectroscopy of precipitation showed the presence of arsenate ions AsO_4^{3-} in them. The kinetic curve of the differential-thermal analysis of the solid sediment characterizes the process of its destruction as a step-wise process — the removal of crystallized water (from 250 °C to 350 °C), the decomposition of manganese hydroarsenate (from 470 °C to 630 °C) and manganese arsenate (from 690 °C to 900 °C). It is established that the process of formation of manganese arsenate is a result of parallel reactions of interaction of sulfate ions with manganese ions with the formation of a sulfate complex, interaction of the manganese sulphate complex with arsenate ions with the formation of manganese hydroarsenate, and the transition of hydroarsenate to manganese arsenate.

Keywords: copper electrolyte, manganese oxide (IV), arsenic; arsenates, hydroarsenate, manganese arsenate, stochastic determinated design of experiments.

Introduction

The deterioration in the quality of raw materials, the need to ensure the selective extraction of all its valuable components and the toughened requirements for environmental protection have revealed huge volumes of various technological solutions that require processing. Technological solutions of electrolytic refining of copper have a great interest. They contain significant amounts of copper and nickel sulfates, sulfuric acid, arsenic, antimony and other components of the copper electrolyte. Decrease in the quality of cathode copper due to excessive accumulation of arsenic in the electrolyte, as well as high toxicity of arsenic compounds, determine arsenic as one of the dangerous impurities of copper electrolyte.

In works [1, 2] pyrolusite, which is a mineral based on manganese oxide (IV), is used as an oxidizer of trivalent arsenic to pentavalent. Considering that manganese arsenate is a compound with a low solubility value, the role of manganese as an arsenic precipitant in the form of arsenates from copper electrolyte, where it is found both in anionic and cationic forms, has become a matter of interest.

According to the literature data [3, 4], during the electrorefining of copper from the anode, 60–80 % of arsenic passes into the electrolyte, the rest goes to the sludge. The distribution of arsenic between the electrolyte and sludge, as well as its form of stay in solution depends on electrolyte's composition and the mode of electrolysis. For example, the presence of As and Sb with different valencies in the electrolyte leads to the precipitation of antimony-arsenic (Sb^{3+} - As^{5+}) and antimony-arsenic (Sb^{5+} - As^{3+}) precipitates. The introduction of zinc sulphide into the strongly acid copper electrolyte [5] led in precipitation of 40 % of arsenic in the form of sulfides.

The physicochemical analysis of multicomponent systems with the participation of arsenic, antimony, and bismuth carried out by us [6, 7] showed that these elements in the form of arsenates, antimonates and bismuths are stable compounds, both in the water and in the oxidizing and reducing media.

Materials and methods

A technological solution of JSC «Kazakhmys» (Balkhash town) with the content of components is used to investigate the process of precipitation of arsenic from copper electrolyte, g/l: Cu — 50,7; Ni — 7,75; As — 7,4; H_2SO_4 — 200,0 and others.

Experiments on the deposition of arsenic from a copper electrolyte were carried out in a reaction thermostated cell with a capacity of 150 cm³. A sample of manganese oxide (IV), taken in the required

amount, was injected into a solution of a copper electrolyte with a predetermined temperature. The temperature of the experiments was maintained with an accuracy of ± 2 °C. The deposition process was carried out with continuous mixing with the duration dictated by the condition of the experimental matrix. After a predetermined time, the precipitate was separated by filtration, the residual arsenic content was determined in the filtrate by the bichromate method after separation of potassium hypophosphite from the hydrochloric acid solution [8]. The solid precipitates were subjected to differential thermal and IR spectroscopy using LABSYSTMEVOTG, DTA, DSC 1600 °C, FSM 1201 Infrared Fourier spectrometer.

Investigation of the process of arsenic precipitation from copper electrolyte with manganese oxide (IV) was carried out by the method of probabilistic determination of the experiment [9, 10] at four levels. The following factors were chosen as factors: the multiplicity of precipitator dosage (MPD) — this is the number of portions into which the planned weight of the precipitant is divided; the ratio of precipitant to arsenic (Mn:As) — this ratio of the required weight parts of the precipitant to the weight part of arsenic (this value is not calculated mathematically and has no dimension); process temperature (t , °C); the concentration of sulfuric acid (H_2SO_4 , g/l); duration of experiment (time, min). For planning the experiment, Table 1 was used.

Table 1

Levels of variable factors in the precipitation of arsenic by manganese oxide (IV)

No. factor	Factor	Definition	Level of factors			
			1	2	3	4
1	MPD	X_1	1	2	3	4
2	Mn:As	X_2	1	1.5	2	2.5
3	t , °C	X_3	25	40	50	60
4	H_2SO_4 , g/l	X_4	120	150	175	200
5	time, min	X_5	15	30	45	60

Results

Using the most common matrix of the probabilistic-deterministic plan of the five-factor experiment, a plan was drawn up (Table 2), in which the level numbers are replaced with their values from Table 1. The column on the right includes the results of the extraction of arsenic (α_e , As) into the precipitate.

Table 2

The plan-matrix layout and the results of the five-factor experiment at four levels of arsenic precipitation with manganese oxide (IV)

No. of experiment	MPD (x_1)	Mn:As (x_2)	t , °C (x_3)	H_2SO_4 , g/l (x_4)	Time, min (x_5)	α_e , As %
1	1	1	25	120	15	47.25
2	1	1.5	40	150	30	55.80
3	1	2	50	175	45	50.40
4	1	2.5	60	200	60	51.95
5	2	1	40	175	60	46.80
6	2	1.5	25	200	45	48.70
7	2	2	60	120	30	66.00
8	2	2.5	50	150	15	72.40
9	3	1	50	200	30	46.40
10	3	1.5	60	175	15	61.30
11	3	2	25	150	60	27.60
12	3	2.5	40	120	45	52.00
13	4	1	60	150	45	45.40
14	4	1.5	50	120	60	31.50
15	4	2	40	200	15	52.85
16	4	2.5	25	175	30	64.40

In order to construct particular dependences of the degree of arsenic deposition with manganese (IV) oxide, the results of the experiments for each factor were averaged using the geometric mean (Table 3).

Table 3

Sampling for the construction of particular dependencies of the degree of arsenic deposition by manganese oxide (IV) in solutions from the considered factors

Factors		Levels of factors				The mean α_e (geometric)
		1	2	3	4	
x_1	α_e	51.35	58.48	46.83	48.54	51.0
x_2	α_e	46.46	49.33	49.21	60.19	
x_3	α_e	46.99	51.86	50.18	56.16	
x_4	α_e	49.19	50.30	55.73	49.98	
x_5	α_e	58.45	58.15	49.13	39.46	

The average values of the arsenic deposition were used to find the approximating function with calculation of the correlation coefficient and significance (Table 4).

Table 4

Correlation coefficients (R) and their significance (t_R) for particular dependencies of the degree of arsenic deposition by manganese oxide (IV)

Function	R	t_R	Significance
$\alpha(x_1) = 56.36 \cdot 0.96x_1$	0.1	0.1	Insignificant
$\alpha(x_2) = 38.93 \cdot 1.17x_2$	0.79	2.98	Significant
$\alpha(x_3) = 42.24 \cdot 1.004x_3$	0.83	3.70	Significant
$\alpha(x_4) = -887.7/x_4 \cdot 57.01x_4$	0.22	0.33	Insignificant
$\alpha(x_5) = 0.44x_5 + 67.795$	0.1	0.1	Insignificant

The statistical description of particular dependences is represented by the generalized Protodyakonov equation. For the precipitation process of arsenic with manganese (IV) oxide:

$$Y_P = (38.93 \cdot 1.17x_2) \cdot (42.24 \cdot 1.004x_3) \cdot 51.0^{-2}.$$

The correlation coefficient of equation $R = 0.80$; and its significance $t_R = 7.86$.

Figure 1 shows the graphical dependencies of the degree of arsenic deposition on all studied factors.

An increase in the multiplicity of precipitator dosage (MPD) to 4 (Fig. 1, a) leads to a decrease in the degree of arsenic precipitation, which is associated with an increase in the rate of the competing manganese sulfate formation reaction.

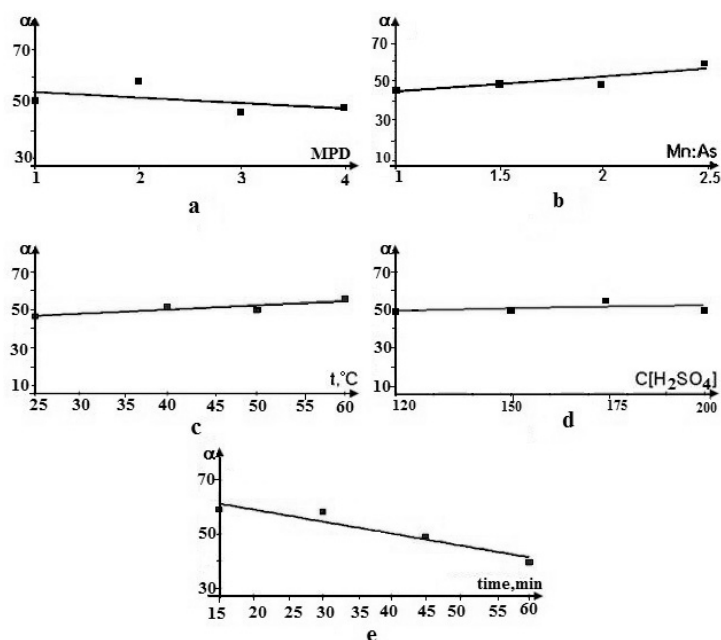


Figure 1. Particular dependencies of arsenic deposition on: the multiplicity of precipitator dosage (a), the ratio of Mn:As (b), temperature (c), the content of sulfuric acid (d), the duration of the experiment (e)

The amount of precipitator (Fig. 1, *b*) positively affects the degree of extraction of arsenic in the sediment, which confirms the sorption nature of the process of its deposition. Factors such as temperature and sulfuric acid concentration (Fig. 1, *c*, *d*) do not significantly influence the transition of arsenic to the solid phase, due to the complexity of the internal processes of formation of the arsenic-containing precipitate. Similar processes were analyzed in [11], where the formation of hydrated complexes of arsenic with iron in acidic solutions was studied.

With an increase in the time of the experiment (Fig. 1, *e*), the decrease in the degree of arsenic precipitation when using manganese oxide (IV) is observed more significantly by 5–10 % every 15 minutes. This is due to the desorption of the cationic form of arsenic from the surface of the precipitant.

To confirm the results of our experiments on the deposition of arsenic by manganese oxide (IV) in the form of arsenate, we analyzed the IR spectrum of the solid precipitate of experiment 8 (Table 2). Analyzing the literature sources [12, 13] in which the data on IR absorption spectra of metal arsenates are given, it is possible to compare data given by the authors with the IR spectrograph obtained by us (Fig. 2).

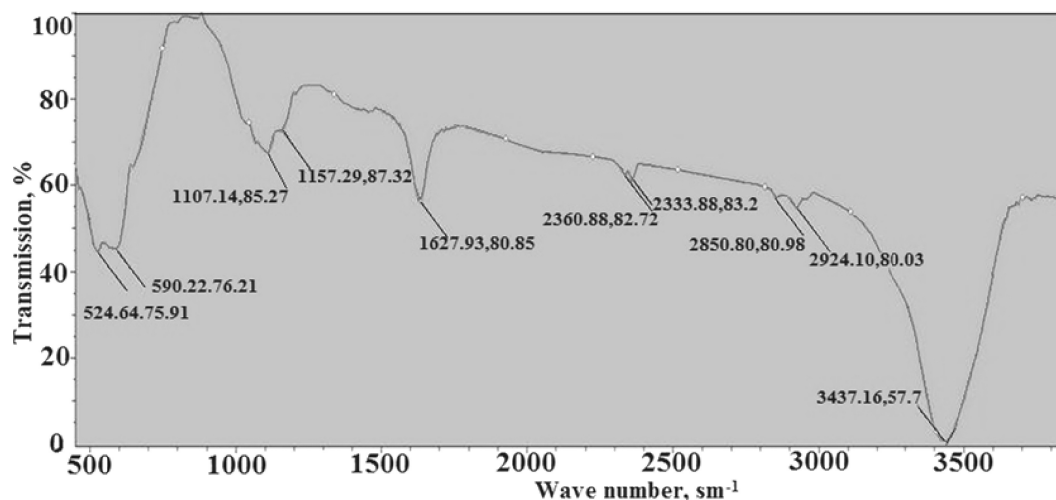


Figure 2. IR spectra of the solid precipitate of the arsenic precipitation experiment with manganese oxide (IV).

The absorption bands at 500–600 cm^{-1} indicate vibrations of the (As-O-As) bridge, and at 800–900 cm^{-1} — (As-O) bridge, i.e. for the presence of manganese arsenate ($\text{Mn}_3(\text{AsO}_4)_2 \cdot 7\text{H}_2\text{O}$) in the investigated solid sediments. In the same intervals, absorption bands of manganese hydroarsenates are observed [12]. The presence of maxima in the spectra in the interval 1130–1080 cm^{-1} indicates the content of manganese sulfate in the composition of the analyzed samples.

The authors of [13] established that manganese hydrosarsenate ($\text{MnHAsO}_4 \cdot 4\text{H}_2\text{O}$) is stable in acidic aqueous solutions in the temperature range 25–75 °C. It is also noted that for manganese phosphates, as for manganese arsenates, acid salts are in equilibrium with strongly acidic solutions.

The $\text{AsO}_4^{3-} \cdot 7\text{H}_2\text{O}$ arsenate ion is characterized by an intense absorption band at 590 cm^{-1} , due to the low symmetry of the $\text{AsO}_4^{3-} \cdot n\text{H}_2\text{O}$ ions. In addition to the intense absorption band of the $\text{AsO}_4^{3-} \cdot 7\text{H}_2\text{O}$ ion, the author [14] presents data on the IR absorption spectra of metaarsenates characterized by the presence of complex intense absorption bands of $\nu(\text{AsO})$ stretching vibrations of the AsO bonds in the 600–850 cm^{-1} region.

Thus, by comparing the above data on the absorption spectra of arsenates with the obtained spectrogram, we confirmed the presence of arsenate ions (AsO_4^{3-}) in the analyzed sample.

To study the kinetics of the process of arsenic precipitation with manganese oxide (IV), a differential thermal analysis of the solid precipitate obtained under the following experimental conditions was carried out: MPD-3; Mn:As = 2.5:1; *t*, °C — 40; $C(\text{H}_2\text{SO}_4)$, g/l — 120; time, min. — 45.

As can be seen from Figure 3, the kinetic curve consists of three stages, and each of the stages is represented by an S-shaped line. This form is explained by the fact that at first the reaction rate increases due to an increase in the rate constant by the Arrhenius equation, and then the rate of destruction decreases in connection with the completion of the decomposition of the test sample.

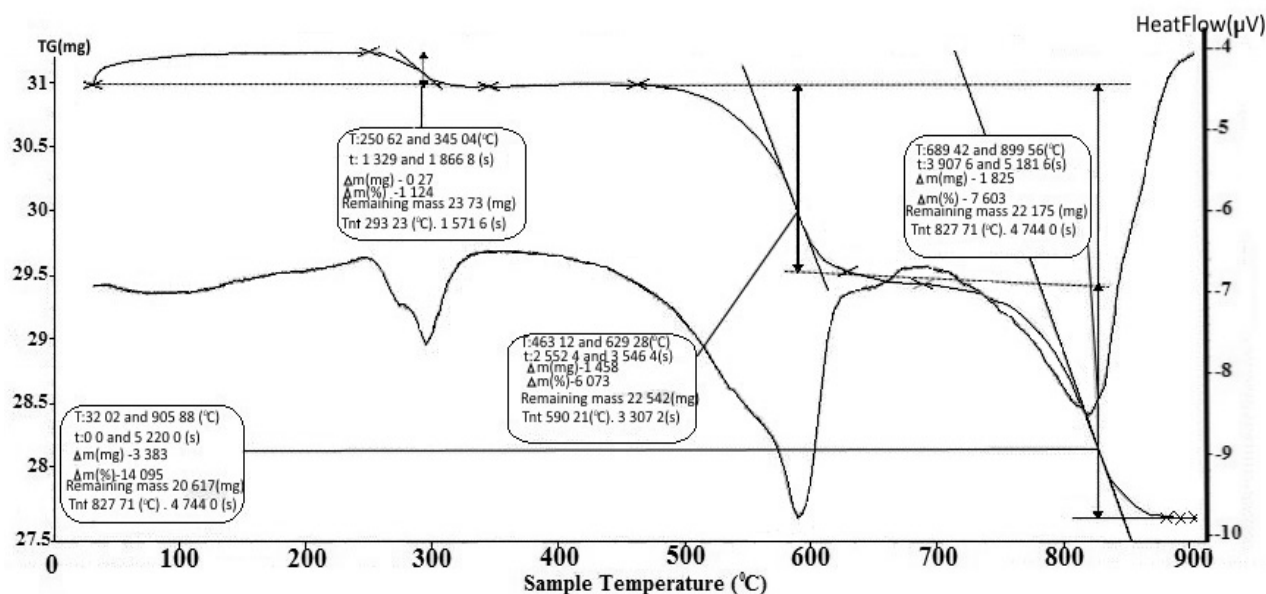


Figure 3. Curve of volatile substances during thermal destruction of solid arsenic-containing precipitate.

Further, the kinetic curve of thermal destruction was subjected to mathematical processing by the method [15]. The data obtained are presented in Table 5.

Table 5

**Results of mathematical processing of the kinetic curve
of thermal destruction of solid arsenic-containing precipitate**

No.	τ , min	m , mg	$m_{i, \max} - m_i$, mg	r_i , mg/min	$r_i / (m_{i, \max} - m_i)$	$-\ln[r_i / (m_{i, \max} - m_i)]$	t , °C	$10^3 / T$, K ⁻¹
1	—	0	—	—	—	—	35	3.25
2	22.10	0	0.27	0.02	0.08	2.53	250	1.91
3	23.99	0.05	0.22	0.04	0.18	1.71	270	1.84
4	25.89	0.14	0.12	0.05	0.42	0.87	290	1.78
5	27.79	0.24	0.025	0.03	1.33	-0.29	310	1.72
6	29.69	0.27	0.001	0.003	3.40	-1.22	330	1.66
7	31.59	0.28	—	—	—	—	350	1.61
8	43.22	0	1.46	—	—	—	470	1.35
9	45.18	0.02	1.43	0.02	0.02	4.09	490	1.31
10	47.14	0.08	1.38	0.04	0.03	3.51	510	1.28
11	49.11	0.17	1.28	0.07	0.05	2.97	530	1.25
12	51.12	0.33	1.12	0.10	0.09	2.44	550	1.22
13	53.13	0.57	0.88	0.16	0.18	1.69	570	1.19
14	55.13	0.99	0.46	0.20	0.44	0.83	590	1.16
15	57.14	1.36	0.09	0.12	1.23	-0.21	610	1.13
16	59.18	1.46	—	—	—	—	630	1.11
17	65.18	0	1.83	—	—	—	690	1.04
18	68.18	0.04	1.78	0.02	0.01	4.34	720	1.01
19	71.20	0.14	1.69	0.06	0.03	3.41	750	0.98
20	74.20	0.36	1.46	0.12	0.08	2.54	780	0.95
21	77.30	0.85	0.98	0.19	0.20	1.62	810	0.92
22	80.30	1.55	0.27	0.16	0.59	0.53	840	0.90
23	83.30	1.80	0.02	0.04	1.88	-0.63	870	0.87
24	86.40	1.83	—	—	—	—	900	0.85

As can be seen from the obtained results, the first stage of thermal destruction takes place in the temperature range from 250 °C to 350 °C, then the change in mass in the temperature range from 350 °C to

470 °C is negligible. The second stage proceeds in the temperature range from 470 °C to 630 °C, the third stage — from 690 °C to 900 °C.

Further, after mathematical processing of the results, graphs of the dependences $-\ln[r_i/(m_{i, \max} - m_i)]$ from $10^3/T$ were plotted (Fig. 4).

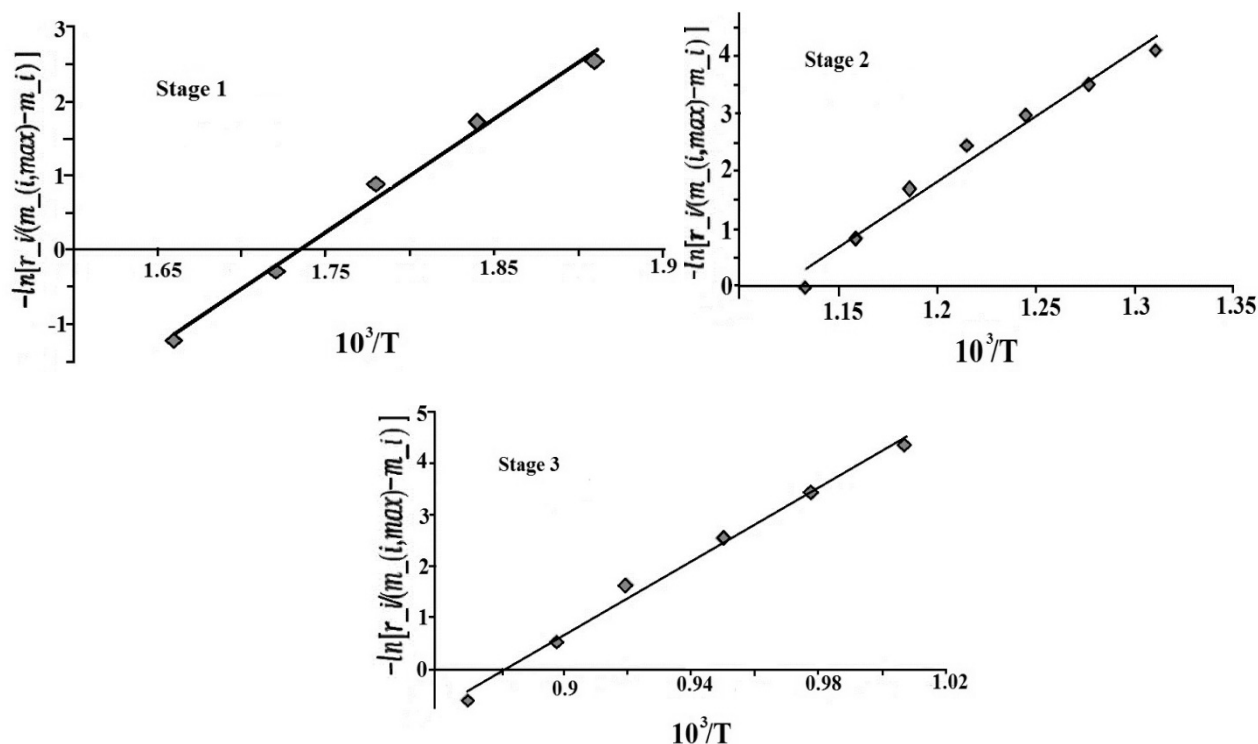


Figure 4. Linearization of the temperature dependence of the rate of thermal destruction of arsenic-containing precipitate

The processing of the obtained direct lines of dependencies of all three stages yielded the following results:

- the first stage refers to the diffusion region — the value of the activation energy is 15.28 kJ/mol;
- the value of the activation energy of 24.81 kJ/mol and the linear dependence of the total arsenic deposition rate on temperature (Fig. 4) suggest the commensurability of the diffusion rate and chemical reaction of the second stage, and indicate the course of the process in the transition region, which is characteristic of the mixed kinetics of heterogeneous processes;
- the third stage refers to the kinetic region — the value of the activation energy is 37.43 kJ/mol.

For the first stage, flowing in the range from 250 °C to 350 °C, corresponds a peak with a temperature value of 300 °C, while the crystallization water is removed.

For the second stage, flowing in the range from 470 °C to 630 °C, there corresponds a peak with a temperature of 600 °C, corresponding to the decomposition of manganese hydrogenarsenate according to the source [16] and further decomposition of manganese oxide (IV) [17].

The third stage, running in the range from 690 °C to 900 °C, corresponds to a peak with a temperature of about 840 °C, at which the process of decomposition of manganese arsenate proceeds [16, 18].

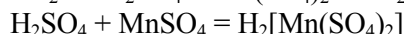
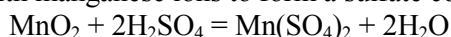
Conclusion

From the analysis of the experimental data on the process of precipitation of arsenic from copper electrolyte with manganese oxide (IV), follows that the highest indices of arsenic extraction into sediment (66.0–72.4 %) are achieved with a relatively short duration of the experiment (15–30 min) and large ratios of precipitant to arsenic (2.0–2.5:1).

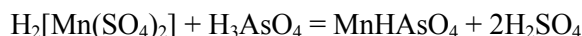
Analysis of the partial dependencies of arsenic deposition from copper electrolyte with manganese oxide (IV), obtained as a result of five-factor experiments (factors: multiplicity of the precipitant dosage, Mn:As ratio, temperature, sulfuric acid concentration, duration of the experiment), the results of differential

thermal analysis and IR spectroscopy of the obtained solid precipitates showed the complexity of the formation of manganese arsenate, which can be represented as a result of parallel reactions:

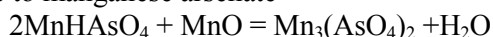
- interaction of sulfate ions with manganese ions to form a sulfate complex



- interaction of manganese sulfate complex with arsenate ions with formation of manganese hydroarsenate



- transition of hydroarsenate to manganese arsenate



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Мыс электролитінен марганец (IV) тотығымен күшәланы тұндыру үрдісін зерттеу

Мақала экспериментті төрт деңгейлі ықтималды-детерминирленген жоспарлау әдісті қолдануымен марганец (IV) тотығымен мыс электролитінен күшәланы бөліп алу үрдісін зерттеуге бағытталған. Таңдалған факторлар болып келесілер табылады: тұндырғышты мөлшерлеу дәрежесі, тұндырғыштың күшәлаға қатынасы, үрдістің температурасы, күкірт қышқылының концентрациясы, эксперименттің ұзақтығы. Күшәланы тұндырудың жеке тәуелділіктерінің сараптамасы бойынша тұндырғыштың мөлшері мен эксперименттің ұзақтығы ұлғаюы үрдістің өтуіне зор әсері көрсетілді. Қатты тұнбаның ИК-спектроскопия нәтижелері тұнбада AsO_4^{3-} арсенат-иондарының бар екендігін көрсетті. Қатты тұнбаның дифференциалды-термиялық талдауының кинетикалық сызығы оның ыдырау үрдісі сатылап өтетінін сипаттайды — кристалданған судың бөлінуі (250 °C бастап 350 °C дейін), марганецтің гидроарсенаты ыдырауы (470 °C бастап 630 °C дейін) және де марганец арсенатының ыдырауы (690 °C бастап 900 °C дейін). Марганец арсенатының түзілуі параллельді реакцияларының нәтижесі болатыны анықталған: сульфат-иондарының марганец иондарымен әрекеттесу нәтижесінде сульфаты комплексін түзілуі, марганец сульфаты комплексінің арсенат иондарымен әрекеттесу барысында марганецтің гидроарсенатын түзілуі және дегидроарсенаттың марганец арсенатына өзгеруі.

Кілт сөздер: мыс электролиті, марганец (IV) тотығы, күшәла, арсенаттар, гидроарсенат, марганец арсенаты, эксперименттің ықтималды-детерминирленген жоспарлауы.

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Исследование процесса осаждения мышьяка из медного электролита оксидом марганца (IV)

Статья направлена на исследование процесса осаждения мышьяка из медного электролита оксидом марганца (IV) с использованием метода вероятностно-детерминированного планирования эксперимента на четырех уровнях. Выбранными факторами являются: кратность дозирования осадителя, отношение осадителя к мышьяку, температура процесса, концентрация серной кислоты, продолжительность эксперимента. Анализ частичных зависимостей осаждения мышьяка показал, что увеличение количества осадителя и продолжительность эксперимента оказали значительное влияние на ход процесса. ИК-спектроскопия твердого осадка показала присутствие в нем арсенат-ионов AsO_4^{3-} . Кинетическая кривая дифференциально-термического анализа твердого осадка характеризует процесс его разложения как ступенчатый процесс — удаление кристаллизованной воды (от 250 °C до 350 °C), разложение гидроарсената марганца (от 470 °C до 630 °C) и разложение арсената марганца (от 690 °C до 900 °C). Установлено, что процесс образования арсената марганца является результатом параллельных реакций: взаимодействия сульфат-ионов с ионами марганца с образованием сульфатного комплекса, взаимодействия комплекса сульфата марганца с ионами арсената с образованием гидроарсената марганца и переход гидроарсената в арсенат марганца.

Ключевые слова: медный электролит, оксид марганца (IV), мышьяк, арсенаты, гидроарсенат, арсенат марганца, вероятностно-детерминированное планирование эксперимента.

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Study and development of the process scheme of barytic raw material leaching

Continuous growth of demand for crude ore leads to accelerated development of high-grade deposits and to putting into operation the impoverished deposits. Consequently specific yield of industrial waste for the unit of products at all the stages of production increases. Development of leaching schemes of barium-containing waste is the purpose of the given article. The search object is barium-containing waste produced at flotation enrichment of barium-polymetal ores. The experiments on water leaching of barium-containing waste in the presence of ammonium fluoride were carried out by means of the design of experiments. In order to research leaching of barium-containing waste, three factors were chosen, namely, leaching temperature (T), leaching time (τ) and percentage of the initial solution on ammonium fluoride (C). The mathematical model of the process was developed and optimal conditions were determined for leaching barium-containing waste that provided production of desilicated concentrate of compound, mass %: SiO_2 — 1.9; BaSO_4 — 67.3; Fe — 8.4; Zn — 1.09; Pb — 0.91; Cu — 0.36. Under laboratory conditions, the scheme of barium-containing waste leaching was developed. Studies of barium-containing waste leaching allowed detecting partial dependence of silicon extraction into the solution on the temperature, time of leaching and concentration of solution. On the basis of significant partial dependencies, the mathematical model of the process was developed by means of which the optimum conditions for leaching were determined. Two products were produced, namely, the ammonium hexafluorosilicate solution and the chemically enriched desilicated barite concentrate.

Keywords: barium, barium-containing waste, fluoride technology, leaching, silicon, ammonium hexafluorosilicate, desilication.

Introduction

Demand for crude ore constantly increases, which leads to accelerated resource recovery and to developing deposits of a low grade. Accelerated development of deposits leads to increasing specific yield in industrial waste per unit of output. The main problem of barium-containing waste is absence of technology and inefficient conventional development methods. The problem of development of barium-containing waste is due to the absence of an efficient application of the conventional treatment technology: acid leaching in the context of the complex mineral composition. Final rejects of treatment plants stored in the tailing dumps belong to barium-containing waste. Disposal are as occupy significant spaces and are the source of pollution of soil, air, and water basins with heavy metals and barite powder.

Treatment of waste of barium-containing poly metal ores has big economic potential. It contains up to 40 % of BaSO_4 , 0.4 % of Cu, 0.8 % of Zn, 0.6 % of Pb by which this waste may be classified as the industrial poly metal barite raw material. It has an advantage over the mineral raw material because expenses for extraction and refinement are not necessary. Waste stocks are significant: up to twenty million tons.

Dissociation of ore minerals with silicon-containing minerals of waste material is a problem of treating this type of raw material. A step-ahead solution of the problem is uncovering a raw material by chemical methods, and, in particular, by fluorine-ammonium method at which in the process of water leaching in presence of ammonium fluorine, silicon goes to the liquid phase from the solid one, because of formation of water-soluble ammonium hexafluorosilicate. The given method has energy consumption advantages over the fluorosulfate method of high-silicon raw material extraction that requires baking at a temperature of up to 400 °C.

The article is devoted to the search for a problem of utilization of barium-containing waste. The solution of the given problem is of ecological and economic significance. The solution of the problem would allow improving the ecologic situation around the enterprises producing the given type of waste.

Water leaching of the barite raw material in the presence of ammonium fluorine and determination of optimal conditions of the process are the main tasks of the article.

Raw material treatment and desilication methods

Hydrochemical and thermochemical processes became ingrained in complex treatment of the high-silicon raw material. The main operation is uncovering the raw material by a chemical interaction with the silicon oxide, that the raw material contains, and leaching.

So, alkaline autoclave desilication of high-silicon copper concentrates would lead to enrichment of initial copper concentrate by all the metals and sulfur, prevent difficulties of copper melting by the modern technological schemes [1].

Hydrochemical autoclave method is applied while extracting alumina from the high-silicon raw material [2]. Its essence is concluded in autoclave leaching of aluminosilicate raw material by strong solutions of sodium hydrate in the presence of lime. Aluminate and sodium silicate pass to the solution, then sodium-calcium hydro-silicate precipitates from the solution. Conditions for high extraction of alumina are superabundance of the free caustic alkali in the solution, a high temperature, and a high concentration of the alkali solution.

It should be mentioned that the given desilication methods while treating high-silicon raw material require the corresponding instrumentation and high measures on safety technique because of application of leaching of the concentrated alkali solution and running the process at high temperatures and pressure.

The most efficient reagents for uncovering silicate bases of high-silicon raw material are elemental fluorine and fluorine hydride, and ammonium fluoride. However, there are several problems, restricting application of F_2 and HF for these purposes. In particular, the use of elemental fluorine will require creation of additional production of fluorine that will increase expenses for final product. Application of HF, as well as of F_2 , will lead to generation of the toxic gas SiF_4 that requires special work and utilization conditions. Therefore, the use of fluorides and bifluorides, ammonium for running desilication is more technologically profitable [3].

In the study [4], we tried the method that includes baking silicon-containing material by ammonium bifluoride at a temperature of 200 °C and removal of generated ammonium hexafluorosilicate at a temperature of 400 °C. The exit gas consisting of $(NH_4)_2SiF_6$, is absorbed by an ammonia water resulting in generation of alumina consisting of precipitates separated by filtration. After separation of alumina, the solution is evaporated. The solid residue consisting of the fluoride and bifluoridemix is baked at a temperature of 180–200 °C with capturing escaping ammonia. Ammonia bifluoride produced after burning is led to burning the next portion of the silicon-containing material.

The most rational method of desiliconization of a silicon-containing material is the hydrochemical method [5] according to which the silicon-containing material is leached by the mix of bifluoride (NH_4HF_2) and fluoride (NH_4F) ammonium at a temperature of 100 °C within 3 hours. Then, highly soluble $(NH_4)_2SiF_6$ is separated by filtration of slurry sludges formed at the pH 5.5–6.0 consisting of hexafluoraluminum ($(NH_4)_3AlF_6$) and hexafluoroferrate ($(NH_4)_3FeF_6$) ammonium, calcium fluorine, magnesium, and other compounds. The $(NH_4)_2SiF_6$ water solution interacts with ammonia water at a temperature of 20–80 °C with sludging of SiO_2 .

In order to decrease material and energy expenses the method of hydrochemical leaching of high-silicon material has been experimentally studied in this publication, in particular, leaching of the silicon-containing barite raw material by the ammonium fluoride solution.

Justification of studies of leaching barite raw materials

Chemical enrichment of barium-containing waste involves its desilication. There are several methods of chemical desilication. One of the methods consists in baking the silica-containing material with ammonium bifluoride at a temperature of 200 °C and removal of generated ammonium hexafluorosilicate at a temperature of 400 °C. We tried this method in the study [6]. The other method consists in processing the material by the ammonium fluoride solution at a temperature of approximately 100 °C. In such event, silicon is connected with operating reagent into ammonium hexafluorosilicate and passes to solution. The second method differs from the first one by smaller energy consumption, simpler instrumentation, and a smaller number of technological operations demands for less number of technological operations.

With the view to determine efficiency of the given desilication method we carried out studies of leaching the barite raw material by means of the ammonium fluoride solutions corresponding to the scheme shown in the Figure 1.

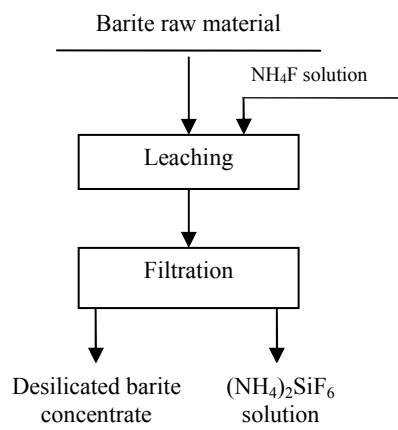


Figure 1. Technological scheme of barite raw material leaching

Leaching the barite raw material may be presented as a corresponding mathematical model. In order to create this model, it is necessary to study influence of the different factors on leaching with involving the method of experiment planning [7].

Studies on leaching are carried out on the waste of flotation enrichment of barite-polymetal ores of the Karagaily deposit—barite raw material of composition, mass. %: SiO_2 — 40.0; BaSO_4 — 37.0; Al_2O_3 — 5.3; Fe — 4.6; S — 6.8; Zn — 0.6; Pb — 0.5; Cu — 0.2.

In order to study the process of leaching barium-containing waste three factors are chosen, namely, leaching temperature (this factor is marked as T), leaching time (τ), and percentage of the initial ammonium fluoride solution (C). The factor change range is shown in Table 1.

Table 1

Factors and levels of their variation for studying the process of barium-containing waste leaching

Factor	Level				
	1	2	3	4	5
T , Temperature, °C	80	85	90	95	100
τ , Time, min.	30	60	80	100	120
C , Solution percentage, %	10	20	30	35	40

For each experiment, a charge of barium-containing waste of a certain weight was taken. Then, it was put into the stainless thermostat container with the ammonium fluoride solution, and leaching was carried out under a set of conditions with interfusion.

On expiration of leaching time, solids and liquids were separated by vacuum filtration. Precipitates on the paper filter were washed off with distilled water. After drying and weighing it was analyzed for silicon containing by the chemical method.

Based on the data obtained from the chemical analysis, extraction of α -silicon into the solution was determined. The results are given in Table 2.

Table 2

Influence of the factors of leaching barium-containing wastes on extraction of silicon into the solution

No. of experience	T , °C	τ , min	C , %	Extraction of silicon into the solution, %	
				αE	αP
1	2	3	4	5	6
1	80	30	10	35.02	37.15
2	80	80	30	40.61	40.09
3	80	60	20	37.80	39.14
4	80	120	40	41.88	41.18
5	80	100	35	42.73	40.68
6	90	30	30	78.06	76.74
7	90	80	20	79.85	80.00

Continuation of Table 2

1	2	3	4	5	6
8	90	60	40	86.96	80.09
9	90	120	35	83.52	82.69
10	90	100	10	80.45	79.62
11	85	30	20	57.12	59.68
12	85	80	40	59.26	63.80
13	85	60	35	58.70	62.67
14	85	120	10	61.55	63.07
15	85	100	30	62.11	64.10
16	100	30	40	92.55	93.42
17	100	80	35	96.70	97.99
18	100	60	10	93.12	93.83
19	100	120	30	99.17	99.67
20	100	100	20	97.05	97.85
21	95	30	35	86.20	87.90
22	95	80	10	87.55	89.87
23	95	60	30	86.68	90.82
24	95	120	20	90.21	93.19
25	95	100	40	88.33	93.82

Supposing that the study function was extraction of silicon from barium-containing waste into the solution we sampled experimental data by levels within factor. The selected experimental values of partial functions are given in Table 3.

Table 3

Experimental values of the particular functions on extraction of silicon to the solution

Function	Levels					Average value
	1	2	3	4	5	
α_1	39.61	59.75	81.77	87.79	95.72	72.33
α_2	69.79	72.65	72.79	74.13	75.27	72.33
α_3	71.54	72.41	73.33	73.57	73.80	72.33

By the experimental values of the functions the dot diagrams of a partial dependence of extraction of silicon into the solution on examined factors were constructed. They are shown in Figure 2.

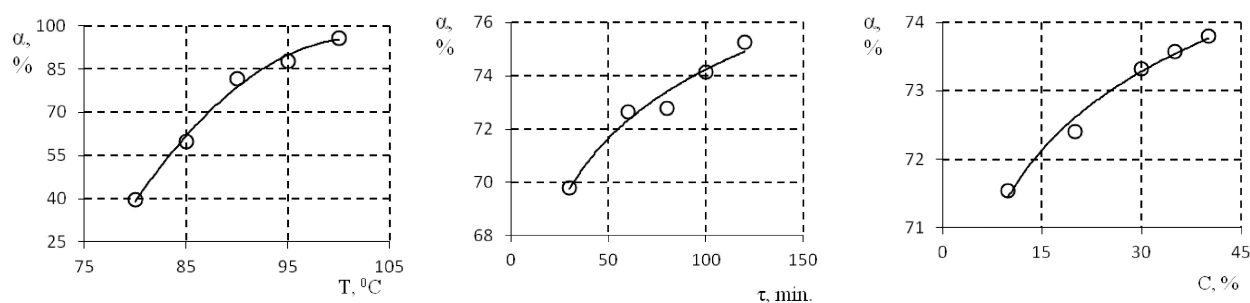


Figure 2. Dependencies of silicon extraction into the solution

By the point data, approximating functions were selected to describe dependence of silicon extraction into the solution on the studied factors of leaching:

$$\alpha_1 = -0.1155T^2 + 23.59T - 1109.0; \quad (1)$$

$$\alpha_2 = 3.716 \ln(\tau) + 57.11; \quad (2)$$

$$\alpha_3 = 1.666 \ln(C) + 67.61. \quad (3)$$

According to those equations the values of partial functions were calculated and their average values were determined. The calculation data are given in Table 4. A minor deviation of the average calculated values from the general average of the experimental value testifies that equations and dot diagrams are closely matched.

Table 4

Calculated values of partial functions by extraction of silicon into the solution

Function	Levels					Average value
	1	2	3	4	5	
α_1	39.00	61.66	78.55	89.66	95.00	72.77
α_2	69.75	72.32	73.39	74.22	74.90	72.92
α_3	71.45	72.60	73.28	73.53	73.76	72.92

Then, the coefficient of nonlinear multiple correlation and the value of the produced partial dependences were determined. The results are given in Table 5.

Table 5

The R coefficient of correlation and its relevance tR for partial functions in extraction of silicon into the solution

Function	R	t_R	Function significance
α_1	0.99	145.9	Significant
α_2	0.98	38.5	Significant
α_3	0.99	137.7	Significant

The analysis of particular dependencies shows that in the matrix experiments leaching temperature exercises the greatest influence on the degree of extraction of silicon into the solution. So, extraction increases by 56 % on average when temperature increases from 80 °C to 100 °C. Extraction increases throughout the entire studied interval tending to saturation.

Dependence of extraction of silicon on the time of leaching and on the concentration of ammonium fluoride is similar. However, they exercise less influence — in the studied time intervals and concentration increase of extraction of silicon averages 5 and 2 %, correspondingly.

The generalized multivariable equation for extraction of silicon into the solution made on the basis of relevant partial dependences looks like that:

$$\alpha = (-0.1155T^2 + 23.59T - 1109.0)(3.716 \ln(\tau) + 57.11)(1.666 \ln(C) + 67.61)72.33^{-2}. \quad (4)$$

This equation is a mathematical model of silicon extraction from barite raw material by leaching ammonium fluoride with a solution. The results (Table 2) that show the considerable relationship with experiment data ($R = 0.99$, $tR = 236.4$) clearly demonstrate that this model is sufficient.

According to the developed model full extraction of silicon into the solution can be expected at a temperature of 95 °C at an ammonium fluoride solution concentration of 25 % and duration of leaching the barite raw material of 80 minutes.

Summary

Studies of leaching barium-containing waste allowed getting particular dependences of extraction of silicon into the solution from temperature leaching time and concentration of solution. On the basis of relevant particular dependences the mathematical model of process is developed, by means of which the optimal leaching conditions are determined. Two products are derived, namely the solution ammonium hexafluorosilicate and the chemically enriched desilicated barite concentrate.

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Бариттік шикізатты сілтілеу процесі схемасын ойлап табу және зерттеу

Зерттеу нысаны барит-полиметалдық кенін флотациялық байыту кезінде алынған баритқұрамдас қалдықтар болып табылады. Мақаланың мақсаты — баритқұрамдас қалдықтарды сілтілеу схемасын ойлап табу. Жоспарлау әдісін қолдану арқылы баритқұрамдас қалдықтарды аммоний фторидінің қатысында сулы сілтілеу эксперименттері өткізілді. Баритқұрамдас қалдықтарды сілтілеу процесін зерттеу үшін үш фактор таңдап алынды — сілтілеу температурасы (T), сілтілеу уақыты (τ) және аммоний фториді бойынша бастапқы ерітіндінің пайыздық концентрациясы (C). Құрамы пайыздық өлшемде SiO_2 — 1.9; BaSO_4 — 67.3; Fe — 8.4; Zn — 1.09; Pb — 0.91; Cu — 0.36 болатын кремнийсіз концентрат алуды қамтамасыз ететін баритқұрамдас қалдықтарды сілтілеудің тиімді шарттары мен үрдістің математикалық үлгісі алынды. Лабораториялық шарттарда баритқұрамдас қалдықтарды сілтілеу схемасы жасалды. Баритқұрамдас қалдықтарды сілтілеу үрдісін зерттеу кремнийді ерітіндіден шығарудың температурадан, сілтілеу уақытынан және ерітінді концентрациясынан жеке тәуелділіктерін алуға мүмкіндік берді. Алынған жеке тәуелділіктер негізінде процестің математикалық үлгісі алынды. Оның көмегімен сілтілеудің тиімді шарттары анықталды. Екі өнім алынды. бірінші өнім — аммоний гексафторосиликат ерітіндісі және екінші өнім — химиялық әдіспен байытылған кремнийсіз баритті концентрат.

Кілт сөздер: барит, барит құрамды қалдықтар, фторидтік технология, сілтілеу, кремний, аммоний гексафторосиликаты, кремнийсіздендіру.

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Исследование и разработка схем процесса выщелачивания баритового сырья

Объектом исследований являются баритсодержащие отходы, полученные при флотационном обогащении барито-полиметаллических руд. Разработка схем выщелачивания баритсодержащих отходов является целью данной статьи. С использованием метода планирования проведены эксперименты по водному выщелачиванию баритсодержащих отходов в присутствии фторида аммония. Для исследования процесса выщелачивания баритсодержащих отходов выбраны три фактора — температура выщелачивания (T), время выщелачивания (τ) и процентная концентрация исходного раствора по фториду аммония (C). Получена математическая модель процесса, и определены оптимальные условия выщелачивания баритсодержащих отходов, обеспечивающие получение обескремненного концентрата состава, масс. %: SiO_2 — 1.9; BaSO_4 — 67.3; Fe — 8.4; Zn — 1.09; Pb — 0.91; Cu — 0.36. В лабораторных условиях разработана схема выщелачивания баритсодержащих отходов. Исследование процесса выщелачивания баритсодержащих отходов позволили получить частные зависимости извлечения кремния в раствор от температуры, времени выщелачивания и концентрации раствора. На основании значимых частных зависимостей получена математическая модель процесса, с помощью которой определены оптимальные условия выщелачивания. Получены два продукта. Первый продукт — раствор гексафторосиликата аммония и второй продукт — обогащенный химическим методом обескремненный баритовый концентрат.

Ключевые слова: барит, баритсодержащие отходы, фторидная технология, выщелачивание, кремний, гексафторосиликат аммония, обескремнивание.

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