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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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АО «Институт топлива, катализа и
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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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ANALYSIS OF THE HYDROCHEMICAL COMPOSITION OF SALT BRINS OF LAKE INDER

Abstract. The article presents an analysis of the hydrochemical composition of the salt brines of the Inder Lake, which consists of three sources Tuzdybulak, Aschybulak and Telepbulak. The analysis shows that the chloride content on Tuzdybulak ranges from 19538 mg/l to 36868 mg/l during the research period from 1961 to 2017, which exceeds the maximum permissible concentration by 55,8-105.3 times; on Aschybulak from 12880 mg/l to 28080 mg/l, the excess is 36.8-80.2 times; on Telepbulak from 11900 mg/l to 26000 mg/l with an excess of 34-74.3 times. Analysis of sodium showed that on Tuzdybulak it is 10,877 mg/l -28,680 mg/l with an excess of the maximum permissible concentration of 54-143.4 times; on Aschybulak from 8430 mg/l to 21697 mg/l with an excess of 42.2-108.5 times; on Telepbulak from 8010 mg/l to 18280 mg/l with an excess of 40.05-91.4 times. This analysis shows that these brines are of the sodium chloride type, while the most saline in terms of sodium and chloride is the Tuzdybulak source. According to the content of calcium cations at the source, Tuzdybulak varies from 860 mg/l to 1499 mg/l, which is 573.3-999.3 times the maximum permissible concentration; at the source of Aschybulak from 930 mg/l to 1325 mg/l, which is 620-883.3 times higher than the MPC; at the source of Telepbulak from 1000 mg/l to 1980 mg/l, which is 666.7-1320 times higher than the MPC. According to sulfate anions at the Tuzdybulak source, from 4096 mg/l to 20077.85 mg/l, which is 8.2–40.2 times higher than the MPC; at the Aschybulak source, from 3370 mg/l to 10841.54 mg / l, which is 6.74-21.6 times higher than the MPC; at the source of Telepbulak from 3360 mg/l to 50816.14 mg/l, which is 6.72-101.6 times higher than the MPC. According to the sulphate-calcium type, the highest content is typical for the Telepbulak source. The analysis of mineralization and solids shows that in salt solutions of Lake Inder they exceed: at the source of Tuzdybulak from 22.3 to 50.9 times; at the source of Aschybulak from 17.8 to 38.5 times; at the source Telepbulak from 17.1 to 33.1 times, which shows that the brines of Lake Inder belong to brine mineral waters.

Key words: Tuzdybulak, Aschybulak, Telepbulak, sodium cations, calcium cations, chloride anions, sulfate anions, salt brine, mineralization, dry residue.

Introduction. As you know, Atyrau region is characterized by difficult climatic conditions. It is located in a semi-desert zone with a sharply continental climate.

In this regard, the organization of a new health resort in the Atyrau region is of great importance for the improvement of the population of the region.

In the region there are necessary mineral resources for the organization of a spa resort in the village of Inderborsk. Rapa Lake Inder has a long history of study [1].

The healing mud of salt lakes is formed in certain geological conditions. Brines that have accumulated in lower areas of the earth, feeding on atmospheric precipitation and other various water sources, mainly under arid conditions, evaporate and form various mineral salts in some parts, and therapeutic mud sludge accumulates under them for a long time.

Healing mud is available on the north coast of Inder Lake. These dirt accumulates at the places of exits of large sources Tuzdybulak, Telepbulak and Aschybulak. Mud yields associated with the source of Telepbulak are approximately 200-250 m long from west to east, 60 m wide from north to south with a visible thickness of 17 cm. The dimensions of the mud outlet associated with the Aschybulak spring are

200 m long, 10 m wide and 10 cm thick. The length of the mud outlet at the Tuzdybulak spring is 210 m, the width is from 54 to 74 m, the thickness is 10-20 cm. The therapeutic mud outlets associated with the Telepbulak spring are approximately 200-250 m long from west to east, north to north wide south up to 60m with a visible power of 17cm. The dimensions of the mud outlet associated with the Aschybulak spring are 200 m long, 10 m wide and 10 cm thick. The length of the mud outlet at the source of Tuzdybulak is 210 m, width is from 54 to 74 m, thickness is 10-20 cm [2].

Methods. In this work, we used methods of comparative analysis of data on the hydrochemical composition of the salt brines of Inder Lake, according to the results of ongoing studies in different years from 1961 to 2017 [2-5]. All results were compared with regulatory documents GOST 26449.1-85, ST RK 1015-200, SanPin 2.1.4.1074-01 and RD 5224.365-2008.

Results. Inder Lake is located in the Atyrau region, 170 km north of Atyrau and 1.2 km from the left bank of the Ural River. Length 13.5 km, maximum width 11 km. Its area is 123 km^2. Inder Lake is fed by atmospheric precipitation and due to the waters of the main aquifer (thickness 14 meters) of the gypsum stratum of the Inder rise, which is unloaded on the northern shore of the lake in the form of numerous descending and ascending sources, the total flow rate of which ranges from 31.0 to 147.5 l/sec (average 60.5 l/sec) [3].

A total of 33 sources were recorded, arising mainly from karst gypsum or from Permian-Triassic sandstones. Three groups of sources have the greatest value in flow rate: 1) Tuzdybulak, Aschybulak on the northeastern outskirts and 2) Telepbulak - on the northwestern part of the lake.

The average annual water consumption is according to sources: Tuzdybulak - 12.3 l/s, Aschybulak - 7.84 l/s and Telepbulak - 9.18 l/s.

In spring and winter, the lake is sometimes covered with a thin layer of brine, and in summer and autumn brine remains only in the northern and northwestern parts, and even then in small areas.

From the north, the lake is surrounded by hills called the Inder Mountains. The southern part of the lake is shallow, imperceptibly passing into the steppe plateau.

The northern part of the lake lies on the southern wing of a large salt dome uplift and has a complex geological structure. The southern, sloping shores of the lake are composed exclusively of the latest Caspian sediments.

The productive stratum of the lake is composed of thick sediments of self-landing cooked high-quality salt. The maximum installed thickness of salt deposits in the lake is 56.2 m.

Indera's lake salt (Figure 1) is divided into five lithological differences: new salt, old salt, granular, pomegranate and black salt. There are no sharp boundaries between them, and their selection is somewhat arbitrary. The main distinguishing features of these salt differences are as follows [4]:

- The new salt is dazzlingly white, finely crystalline (the size of halite crystals is from fractions of mm to 2-5 mm), densely cemented. It is difficult to break with a shovel, easily breaks through with a crowbar. New salt covered almost the entire surface of the salt.
- The old salt tightly cemented 0.05-0.50; yellowish gray, medium crystalline, clay-carbonate with rare gypsum crystals.
- The bulk is transparent, light gray, crystalline, friable, in some places slightly cemented, slightly contaminated with clay-clay material. Easy to take with a shovel. When driving wells, it easily crumbles from the walls. In this regard, wells can only be cased.
- The grenade differs from the above differences in its well-formed halite crystals. The maximum dimensions of the latter are 15-26mm. The salt is clear, light gray, sometimes pinkish, coarse-grained. Small crystals of gypsum and an admixture of carbonate-clay material are observed, rarely in significant quantities. Pomegranate is more difficult to drill than granular, due to the cementation of the rock.
- The black salt gray, dark gray, dense, silted, gypsum, self-salt. The structure is medium and large crystalline. The sizes of halite crystals range from 5-20 mm. A distinctive feature from other differences is a rather significant contamination with clayey-salty carbonate material, gypsum and a sharply increased density, in contrast to grenades and granules. The black salt lays the salt stratum and salty, clay-sand saline and gypsum formations. The salt stratum of Lake Inder has a high porosity reaching 40%. Due to this, the lake has reserves (about 1 billion m^3) of highly mineralized brine, the chemical composition of which is characterized by more or less constancy.

Figure 1 - Inder Lake self-settling salt

Mineral mud or black silts with healing properties are classified as fine. Mud solution is less than 50%. In the mud, particles with a diameter of more than 0.25 mm (clogging) are absent. The colloidal absorption complex is very significant.

Inder mud in its component composition has balneological properties.

The mud of the lake is silt with a strong odor of hydrogen sulfide. The water content in the peloid is 30-35%, and sulphurous iron - about 42 grams per kg of mud, the salt concentration is very high - more than 200 grams per kg of raw mud. The crystalline skeleton consists of calcium carbonates and sulfates. Inder mud is homogeneous black, oily, sticky with the smell of hydrogen sulfide. There are sites littered with sand particles [5].

100 grams of the peloid contains hydrogen sulfide - 250 mg, organic substances - 1.54 g; carbonates in terms of calcium carbonate - 8.5, specific gravity - 1.56; heat capacity - 0.32 calories. Peloid reserves in the lake are significant.

According to the main physical and chemical indicators, the mud of the Inder Lake is: according to the content of water-soluble salts in the mud solution (in g/l) - to salt-saturated (more than 150), according to the content of sulfides (FeS as a percentage of natural mud) - highly sulfide (more than 0.50) , according to the reaction of the medium (pH) - slightly alkaline (7.0-9.0) [6].

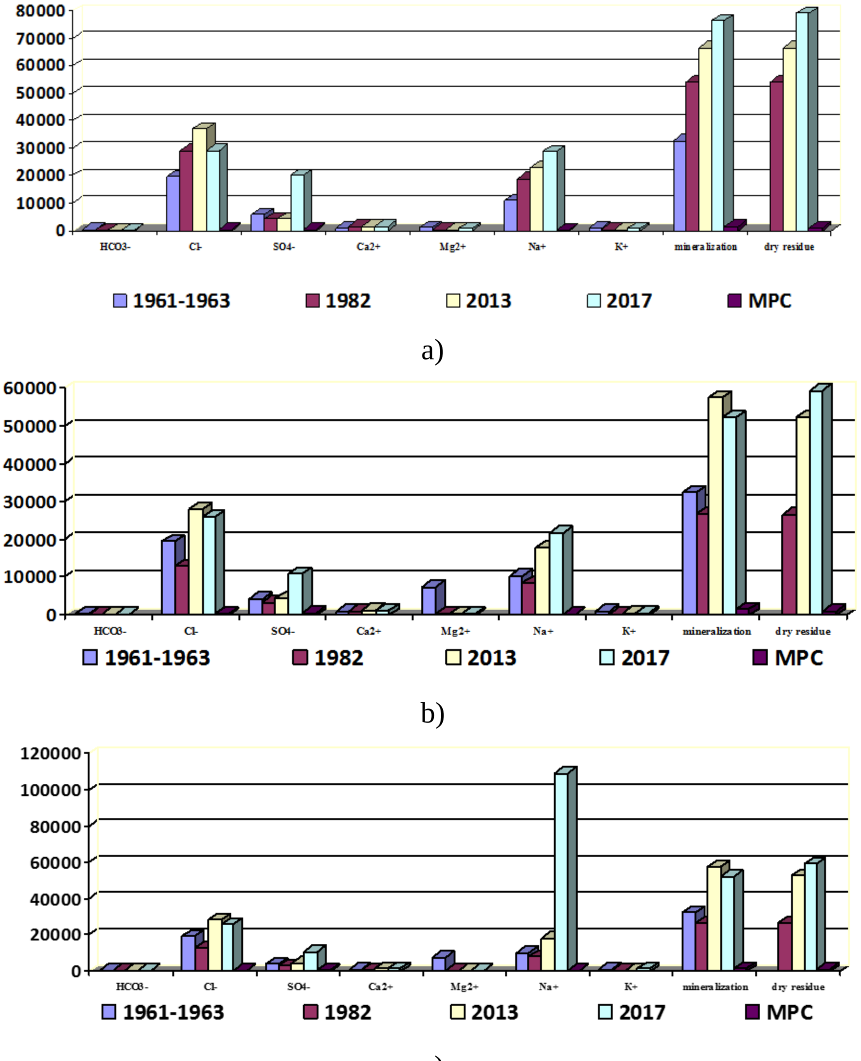
The water extract of the mud of Lake Inder consists of (g/l): calcium 0.29; magnesium 0.40; sodium 0.47; potassium 0.05; no carbonates detected, bicarbonates 0.009; chlorides 2.70; sulfates 1.20 and a dense residue of 6.20, with a pH value of -7.27 [7].

Their balneological value is determined by their moisture capacity (natural humidity), texture (shear resistance), the degree of clogging by large fractions, heat capacity and heat holding ability, mineralization of the mud solution, the presence of hydrogen sulfide and iron sulfides, redox potential and the reaction of the medium.

The requirements for the quality of therapeutic mud include such normative indicators, the mismatch of which excludes the possibility of therapeutic use of preloads [8]:

- humidity determines the consistency of the mud mass, which only at a certain water content can remain plastic, retain on the patient’s body and have a high heat-holding ability;
- contamination with mineral particles or plant debris worsens the plasticity of the mud, and in the presence of large inclusions (crystals, fragments of shells, etc.) causes burns;
- shear resistance characterizes the plasticity of the mud procedural mass and, therefore, its suitability for mud applications [9].

Discussion. As can be seen from the diagrams in Figure 2, the chemical composition of aqueous salt solutions is dominated by the content of chloride anions and sodium cations at all three sources:



a)

b)

c)

Figure 2 - Analysis of the results of the hydro chemical composition of Inder Lake for the period from 1961 to 2017
a) the source of Tushybulak; b) the source of Aschybulak; c) the source of Telepbulak

• the chloride content on Tuzdybulak is from 19538 mg/l in 1961-1963 up to 36868 mg/l in 2013; on Aschybulak from 12880 mg/l in 1982 mg/l to 28080 in 2013; on Telepbulak from 11,900 mg/l in 2017 to 26,000 mg/l in 2013.

• the sodium content on Tuzdybulak is from 10877 mg/l in 1961-1963 up to 28680 mg/l in 2017; on Aschybulak from 8430 mg/l in 1961-1963 until 21697 mg/l in 2017; on Telepbulak from 8010 mg/l in 1982 to 18280 mg/l in 2013 [10].

These data indicate that the mud solution of Lake. Inder refers to the sodium chloride type.

In accordance with regulatory documents (GOST 26449.1-85), the concentration of chlorides in the MPC of chlorides is 350 mg/l, while at the sources of Lake Inder they exceed 55,8 to 105.3 times at the source of Tuzdybulak; from 36.8 to 80.2 times at Aschybulak and from 34 to 74.3 times at Telepbulak source [11].

The maximum permissible concentration of sodium according to RD 5224.365-2008 is 200 mg/l, while in salt solutions of Inder Lake they exceed: from 54 to 143.4 times at the source of Tuzdybulak; from 42.2 to 108.5 at Aschybulak and from 40.05 to 91.4 times at the source of Telepbulak [12].

The content of calcium cations is lower than the content of sodium cations, but despite this, they exceed the maximum permissible concentration, which is 1.5 mg / l for drinking water according to SanPin 2.1.4.1074-01. The content of calcium cations is: at the source of Tuzdybulak from 860 mg / l in 1961-1963. up to 1499 mg l in 2013, which is 573.3-999.3 times more than the MPC; at the Aschybulak source, from 930 mg/l in 1982 to 1325 mg/l, which is 620-883.3 times higher than the MPC; at the source Telepbulak from 1000 mg/l to 1980 mg/l, which is 666.7-1320 times higher than the MPC [13].

The content of sulfate anions is lower than the content of chlorine anions, but exceed the MPC, which is 500 mg/l according to the standard ST RK 1015-2000. The content of sulfate anions is: at the Tuzdybulak source from 4096 mg/l in 2013 to 20077.85 mg/l in 2017, which is 8.2–40.2 times higher than the MPC; at the Aschybulak source, from 3370 mg/l in 1982 to 10,841.54 mg/l in 2017, which is 6.74-21.6 times higher than the MPC; at the source Telepbulak from 3360 mg/l in 1982 to 50816.14 mg/l in 2017, which is 6.72-101.6 times higher than the MPC [14].

Thus, the saline solutions of Lake Inder can also be attributed to the sulfate-calcium type.

The increased content of salts of sodium chloride and calcium sulfate lead to an increase in the salinity of the saline solution, which is: for the source of Tuzdybulak from 33481 mg/l in 1961-1963 up to 76,400 mg/l in 2017, for the Aschybulak source from 26,710 mg/l in 1982 to 57,700 mg/l in 2017, for the Telepbulak source from 2,650 mg/l in 1982 to 49580 mg/l in 2013. According to GOST 26449.1-85, the MPC of mineralization is 1500 mg/l, in salt solutions of Inder Lake they exceed: at the source of Tuzdybulak from 22.3 to 50.9 times; at the source of Aschybulak from 17.8 to 38.5 times; at the source of Telepbulak from 17.1 to 33.1 times [15].

According to the classification, depending on the total salinity, the waters of Lake Indera belong to brine mineral waters.

According to the dry residue, the same pattern is observed as with saline salinity with a slight deviation of up to 10%: at the Tuzdybulak source from 54150 mg/l in 1982 to 78808 mg/l in 2017, which exceeds the MPC equal to 1000 mg/l according to GOST 26449.1-85 in 54.15-78.8 times; at the source of Aschybulak from 26570 mg/l in 1982 to 59406 mg/l in 2017, which exceeds the MPC by 26.57-59.41 times; at the source of Telepbulak from 25650 mg/l in 1982 to 49654 mg/l in 2013, which exceeds the MPC by 25.65-49.65 times. Dry solids data for 1961-1963 not available [16].

Conclusion A comparative analysis of the hydrochemical composition showed that the saline solution of Lake Inder belongs to the sodium chloride and calcium sulfate type. According to the MPC, the composition of brines exceeds the content of sodium cations from 40 to 143 times, calcium from 17 to 50 times; chloride anions from 34 to 105 times; sulfate anions from 6 to 101 times. It should be noted that the content of chlorine anions and sodium cations is higher at the source of Tuzdybulak, the content of sulfate anions and calcium cations is higher at the source of Telepbulak. Thus, the rosol of the source Tuzdybulak belongs to the sodium chloride, and the source of Telepbulak to the sulfate-calcium type [17].

Depending on the total mineralization and solids, it can be concluded that the brine of the Tuzdybulak spring is the most mineralized.

Thus, the physico-chemical study of the therapeutic mud of Inder Lake in the Atyrau region allows us to conclude that they meet the requirements for mud for therapeutic use. Unfortunately, the studied resources of high-quality therapeutic mud of Inder Lake are insignificant and cannot be used on an industrial scale [18].

The unique chemical composition of therapeutic mud in combination with brine baths makes Lake Inder attractive for recreation of citizens of Kazakhstan and vacationers from neighboring regions of Russia [19].

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ИНДЕР КӨЛІНІҢ ТҰЗДЫ ТҰЗДЫҚТЫҢ ГИДРОХИМИЯЛЫҚ ҚҰРАМЫН ТАЛДАУ

Аннотация. Мақалада Тұздыбұлақ, Ащыбұлақ және Телепбұлақ үш көзден тұратын Индер көлінің тұзды тұздарының гидрохимиялық құрамына талдау берілген. Судың орташа жылдық шығыны көздерге сәйкес: Тұзбұлақ - 12,3 л/с, Ащыбұлақ - 7,84 л/с және Телепбұлақ - 9,18 л/с. Көлдің балшықтары күкіртсутектің күшті иісі бар тұнбаға айналады. Пелоидтағы су мөлшері 30-35% құрайды, ал темір сульфиді әр балшық үшін шамамен 42 грамм, тұз концентрациясы өте жоғары - шикі балшықтың әр килограмына 200 грамнан астам. Кристалл қаңқасы кальций карбонаттары мен сульфаттардан тұрады. Ішіндегі балшық біртекті қара, майлы, күкіртсутегі иісімен жабысқақ. Құм бөлшектері бар жерлер бар [5].

100 грамм пелоид құрамында күкіртсутегі бар - 250 мг, органикалық заттар - 1,54 г; кальций карбонаты бойынша карбонаттар - 8,5, ерекше ауырлық күші - 1,56; жылу сыйымдылығы - 0,32 калория. Көлдегі пелоид қоры айтарлықтай.

Негізгі физикалық және химиялық көрсеткіштерге сәйкес Индер көлінің балшықтары: балшық ерітіндісіндегі суда еритін тұздардың құрамына сәйкес (г/л) - тұзға қаныққан (150-ден астам), сульфидтердің құрамына сәйкес (табиғи балшықтың пайыздық құрамындағы FeS) - жоғары сульфидті (0,50-ден жоғары), ортаның реакциясына сәйкес (pH) - сәл сілтілі (7.0-9.0).

Индер көлінің балшық суының сығындысы құрамы (г/л): кальций 0,29; магний 0,40; натрий 0,47; калий 0,05; карбонаттар анықталмады, бикарбонаттар 0,009; хлоридтер 2.70; сульфаттар 1,20 және қатты қалдық 6,20, pH -7,27.

Талдау көрсеткендей, Тұздыбұлақтағы хлоридтің мөлшері зерттеу кезеңінде 1961 жылдан 2017 жылға дейін 19538 мг/л-ден 36868 мг/л аралығында болады, бұл шекті рауалды мөлшерден 55,8-105,3 есе асады; Ащыбұлақ бойынша 12880 мг/л-ден 28080 мг/л дейін, асып кетуі 36,8-80,2 есе; Телебұлақта 11900 мг л-ден 26000 мг/л-ге дейін, 34-74,3 есе артық. Натрий талдауы бойыншаТұздыбұлақта 10,877 мг/л -28,680 мг/л құрайды, бұл шекті рауалды мөлшерден 54-143,4 есе асады; Ащыбұлақ бойынша 8430 мг/л-ден 21697 мг/л-ге дейін, 42,2-108,5 есе; Телепбұлақ бойынша 8010 мг/л-ден 18280 мг/л-ге дейін, 40,05-91,4 есе артық. Бұл талдау көрсеткендей, бұл тұздықтар натрий хлориді түріне жатады, ал тұзды тұздың ең көп мөлшері Тұздыбұлақ көзі болып табылады. Көздердегі кальций катиондарының құрамы бойынша Тұздыбұлақ 860 мг/л-ден 1499 мг/л-ге дейін өзгереді, бұл шекті рауалды мөлшерден 573,3-999,3 есе; Ащыбұлақ көзінде 930 мг/л-ден 1325 мг/л дейін, бұл ШРМК-ден 620-883,3 есе жоғары; Телепбұлақ көзінде 1000 мг л бастап 1980 мг/л дейін, бұл ШРМ-ден 666,7-1320 есе жоғары. Тұздыбұлақ көзіндегі сульфат аниондары бойынша 4096 мг/л-ден 2007,75 мг/л-ге дейін, бұл ШРМ-ден 8,2-40,2 есе жоғары; Ащыбұлақ көзінде 3370 мг/л-ден 10841,54 мг/л дейін, бұл ШРМ-ден 6,74-21,6 есе жоғары; Телепбұлақ көзінде 3360 мг/л-ден 50816,14 мг/л-ге дейін, бұл ШРМ-ден 6,72-101,6 есе жоғары. Сульфат-кальций түріне сәйкес Телепбұлақ көзі үшін ең жоғары мазмұны тән. Минералдану мен қатты заттарды талдау Индер көлінің тұзды ерітінділерінде, олар: Тұздыбұлақ көзінде 22,3-тен 50,9 есеге дейін; Ащыбұлақ көзінде 17,8-ден 38,5 есеге дейін; Телепбұлақ көзінде 17,1-ден 33,1 есеге дейін, бұл Индер көлінің тұздары тұзды минералды суларға жататындығын көрсетеді.

Зерттеулер Индер көлінің тұзды ерітіндісі натрий хлориді мен кальций сульфатының түріне жататынын көрсетті. Тұздықтардың құрамында ШРМ сәйкес натрий катиондарының мөлшері 40-тан 143-ке, кальций 17-ден 50 есеге дейін; хлоридті аниондар 34-тен 105 есеге дейін; сульфат аниондары 6-дан 101 есеге дейін. Тұздыбұлақ көзінде хлорлы аниондар мен натрий катиондарының мөлшері жоғары, сульфат аниондары мен кальций катиондарының мөлшері Телепбұлақтың қайнар көздерінде жоғары екенін атап өткен жөн. Сонымен, Тұздыбұлақ бұлағының тұздылығы натрий хлоридті, ал Телепбұлақ бұлағы кальций сульфатты түріне жатады. Жалпы минералдану мен қатты заттарға байланысты Тұздыбұлақ бұлағының тұздылығы ең минералданған деген қорытынды жасауға болады.

Сонымен, Атырау облысындағы Индер көлінің емдік балшықтарын физикалық-химиялық зерттеу олардың терапевтік пайдалануға арналған балшыққа қойылатын талаптарға сәйкес келеді деген қорытынды жасауға мүмкіндік береді. Өкінішке орай, Индер көлінің жоғары сапалы емдік балшықтарының зерттелген қорлары аз, сондықтан оларды өнеркәсіптік масштабта пайдалану мүмкін емес.

Түйін сөздер: Тұздыбұлақ, Ащыбұлақ, Телепбұлақ, натрий катиондары, кальций катиондары, хлорид аниондары, сульфат аниондары, тұзды тұз, минералдану, құрғақ қалдық.

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АНАЛИЗ ГИДРОХИМИЧЕСКОГО СОСТАВА СОЛЕВЫХ РАССОЛОВ ОЗЕРА ИНДЕР

Аннотация. В статье дан анализ гидрохимического состава солевых рассолов озера Индер, который состоит из трех источников Туздыбулак, Ащыбулак и Телепбулак. Средний годовой расход воды составляет по источникам: Тузбулак – 12,3 л/сек, Ащыбулак – 7,84 л/сек и Телепбулак – 9,18 л/сек. Грязь озера иловая с сильным запахом сероводорода. Содержание воды в пелоиде 30-35%, а сернистого железа – около 42 граммов на кг грязи, концентрация солей очень высокая – более 200 грамм на кг сырой грязи. Кристаллический скелет состоит из карбонатов и сульфатов кальция. Индерская грязь однородная черная, маслянистая, липкая с запахом сероводорода. Встречаются участки, засоренные песчаными частицами [5].

В 100 граммах пелоида содержится сероводорода – 250 мг, органических веществ – 1,54 гр; карбонатов в пересчете на карбонат кальция – 8,5, удельный вес – 1,56; теплоемкость – 0,32 калорий. Запасы пелоидов в озере значительные.

По основным физико-химическим показателям грязь озера Индер относится: по содержанию водорастворимых солей в грязевом растворе (в г/л) – соленасыщенным (более 150), по содержанию сульфидов (FeS в процентах к естественной грязи) – сильносульфидным (более 0,50), по реакции среды (рН) – слабощелочным (7,0-9,0) [6].

Водная вытяжка грязи озера Индер состоит (г/л): кальций 0,29; магний 0,40; натрий 0,47; калий 0,05; карбонаты не обнаружены, гидрокарбонаты 0,009; хлориды 2,70; сульфаты 1,20 и плотный остаток 6,20, при значении рН -7,27

Проведенный анализ показывает, что содержание хлоридов составляет на Туздыбулаке от 19538 мг/л до 36868 мг/л в периоды исследований с 1961 до 2017 г., что превышают предельно-допустимую концентрацию в 55, 8-105,3 раз.; на Ащыбулаке от 12880 мг/л до 28080 мг/л, превышение составляет 36,8-80,2 раз; на Телепбулаке от 11900 мг/л до 26000 мг/л с превышением 34-74,3 раз. Анализ по натрию показал, что на Туздыбулаке составляет 10877 мг/л -28680 мг/л с превышением предельно-допустимой концентрацией 54-143,4 раз; на Ащыбулаке от 8430 мг/л до 21697 мг/л при превышении в 42,2-108,5 раз; на Телепбулаке от 8010 мг/л до 18280 мг/л при превышении 40,05-91,4 раз. Данный анализ показывает, что данные рассолы относятся к хлоридно-натриевому типу, при этом наиболее соленым по натрию и хлоридам является источник Туздыбулак. По содержанию катионов кальция на источнике Туздыбулак варьирует от 860 мг/л до 1499 мг/л, что в 573,3-999,3 раза больше предельно-допустимой концентрации; на источнике Ащыбулак от 930 мг/л до 1325 мг/л, что в 620-883,3 раз выше ПДК; на источнике Телепбулак от 1000 мг/л до 1980 мг/л, что в 666,7-1320 раз превышает ПДК. По сульфат-анионам на источнике Туздыбулак от 4096 мг/л до 20077,85 мг/л, что в 8,2-40,2 раза выше ПДК; на источнике Ащыбулак от 3370 мг/л до 10841,54 мг/л, что в 6,74- 21,6 раз превышает ПДК; на источнике Телепбулак от 3360 мг/л до 50816,14 мг/л, что в 6,72-101,6 раз превышает ПДК. По сульфатно-кальциевому типу наиболее высокое содержание характерно для источника Телепбулак. Анализ по минерализации и сухому остатку показывает, что в солевых растворах озера Индер они превышают: на источнике Туздыбулак от 22,3 до 50,9 раз; на источнике Ащыбулак от 17,8 до 38,5 раз; на источнике Телепбулак от 17,1 до 33,1 раз, что показывает, что рассолы озера Индер относятся к рассольным минеральным водам.

Исследования показали, что солевой раствор озера Индер относится к хлоридно-натриевому и сульфатно-кальциевому типу. В составе рассолов, согласно ПДК, превышает содержание катионов натрия от 40 до 143 раз, кальция от 17 до 50 раз; анионов хлорида от 34 до 105 раз; анионов сульфата от 6 до 101 раза. Необходимо отметить, что содержание анионов хлора и катионов натрия выше на источнике Туздыбулак, содержание сульфат анионов и катионов кальция выше на источнике Телепбулак. Таким образом, рассол источника Туздыбулак относится к хлоридно-натриевому, а источника Телепбулак – к сульфатно-кальциевому типу. В зависимости от общей минерализации и сухого остатка можно сделать вывод, что к наиболее минерализованным относится рассол источника Туздыбулак.

Таким образом, физико-химическое изучение лечебной грязи озера Индер Атырауской области позволяет сделать вывод об их соответствии требованиям, предъявляемым к грязям для лечебного использования. К сожалению, изученные ресурсы высококачественной лечебной грязи Индерского озера незначительные и использовать их в промышленном масштабе не представляется возможным

Ключевые слова: Туздыбулак, Ащыбулак, Телепбулак, катионы натрия, катионы кальция, хлорид-анионы, сульфат-анионы, солевой рассол, минерализация, сухой остаток.

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RESEARCH AND ANALYSIS OF DRIED KISHMISH AND RAISINS FROM GRAPES OF SOUTH KAZAKHSTAN

Abstract. Dried fruits, including raisins, are of particular interest in nutritional studies due to its unique chemical composition and natural qualities, which make raisins an attractive source of nutrients. Research and analysis of kishmish and dried raisins was performed in the department "Food Engineering" of M. Auezov SKSU. Dried fruits were prepared by scientifically justified and developed technology of drying fruits to obtain domestic environmentally friendly dried grapes by infrared irradiation after pre-treatment of raw materials without the use of chemical reagents.

From this study, it can be concluded that the kishmish and raisins obtained from grapes varieties “Kishmish black”, “Bulls-eye”, grown in South Kazakhstan region contain sufficient amount of sucrose (5.17 and 4.75 respectively). Given samples also show high contents ofpotassium (17.98 and 33.02 respectively), calcium (1.19 and 2.07 respectively), phosphorus (1.41and 4.47 respectively), but iron contents is much less (0.21and 0.27 respectively) than usually.

Consumers and stakeholdersmay get benefits by production and realization of suggested kishmish and raisins as regional brands of Kazakhstan or products with geographical indications (GI).

In the future it is necessary to carry out a lot of work on branding the products offered by the authors, provided that it will satisfy the following values, such as technological novelty, rarity and uniqueness of the product, environmental friendliness of the manufacture and use of the product.

Keywords: drying of fruits, grapes, kishmish, raisins, biochemical composition, minerals.

INTRODUCTION

Attention to the problem of nutrition is constantly growing both from the various segments of the population, and from the side of scientific research. At present, modern society is trying to adhere to a healthy lifestyle, to eat balanced foods that contain the necessary substances that support the normal functioning of the body. In the period of exacerbation of chronic diseases (in spring and autumn), as well as in winter, to compensate for the lack of vitamins, micro and macro elements, the pharmaceutical industry offers a wide range of chemically synthesized multicomponent vitamin and mineral complexes. Such complexes are significantly different from native forms, and are characterized by insufficient digestibility by the body [1-3].

In this regard, as sources of vitamins, micro- and macroelements and dietary fiber, as well as a wide range of bioactive components, it is advisable to introduce dried products in a natural or industrial way - dried fruits. It should be noted that modern industrial drying technologies make it possible to preserve most of the biologically active substances in dry fruits, and their amount will be higher than in fresh raw materials due to the removal of moisture from the fruits [4,5].

Dried fruits, including raisins, are of particular interest in nutritional studies due to its unique chemical composition and natural qualities, which make raisins an attractive source of nutrients. Raisins, like other fruits, are free of fats, saturated fats and cholesterol. They are a source of dietary fiber, fructooligasaccharides (fructans), tartaric acid and fruit acid, polyphenolic substances, minerals - potassium, phosphorus, magnesium, iron[6,7].

For the preparation of dried grape products use a crop of special varieties. About 95% of the dried products of all countries of the world are produced from seedless grapes and about 5% - grapes with seed. Dried products made from seedless species are called kishmish and currant, and made from grapes with seed are called raisins. Seedless grape varieties are represented by two groups: kishmish (Round kishmish, Oval kishmish, Black kishmish) and currant (Black currant, White currant, Pink currant). The main grapes of raisins are “Bulls-eye”, Sultani, Tayfi Pink,etc.[8].

Commercial and taste qualities of dried grapes are determined primarily by the quality of raw materials. The following basic requirements are imposed on fresh grapes intended for drying: the consistency of the pulp of the berries must be dense and fleshy, otherwise dried berries are poorly made, wrinkled and have no attractive appearance, in addition, the yield of dried produce is reduced. A mandatory indicator for kishmish and raisins is the high sugar content of the berry juice. The yield of dried products directly depends on its level. For a group of kishmish, it should be at least 23-25%, raisins - at least 22-23%. In their composition, the grapes must be loose, medium-loose or friable; otherwise the process of drying them becomes more difficult. Valuable properties of grape varieties intended for the preparation of dried products are seedlessness and early ripening of berries [9-11].

Thus, the development of technology for producing domestic dried fruits: kishmish and raisins with seeds are very relevant.

MATERIALS AND METHODS

At different stages of work, the objects of the study were local species of grapes “Kishmish black”, “Bulls-eye” obtained in the local markets and dried fruits –kishmish and raisins.

Experimental drying was carried out on a drying unit SD-4 of the department "Food Engineering" of M. Auezov SKSU according to the innovative patent of the Republic of Kazakhstan for No. 20923; as a result dried fruits in the form of kishmish and raisins were obtained.

Analysis of dried fruits were carried out in the Experimental and Regional Laboratory of Engineering Profile Constructional biochemical material (IRLIP “KBM”) at M. Auezov South Kazakhstan State University and at the scientific and laboratory base of the testing laboratory of Academy of Nutrition - Nutritest LLP (Almaty) using all standard and generally accepted methods.

RESULTS AND DISCUSSION

Present investigation was carried out to research and analyze kishmish and raisins from grapes of South Kazakhstan, obtained by scientifically justified and developed technology of drying fruits to obtain domestic environmentally friendly dried grapes by infrared irradiation after pre-treatmentof raw materials without the use of chemical reagents[12]. Special pre-treatment of raw materials allows to emphasize the naturalness of the taste of the products, as well as to preserve all the necessary useful properties (vitamins and minerals).

Raisins, as part of the daily diet, have a combination of attractive, sweet taste and high nutritional value. Chemical composition of raisins includes essential nutrients, soluble and insoluble dietary fibers, as well as biologically active health components.

Table 1 shows nutrient compositions of kishmish (seedless raisins) and raisins with seeds of “Bulls-eye” grapes. Both raisins and kishmish provide similar amounts of sugar (62.60g and 62.24g, respectively), divided almost equally between fructose and glucose with sufficient amounts of sucrose. Raisins, like allfruits, are high in potassium and low in sodium. Compared to other fruits, they are high in magnesium, calcium, phosphorus and iron (Table 2, Figures 1,2).

Table 1 - Biochemical composition of Kishmish (seedless raisins) and Raisins with seeds of “Bulls-eye” grapes

Nutrient	Kishmish (seedless raisins)	Raisins with seeds of “Bulls-eye” grapes
Water, %	21.4	20.,39
Energy, kcal on 100 g	308	313
Carbohydrate,%	73.0	75.0
Sugars (total),%	62.6	62.24
Glucose,%	27.75	28.32
Fructose,%	29.68	29.75
Sucrose,%	5.17	4,75
Proteins,%	2.86	2,26
Fats,%	0.54	0.49
Mass fraction of ash,%	2.16	1.86

The competitiveness and advantage of dried fruit products produced by the developed technology is to obtain environmentally friendly products without the use of chemical preservatives and reagents. One of the main advantages of dried fruits in the south of Kazakhstan is high sugar content and aroma. In summer, solar air insolation is from + 35-45 °C in the shade and fruits grown in a dry, hot climate accumulate sucrose and fructose to the maximum. In dried fruits made in Turkey and Greece, located near the Black Sea due to high humidity, the sugar content in dried fruits is much less. So, content of sucrose of Kishmish (seedless raisins) and Raisins with seeds of “Bulls-eye” grapes of South Kazakhstan -5.17 and 4.75 respectively and for dried fruits made in Turkey and Greece, located near the Black Sea – approximately 0.14-0.98 [13-15].

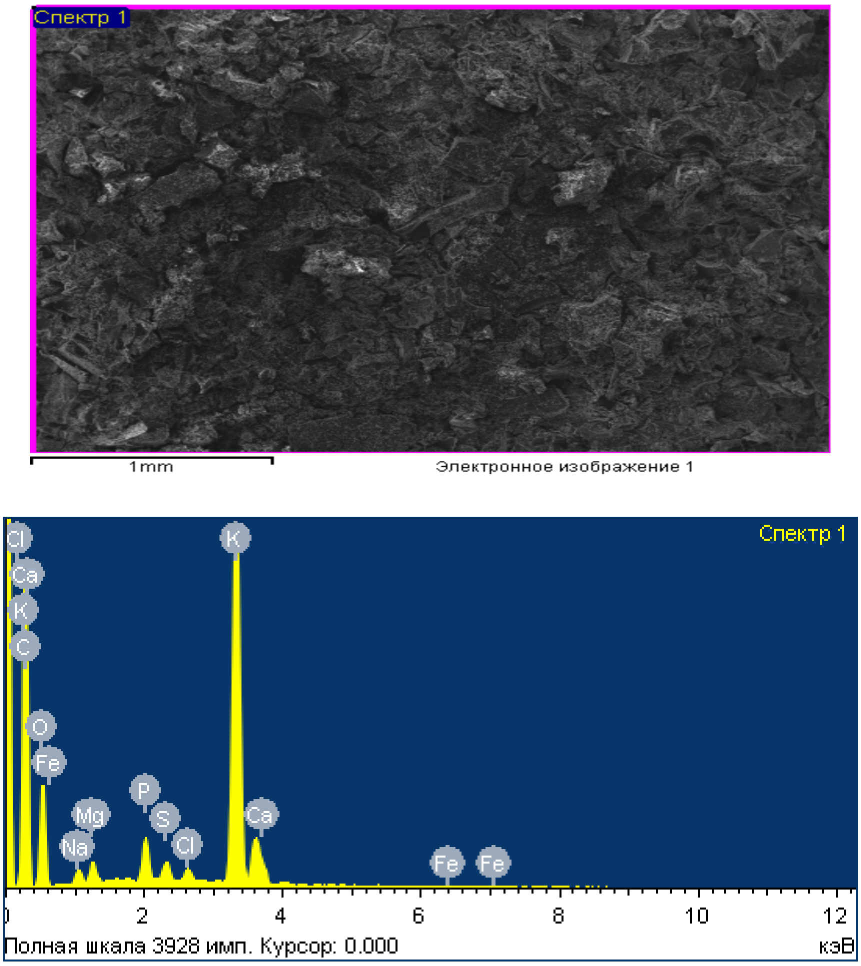

Figure 1 - Micro picture of Kishmish (seedless raisins)

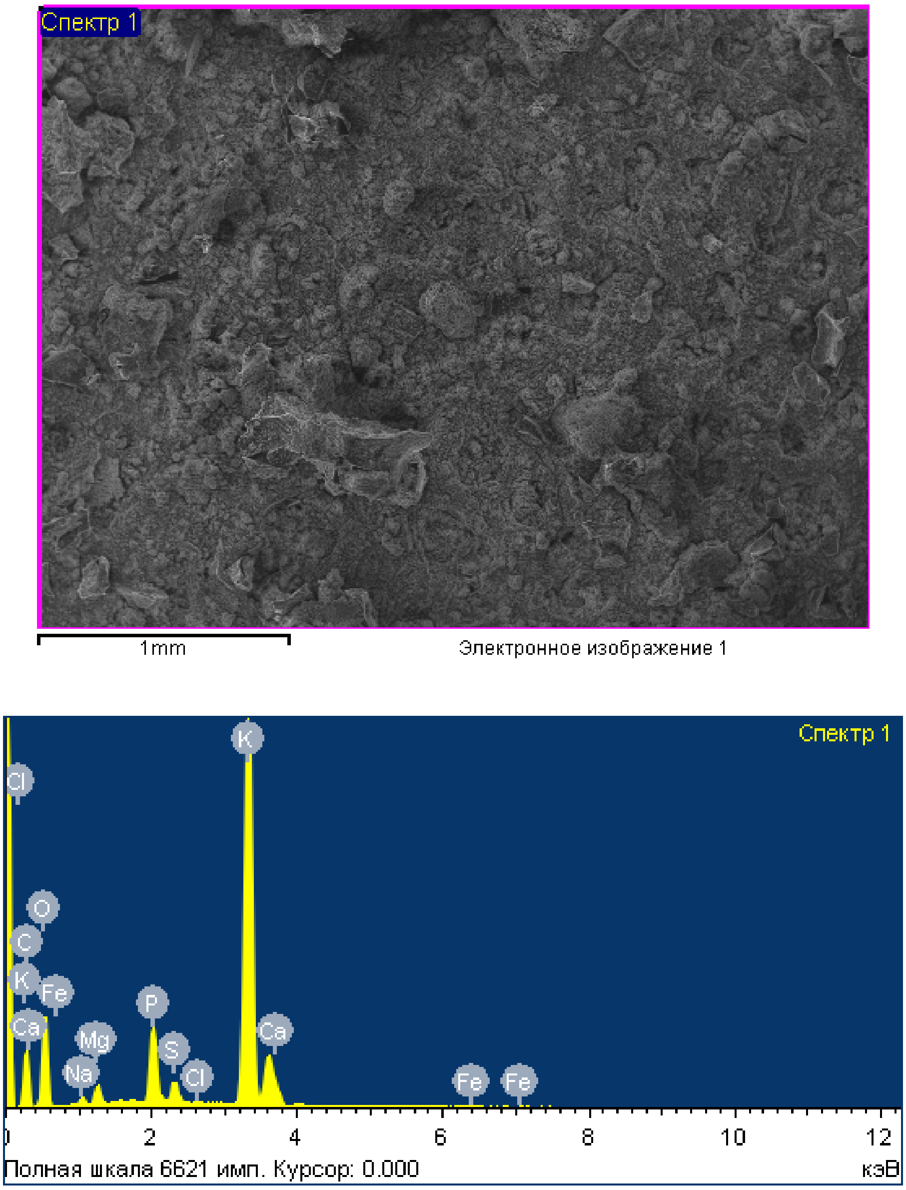

Figure 2 - Micro picture of Raisins with seeds of “Bulls-eye” grapes

Table 2 - Mineral composition of Kishmish (seedless raisins)
and Raisins with seeds of “Bulls-eye” grapes

Kishmish (seedless raisins)		Raisins with seeds of “Bulls-eye” grapes	
Element	Weight, %	Element	Weight, %
C	52.33	C	21.43
O	24.42	O	35.27
Na	0.80	Na	0.84
Mg	0.73	Mg	1.20
P	1.41	P	4.47
S	0.63	S	1.27
Cl	0.50	Cl	0.17
K	17.98	K	33.02
Ca	1.19	Ca	2.07
Fe	0.21	Fe	0.27

CONCLUSIONS

Current research shows, that using progressive technology of infrared drying of fruits will allow you to get dried fruits with high consumer and taste. Thus, sucrose is retained to the maximum extent possible in the products obtained, the mass fraction of which in the kishmish is 5.17% with an energy value of 308 kcal/100g, and the mass fraction of sucrose in raisins with seeds is 4.75% with an energy value of 313kcal / 100g. In conclusion, raisins are rich in main minerals which are important for activity and maintenance.So, minerals as iron, potassium, magnesium, calcium, etc, and other biologically active substances are preserved in dry fruits, as well as taste nutritional values are kept. Furthermore, consumers and stakeholders may get benefits by production and realization of suggested kishmish and raisins as regional brands of Kazakhstan or products with geographical indications (GI)[16].

In the future it is necessary to carry out a lot of work on branding the products offered by the authors, provided that it will satisfy the following values, such as technological novelty, rarity and uniqueness of the product, environmental friendliness of the manufacture and use of the product.

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ОҢТҮСТІК ҚАЗАҚСТАННЫҢ ЖҮЗІМІНЕН ЖАСАЛҒАН КИШМИШ ПЕН МЕЙІЗДІ ЗЕРТТЕУ ЖӘНЕ ТАЛДАУ

Аннотация. Тамақтану проблемасына халықтың әртүрлі топтары тарапынан да, ғылыми зерттеулер тарапынан да үнемі назар аударылып келеді. Қазіргі уақытта қазіргі қоғам салауатты өмір салтын ұстануға тырысады, құрамында ағзаның қалыпты жұмысын қамтамасыз ететін қажетті заттар бар теңдестірілген тағамдар бар. Созылмалы аурулардың асқыну кезеңінде (көктемде және күзде), сондай-ақ қыста дәрумендер, микро және макроэлементтердің тапшылығын толтыру үшін фармацевтика өнеркәсібі химиялық синтезделген көп компонентті витаминді-минералды кешендердің кең спектрін ұсынады. Мұндай кешендер табиғи формалардан едәуір ерекшеленеді және ағзаның жеткіліксіз сіңімділігімен сипатталады.

Кептірілген жемістер, мейізді қоса алғанда, өзінің бірегей химиялық құрамы мен табиғи қасиеттерінің арқасында қоректік заттардың тартымды көзі болып табылады. Кішмиш және кептірілген мейізді зерттеу және талдау М. Әуезов ат. ОҚМУ-да "Тамақ инженерия" кафедрасында жүргізілді. Кептірілген жемістер химиялық реагенттерді пайдаланбай шикізатты алдын ала өңдегеннен кейін отандық экологиялық таза кептірілген жүзім алу үшін ғылыми негізделген және әзірленген жеміс кептіру технологиясы бойынша дайындалған.

Осы зерттеуден Оңтүстік Қазақстан облысында өсірілген "Қара кишмиш", "Бычий глаз" жүзім сорттарынан алынған кішмиш пен мейіз құрамында жеткілікті сахароза (тиісінше 5,17 және 4,75) бар деген қорытынды жасауға болады. Бұл үлгілер сондай-ақ калийдің (тиісінше 17,98 және 33,02), кальций (тиісінше 1,19 және 2,07), фосфордың (тиісінше 1,41 және 4,47) жоғары құрамын көрсетеді, бірақ темірдің мөлшері әдетте қарағанда әлдеқайда аз (тиісінше 0,21 және 0,27).

Тұтынушылар мен мүдделі тараптар үшін Қазақстанның өңірлік брендтері немесе географиялық көрсеткіштері бар өнімдер (GI) ретінде айтылған өнімдерді жасау және тарату өте пайдалыболуы мүмкін.

Болашақта авторлар ұсынған өнімдерді брендтеу бойынша көп жұмыс атқару қажет, егер ол технологиялық жаңашылдығы, өнімнің сирек және бірегейлігі, өнімді өндіру мен пайдаланудың экологиялық қауіпсіздігі сияқты келесі құндылықтарды қанағаттандыратын болса.

Түйін сөздер: жеміс кептіру, жүзім, кишмиш, мейіз, биохимиялық құрамы, минералдар.

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ИССЛЕДОВАНИЕ И АНАЛИЗ СУШЕНОГО КИШМИША И ИЗЮМА ИЗ ВИНОГРАДА ЮЖНОГО КАЗАХСТАНА

Аннотация. Внимание к проблеме питания постоянно растет как со стороны различных слоев населения, так и со стороны научных исследований. В настоящее время современное общество старается придерживаться здорового образа жизни, есть сбалансированные продукты, содержащие необходимые вещества, поддерживающие нормальное функционирование организма. В период обострения хронических заболеваний (весной и осенью), а также зимой, чтобы восполнить недостаток витаминов, микро- и макроэлементов, фармацевтическая промышленность предлагает широкий спектр химически синтезированных многокомпонентных витаминно-минеральных комплексов. Такие комплексы значительно отличаются от нативных форм и характеризуются недостаточной усвояемостью организмом.

Сухофрукты, включая изюм, представляют особый интерес в исследованиях в области питания благодаря своему уникальному химическому составу и природным качествам, которые делают изюм привлекательным источником питательных веществ. Исследования и анализ кишмишного и сушеного изюма проводились на кафедре «Пищевая инженерия» ЮКГУ им. М. Ауэзова. Сухофрукты готовили по научно обоснованной и разработанной технологии сушки плодов для получения отечественного, экологически чистого сушеного винограда инфракрасным излучением после предварительной обработки сырья без использования химических реагентов.

Из этого исследования можно сделать вывод, что кишмиш и изюм, полученные из сортов винограда «Кишмиш черный», «Бычий глаз», выращенных в Южно-Казахстанской области, содержат достаточное количество сахарозы (5,17 и 4,75 соответственно). Данные образцы также показывают высокое содержание калия (17,98 и 33,02 соответственно), кальция (1,19 и 2,07 соответственно), фосфора (1,41 и 4,47 соответственно), но содержание железа намного меньше (0,21 и 0,27 соответственно), чем обычно.

Потребители и заинтересованные стороны могут получить выгоды от производства и реализации предлагаемых кишмишей и изюма в качестве региональных брендов Казахстана или продуктов с географическими указаниями (GI).

Необходмо провести в дальнейшем большую работу по брендированию предлагаемых авторами продукции при условии, что она будет удовлетворять следующим ценностям, как технологическая новизна, редкость и уникальность продукта, экологичность изготовления и использования продукта.

Ключевые слова: сушка фруктов, виноград, кишмиш, изюм, биохимический состав, минералы.

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SYNTHESIS AND STRUCTURE OF DIETHYL-2,6-DIMETHYL-PYRIDIN-3,5-DICARBOXYLATE

Abstract. The article is devoted to the development of a preparatively convenient method for the synthesis of diethyl-2,6-dimethylpyridin-3,5-dicarboxylate. The data on the synthesis of diethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate obtained by three-component cyclocondensation of two equimolar amounts of acetoacetic ester, urotropine and ammonium acetate by the Ganch method are presented. It was shown that when ethanol was boiled for 2 h, diethyl 2,6-dimethyl-1,4-dihydropyridin-3,5-dicarboxylate with sodium nitrite in acetic acid led to the formation of the corresponding aromatic pyridine. The structures of the synthesized compounds were studied by ^{1}H and ^{13}C NMR spectroscopy, as well as by the data of two-dimensional spectra of COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C). The values of chemical shifts, multiplicity, and integrated intensity of 1H and 13C signals in one-dimensional NMR spectra were determined. Using spectra in the formats COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C), homo- and heteronuclear interactions were established, confirming the structure of the studied compounds.

Keywords: Ganch reaction, 1,4-dihydropyridines, ^{1}H and ^{13}C NMR spectra, diethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate.

Introduction

It is known that the derivatives of the Ganch reaction - 1,4-dihydropyridines, are of great interest not only in terms of their possible preparative modification and possessing a wide range of pharmacological activity, but also the constant detection and identification of derivatives of new forms of biological activity among this class of derivatives [1-12]. The chemical oxidation reaction of 1,4-dihydropyridines has been well studied; a number of both organic and inorganic reagents are used as oxidizing agents [13-19].

Methods

^{1}H and ^{13}C NMR spectra of compounds **1, 2** were recorded in DMSO-d_6 on a JNM-ECA 400 spectrometer (399.78 and 100.53 MHz on ^{1}H and ^{13}C nuclei, respectively) of the Jeol company from Japan. The survey was carried out at room temperature using a DMSO-d_6 solvent. Chemical shifts are measured relative to the signals of residual protons or carbon atoms of a deuterated solvent.

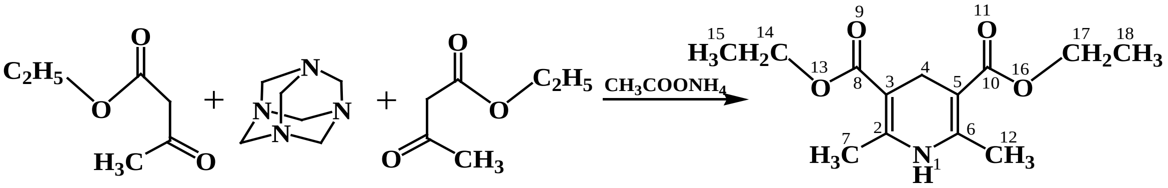
Experimental part

Diethyl-2,6-dimethyl-1,4-dihydropyridin-3,5-dicarboxylate (**1**)**.** A mixture of 15.6 g (0.12 mol) of acetoacetic ester, 1.54 g (0.01 mol) of urotropin and 4.62 g (0.06 mol) of ammonium acetate in 60 ml of ethanol is boiled for 1 hour. The solution is cooled, the precipitate is filtered off. Yield 2.50 g (90.0%), temperature melting 189-190°C.

Diethyl-2,6-dimethylpyridin-3,5-dicarboxylate (**2**)**.** To a suspension of 1.27 g (0.005 mol) of diethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate in 15 ml of acetic acid at room temperature, 0.69 g (0.01 mol) of sodium nitrite was added in portions. After all sodium nitrite was added, the reaction mixture was stirred for 2 hours at room temperature. Then it is poured onto ice, neutralized with ammonia and the precipitated product 2 is filtered off, washed with water. Yield 1.13 g (89.7%), temperature melting 74-75°C.

Results and discussions

In order to obtain and further modify the new derivatives of symmetric 1,4-dihydropyridines, a three-component cyclocondensation of two equimolar amounts of acetoacetic ester was carried out by the Ganch method. Instead of formaldehyde and ammonia in the classic version of the Ganch synthesis, it used urotropine and ammonium acetate. Ethanol was chosen as a solvent. The reaction time was monitored by TLC. As a result of the reaction, after 1 h of boiling the mixture, a light yellow precipitate formed, which after filtration did not require additional purification, since According to the ^{1}H and ^{13}C NMR spectra, it turned out to be analytically pure product **1**.



1

In the ^{1}H NMR spectrum of compound **1**, the equivalent methyl protons H-15, 15, 15, 18, 18, 18 of the ethyl carboxylate groups appeared as a six-proton triplet at 1.14 ppm with ^{3}J 7.2 Hz. The neighboring equivalent methylene protons H-14, 14, 17, 17 of the ethyl carboxylate substituent resonated with a four-proton quadruplet signal at 4.01 ppm, respectively with ^{3}J 6.8 Hz. Equivalent methyl protons H-7, 7, 7, 12, 12, 12, which do not have protons splitting them in the neighborhood, were manifested by the expected six-proton singlet at 2.02 ppm. At 3.06 ppm atoms of H-4, 4 of the dihydropyridine fragment were resonated by a two-proton singlet. In the weakest field at 8.25 ppm single-proton singlet protons H-1 of the dihydro-pyridine nucleus appeared.

In the ^{13}C NMR spectrum of compound **1**, signals of equivalent ethyl carboxylate groups appeared at 14.92 (C-15, 18), 59.46 (C-14, 17) and 167.65 (C-8, 10) ppm. The carbon atoms of the equivalent methyl substituents C-7, 12 resonated at 18.47 ppm. The carbon atoms of the dihydropyridine fragment are observed at 25.23 (C-4), 97.52 (C-3, 5) and 147.09 (C-2, 6) ppm.

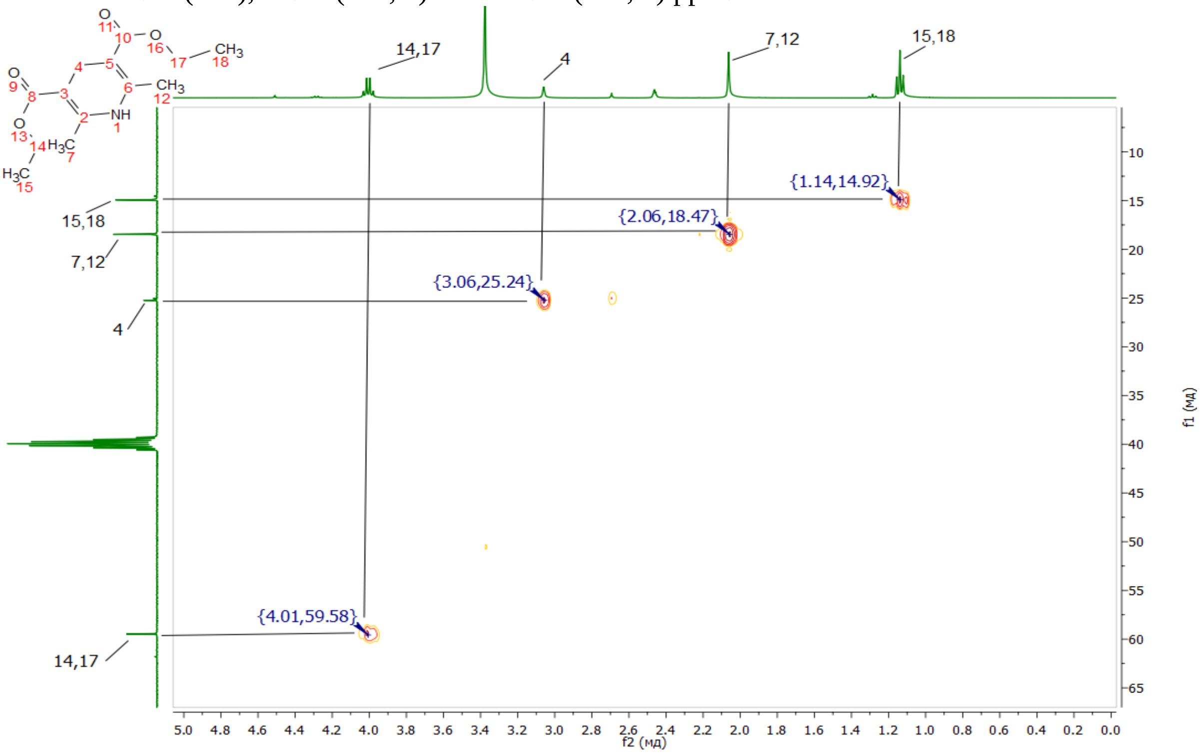


Figure 1 – Spectrum survey of HMQC compound **1** in DMSO

The structure of compound **1** was also confirmed by the methods of two-dimensional NMR spectroscopy COSY (^1H-^1H) and HMQC (^1H-^{13}C), which allows one to establish spin-spin interactions of a homo- and heteronuclear nature (Figs. 1 and 2). The observed correlations in the molecule are presented in the diagrams. In the spectra of ^1H-^1H COSY compounds, spin-spin correlations are observed through three bonds of the neighboring methyl and methylene protons of the ethyl carboxylate fragments $H^{15,18}$-$H^{14,17}$ with coordinates at 1.11, 4.01 and 4.00, 1.14 ppm. Heteronuclear interactions of protons with carbon atoms through one bond were established using ^1H-^{13}C HMQC spectroscopy for all pairs present in the compound: $H^{15,18}$-$C^{15,18}$ (1.14, 14.92), $H^{7,12}$-$C^{7,12}$ (2.06, 18.47) , H^4-C^4 (3.06, 25.24) and $H^{14,17}$-$C^{14,17}$ (4.01, 59.58).

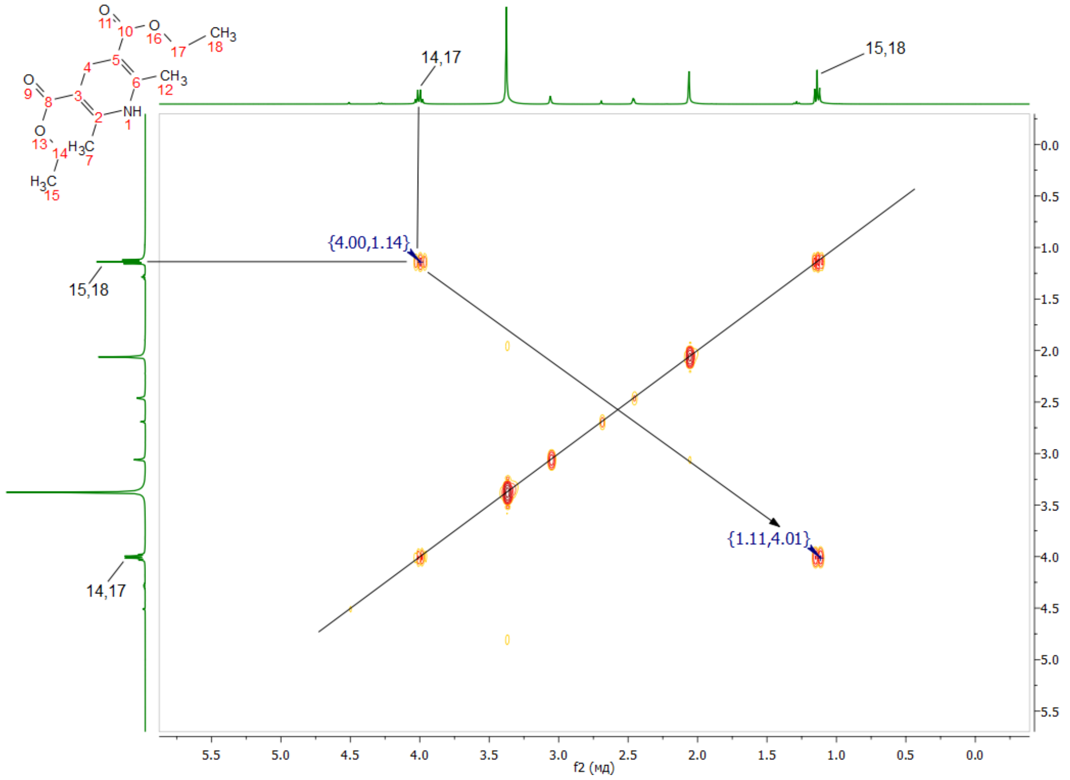
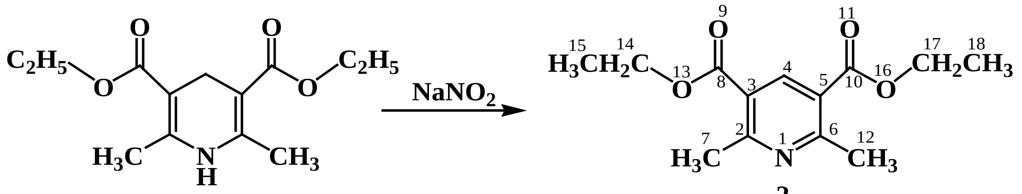


Figure 2 – Survey of the spectrum of COSY compound **1** in DMSO

Oxidative dehydrogenation of diethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **1** to the corresponding aromatic pyridine **2** was carried out with sodium nitrite in acetic acid. As a result of the reaction, diethyl-2,6-dimethylpyridin-3,5-dicarboxylate **2** was isolated in analytically pure form with a yield of 89.7%.



1 **2**

In the ^1H NMR spectrum of compound **2**, the equivalent methyl protons H-15, 15, 15, 18, 18, 18, 18 of the ethyl carboxylate groups showed a six-proton triplet at 1.28 ppm with ^3J 6.8 Hz (Fig. 3). The neighboring equivalent methylene protons H-14, 14, 17, 17 of the ethyl carboxylate substituent resonated with a four-proton quadruplet signal, respectively, at 4.27 ppm with ^3J 6.8 Hz. Equivalent methyl protons H-7, 7, 7, 12, 12, 12, which do not have protons splitting them in the neighborhood, were manifested by the expected six-proton singlet at 2.67 ppm. In the aromatic region, a single-proton singlet at 8.44 ppm. the pyridine proton H-4 resonated.

In the ^{13}C NMR spectrum of compound **2**, signals of equivalent ethyl carboxylate groups appeared at 14.53 (C-15, 18), 61.77 (C-14, 17) and 165.65 (C-8, 10) ppm (fig. 4). The carbon atoms of the equivalent methyl substituents C-7, 12 resonated at 25.00 ppm. The carbon atoms of the pyridine fragment are observed at 123.11 (C-3, 5), 140.43 (C-4) and 161.83 (C-2, 6) ppm.

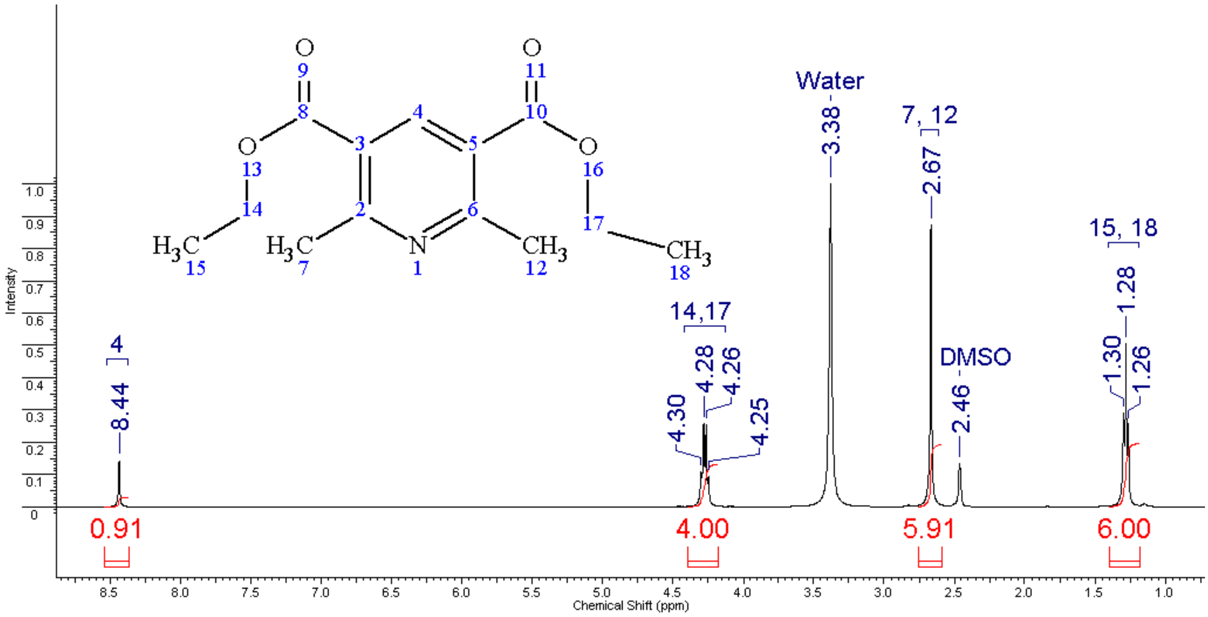


Figure 3 – Survey of the NMR ^{1}H spectrum of compound **2** in DMSO

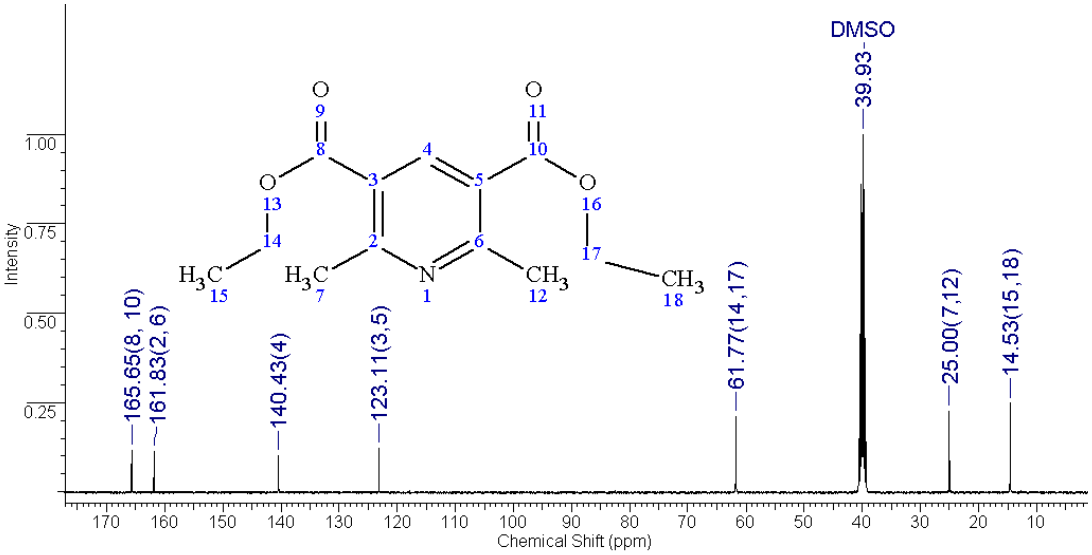


Figure 4 – Survey of the NMR ^{13}C spectrum of compound **2** in DMSO

The structure of compound **2** was also confirmed by two-dimensional NMR spectroscopy COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C), which allows one to establish spin-spin interactions of a homo- and heteronuclear nature (Fig. 5). The observed correlations in the molecule are presented in the diagrams. In the spectra of the ^{1}H-^{1}H COSY compound, spin-spin correlations are observed through three bonds of the neighboring methyl and methylene protons of the ethyl carboxylate fragments H^{15,18}-H^{14,17} with coordinates at 1.26, 4.27 and 4.26, 1.28 ppm. Heteronuclear interactions of protons with carbon atoms through one bond were established using ^{1}H-^{13}C HMQC spectroscopy for all pairs present in the compound: H^{15,18}-C^{15,18} (1.27, 14.63), H^{7,12}-C^{7,12} (2.66, 25.04) H^{14,17}-C^{14,17} (4.28, 61.57); and H^4-C^4 (8.42, 140.33).

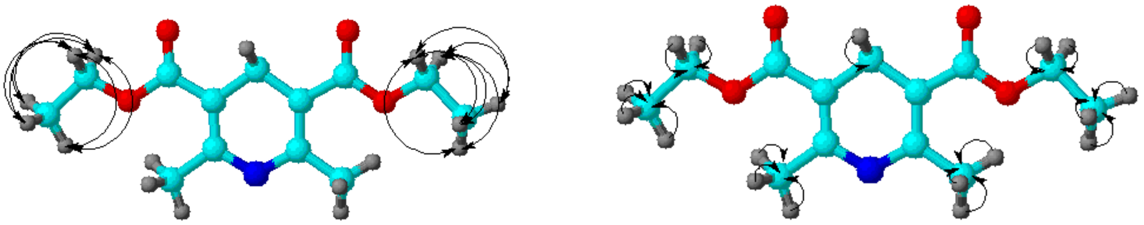


Figure 5 – Correlation scheme in the spectra of COSY (a) and HMQC (b) of compound **2**

Thus, we synthesized diethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate and developed a fairly simple and effective method for producing diethyl-2,6-dimethylpyridin-3,5-dicarboxylate, the structure of which is proved ^{1}H and ^{13}C NMR spectroscopy, as well as the data of two-dimensional spectra of COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C).

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ДИЭТИЛ-2,6-ДИМЕТИЛПИРИДИН-3,5-ДИКАРБОКСИЛАТ СИНТЕЗІ ЖӘНЕ ҚҰРЫЛЫСЫ

Аннотация. Мақала диэтил-2,6-диметилпиридин-3,5-дикарбоксилат синтезінің қолайлы әдісін іздестіруге арналған. Ганч әдісі бойынша ацетоуксус эфирі, уротропин және аммоний ацетатының екі эквимольді мөлшерінде үшкомпонентті циклоконденсациямен алынған диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилатты синтездеу бойынша зерттеу деректері қарастырылған. Конденсация процесінің еріткіші ретінде этанол таңдалды. Реакция уақыты ЖҚХ көмегімен бақыланды. Реакцияның нәтижесінде қоспаны 1 сағат қайнатқаннан кейін ашық-сары тұнба түзілді, ол сүзуден кейін қосымша тазартуды талап етпеді, өйткені ЯМР ^{1}Н және ^{13}С спектріне сәйкес ол аналитикалық таза өнім болып шықты. Диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилаттың тотығу дегидрленуі тиісті ароматты пиридинге дейін сірке қышқылында натрий нитриті қатысуы арқылы жүргізіледі. Реакция нәтижесінде диэтил-2,6-диметилпиридин-3,5-дикарбоксилат 89,7% шығымымен аналитикалық таза түрде бөлінді. Синтезделген қосылыстардың құрылысы ЯМР ^{1}Н - және ^{13}С-спектроскопия әдістерімен, сондай-ақ COSY (^{1}H-^{1}H) және HMQC (^{1}H-^{13}C) екі өлшемді спектрлерінің деректерімен зерттелді. Біректлшемді ЯМР спектрлерінде ^{1}Н және ^{13}С сигналдардың интегралдық қарқындылығы, мультиплеттілігі және химиялық ығысу мәндері анықталды. COSY (^{1}H-^{1}H) және HMQC (^{1}H-^{13}C) форматтарында спектрлер көмегімен зерттелетін қосылыстардың құрылымын растайтын гомо - және гетероядролық өзара әрекеттесулер орнатылды. Диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилат қосылысының ^{1}Н ЯМР спектрінде метильді протондар Н-15, 15, 15, 18, 18, 18 этилкарбоксилатты топтар 1.14 м.б. ^{3}J 7.2 Гц кезінде алты триплетпен пайда болатындығы айқындалды. ^{13}С спектрінде диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилат қосындысының этилкарбоксилат топтарының эквивалентті сигналдары 14.92 (С-15, 18), 59.46 (С-14, 17) және 167.65 (С-8, 10) м.б. кезінде айқын көрінген. С-7, 12 эквивалентті метильді орынбасарларының көміртекті атомдары 18.47 м.б. кезінде резонацияланған. Дигидропиридинді фрагменттің көміртегі атомдары 25.23 (С-4), 97.52 (С-3, 5) және 147.09 (С-2, 6) м.б. аймағында анықталды. Сондай-ақ диэтил-2,6-диметилпиридин-3,5-дикарбоксилаттың ЯМР ^{1}Н спектрінде эквивалентті метильді протондары Н-15, 15, 15, 18, 18, 18 этилкарбоксилатты топтар 1.28 м.б. ^{3}I 6.8 Гц кезінде алты триплетпен көрінетіні анықталған, ал ЯМР ^{13}С спектрінде карбоксилатты топтардың эквивалентті этил сигналдары 14.53 (С-15, 18), 61.77 (С-14, 17) және 165.65 (С-8, 10) м.б. кезінде байқалды. С-7, 12 эквивалентті метильді орынбасарларының көміртекті атомдары 25.00 м.б. кезінде резонацияланды. Пиридинді фрагменттің көміртегі атомдары 123.11 (С-3, 5), 140.43 (С-4) және 161.83 (С-2, 6) м.б. байқалған.

Түйін сөздер: Ганч реакциясы, 1,4-дигидропиридиндер, ЯМР ^{1}Н - және ^{13}С-спектрлер, диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилат.

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СИНТЕЗ И СТРОЕНИЕ ДИЭТИЛ-2,6-ДИМЕТИЛПИРИДИН-3,5-ДИКАРБОКСИЛАТА

Аннотация. Статья посвящена разработке препаративно удобного способа синтеза диэтил-2,6-диметилпиридин-3,5-дикарбоксилата. Приведены данные по синтезу диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилата, полученного трехкомпонентной циклоконденсацией двух эквимольных количеств ацетоуксусного эфира, уротропина и ацетата аммония по методу Ганча. В качестве растворителя процесса конденсации был выбран этанол. Время реакции контролировали с помощью ТСХ. В результате реакции после 1 ч кипячения смеси образовывался светло-желтый осадок, который после фильтрации не требовал дополнительной очистки, поскольку, согласно спектрам ЯМР ^{1}Н и ^{13}С, он оказался аналитически чистым продуктом. Окислительное дегидрирование диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилата до соответствующего ароматического пиридина проведено в присутствии нитрита натрия в уксусной кислоте. В результате реакции был выделен диэтил-2,6-диметилпиридин-3,5-дикарбоксилат в аналитически чистом виде с выходом 89,7 %. Исследованы строения синтезированных соединений методами ЯМР ^{1}Н- и ^{13}С-спектроскопии, а также данными двумерных спектров COSY (^{1}Н-^{1}Н) и HMQC (^{1}Н-^{13}С). Определены значения химических сдвигов, мультиплетность и интегральная интенсивность сигналов ^{1}Н и ^{13}С в одномерных спектрах ЯМР. С помощью спектров в форматах COSY (^{1}Н-^{1}Н) и HMQC (^{1}Н-^{13}С) установлены гомо- и гетероядерные взаимодействия, подтверждающие структуру исследуемых соединений. Зафиксировано, что в спектре ЯМР ^{1}Н диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилата метильные протоны Н-15, 15, 15, 18, 18, 18 этилкарбоксилатных групп проявились шестипротонным триплетом при 1.14 м.д. с ^{3}J 7.2 Гц. В спектре ЯМР ^{13}С диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилата сигналы эквивалентных этилкарбоксилатных групп обнаружено при 14.92 (С-15, 18), 59.46 (С-14, 17) и 167.65 (С-8, 10) м.д. Углеродные атомы эквивалентных метильных заместителей С-7, 12 резонировано при 18.47 м.д. Атомы углерода дигидропиридинового фрагмента наблюдено при 25.23 (С-4), 97.52 (С-3, 5) и 147.09 (С-2, 6) м.д. Также выяснено, что в спектре ЯМР ^{1}Н диэтил-2,6-диметилпиридин-3,5-дикарбоксилата эквивалентные метильные протоны Н-15, 15, 15, 18, 18, 18 этилкарбоксилатных групп проявляются шестипротонным триплетом при 1.28 м.д. с ^{3}J 6.8 Гц, а в спектре ЯМР ^{13}С сигналы эквивалентных этилкарбоксилатных групп резонируют при 14.53 (С-15, 18), 61.77 (С-14, 17) и 165.65 (С-8, 10) м.д. Углеродные атомы эквивалентных метильных заместителей С-7, 12 резонировались при 25.00 м.д. Атомы углерода пиридинового фрагмента наблюдено при 123.11 (С-3, 5), 140.43 (С-4) и 161.83 (С-2, 6) м.д.

Ключевые слова: реакция Ганча, 1,4-дигидропиридины, ЯМР ^{1}Н- и ^{13}С-спектры, диэтил-2,6-диметил-1,4-дигидропиридин-3,5-дикарбоксилат.

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ESTIMATION OF OIL PRODUCTS CONTENT IN SOIL AND WATER OBJECTS IN THE AREA OF LOCATION OF SLUDGE DRESSERS ON THE COAST OF THE VOLGA RIVER

Abstract. The article assesses the quantitative composition of petroleum products at oil waste storage areas near the confluence of the Volga River and its Kizan branch of the Volga Region of the Astrakhan Region. Studies were conducted of soil samples at different depths in two pits and groundwater, groundwater and bottom sediments. In the studied two wells, the maximum excess is observed from 104 to 260 times in the second well, while in the first well the oil content exceeds from 67.5 to 133 times. The content of heavy metals also exceeded the maximum permissible concentration, for example, total chromium 168 times and 2040 times and arsenic 1.7 times and 2.6 times, respectively, in the first and second wells. According to the results of groundwater research, the oil content exceeds 88 and 14.4 times for the 1st oil well and 520 and 86.6 times for the 2nd well. On the Volga River section, located at the 200th distance from the oil, the content of oil products in the water is lower than the MPC, however, far from the coast, the studied indicator is higher than the MPC for fishery reservoirs with a maximum at a distance of 1000 m from the second oil tank. The maximum content of petroleum products (18719.3 ± 4679.8 mg / kg) in bottom sediments was observed in the area of oil tank No. 2, which exceeded the control variant by more than 36 times. Research shows that the second hole is the most polluted.

Key words: oil pit, oil products, heavy metals, maximum permissible concentration, soil, groundwater, bottom sediments.

Introduction. The oil pits in Sokolovo at one time were intended for the storage of oil products, which were earthen excavations with sloping walls where they temporarily stored oil, kerosene, fuel oil and other oil products. To ensure stability along the sides, oil pits were furnished with wooden bars. When filling such a pit with oil, it was absorbed and filled with water in order to reduce the pit. At this time, the remains of the pipeline system pipe and the wooden fortifications of one of the Sokolovskoye oil fields remained. Then they were used to receive oily waste after from all oil bases in the Astrakhan region.

Sokolovo oil pits are located at the confluence of the Volga River and its Kizan branch. In the hydrographic network of the Volga delta, the main channel is distinguished - the watercourse of the largest category, as well as hoses, ducts, eric and banks, differing in morphometric and hydraulic characteristics. A characteristic type of delta watercourses are proranes - natural ones that occur when water breaks out from one flood to another and artificial ones created for water exchange and fish passage [1].

Administratively, the contaminated territory of the Sokolovo oil pit object is located in the Volga region of the Astrakhan region within the boundaries of the municipality of Tatarobashmakovsky Village Council on the lands of the settlement [2].

Methods. Laboratory tests of soil samples for the content of PAHs were carried out by the accredited laboratory of the Federal State Institution SevKasptekhmordirektsiya (PDN F 16.1: 2.2.3: 3.62-09).

Sample preservation method: freezing. Sample volume: 1.0 kg.

Measurement Method: IKS - spectrometric; HPLC

Determination of the mass fraction of NP in soil samples is carried out by IR spectrometry. The method is based on the extraction of NP from the soil with a solvent at room temperature. The concentration of hydrocarbons in a soil sample is determined by the optical density measured on an IR spectrometer.

Of the traditional solvents for the infrared region, carbon tetrachloride is most suitable, since it is most transparent in this area.

HPLC allows the simultaneous separation of complex samples into their constituent components, detecting most components, measuring the concentration of one or more compounds (depending on specific analytical tasks and the availability of standard samples) [3].

For the study, soil samples were taken of two oil disposal pits located in the Volga region of the Astrakhan region and water samples from both the shore and from the vessel and from bottom sediments.

Results and discussion. The results of laboratory tests of soil samples taken during the reconnaissance survey of the coastal strip are presented in table 1.

Table 1 - Contaminant content in soil

Name of pollutants	MPC$_{soil}$, mg / kg	UEC$_{soil}$ sand / loam, mg / kg	The content of pollutants, mg / kg	
			oil pit number 1	oil pit number 2
Oil products		1000	**from 67500 to 133000**	**from 104000 to 260000**
HM (gross form):				
lead	32		up to 4,48	up to 5,98
copper		33/132	up to 8,27	up to 8,26
cadmium		0,5/2,0	up to 0,09	up to 0,09
nickel		20/80	up to 18,1	up to 18,1
zinc		55/220	up to 20,5	up to 20,6
common chrome (6+)	0,05	-	**up to 8,38**	**up to 102,0**
mercury	2,1		up to 0,027	up to 0,022
arsenic	2,0		**up to 3,40**	**up to 5,3**

The data in the table indicate that in the soil of the coastal strip of oil pit No. 1, the content of oil products exceeds the MEA (maximum estimated amount) by a minimum of 67.5, and a maximum of 133 times. For oil pit No. 2, this excess is from 104 to 260 times. Such indicators of oil products characterize the level of land pollution with chemicals as very high [4].

According to the calculation of the integral index of pollution Zc, according to the degree of pollution with chemicals, the coastal ground soils are classified as “dangerous” and “extremely dangerous”. Sanitary regulations have recommended on such lands the implementation of measures to reduce pollution and the binding of toxicants in soils, the organization and monitoring of toxicants in soils, groundwaters and local water sources [5].

An important circumstance is the excess of MPC for such heavy metals as total chromium (168 times for oil pit No. 1 and 2040 times for oil pit No. 2) and arsenic (1.7 times for oil pit No. 1 and 2.6 times for oil pit No. 2). Due to the fact that the coastal strip is located 100m from the beach and is often visited by vacationers, fishing enthusiasts and local residents, this level of pollution poses a threat to human health. The problem is exacerbated by the destruction of the coast and the ingress of contaminated soil in the river Kizan, which is a source of centralized water supply and a reservoir of the highest category of fishery use, is a place of reproduction of fish stocks of the Volga-Caspian basin.

Given the highest excess concentration, a particular danger in this case is chromium. Despite the biological needs for it, its high concentrations are toxic. Chromium has a generally poisonous, irritating, cumulative, allergic, carcinogenic and mutagenic effect on the human and animal organism. According to published data, chromium is able to penetrate intact human skin in contact with an aqueous solution (hexavalent chromium in doses of 0.25; 0.025 and 0.005 mg / kg). Which leads to severe damage to the enzymatic system of the liver, with manifestations of embryotoxic and mutagenic effects [6]. In general, the data in the table indicate that the most polluted and therefore most dangerous is oil pit No. 2, which is located 10 meters from the residential development. At the end of it is the pumping station of the cottage village. This situation requires urgent decision-making in order to prevent environmental dangers to the local population.

In soils, oil and oil products cause deep, irreversible changes in the morphological, physical, physicochemical, and microbiological properties of soils, and with a strong and very strong degree of contamination, they can provoke significant changes in the soil profile, and as a result, loss of fertility and exclusion of the territory from agricultural use [7].

The figure shows that the maximum amount of oil products was noted in the second oil pit at a depth of 1 and 4 m. For the first oil pit, the highest content of oil products was recorded at a depth of 2 m.

Such indicators of oil products characterize the level of land pollution with chemicals as very high and medium [8].

According to the degree of pollution with chemicals, the soil is classified as “moderately dangerous” and “dangerous” [5].

Sanitary rules imply control over the content of pollutants in all environmental objects, including soil, surface and groundwater, and a list of measures to reduce their impact on vegetation [5].

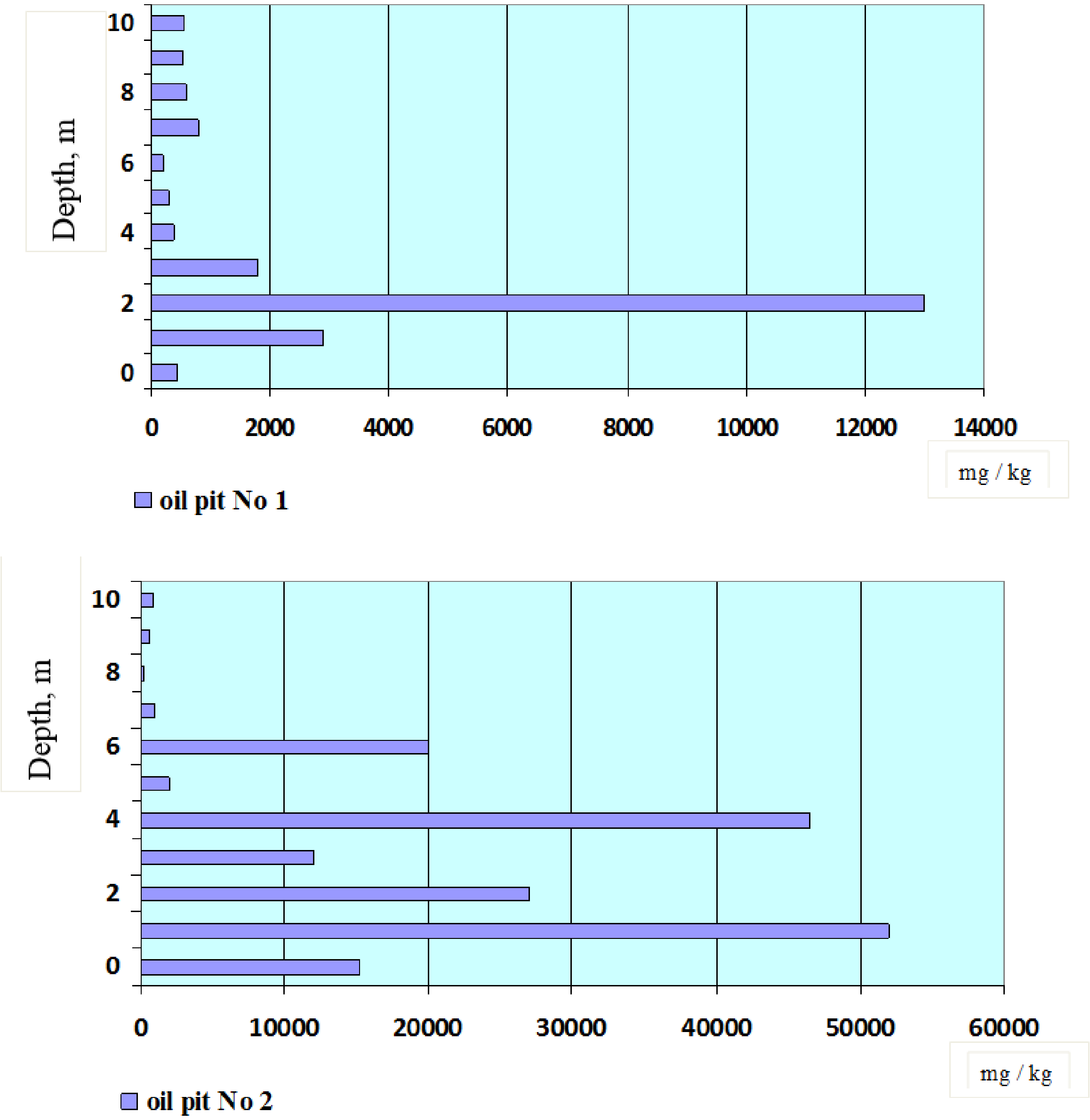

Figure 1 - The content of petroleum products in soil at different depths

The indicators presented in the figure show that the most polluted oil products in depth is also oil pit No. 2.

The results of laboratory tests of groundwater selected during the drilling of engineering and geological wells are presented in table 2.

Table 2 - The content of petroleum products in groundwater

MPCAw, mg / dm^3 (reservoirs of fishery significance)	MPCw, mg / dm^3 (reservoirs of household and cultural and domestic water use)	Contaminant content, mg / ^{dm3}	
		oil pit No. 1	oil pit No. 2
0,05	0,3	4,4	26,0

The standards for maximum permissible concentrations of pollutants in the water of fishery facilities are established by order of the Federal Agency for Fisheries dated January 18, 2010 No. 20.

The standards for maximum permissible concentrations of pollutants in the water of water bodies of domestic, drinking, and cultural and domestic water use (GN 2.1.5.1315-03) are established by the Resolution of the Chief State Sanitary Doctor of the Russian Federation of April 30, 2003. No. 78 [9].

The data in Table 2 indicate an excess of oil products in groundwater by 88 and 14.4 times for the 1st oil pit and 520 and 86.6 times for the 2nd oil pit, taking into account the fact that the Kizan River is both a fishery and household and cultural purposes.

It should be noted that the increased content of petroleum products in groundwater indicates their high migration activity. And since the unloading of groundwater occurs in the river Kizan there is a risk of these pollutants entering the river [10].

To determine the oil content in the water, samples were taken both from the shore and from the vessel. The results of laboratory tests of water samples are presented in table 3.

Table 3 - The content of petroleum products at various points of sampling

No.	Water sampling site	MPCAw, mg / dm^3 (reservoirs of fishery significance)	MPCw, mg / dm^3 (reservoirs of household and cultural and domestic water use)	Oil content in samples, mg / dm^3	
				ship samples (50m from the coast)	samples from the shore
1	River Volga upstream (200 m) from the river Kizan	0,05	0,3	0,02±0,02	-
2	River Volga downstream (200 m) from the river Kizan			0,03±0,02	-
3	River Kizan (beach, control)	0,05	0,3	0,06±0,02	0,06±0,02
4	oil pit No. 1			0,04±0,02	0,18±0,06
5	oil pit No. 2			0,05±0,02	0,21±0,07
6	500 m downstream			0,05±0,02	0,13±0,04
7	1000 m downstream			0,03±0,01	0,28±0,10

The results of the table indicate that in the Volga River, located at the 200th distance from the oil industry, the content of oil products in the water is below the MPC. But already in the control, both offshore and far from it, this indicator exceeds the MPC for fishery reservoirs by 0.01 mg / dm^3 and has the same values for both samples (0.06 ± 0.02 mg / dm^3).

In further samples, the results are dramatically different depending on the sampling points. The coastal part is characterized by an excess of the studied indicator relative to the MPC value for reservoirs of fishery value with a maximum at a distance of 1000m downstream from the 2nd oil well. For samples 50m from the coast, the situation is more favorable, since the content of petroleum products meets the standards.

Thus, the research results indicate the direct impact of Sokolovo oil on water pollution by oil products near the coast of the Kizan branch.

An important indicator of the ecological state of the catchment is the chemical composition of bottom sediments. Bottom river deposits, accumulating and concentrating petroleum hydrocarbons, resins, heavy metals, are a representative indicator of pollution. Knowledge of the natural concentrations of heavy metals in the bottom sediments of rivers makes it possible to judge the state of their purity or contamination [11]. The results of laboratory tests of samples of bottom sediments taken from the vessel by the grab bottom grab DG-0.16 are presented in table 4.

Table 4 - The content of petroleum products in bottom sediments at various points of sampling

No	Sampling point	Petroleum products, mg / kg
1	River Kizan (beach, control)	513,9±128,5
2	oil pit No. 1	14994,5±3748,6
3	oil pit No. 2	18719,3±4679,8
4	500 m downstream	807,7±201,9
5	1000 m downstream	474,8±118,7

As can be seen from the table, the maximum content of petroleum products (18719.3 ± 4679.8 mg/kg) in bottom sediments was observed in the area of oil pit No. 2, which exceeded the control variant by more than 36 times. The minimum value (474.8 ± 118.7 mg / kg) was recorded at a distance of 1000 m downstream from the test object, and in the control (beach) the value of this indicator was slightly higher ($P < 0.05$).

Thus, a gradual increase in pollution of bottom sediments by oil products from control to oil pit No. 2 is observed, after which the picture changes in the direction of decreasing this indicator. Consequently, there is a clear dependence of the impact of Sokolovo oil on pollution of bottom sediments by oil products of the adjacent water area.

Conclusion. The petroleum product indices at oil pit No. 1 (from 67500 to 133000 mg / kg) and No. 2 (from 104000 to 260,000 mg / kg) characterize the level of land pollution with chemicals as very high.

The maximum content of oil products is observed in the second oil pit at a depth of 1 and 4 m (51400 and 46100 mg / kg, respectively). For the first oil pit, the highest content of oil products was recorded at a depth of 2 m (13000 mg / kg), which characterizes the level of land pollution with chemicals as very high and medium [12].

At the Volga River, located 200th from oil, the oil content in the water is below the MPC, although this indicator exceeds the MPC for fishery reservoirs by 0.01 mg / dm^3 and has the same values for both samples (0.06 ± 0.02 mg / dm^3). Away from the coast, the studied indicator is characterized by an excess relative to the MPC value for reservoirs of fishery value with a maximum at a distance of 1000 m from the 2nd oil pit. For samples from water (from a vessel), the content of petroleum products meets the standards.

The content of oil products in groundwater is 88 and 14.4 times higher than those for first oil pit and 520 and 86.6 times for second oil pit, taking into account the fact that the Kizan River is a reservoir of fishery, household and cultural purposes [13].

The maximum content of petroleum products (18719.3 ± 4679.8 mg / kg) in bottom sediments was observed in the area of oil pit No. 2, which exceeded the control variant by more than 36 times. The minimum value (474.8 ± 118.7 mg / kg) was recorded at a distance of 1000 m downstream from the test object.

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ЕДІЛ ӨЗЕНІНІҢ ЖАҒАЛАУЫНДА ҚАЛДЫҚТЫ ТОҒАНДА ОРНАЛАСҚАН АЙМАҚТА ТОПЫРАҚ ЖӘНЕ СУ ОБЪЕКТІЛЕРІНДЕ МҰНАЙ ӨНІМДЕРІНІҢ ҚҰРАМЫН БАҒАЛАУ

Аннотация. Мақалада Еділ өзені мен Астрахань облысының Еділ бойындағы Кизан тармағының жанындағы мұнай қалдықтары қоймаларындағы мұнай өнімдерінің сандық құрамы бағаланады. Соколоводағы шұңқырлар бір кездері мұнай, керосин, мазут және басқа да мұнай өнімдерін уақытша сақтайтын көлбеу қабырғалары бар жер қазбалары болған мұнай өнімдерін сақтауға арналған. Топырақ үлгілерін зерттеу екі шұңқырда және жер асты суларында, жер асты сулары мен түбіндегі шөгінділерде әртүрлі тереңдікте жүргізілді. Зерттелген екі ұңғыманың екінші ұңғымада максималды жоғарылау 104-тен 260 есеге дейін, ал бірінші ұңғымада мұнайдың мөлшері 67,5-тен 133-ке дейін байқалды. Сондай-ақ, ауыр металдардың құрамы шекті рауалды мөлшерден асып кетті, мысалы, жалпы хром 168 есе және 2040 есе, мышьяк 1,7 есе және бірінші ұңғымаларда сәйкесінше 2,6 есе. Бұл жағдайда ең қауіпті - бұл хром, ол улы, тітіркендіргіш, кумулятивті, аллергиялық, канцерогендік және мутагендік әсерге ие. Топырақтағы мұнай өнімдерінің мөлшері екінші ұңғымада 1 м тереңдікте 51400 мг / кг-ға дейін және 4 м тереңдікте - 461000 мг/кг дейін жоғарылауымен сипатталады, сонымен қатар жер бетінде мұнай өнімдерінің мөлшері 15000 мг / кг, 2 метр тереңдікте 27000 мг / кг, 6 м тереңдікте - 20 000 мг / кг тең. Алғашқы мұнай құятын ыдыста 2 м тереңдігі 13000 мг / кг мұнай өнімдерінің ең көп мөлшері сипатталады, бұл 2 мұнай құятын қоймадағы ең көп мөлшерден 3 есе төмен. 1 және 3 метр тереңдікте майдың мөлшері 2000 мг / кг құрайды, басқа тереңдікте - 0, 4, 5, 6, 7, 8, 9, 10 метр, олар 1000 мг / кг-дан аз. Екінші мұнай резервуарында 2000 мг / кг-нан төмен топырақтағы мұнай өнімдерінің құрамы тек 7-ден 10 метр тереңдікте болады.

Жер асты суларын зерттеу нәтижелері бойынша мұнайдың құрамы 1-ші ұңғыма үшін 88 және 14,4 еседен, ал 2-ші ұңғымадан 520 және 86,6 еседен асады. Жер асты суларындағы мұнай өнімдерінің жоғарылауы олардың көші-қон белсенділігінің жоғары екендігін көрсетеді. Өзенде жер асты суларының түсуі орын алады. Кизанда осы ластаушы заттардың өзенге ену қаупі бар. Мұнай өнеркәсібінен 200-қашықтықта орналасқан Волга өзенінің учаскесінде судағы мұнай мөлшері ШРМ-нен төмен, дегенмен, жағалаудан алыс жерде, зерттелген көрсеткіш 2-ші мұнай резервуарынан максималды 1000 м қашықтықта балық аулау су қоймалары үшін ШРМ мәнінен жоғары. Төменгі шөгінділердегі мұнай өнімдерінің максималды мөлшері (18719,3 ± 4679,8 мг / кг) №2 мұнай резервуарының аумағында байқалды, бұл бақылау нұсқасынан 36 есе асып түсті. Ең төменгі мәні (474,8 ± 118,7 мг / кг) сынақ объектісінен 1000 м қашықтықта тіркелді, ал бақылауда (жағажайда) бұл көрсеткіш шамалы жоғары болды ($P < 0.05$). Осылайша, мұнай шөгінділерінің мұнай өнімдерімен бақылаудан №2 мұнай резервуарына дейін ластануының біртіндеп артуы байқалады, содан кейін көрініс осы көрсеткіштің төмендеуіне қарай өзгереді. Демек, Соколовское мұнайының әсер етуінің түбіндегі шөгінділерді іргелес су аймағының мұнай өнімдерімен ластануына айқын тәуелділігі бар.

Қорытындылай келе, зерттеу нәтижелері №1 мұнай кеніштеріндегі мұнай өнімдерінің көрсеткіштері (67,500-ден 133 000 мг / кг-ға дейін) және №2 (104 000-нан 260 000 мг / кг-ға дейін) жердің химиялық заттармен ластану деңгейінің өте жоғары екенін сипаттайды. Мұнай өнімдерінің ең көп мөлшері екінші мұнай кенішінде 1 және 4 м тереңдікте байқалады (сәйкесінше 51400 және 46100 мг / кг). Алғашқы мұнай резервуарда мұнай өнімдерінің ең жоғары мөлшері 2 м (13000 мг / кг) тереңдікте тіркелді, бұл жердің химиялық заттармен ластану дәрежесін өте жоғары және орташа деп сипаттайды. Мұнайдан 200-ші жерде орналасқан Волга өзенінің суында мұнай құрамы ШРМ-ден төмен, дегенмен бұл көрсеткіш балық шаруашылығы су айдындары үшін ШРМ-ден 0,01 мг / дм^{3}-ге асады және екі үлгі үшін де бірдей (0,06 ±) 0,02 мг / дм^{3}). Кизан өзенінің балық шаруашылығы, тұрмыстық және мәдени мақсаттағы су қоймасы болғандығын ескере отырып, жер асты суларындағы мұнай өнімдерінің мөлшері бірінші мұнай кенішіне қарағанда 88 және 14,4 есе, 2 резервуарда 520 және 86,6 есе жоғары.

Төменгі шөгінділердегі мұнай өнімдерінің максималды мөлшері (18719,3 ± 4679,8 мг / кг) №2 мұнай резервуарының аумағында байқалды, бұл бақылау нұсқасынан 36 есе асып түсті. Ең төменгі мәні (474,8 ± 118,7 мг / кг) сынақ объектісінен 1000 м қашықтықта тіркелді. Зерттеу нәтижелері екінші ұңғыманың ең көп ластанғанын көрсетеді.

Түйін сөздер: мұнайқалдықты тоған, мұнай өнімдері, ауыр металдар, шекті рауалды мөлшер, топырақ, жер асты сулары, су түбіндегі шөгінділер.

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ОЦЕНКА СОДЕРЖАНИЯ НЕФТЕПРОДУКТОВ В ПОЧВЕННЫХ И ВОДНЫХ ОБЪЕКТАХ В РАЙОНЕ РАСПОЛОЖЕНИЯ ШЛАМОНАКОПИТЕЛЕЙ НА ПОБЕРЕЖЬЯХ РЕКИ ВОЛГА

Аннотация. В статье дана оценка по количественному составу нефтепродуктов в местах хранения отходов нефти в районе слияния реки Волга и ее рукава Кизань Приволжского района Астраханской области. Нефтяные ямы в Соколово в свое время были предназначены для хранения нефтепродуктов, представляющие собой земляные выемки с наклонными стенками, где временно хранили нефть, керосин, мазут и прочие нефтепродукты. Были проведены исследования проб почвы на разных глубинах в двух ямах и подземных, грунтовых вод и донных отложений. В исследуемых двух ямах отмечается максимальное превышение от 104 до 260 раз во второй яме, тогда как в первой яме содержание нефтепродуктов превышает от 67,5 до 133 раз. По содержанию тяжелых металлов также отмечается превышение предельно-допустимой концентрации, например, по хрому общему в 168 раз и в 2040 раз и по мышьяку в 1,7 раз и 2,6 раз соответственно в первой и второй ямах. Наиболее опасным при этом является хром, который очень токсичен, оказывая отравляющее, раздражительное, кумулятивное, аллергическое, канцерогенное и мутагенное действие. Содержание нефтепродуктов в почве характеризуется повышенным содержание во второй яме на глубине 1 м до 51400 мг/кг и на глубине 4 м – 461000 м. При этом на поверхности земли содержание нефтепродуктов составляет 15000 мг/кг, на глубине 2 метров 27000 мг/кг, на глубине 6 м – 20000 мг/кг. В первой нефтеяме самым максимальным содержанием нефтепродуктов характеризуется глубина 2 м с 13000 мг/кг, что более чем в 3 раза ниже максимального содержания во 2 нефтеяме. На глубине 1 и 3 метров содержание нефтепродуктов составляет около 2000 мг/кг, на других глубинах – 0, 4, 5, 6, 7, 8, 9, 10 метрах они составляют менее 1000 мг/кг. Во второй нефтеяме содержание нефтепродуктов в почвогрунте ниже 2000 мг/кг характерно только на глубинах от 7 до 10 метров.

По результатам исследований подземных вод содержание нефтепродуктов превышает в 88 и 14,4 раз для 1-ой нефтеямы и 520 и 86,6 раз для 2-ой ямы. Повышенное содержание нефтепродуктов в грунтовых водах говорит о высокой их миграционной активности. И так как разгрузка грунтовых вод происходит в р. Кизань, существует угроза попадания этих загрязнений в реку. На участке р.Волга, находящейся в 200-ом отдалении от нефтеям, содержание нефтепродуктов в воде ниже ПДК, однако в**дали от берега характерно превышение исследуемого показателя относительно значения ПДК для водоемов рыбохозяйственного значения с максимумом на расстоянии 1000м от 2-ой нефтеямы.** Максимальное содержание нефтепродуктов (**18719,3±4679,8 мг/кг**) в донных отложениях отмечалось в районе нефтеямы №2, что превосходило контрольный вариант более чем в 36 раз. Минимальное значение (**474,8±118,7 мг/кг)** было зарегистрировано на расстоянии 1000м по течению от исследуемого объекта, причем в контроле (пляж) величина данного показателя была несколько выше ($P < 0,05$). Таким образом, наблюдается постепенное нарастание загрязнения донных отложений нефтепродуктами от контроля до нефтеямы №2, после чего картина меняется в сторону снижения данного показателя. Следовательно, прослеживается четкая зависимость воздействия Соколовских нефтеям на загрязнение донных отложений нефтепродуктами прилегающей водной площади.

В заключении, результаты исследований показывают, что показатели содержания нефтепродуктов на нефтеямах №1 (от 67500 до 133000мг/кг) и №2 (от 104000 до 260000мг/кг) характеризуют уровень загрязнения земель химическими веществами как очень высокий. Максимальное содержание нефтепродуктов наблюдается во второй нефтеяме на глубине 1 и 4 м (51400 и 46100 мг/кг, соответственно). Для первой нефтеямы наибольшее содержание нефтепродуктов зарегистрировано на глубине 2м (13000 мг/кг), что характеризует уровень загрязнения земель химическими веществами как очень высокий и средний. На участке р.Волга, находящейся в 200-ом отдалении от нефтеям, содержание нефтепродуктов в воде ниже ПДК, хотя данный показатель превышает ПДК для водоемов рыбохозяйственного значения на 0,01 мг/ дм^3 и имеет для обеих проб одинаковые значения (**0,06±0,02 мг/дм^3).** Содержания нефтепродуктов в подземных водах в 88 и 14,4 раз превышают таковые для 1 нефтеямы и 520 и 86,6 раз для 2 ямы с учетом того, что р.Кизань является как водоемом рыбохозяйственного, так хозпитьевого и культурно-бытового назначения [13].

Максимальное содержание нефтепродуктов (**18719,3±4679,8 мг/кг**) в донных отложениях отмечалось в районе нефтеямы №2, что превосходило контрольный вариант более чем в 36 раз. Минимальное значение (**474,8±118,7 мг/кг)** было зарегистрировано на расстоянии 1000м по течению от исследуемого объекта. Результаты исследований показывают, что наиболее загрязненной является вторая яма.

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SYNTHESIS AND STRUCTURED N-ACYL AND THIOUREA DERIVATIVES CITIZINE AND ANABAZINE

Abstract. This work presents the results of studies on the chemical transformation of the alkaloids molecules cytisine and anabazine to obtain their N-cinnamoyl derivatives, as well as possible ways for their further modification. The optimal conditions for the preparation of N-cinnamoylcytisine and N-cinnamoylanabazine in the acylation reactions of alkaloids with cinnamoyl chloride are considered. Hydrazinolysis of the resulting N-cinnamoylcytisine and N-cinnamoylanabazine was carried out. It was shown that the interaction of acrylamide derivatives of alkaloids with hydrazine hydrate in ethanol leads to the formation of the corresponding pyrazole derivatives resulting from the intramolecular cyclocondensation of hydrazones of N-cinnamoyl derivatives. By the interaction of cinnamoylisothiocyanate with the above alkaloids, new thiourea derivatives are synthesized. The structures of the synthesized compounds were studied by ^{1}H and ^{13}C NMR spectroscopy, as well as by the data of two-dimensional spectra of COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C). The values of chemical shifts, multiplicity, and integrated intensity of ^{1}H and ^{13}C signals in one-dimensional NMR spectra were determined. Using spectra in the formats COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C), homo- and heteronuclear interactions were established, confirming the structure of the studied compounds.

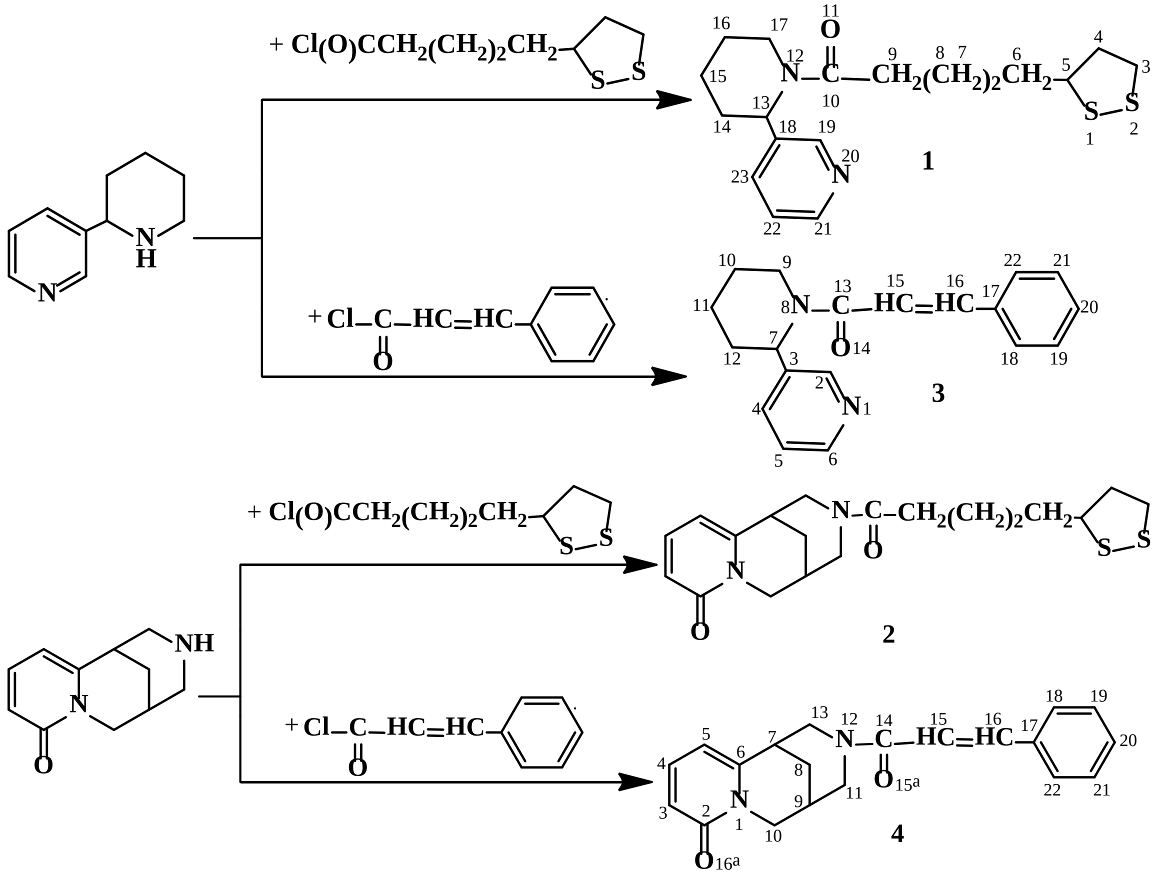
Key words: alkaloid, cytisine, anabazine, chemical transformation, N-acyl moiety, acid chloride.

Introduction

Interest in research on the chemical transformation of the alkaloids cytisine and anabazine is due to the wide spectrum of biological activity of their derivatives. To date, a large number of derivatives of alkaloids of cytisine and anabazine with various groups at the nitrogen atom have been synthesized [1-13]. The development of research on the search for new bioactive compounds has prompted us to synthesize a number of cinnamoyl derivatives of the above alkaloids. Many cinnamoyl derivatives are recommended for use as promising drugs for the treatment and / or prevention of arterial and/or venous thrombosis, acute coronary syndromes, restenosis, stable angina, cardiac arrhythmias, myocardial infarction, hypertension, heart failure, stroke [14, 15]. Lipoic acid (lipoate, vitamin N) is an important antioxidant; it plays the role of coenzyme in oxygen metabolism, especially in the pyruvate dehydrogenase complex [16]. The work of a number of researchers showed [14] that, when a hydrogen atom is replaced with nitrogen by acyl radicals, toxicity decreases and interesting biological properties manifest. There is a report in the literature of the authors of [17] who studied the reaction of the interaction of cytisine with cinnamic acid chloride in toluene, and the final product was obtained in low yield (45%). In the literature there is no information about obtaining a similar derivative of anabazine.

Results and discussions

Continuing studies on the modification of the cytisine and anabazine molecules, we synthesized their new acyl derivatives by reaction with acid chlorides of 5-[(3R)-dithiolan-3-yl]pentanoic (lipoic) and 3-phenylacrylate (cinnamoyl chloride) acids. The acylation reactions were carried out in absolute benzene in the presence of triethylamine under cooling. As the results of studying these reactions have shown, the interaction reactions in benzene proceed smoothly and lead to the formation of N-acyl derivatives of anabazine **1**, **3** and cytisine **2**, **4** with satisfactory yields.



The synthesized compounds **1**, **2** are oils, and **3**, **4** are white crystalline substances readily soluble in organic solvents.

The structure of compounds **1-4** was confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy, two-dimensional spectra of COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C).

In the IR spectra of compounds **1-4**, the absorption bands of amide carbonyl appear in the regions of 1648 and 1643 cm^{-1}, respectively.

In the ^{1}H NMR spectrum of compound **1** in a broadband, high-field, twelve-proton multiplet at 1.05-1.83 ppm the alicyclic and aliphatic protons N-16, 16, 15, 15, 14, 14, 8, 8, 6, 6, 4, 4 were located. In a four-proton multiplet at 2.35-2.43 ppm the aliphatic protons H-7, 7, 9, 9 were located. In the broadened singlet signals, H-17ax protons, 3.58 - H-5, 3.75 - H-17eq, 5.76 - H-13 and 7.34 ppm were located at 2.82. - H-22. The remaining protons were located in multiplet signals at 3.09-3.14 (2H, H-3, 3), 7.53–7.55 (1H, H-23), and 8.37-8.42 ppm. (2H, H-19, 21).

In the ^{13}C NMR spectrum of compound **1**, the signals of the dithiolan fragment appeared at 38.64 (C-3), 40.02 (C-4) and 56.74 (C-5) ppm. The carbon atoms of the aliphatic chain appeared at 25.21 (C-8), 27.55 (C-7), 32.88 (C-9) and 34.76 (C-6) ppm. The carbon nuclei of the piperidine and pyridine nuclei resonated at 26.01 (C-16), 29.03 (C-14), 42.06 (C-17), 48.96 (C-13), 124.11 (C-22), 134.95 (C-23), 135.60 (C-18), 148.11 (C-19) and 148.65 (C-21) ppm. Carbon atoms of the carbonyl group C-10 were observed at 172.05 ppm.

The structure of compound **1** was also confirmed by two-dimensional HMQC NMR spectroscopy (^{1}H-^{13}C), which allows one to establish spin-spin interactions of a heteronuclear nature (Fig. 1). The observed correlations in the molecule are presented in the diagram. Heteronuclear interactions of protons with carbon atoms through one bond were established using ^{1}H-^{13}C HMQC spectroscopy for the following pairs present in the compound: H^{14}-C^{14} (1.39, 29.71), H^{15}-C^{15} (1.53, 20.41), H^8-C^8 (1.52, 25.70), H^6-C^6 (1.53, 35.53), H^4-C^4 (1.83, 40.03, H^9-C^9 (2.44, 33.48), H^{17}-C^{17} (2.83, 42.69), H^5-C^5 (3.59, 57.33), H^{17}-C^{17} (3.80, 42.60), H^{13}-C^{13} (5.76, 49.54), H^{22}-C^{22} (7.35, 124.57), H^{23}-C^{23} (7.55, 135.36), $H^{19,21}$-$C^{19,21}$ (8.43, 148.45).

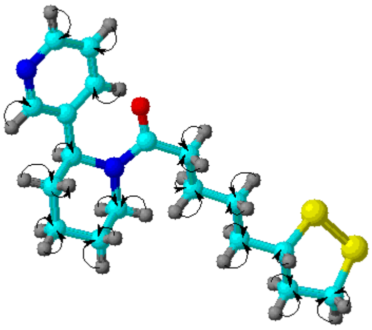


Figure 1 – The correlation scheme in the spectrum of HMQC compound **1**

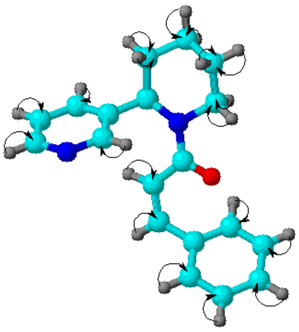


Figure 2 – The correlation scheme in the spectrum of HMQC compound **3**

From an analysis of ^{1}H NMR spectra of N-cinnamoylanabazine (**3**) and N-cinnamoylcytisine (**4**), one can assume the presence of several N-CO and CO-CH = CH-C_6H_5 isomers rotational in bonds. Since the barriers of these rotations are not large, they can lead to both the registration of spectra from several conformers and simply to a substantial broadening of the lines of the spectrum. In some cases, this did not allow the unambiguous assignment of signals.

The ^{1}H NMR spectrum of compound **3** was studied in most detail, where the piperidine cycle signals manifested themselves as multiplets at 1.30-1.42 (1H, H^{11ax}), 1.54-1.57 (2H, $H^{11eq,10ax}$), 2.36-2.46 (1H, H^{12ax}) and 3.43-3.46 (1H, H^{9ax}) ppm and broadened singlets at 1.79 (1H, H^{10eq}), 2.87 (1H, H^{12eq}), 4.22 (1H, H^{9eq}) and 5.87 (1H, H^7) ppm. Unsaturated aliphatic protons H15 and H16 resonated with a multiplet in the region of 7.56–7.69 ppm. Aromatic phenyl and pyridine protons manifested themselves as multiplets at 7.30-7.34 (5H, $H^{5,18,19,21,22}$), 7.56-7.69 (2H, $H^{4,20}$) and 8.44-8.47 (2H, $H^{2.6}$) ppm.

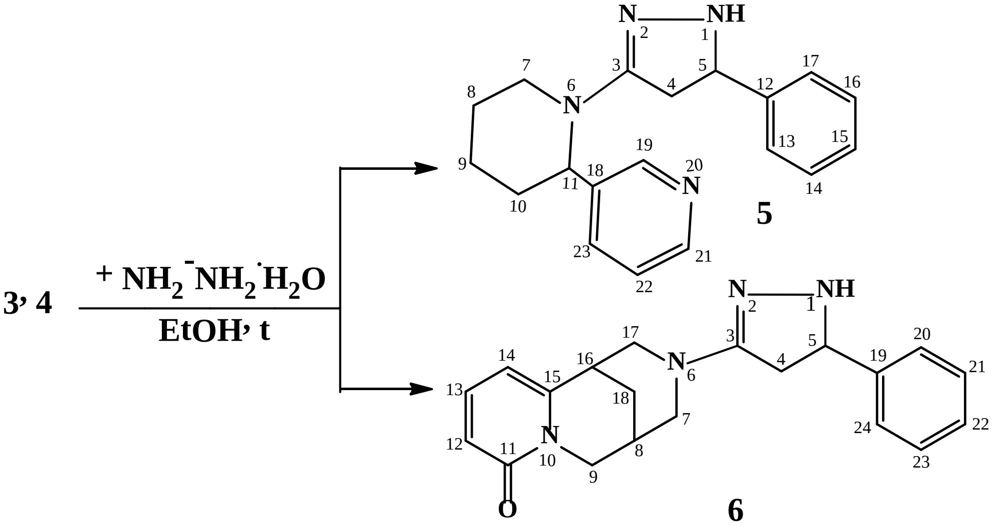
In the ^{13}C NMR spectrum of compound **3**, the signals of the carbon atoms of the piperidine ring appeared at 19.72 (C^{11}), 26.19 (C^{10}), 27.61 (C^{12}), 48.23 (C^9) and 49.84 (C^7) ppm. The carbon atoms of the phenyl and pyridine fragments are observed at 124.13 (C^5), 128.58 (C^3), 128.80 (C^{20}), 129.23 ($C^{19,21}$), 130.05 ($C^{18,22}$), 134.92 (C^4), 135.68 (C^{17}), 148.28 (C^6) and 148.65 (C^2) ppm. Signals with chemical shifts at 118.83 and 142.68 ppm. correspond to carbon atoms in the double bond of C^{15} and C^{16}, respectively. In the field of a weak field at 166.27 ppm the carbon atoms of the C^{13} carbonyl group were resonated.

The structure of compound **3** was also confirmed by two-dimensional HMQC NMR spectroscopy (^{1}H-^{13}C), which allows one to establish spin-spin interactions of a heteronuclear nature (Figure 2). The observed correlations in the molecule are presented in the diagram. Heteronuclear interactions of protons with carbon atoms through one bond were established using 1H-13CHMQC spectroscopy for the following pairs present in the compound: H^{11}-C^{11} (1.56, 20.37), H^{10}-C^{10} (1.60, 26.65), H^{12}-C^{12} (2.34, 28.02), H^9-C^9 (4.24, 42.78), H^7-C^7 (5.90, 50.36), H^5-C^5 (7.31, 124.58), $H^{18,19,20,21,22}$-$C^{18,19,20,21,22}$ (7.28, 129.33), H^{15}-C^{15} (7.60, 119.22), H^4-C^4 (7.55, 135.27), H^{16}-C^{16} (7.56, 143.13) и $H^{2,6}$-$C^{2,6}$ (8.45, 148.86).

The chemical shifts of the cinnamoyl moieties associated with the anabazine and cytisine groups are similar in the ^{1}H and ^{13}C NMR spectra. A slight predominance of the mesmeric effect of the cytisine fragment leads to a slight shift to the weakly field region of the signals of the cinnamoyl fragments in compound **4** as compared with derivative **3**. Thus, the olefin protons of the cinnamoyl group H^{15} and H^{16} of compound **4** appear at 6.49-6.75 and 7.16-7.64 ppm. respectively, whereas similar olefin protons of compound **3** resonate in one region at 7.56-7.69 ppm. The same situation is observed for free-standing C^{13} carbonyl atoms: in the spectrum of compound **3**, they appeared at 166.27 ppm, and in the case of compound **4**, at 165.65 ppm.

The cyclocondensation reaction of hydrazines with α, β-unsaturated ketones is an important synthetic approach to the preparation of 1,2-azoles. Some pyrazole derivatives exhibit the properties of analgesics and platelet aggregation inhibitors [18], have a strong antibacterial [19] and anesthetic [20] effect.

In order to further study the properties and possibilities of transformation of the obtained N-cinnamoylanabazine (**3**) and N-cinnamoylcytisine (**4**), we studied their interaction with hydrazine hydrate. It was found that the interaction of acrylamide derivatives **3**, **4** with hydrazine hydrate in ethanol leads to the formation of the corresponding pyrazole derivatives **5** and **6**, which are formed, possibly as a result of intramolecular cyclocondensation of the intermediate hydrazones formed.



In the ^{1}H NMR spectrum of compound **6** in the most strongly field region of the spectrum at 1.87-1.99 ppm two-proton multiplet manifested cytisine protons H-18. In the broadband multiplet at 2.25-3.33 ppm the six-proton multiplet resonated with the cytisine protons H-8, H-16 and H-7 and the pyrazole protons H-4. In the next five-proton multiplet at 3.58-4.63 ppm. the cytisine protons H-17 and H-9 and the other pyrazole proton H-5 were located. At 6.11-6.20 ppm protons H-12 and H-14 of the pyrazole ring resonated with a two-proton multiplet. In the seven-proton multiplet at 6.97-7.64 ppm housed the cytisine proton H-13, the proton of the amino group H-1 and the aromatic protons H-20-24.

In the ^{13}C NMR spectrum of compound **6**, the signals of carbon atoms of cytisine rings are observed at 25.80 (C-18), 27.52 (C-8), 33.76 (C-16), 48.75 (C-9), 49.18 (C-7), 51.21 (C-17), 105.27 (C-14), 116.31 (C-12), 139.30 (C-13), 150.19 (C-15) and 170.85 (C-11) ppm. Signals with chemical shifts at 34.79, 52.82, and 162.64 ppm. correspond to carbon atoms C-4, C-5 and C-3, respectively. Carbons of the aromatic ring appeared at 126.32 (C-22), 128.51 (C-21, 23), 129.25 (C-20, 24) and 141.62 (C-19) ppm.

The structure of compound **6** was also confirmed by two-dimensional HMQC (^{1}H-^{13}C) NMR spectroscopy, which allows one to establish spin-spin interactions of a heteronuclear nature. The observed correlations in the molecule are shown in Figure 3. Heteronuclear interactions of protons with carbon atoms through one bond were found for pairs: H^{18}-C^{18} (1.88, 26.44), H^8-C^8 (2.44, 28.40), H^{16}-C^{16} (2.52, 34.62), H^7-C^7 (2.74, 48.79), H^4-C^4 (3.10, 34.89), H^5-C^5 (4.22, 53.55), H^{17}-C^{17} (4.43, 51.92), H^9-C^9 (4.53, 48.45), H^{14}-C^{14} (6.15, 105.77), H^{12}-C^{12} (6.21, 117.00), $H^{21,23}$-$C^{21,23}$ (7.09, 129.08), H^{22}-C^{22} (7.12, 126.67), $H^{20,24}$-$C^{20,24}$ (7.32, 129.32) и H^{13}-C^{13} (7.28, 139.80).

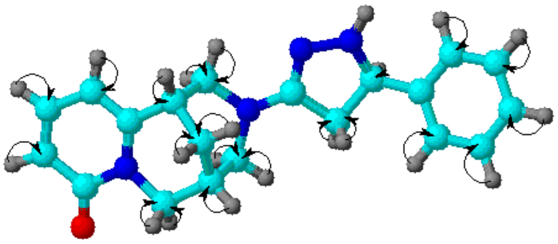
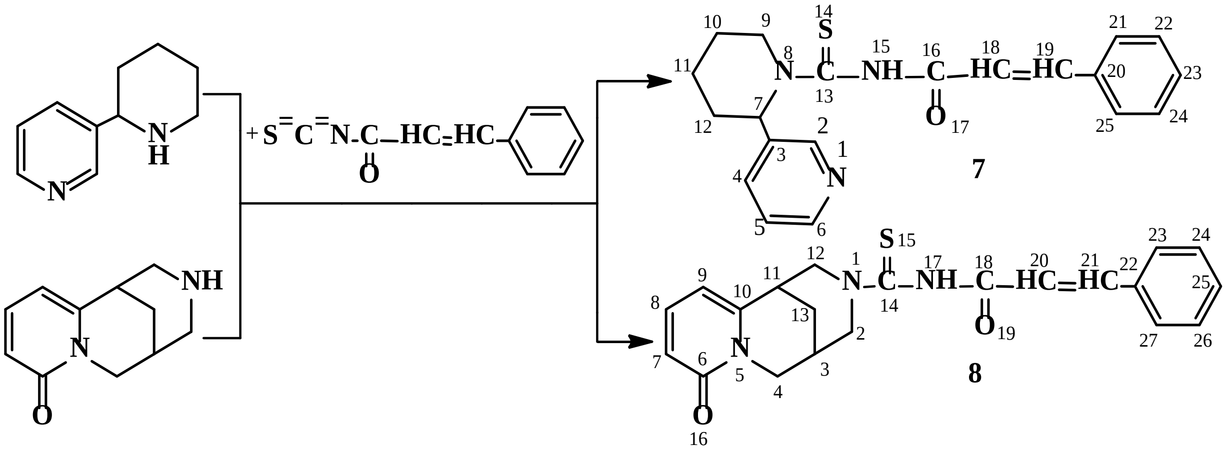


Figure 3 – The correlation scheme in the spectrum of HMQC compound **6**

NMR spectroscopic study of the obtained pyrazole derivatives **5** and **6** showed that the anabazine and cytisine fragments mainly retain their regions of chemical shifts in the ^{1}H and ^{13}C NMR spectra upon transition from cinnamoyl derivatives to pyrazole.

In order to expand the possibility of functionalization of cytisine and anabazine molecules, it was interesting to synthesize new thiourea derivatives **7**, **8** by interaction with cinnamoylisothiocyanate. Cinnamoylisothiocyanate was prepared by reacting cinnamic acid chloride with potassium thiocyanate in acetone under heating. The obtained cinnamoylisothiocyanate reacted with anabazine and cytisine to form the corresponding derivatives **7** and **8**.



The resulting target products **7**, **8** are well crystallized white crystalline substances with moderate solubility in organic solvents.

The structure and individuality of the synthesized compounds **7**, **8** were confirmed by IR, ^{1}H NMR spectroscopy and thin-layer chromatography.

In the IR spectra of the synthesized compounds **7**, **8**, there is an absorption band in the region of 1465 and 1550 cm^{-1}, characteristic of the C=S group, absorption bands of the amide group of C(O)NH appear in the region of 1691 and 1689 cm^{-1}. The intense spectrum of the amide group (N-C=O) cytisine alkaloid in the 1648 cm^{-1} region is present in the IR spectrum of compound **8**.

In the ^{1}H NMR spectrum of compound **7**, the piperidine cycle signals manifested themselves as multiplets at 0.99-1.00 (H^{10ax}), 1.31-1.34 (H^{11ax}), 2.52-2.55 (^{H12eq}) and 3.00-3.05 (H^{9ax}) ppm. Unsaturated protons H^{18} and H^{19} resonated with doublets at 6.87 (^{3}J 16.0 Hz) and 7.65 (^{3}J 15.6 Hz) ppm. Aromatic phenyl and pyridine protons were manifested by broadened singlets at 7.39 (H^{5,22,23,24}), 7.86 (H^{4}) and 8.66 (H^{2}) and doublets at 7.58 (H^{21,25}, ^{3}J 6.4 Hz) and 8.47 (H^{6}, ^{3}J 4.1 Hz) ppm The proton of the H^{15} amide bond resonated with a broadened singlet in the weakest field of the spectrum at 10.85 ppm.

In the ^{13}C NMR spectrum of compound **7**, the signals of the carbon atoms of the piperidine cycle appeared at 18.99 (C^{11}), 26.02 (C^{10}), 27.49 (C^{12}), 48.27 (C^{9}) and 59.00 (C^{7}) ppm. Carbon atoms of the phenyl fragment are observed at 128.49 (C^{21,25}), 129.60 (C^{22,24}), 130.83 (C^{23}) and 133.35 (C^{20}) ppm. The carbon atoms of the pyridine ring resonated at 124.11 (C^{5}), 134.93 (C^{3,4}), 148.52 (C^{2}) and 148.65 (C^{6}) ppm. Signals with chemical shifts at 120.80 and 143.27 ppm correspond to carbon atoms in the double bond of C^{18} and C^{19}, respectively. In the field of a weak field at 162.64 and 181.61 ppm. the amide and thioamide carbon atoms of C^{16} and C^{13} resonated, respectively.

The structure of compound **7** was also confirmed by two-dimensional NMR spectroscopy HMQC (^{1}H-^{13}C). The proposed correlation scheme is presented in the scheme.

In the analysis of ^{1}H NMR spectra of compounds **7**, **8**, characteristic proton signals for the alkaloid part are observed. Moreover, the anabazine and cytisine fragments mainly retain their regions of chemical shifts in the ^{1}H and ^{13}C NMR spectra, as is the case with cinnamoyl compounds **3**, **4** and pyrazole **5**, **6** nature.

Thus, for the first time, we obtained new N-acyl and thiourea derivatives of anabazine and cytisine, investigated the possibilities of their further chemical transformation into new potentially bioactive substances.

Experimental part

^{1}H and ^{13}C NMR spectra of compounds **1-8** were recorded on a JNM-ECA Jeol 400 spectrometer (frequencies 399.78 and 100.53 MHz, respectively) using a DMSO-d_6 solvent. Chemical shifts are measured relative to the signals of residual protons or carbon atoms of DMSO-d_6. The reaction progress and the purity of the obtained compounds were monitored by thin layer chromatography on SilufolUV-254 plates in isopropyl alcohol-ammonia-water 7:2:1, ethanol-chloroform 1:4 systems. The plates showed iodine vapor. The reaction products were isolated by recrystallization or column chromatography on alumina. All solvents used in the work were purified and absolutized by standard methods [21].

General procedure for the preparation of N-lipoylanabazine (1) and N-lipoylcytisine (2). To a solution of 1.425 g (8.78 mmol) of anabazine or 1.67 g (8.78 mmol) of cytisine, 1.22 ml (8.78 mmol) of triethylamine in 50 ml of benzene, a solution of 1.974 g (8.78 mmol) of lipoyl chloride [obtained from 4.5 g (21.95) was added with stirring mmol) of lipoic acid and 3.264 g (27.43 mmol) of thionyl chloride] dissolved in 25 ml of benzene. The reaction mixture was stirred for 3 hours at room temperature until a precipitate formed. The precipitate was filtered off, the mother liquor was evaporated, the residue was chromatographed on silica gel (eluent: benzene-chloroform). 0.92 g (64.56%), lipoylanabazine (**1**) and 1.28 g (76.60%), lipoylcytisine (**2**) were isolated as yellowish thick oils.

N-Cinnamoylanabazine (3). To a solution of 3 g (18.49 mmol) of anabazine in 150 ml of benzene, 2.57 ml (18.49 mmol) of triethylamine and a solution of 3.08 g (18.49 mmol) of cinnamoyl chloride in 50 ml of benzene were added with stirring. The reaction mixture was stirred for 3 hours at room temperature until a precipitate formed. The precipitated precipitate of triethylamine hydrochloride was filtered off, the mother liquor was evaporated, and the residue was chromatographed on alumina (eluent benzene, benzene-ethyl acetate, 100:1). Received 2.87 g (95.6%), N-cinnamoylanabazine (**3**) in the form of white crystals with so m.p. 95-98°C.

N-Cinnamoylcytisine (4). To a solution of 1.14 g (6.0 mmol) of cytisine in 50 ml of benzene, 0.6 g (6.0 mmol) of triethylamine and a solution of 1 g (6.0 mmol) of cinnamoyl chloride in 20 ml of benzene were added with stirring. The reaction mixture was stirred for 3.3 hours at room temperature until a precipitate formed. The precipitate of triethylamine hydrochloride was filtered off, the mother liquor was evaporated, and the residue was treated with diethyl ether. Obtained 0.95 g (95%), N-cinnamoylcytisine (**4**) in the form of a white powder with a yellowish tinge with so pl. 130-134°C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.86-1.97 m (2H, $H^{8,8}$), 2.44 expanded singlet (1H, H^{9}), 2.90-3.40 m (3H. $H^{7,11ax,13ax}$), 3.63-3.97 m (2H, $H^{10ax,10eq}$), 4.24-4.65 m (2H, $H^{11eq,13eq}$, 6.14 d (2H, $H^{3,5}$. ^{3}J 6.1), 6.49-6.75 m (1H, H^{15}), 7.16-7.64 m (7H, $H^{4,15,18\text{-}22}$). ^{13}C NMR spectrum, δ_C, ppm: 25.95 (C^{8}), 27.86 (C^{9}), 35.13 (C^{7}), 49.05 (C^{10}), 51.31 (C^{11}), 53.04 (C^{13}), 105.29 (C^{5}), 116.40 (C^{3}), 128.85 (C^{15}), 129.24 ($C^{18,19,21,22}$), 129.99 (C^{20}), 135.55 (C^{4}), 139.09 (C^{16}), 141.32 (C^{17}), 150.47 (C^{6}), 162.66 (C^{2}), 165.65 (C^{14}) ppm. Cross peaks of HMQC NMR spectra (^{1}H-^{13}C), ppm: H^{8}-C^{8} (1.96, 26.60), H^{9}-C^{9} (2.44, 28.48), H^{7}-C^{7} (3.13, 35.65), H^{10ax}-C^{10ax}(3.59, 49.56), H^{10ax}-C^{10ax}(3.98, 49.58), H^{5}-C^{5} (6.14, 105.76), H^{3}-C^{3} (6.12, 116.82) и $H^{18,19,21,22}$-$C^{18,19,21,22}$ (7.37, 129.52).

1-(5-Phenyl-4,5-dihydro-1H-pyrazol-3-yl)anabazine (5). 2.33 g (7.97 mmol) of N-cinnamoylanabazine (**3**) was dissolved in 100 ml of ethanol and 1.9 ml was added dropwise. 39.85 mmol) hydrazine hydrate. The reaction mixture was stirred for 1 hour at 25°C and an additional (**7**) hours at 70-75°C, cooled and evaporated. The resulting mass was dissolved in $CHCl_3$ (300 ml), washed with water (3×60 ml) and dried over $MgSO_4$. The desiccant was filtered off, the solvent was evaporated under reduced pressure, the residue was chromatographed on an alumina column (eluent: benzene, benzene-chloroform, 100: 1). 2.028 g (87.03%) of product **5** was isolated as a yellow-green thick oil. ^{1}H NMR spectrum, δ, ppm. (J, Hz): 1.31-1.52 m (1H. H^{9ax}), 1.53-1.61 m (3H, $H^{8ax,10ax,9eq}$), 1.70-1.88 m (1H, H^{8eq}), 2.18-2.40 m (1H, H^{10eq}), 2.76-2.84 m (2H, $H^{4ax,7ax}$), 2.96-2.98 m (1H, H^{7eq}), 3.58-3.65 m (2H, $H^{4eq,H\text{-}11}$), 4.58 widened singlet (1H, H^{1}), 5.12-5.21 m (1H, H^{5}), 7.18-7.22 m (3H, $H^{14,15,16}$), 7.25-7.37 m (4H, $H^{13,17,22,23}$), 8.40-8.50 (2H, $H^{19,21}$). Cross peaks of COSY NMR spectra (^{1}H-^{1}H), ppm: H^{4ax}-H^{5} (2.76, 5.16 and 5.16, 2.75), $H^{13,17}$-$H^{14,16}$ (7.34, 7.16 and 7.16, 7.34), $H^{21,23}$-H^{22} (8.39, 7.34 and 7.34, 8.39). Cross peaks of HMQC NMR spectra (^{1}H-^{13}C), ppm: H^{4ax}-C^{4} (2.75, 42.19), H^{4eq}-C^{4} (3.64, 42.19), H^{5}-C^{5} (5.20, 70.38), H^{8ax}-C^{8} (1.53, 25.86), H^{8eq}-C^{8} (1.73, 25.86), H^{9ax}-C^{9} (1.37, 19.54), H^{9eq}-C^{9} (1.61, 19.54), H^{10eq}-C^{10} (2.25, 26.85), H^{11}-C^{11} (3.58, 42.12), H^{22}-C^{22} (7.34, 134.83).

1-(5-Phenyl-4,5-dihydro-1H-pyrazol-3-yl)cytisine (6). 0.33 g (1.03 mmol) of N-cinnamoylcytisine (**2**) was dissolved in a minimum amount of ethanol (~ 15 ml) and 0.50 ml was added dropwise (10.28 mmol) hydrazine hydrate. The reaction mixture was stirred for 2 hours at 25°C and an additional 6 hours at 70-75°C, cooled and evaporated. The resulting mass was dissolved in $CHCl_3$ (100 ml), washed with water (3×20 ml) and dried over $MgSO_4$. The drying agent was filtered off, the solvent was evaporated under reduced pressure, the residue was chromatographed on an alumina column (eluent: petroleum ether, petroleum ether-benzene, 100:1). 0.283 g (85.75%) of product **6** was isolated in the form of yellow needle crystals with a melting point of 122-125°C. ^1H NMR spectrum, δ, ppm. (J, Hz): 1.87-1.99 m (2H, $H^{18,18}$), 2.25-3.33 m (6H. $H^{4,4,7,7,8,16}$), 3.58-4.63 m (5H, $H^{5,9,9,17,17}$), 6.11-6.20 m (2H, $H^{12,14}$), 6.97-7.64 m (7H, $H^{1,13,20\text{-}24}$). ^{13}C NMR spectrum, δ_C, ppm: 25.80 (C^{18}), 27.52 (C^8), 33.76 (C^{16}), 34.79 (C^4), 48.75 (C^9), 49.18 (C^7), 51.21 (C^{17}), 52.82 (C^5), 105.27 (C^{14}), 116.31 (C^{12}), 126.32 (C^{22}), 128.51 ($C^{21,23}$), 129.25 ($C^{20,24}$), 139.30 (C^{13}), 141.62 (C^{19}), 150.19 (C^{15}), 162.64 (C^3), 170.85 (C^{11}). Cross peaks of HMQC NMR spectra (^1H-^{13}C), ppm: H^{18}-C^{18} (1.88, 26.44), H^8-C^8 (2.44, 28.40), H^{16}-C^{16} (2.52, 34.62), H^7-C^7 (2.74, 48.79), H^4-C^4 (3.10, 34.89), H^5-C^5 (4.22, 53.55), H^{17}-C^{17} (4.43, 51.92), H^9-C^9 (4.53, 48.45), H^{14}-C^{14} (6.15, 105.77), H^{12}-C^{12} (6.21, 117.00), $H^{21,23}$-$C^{21,23}$ (7.09, 129.08), H^{22}-C^{22} (7.12, 126.67), $H^{20,24}$-$C^{20,24}$ (7.32, 129.32), H^{13}-C^{13} (7.28, 139.80).

3-Phenyl-N-(anabazinocarbonothioyl)acrylamide (7). 1.62 g (0.01 mol) of anabazine was dissolved in 5 ml of acetone, then a solution (0.011 mol) of cinnamoylisothiocyanate in 10 ml of acetone was added dropwise with vigorous stirring. The mixture was stirred for 1 h at a temperature of 30°C. The completion of the reaction was monitored by TLC. The solution was cooled, the precipitated fine precipitate was filtered off, washed with a small amount of diethyl ether. After recrystallization from 2-propanol, 2.82 g (80.4%) of a white powder of 5 s melted was obtained. 150-151°C. The data of elemental analysis of compound **7** answered calculated. $C_{20}H_{21}N_3OS$. ^1H NMR spectrum, δ, ppm (J, Hz): 0.99-1.00 m (1H, H^{10ax}), 1.31-1.34 m (1H, H^{11ax}), 1.44-1.65 m (2H, $H^{10eq,11eq}$), 1.88-2.00 m (1H, H^{12ax}), 2.52-2.55 m (1H, H^{12eq}), 3.00-3.05 m (1H, H^{9ax}), 3.73-3.87 m (1H, H^{9eq}), 6.72 widened singlet (1H, H^7), 6.87 d (1H, H^{18}, ^3J 16.0), 7.39 widened singlet (4H, $H^{5,22,23,24}$), 7.58 d (2H, $H^{21,25}$, ^3J 6.4), 7.65 d (1H, H^{19}, ^3J 15.6), 7.86 widened singlet (1H, H^4), and 8.47 d (1H, H^6, ^3J 4.1), widened singlet 8.66 (1H, H^2), 10.85 widened singlet (1H, H^{15}). ^{13}C NMR spectrum, δ_C, ppm: 18.99 (C^{11}), 26.02 (C^{10}), 27.49 (C^{12}), 48.27 (C^9), 59.00 (C^7), 120.80 (C^{18}), 124.11 (C^5), 128.49 ($C^{21,25}$), 129.60 ($C^{22,24}$), 130.83 (C^{23}), 133.35 (C^{20}), 134.89 (C^4), 134.93 (C^3), 143.27 (C^{19}), 148.52 (C^2), 148.65 (C^6), 162.64 (C^{16}), 181.61 (C^{13}). Cross peaks of HMQC NMR spectra (^1H-^{13}C), ppm: H^{10ax}-C^{10} (1.00, 26.67), H^{11ax}-C^{11} (1.28, 19.67), H^{11eq}-C^{11} (1.55, 19.70), H^{10eq}-C^{10} (1.55, 26.80), H^{12ax}-C^{12} (1.90, 28.20), H^{12eq}-C^{12} (2.57, 28.11), H^{9ax}-C^9 (3.03, 48.86), H^{9eq}-C^9 (3.91, 48.87), H^7-C^7 (6.74, 59.48), H^{18}-C^{18} (6.90, 121.09), H^5-C^5 (7.39, 124.50), $H^{22,23,24}$-$C^{22.23.24}$ (7.40, 130.11), $H^{21,25}$-$C^{21,25}$ (7.58, 128.91), H^4-C^4 (7.87, 135.37), H^{19}-C^{19} (7.68, 143.50), H^6-C^6 (8.47, 148.93), H^2-C^2 (8.54, 148.93).

N-Citisino-3-carbonothioylphenylacrylamide (8). 1.9 g (0.01 mol) of cytisine was dissolved in 20 ml of acetone, then a solution (0.011 mol) of cinnamoylisothiocyanate in 10 ml of acetone was added dropwise with vigorous stirring. The reaction mixture, transparent with a yellow tint, was stirred for 2 hours at a temperature of 30^0C. The completion of the reaction was monitored by TLC. The solution was cooled, the precipitated white crystalline precipitate was filtered off, washed with a small amount of diethyl ether. After recrystallization from benzene, 2.32 g (61.3%) of white matter were obtained, 6 s. Mp. $177\text{-}178^0C$. The data of elemental analysis of compound **8** answered calculated. $C_{21}H_{21}N_3O_2S$. ^1H NMR spectrum, δ, ppm (J, Hz): 1.84-1.87 m (1H, H^3), 2.47 widened singlet (1H, H^{13ax}), 2.65 widened singlet (1H, H^{13eq}),3.12 widened singlet (1H, H^{11}), 3.28 widened singlet (1H, H^{2ax}), 3.36-3.38 m (1H, H^{2eq}), 3.57-3.61 m (1H, H^{12ax}), 3.79-3.88 m (1H, H^{4ax}), 3.98-4.01 m (1H, H^{12eq}), 4.22-4.25 m (1H, H^{4eq}), 6.08-6.10 m (1H, H^9), 6.18-6.20 m (1H, H^7), 6.68-6.79 m (1H, H^{20}), 7.32-7.53 m (7H, $H^{8,21,23\text{-}26}$), 10.53 widened singlet (1H, H^{17}). ^{13}C NMR spectrum, δ_C, ppm: 25.31 (C^3), 28.90 (C^{13}), 35.47 (C^{11}), 48.41 (C^4), 55.45 (C^2), 58.68 (C^{12}), 105.08 (C^9), 116.95 (C^7), 120.86 (C^{20}), 128.43 ($C^{23,27}$), 128.85 ($C^{24,26}$), 129.57 (C^{25}), 130.79 (C^{22}), 139.36 (C^8), 142.85 (C^{21}), 149.42 (C^{10}), 161.97 (C^6), 162.70 (C^{18}), 180.65 (C^{14}). Cross peaks of HMQC NMR spectra (^1H-^{13}C), ppm: H^3-C^3 (1.87, 25.98), H^{13ax}-C^{13} (2.47, 29.50), H^{13eq}-C^{13} (2.66, 29.50), H^{11}-C^{11} (3.12, 36.12), H^2-C^2 (3.36, 56.72), H^{12ax}-C^{12} (3.53, 59.30), H^{4ax}-C^4(3.84, 49.34), H^{12eq}-C^{12} (3.98, 57/98), H^{4eq}-C^4 (4.24, 49.34), H^9-C^9 (6.09, 105.49), H^7-C^7 (6.20, 117.26), H^{20}-C^{20} (6.74, 121.45), H^8-C^8 (7.26, 139.76), $H^{23\text{-}27}$-$C^{23\text{-}27}$ (7.32, 129.27), H^{21}-C^{21} (7.52, 142.80).

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ЦИТИЗИН ЖӘНЕ АНАБАЗИННІҢ ЖАҢА N-АЦИЛЬДІ ЖӘНЕ ТИОМОЧЕВИНДІ ТУЫНДЫЛАРЫНЫҢ СИНТЕЗІ МЕН ҚҰРЫЛЫСЫ

Аннотация. Ұсынылған жұмыста цитизин және анабазин алкалоидтары молекулаларының химиялық трансформациясы бойынша зерттеулердің нәтижелері, олардың N-циннамоильді туындылары, сондай-ақ оларды одан әрі қарай модификациялаудың ықтимал жолдары келтірілген. Цитизин мен анабазин алкалоидтарының ацилденген туындылары қатарынан жаңа биологиялық белсенді қосылыстарды іздестіру мақсатында циннамоилхлоридпен әрекеттесу реакциясы жүргізіліп, нәтижесінде одан әрі өзгеру мүмкіндіктеріне ие болатын N-циннамоилцитизин және N-циннамоиланабазин туындылары синтезделді. Еріткіштің табиғатына және ортаның сипатына байланысты зерттелетін реакцияларды жүзеге асырудың оңтайлы шарттары қарастырылған. Зерттелетін алкалоидтардың ацилдену реакциясы триэтиламиннің қатысуымен бензолда жақсы жүреді, сонымен қатар сәйкесінше 75 және 95% шығымдарды құрайтын тиісті анабазин мен цитизин алкалоидтары туындыларының пайда болуына әкеліп соқтырады. N-циннамоилцитизин және N-циннамоиланабазин туындыларын түзетін гидразинолиз реакциясы жүзеге асырылды. Алкалоидтардың акриламидті туындыларының этанолдағы гидразингидратпен өзара әрекеттесуі тиісті пиразолды туындылардың пайда болуына алып келеді және олар гидразондардың N-циннамоильді туындыларының молекулалық циклоконденсациясының нәтижесі болып табылады. Цитизин мен анабазиннен алынған N-циннамоильді туындылары гидразингидратпен өзара әрекеттесу реакцияларында одан әрі зерттелінеді. Этанолды ортада жүргізілген реакцияның нәтижесінде олардың тиісті пиразол туындылары алынды. Реакциялық ортадан бөлінген пиразолды қосылыстар аралық өнім түзетін гидразондардың ішкі молекулалық циклоконденсациясының нәтижесі болуы мүмкін. Циннамоилизотиоцианаттың жоғарыда көрсетілген алкалоидтармен өзара әрекеттесуі жаңа тиомочевиналы туындылардың синтезін жүзеге асырды. Цитизин және анабазин алкалоидтарының циннамоилизотиоционатпен өзара әрекеттесуі нәтижесінде олардың жаңа ацильді туындылары алынды. Циннамоилизотиоцианат корич қышқылының калий роданидімен ацетонда қыздыру арқылы өзара әрекеттесуі барысында синтезделінді. Синтезделген қосылыстардың құрылысы ЯМР ^{1}Н - және ^{13}С-спектроскопия әдістерімен, сондай-ақ COSY (^{1}Н-^{1}Н) және HMQC (^{1}Н-^{13}С) екі өлшемді спектрлерінің деректерімен зерттелді. Бір өлшемді ЯМР спектрлерінде ^{1}Н және ^{13}С сигналдардың интегралдық қарқындылығы, мультиплеттілігі және химиялық ығысу мәндері анықталды. COSY (^{1}Н-^{1}Н) және HMQC (^{1}Н-^{13}С) форматтарында спектрлер көмегімен зерттелетін қосылыстардың құрылымын растайтын гомо - және гетероядролық өзара әрекеттесулер орнатылды.

Түйін сөздер: алкалоидтар, цитизин, анабазин, химиялық трансформация, N-ацильді фрагмент, циннамоил хлорангидриді

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СИНТЕЗ И СТРОЕНИЕ НОВЫХ N-АЦИЛЬНЫХ И ТИОМОЧЕВИННЫХ ПРОИЗВОДНЫХ АЛКАЛОИДОВ ЦИТИЗИН И АНАБАЗИН

Аннотация. В представленной работе приведены результаты исследований по химической трансформации молекул алкалоидов цитизин и анабазин с получением их N-циннамоильных производных, а также возможные пути их дальнейшей модификации. С целью поиска новых биоактивных соединений в ряду ацилированных производных алкалоидов цитизина и анабазина нами исследованы реакции с циннамоилхлоридом и возможности дальнейших превращений образующихся N-циннамоилцитизина и N-циннамоиланабазина. Рассмотрены оптимальные условия осуществления изучаемых реакций в зависимости от природы растворителя и характера среды. Установлено, что ацилирование изучаемых алкалоидов успешно протекает гладко в бензоле в присутствии триэтиламина и приводят к образованию соответствующих производных анабазина и цитизина с выходами 75 и 95% соответственно. Осуществлен гидразинолиз образующихся N-циннамоилцитизина и N-циннамоиланабазина. Показано, что взаимодействие акриламидных производных алкалоидов с гидразингидратом в этаноле приводит к образованию соответствующих пиразоловых производных, которые, возможно, являются результатом внутримолекулярной циклоконденсации гидразонов N-циннамоильных производных. Полученные N-циннамоильные производные цитизина и анабазина подвергнуты дальнейшему изучению в реакциях взаимодействия с гидразингидратом. В результате проведенных реакций в среде этанола были получены соответствующие их пиразольные производные. Сделано предположение, что выделенные из реакционной среды пиразольные соединения, возможно, являются результатами внутримолекулярной циклоконденсации промежуточно образующихся гидразонов. Взаимодействием циннамоилизотиоцианата с вышеуказанными алкалоидами осуществлен синтез новых тиомочевинных производных. Взаимодействием цитизина и анабазина с циннамоилизотиоционатом получены новые ацильные производные. Циннамоилизотиоцианат был получен взаимодействием хлорангидрида коричной кислоты с роданистым калием в ацетоне при нагревании. Исследованы строения синтезированных соединений методами ЯМР ^{1}Н- и ^{13}С-спектроскопии, а также данными двумерных спектров COSY (^{1}H-^{1}H) и HMQC (^{1}H-^{13}C). Определены значения химических сдвигов, мультиплетность и интегральная интенсивность сигналов ^{1}Н и ^{13}С в одномерных спектрах ЯМР. С помощью спектров в форматах COSY (^{1}H-^{1}H) и HMQC (^{1}H-^{13}C) установлены гомо- и гетероядерные взаимодействия, подтверждающие структуру исследуемых соединений.

Ключевые слова: алкалоиды, цитизин, анабазин, химическая трансформация, N-ацильный фрагмент, хлорангидрид циннамоила.

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ANODIC DISSOLUTION OF TITANIUM IN SULFURIC ACID BROMIDE SOLUTIONS

Abstract. Titanium is inert in many different oxidizing environments, prone to passivation. The metal is chemically insoluble in acids, resistant to corrosion and environmental impacts. In the present work, the dissolution behavior of titanium electrode in the sulfuric acid bromide solution under anodic polarization was shown for the first time and laws of the process were determined. The effect of the anode current density (200-1200 A/m^2), potassium bromide solution (1.0-5.0 M) and sulfuric acid concentration (0.5-2.5 M), solution temperature (25-80 ˚C) and electrolysis duration (0.5-2 hours) on the current output of titanium dissolution were considered. With an increase the current density at the anodic polarized titanium electrode from 200 A/m^2 to 600 A/m^2, the current output (CO) of titanium dissolution increases, and at higher current densities, a decrease in CO of titanium dissolution is observed due to the appearance of an oxide coating on titanium surface. The influence of the Br$^-$ ion concentration and the sulfuric acid concentration was studied separately with the aim of systematically studying the effect of the electrolyte nature on the dissolution of titanium. With an increase of the bromide ions concentration, poorly soluble bromide compounds are formed, which leads to a decrease in the CO of the anodic dissolution of titanium. An increase in the concentration of sulfuric acid, i.e. the concentration of hydrogen ions contributes to the dissolution of titanium, the CO of the anodic dissolution of titanium increases. A 1.5 times increase in the CO of titanium was observed upon acidification of an aqueous electrolyte containing Br$^-$ ions with 0.5 M sulfuric acid and an increase in the concentration of bromide ions. However, with an increase in the concentration of sulfuric acid in the bromide solution, the CO of the anodic dissolution of titanium increased significantly and reached 70%. The CO of titanium dissolution has a maximum value in a 2.5 M solution of sulfuric acid and in a 1.0 M solution of potassium bromide. The reaction order of the electrode process during electrolysis with sulfuric acid was calculated and it was shown that the reaction proceeds under diffuse conditions. An increase in the duration of electrolysis leads to concentration polarization due to the accumulation of electrolysis products on the electrode surface and slows down the electrochemical dissolution of titanium. The CO of the dissolution of the titanium electrode abnormally decreases with increasing temperature of the electrolyte. The influence of the basic electrochemical parameters on the dissolution of the titanium anode was studied and the optimal conditions for its dissolution were established. It was found that under optimal electrolysis conditions, the current output of dissolution of titanium has a value of more than 70%.

Key words: titanium, electrolysis, current output, anodic dissolution, potassium bromide, sulfuric acid.

In comparison with pure chemical methods, electrochemical methods allow to obtain high quality products in a simple and inexpensive way. In addition, it contributes to the development of new methods for the study and protection of corrosion processes in metals [1]. Also electrochemical methods will give an opportunity to investigate the electrochemical dissolution behavior of Ti alloys in aqueous solutions and explain the unique phenomena during its dissolution [2].

The specific properties of titanium and its alloys, such as lightness and corrosion resistance, have been widely used in all fields from aviation to nuclear production. Titanium is a thermodynamically active metal, but the oxide shell, which is always on its surface, allows this metal to have a stable corrosion resistance [3, 4].

Obtaining compounds of high melting temperature soluble and sparingly soluble metals by the electrochemical methods is one of the topical issues of today [5 - 7].

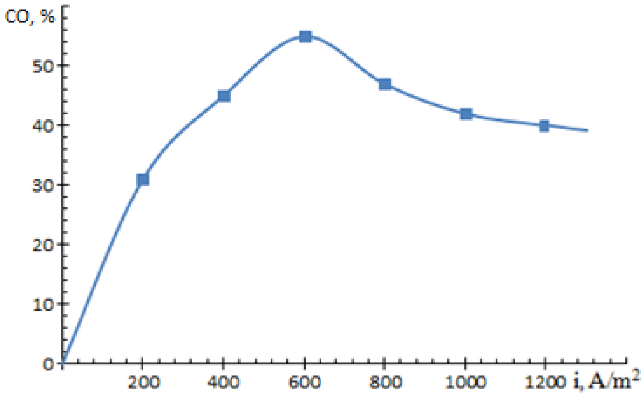
It is well-known from literature data that titanium electrode in sulfate, chloride, neutral and acid solutions does not dissolve in the anodic polarization. Titanium oxide (Ti_xO_y) appears on the surface of anode polarized titanium electrodes and the current passage through the electrochemical circuit stops [8]. In the studies of A.B. Bayeshov and other scientists, the intensive dissolution of titanium electrode by forming salts in the sulfate, chloride, fluoride acid solutions when polarized with 50 Hz alternating current was shown [9 - 11]. The study investigated electrochemical properties of titanium electrode polarized with industrial alternating current in the media containing fluoride ions and in the phosphorus, hydrochloric, sulfuric acid media and provided optimal conditions for titanium electrode dissolution. The study result determined titanium electrode dissolution with high current output in various acidic environments containing fluoride ions. As a result, it was shown the possibility to obtain titanium salts [12, 13].

In our previous studies, titanium oxidation current was recorded by cyclic polarization curves and an intensive dissolution of titanium electrodes polarized by industrial alternating current of 50 Hz frequency in bromide acidic media was shown [14, 15].

The literature review results showed that the electrochemical properties of titanium electrode in bromide aqueous media were not fully studied [16 - 22].

In the present work, for the first time, we present the study results of the anodic dissolution laws of titanium electrode polarized by the direct current. The effect of the main parameters (current density, solution temperature and electrolyte concentration) on electrochemical dissolution process of titanium electrodes was considered.

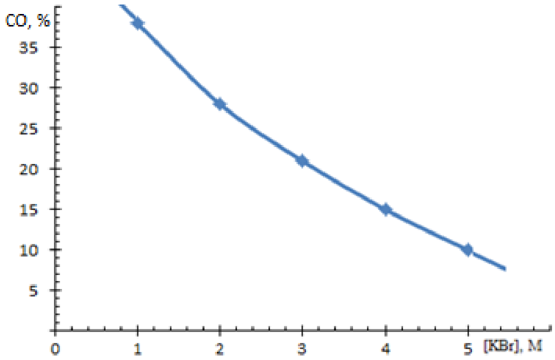
Figure 1 describes the current density effect on current output of titanium electrode dissolution polarized by anodic current in sulfuric acid bromide solution. From the study results, it is possible to see an increase of the current output of titanium electrode dissolution from 31% to 55% when the current density was increased in the range from 200 to 1200 A/m^2, while a slight decrease up to 47% can be observed beginning from 600 A/m^2. The decrease in the current output of titanium dissolution at a current density of 800-1200 A/m^2 is due to the formation of oxidized layer on the titanuim surface during high current density and the occurrence of the passivation process or additional reactions.



[KBr]=1 M, [H_2SO_4]=0,5 M, τ=0,5 h.

Figure 1 - The current density effect in the titanium electrode on the current output of titanium dissolution polarized by anodic current

The effect of potassium bromide concentration on the dissolution properties of direct current (DC) polarized titanium in bromide aqueous solutions was studied in neutral medium without the presence of acid (Figure 2). The studies result showed that, as the potassium bromide concentration was increased in the range of 1.0-5.0 M, the current output of titanium electrode dissolution decreases from 38% to 10%. This phenomenon is due to a solubility decrease of the titanium bromide formed on the titanium surface.



i=600 A/m^2, τ=0,5 h.

Figure 2 - The potassium bromide concentration effect on current output of titanium electrode dissolution polarized by anodic current

The following figure shows titanium electrodes used in electrolysis (Figure 3). It is possible to observe the complete insolubility of the cathode polarized electrode and the active dissolution of the anode polarized titanium electrode.

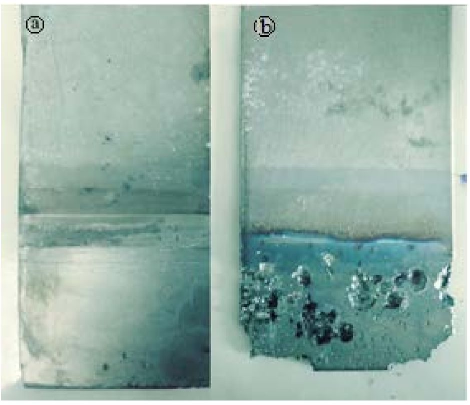
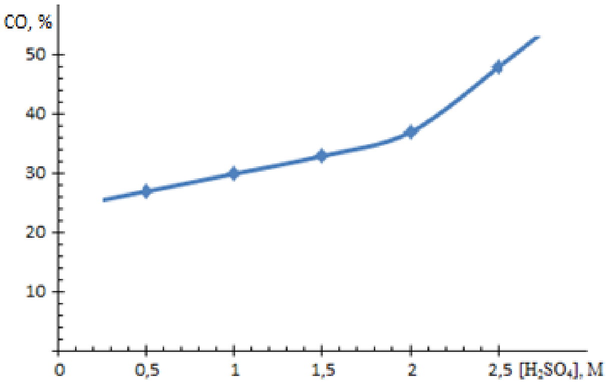


Figure 3 - The surface state of titanium electrodes used during electrolysis: (a) is used as cathode and (b) as anode

In the following study, the current output of titanium was investigated in the presence of sulfuric acid since the current output of titanium dissolution in bromide aqueous solutions had low value (Figure 4). When the sulfuric acid concentration is increased up to 0.5-2.0 M, the current output value of the titanium dissolution gradually increases from 26.7% to 48%. This phenomenon is due to the interaction of sulfate ions with titanium ions and its creation of a favorable condition for the formation of titanium soluble salt.



i=600 A/м^2, τ=0,5 h.

Figure 4 - Sulfuric acid concentration effect on current output of titanium electrode dissolution polarized by anodic current

It should be noted that the electrolyte color is white-yellow and it forms white loose tissues in the range of 0.5-1.0 M sulfuric acid concentration, while in the range of 1.5-2.5 M the electrolyte color changes to blue purple and a blue colored thick layer appears (Figure 5). The appearance of the white tissue is due to the discharge of hydrogen ions in the cathode and the increase of the electrolyte pH and the hydrolysis of titanium ions, and blue-purple colour shows the formation of titanium (III) sulfate.

The potassium bromide concentration effect was investigated in the solution in which the potassium bromide solution was oxidized with 0.5 M sulfuric acid since the current output of the anode current polarized titanium electrode does not exceed 48% in the sulfuric acid media (Figure 6a). The more the potassium bromide concentration is increased, the less a decrease in current output is observed.

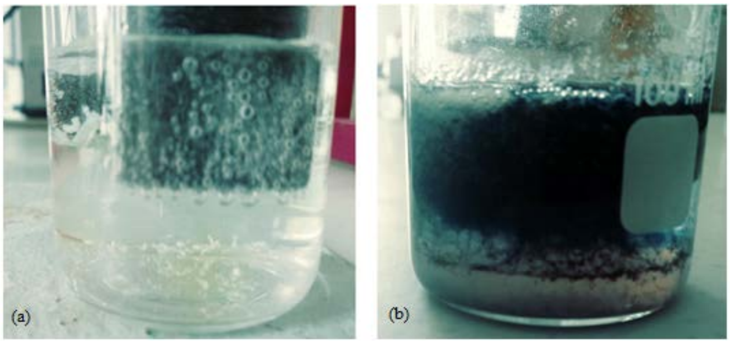
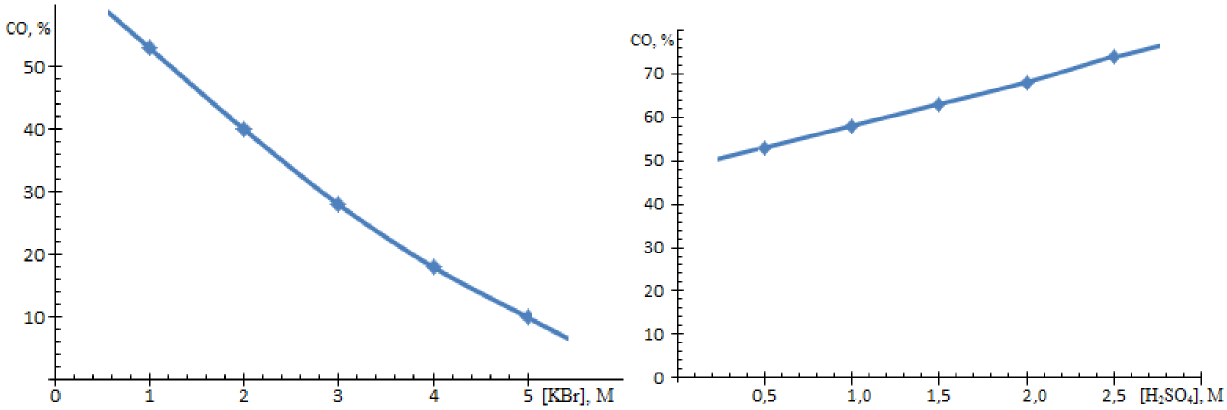


Figure 5 - Electrolytes that are changed in color as a result of electrolysis:
(a) – at the initial stage, (b) – the change by the end of reaction

Initially, 1.0 M potassium bromide and 0.5 M sulfuric acid oxidized bromide ions contributed to better titanium dissolution (CO - 53%), and the weak solubility of the electrolyte due to the increase of the potassium bromide concentration can be explained by the formation of bromide compounds and the passivation of titanium electrode surface.

At this point, as the potassium bromide concentration effect (Figure 6a) was considered, the current output value of titanium dissolution was reduced to a straight line, but it should be noted that in comparison with it the total current output increases 1.5 times.

Figure 6(b) shows the sulfuric acid concentration effect on current output of anode current polarized titanium electrode dissolution in electrolyte containing 1.0 M potassium bromide.



i=600 A/m^2, [H_2SO_4]=0,5 M, τ=0,5 h. (a) i=600 A/m^2, [KBr]=1,0 M, τ=0,5 h. (b)

Figure 6 - Potassium bromide (a) and Sulfuric acid (b) concentration effect
on current output of titanium electrode dissolution polarized by anodic current

As the hydrogen ions concentration in the solution is increased, a gradual increase of the current output value of titanium dissolution is observed. The increase of the sulfate ions concentration creates a favorable condition for the titanium dissolution. According to this dependence result (Table 1) the reaction rate for bromide ions calculated which was equal to 0.5.

Table 1 - Electrode reactions rate on sulfuric concentrations acid during the electrolysis

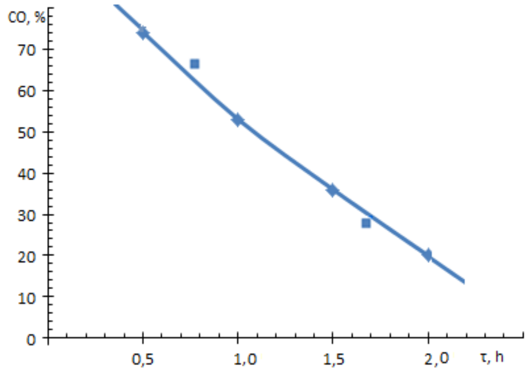
№	C_{el}	lgC=x	I	y=lgi	x·y	x^2
1	0,5	-0,301	500	2,69	-0,809	0,09
2	1	0	550	2,74	0	0
3	1,5	0,176	600	2,78	0,489	0,03
4	2	0,301	650	2,81	0,84	0,09
5	2,5	0,397	700	2,84	1,13	0,157
Σ	-	0,57	-	13,858	1,65	0,367

The calculations were made in accordance to the table 1 and the reaction rate was calculated according to the following formula:

$$b = \frac{n\sum x \cdot y - \sum x \cdot \sum y}{n\sum x^2 - \left(\sum x\right)^2} = \frac{5 \cdot (1{,}65) - (0{,}57 \cdot 13{,}858)}{5 \cdot 0{,}157 - (0{,}367)^2} = 0{,}5$$

This, in turn, indicates that the reaction takes place in a diffusion environment.

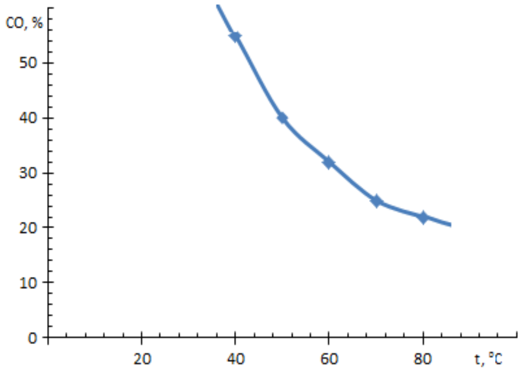
The following figure shows the electrolysis duration effect on the current output of titanium electrode dissolution (Fig. 7). As the electrolysis duration increases, the current output decreases; it can be explained by the occurrence of concentration polarization due to the accumulation of electrolysis products on the electrode surface as the electrolysis time increases.



i=600 A/m^2, [KBr]=1,0 M, [H_2SO_4]=0,5 M

Figure 7 - The electrolysis duration effect on the current output of titanium electrode dissolution polarized by anodic current

The electrolyte temperature effect on the current output of DC polarized titanium electrode dissolution was considered (Figure 8). When the electrolyte temperature increased, a decrease of the current output from 55.4% to 27.6% was defined. The explanation of this anomalous phenomenon requires additional studies.



i=600 A/m^2, [KBr]=1,0 M, [H_2SO_4]=0,5 M, τ=0,5 h

Figure 8 - The electrolyte temperature effect on the current output of titanium electrode dissolution polarized by anodic current

In conclusion, the electrochemical properties of the anode current polarized titanium in the acid bromide solution were investigated for the first time. The increase of the bromide ions concentration leads to a decrease in the current output of titanium anode dissolution, while the increase of the sulfuric acid concentration in the titanium anode dissolution increases the current output of titanium anode dissolution. In optimum conditions, it was shown that the current output of titanium dissolution was above 70%.

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КҮКІРТ ҚЫШҚЫЛДЫ БРОМИД ЕРІТІНДІЛЕРІНДЕГІ ТИТАННЫҢ АНОДТЫ ЕРУІ

Аннотация. Титан көптеген тотықтырғыш орталарда инерттілігімен ерекшеленеді, пассивацияға бейім. Металл қышқылдарда химиялық жолмен ерімейді, коррозияға және қоршаған орта әсеріне төзімді. Қазіргі таңда қолданылу аясы кең болғандықтан титанды ерітіп, түрлі қосылыстарын алудың маңызы үлкен. Ұсынылып отырған жұмыста күкірт қышқылымен қышқылданған бромидті сулы ерітіндісінде анодты поляризациялау кезінде титан электродының еритіндігі алғаш рет көрсетілді және процестің заңдылықтары анықталды. Титан электродының анодты еруінің ток бойынша шығымына ток тығыздығының (200-1200 А/м^2), калий бромиді (1,0-5,0 М) және күкірт қышқылы (0,5-2,5 М) концентрацияларының, ерітінді температурасының (25-80 ˚С), электролиз ұзақтығының (0,5-2 сағ.) әсерлері қарастырылды. Анодты поляризацияланған титан электродындағы ток тығыздығын 200 А/м^2-ден 600 А/м^2-ге арттырғанда, титанның еруінің ток бойынша шығымы (ТШ) жоғарылап, одан жоғары ток тығыздықтарында титанның бетінде тотықты қабаттың пайда болуына байланысты ток бойынша шығымның төмендейтіндігі көрсетілді. Титанның еруіне электролит табиғатының әсерін жүйелі зерттеу мақсатында Br$^-$ иондарының концентрациясының және күкірт қышқылы концентрациясының әсерлері жеке зерттелді. Бромид иондарының концентрациясының артуымен нашар еритін бромид қосылыстары түзіліп, нәтижесінде титанның анодты еруінің ток бойынша шығымы төмендейтіндігі көрсетілді. Күкірт қышқылы концентрациясының өсуімен, демек, сутек иондарының концентрациясының артуы титанның еруіне ықпал жасап, титанның анодты еруінің ток бойынша шығымы жоғарылайтындығы анықталды. Құрамында Br$^-$ иондары бар сулы электролитті 0,5 М күкірт қышқылымен қышқылдап, бромид иондарының концентрациясын жоғарылатқанда титан еруінің ток бойынша шығымы 1,5 есе артуы байқалды. Ал, бромидті ерітіндідегі күкірт қышқылының концентрациясын арттырғанда титанның анодты еруінің ток бойынша шығым мәні анағұрлым артып, 70%-ға жетті. Титанның еруінің ток бойынша шығымы 2,5 М күкірт қышқылы және 1,0 М калий бромиді ерітіндісінде максималды мәнді көрсетті. Электролиз кезінде жүретін электродтық реакцияның күкірт қышқылы бойынша реакция реті есептеліп, реакцияның диффузиялық ортада жүретіндігін көрсетті.

Электролиз ұзақтығын арттырған сайын электрод бетінде электролиз өнімдерінің жинақталуына байланысты концентрациялық поляризация туындап, нәтижесінде титанның электрохимиялық еруі баяулайтындығы көрсетілді. Электролит температурасының жоғарылауымен титан электродының еруінің ток бойынша шығымы аномальды төмендейтіндігі анықталды. Титанның анодты еруіне негізгі электрохимиялық параметрлердің әсерлері жүйелі зерттеліп, оның еруінің оңтайлы жағдайлары қалыптастырылды. Электролиздің оңтайлы жағдайларында титан еруінің ток бойынша шығымы 70%-дан жоғары болатыны анықталды.

Түйін сөздер: титан, электролиз, ток бойынша шығым, анодты еру, калий бромиді, күкірт қышқылы.

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АНОДНОЕ РАСТВОРЕНИЕ ТИТАНА В СЕРНОКИСЛЫХ БРОМИДНЫХ РАСТВОРАХ

Аннотация. Титан отличается инертностью во многих окислительных средах, склонен к пассивации. Металл химически нерастворим в кислотах, устойчив к коррозии и воздействиям окружающей среды. В настоящее время в связи с широкой областью применения растворение титана с получением различных его соединений является очень актуальным. В данной работе впервые показана возможность растворения титанового электрода при анодной поляризации в сернокислых бромидных водных растворах и определены закономерности процесса. Рассмотрено влияние плотности анодного тока (200-1200 А/м^2), концентрации раствора бромида калия (1,0–5,0 М) и серной кислоты (0,5–2,5 М), температуры раствора (25–80˚С), продолжительности электролиза (0,5–2 часа) на выход по току анодного растворения титанового электрода. При повышении плотности тока на анодно-поляризованном титановом электроде от 200 $А/м^2$ до 600 $А/м^2$ выход по току (ВТ) растворения титана повышается, а при более высоких плотностях тока наблюдалось снижение выхода по току растворения титана из-за появления оксидного покрытия на поверхности титана. Влияние концентрации иона Br^- и концентрации серной кислоты исследовалось отдельно с целью систематического изучения влияния природы электролита на растворение титана. Показано, что с увеличением концентрации бромид-ионов образуются плохо растворимые бромидные соединения, что приводит к уменьшению выхода по току анодного растворения титана. Установлено, что увеличение концентрации серной кислоты, т.е. концентрации ионов водорода способствует растворению титана, выход по току анодного растворении титана увеличивается. Увеличение выхода по току титана в 1,5 раза наблюдалось при подкислении водного электролита, содержащего ионы Br^- 0,5 М серной кислотой и повышении концентрации бромид-ионов. Однако с увеличением концентрации серной кислоты в растворе бромида выход по току анодного растворения титана значительно увеличился и достиг 70%. Выход по току растворения титана имеет максимальное значение в 2,5 М растворе серной кислоты и в 1,0 М растворе бромида калия. Рассчитан порядок реакции электродного процесса при электролизе по серной кислоте и показано, что реакция протекает при диффузном режиме.

Показано, что увеличение продолжительности электролиза приводит к концентрационной поляризации из-за накопления продуктов электролиза на поверхности электрода и замедляет электрохимическое растворение титана. Было обнаружено, что с повышением температуры электролита выход по току растворения титанового электрода аномально снижается. Изучено влияние основных электрохимических параметров на растворение титанового анода и установлены оптимальные условия его растворения. Было установлено, что при оптимальных условиях электролиза выход по току растворения титана имеет значение более 70%.

Ключевые слова: титан, электролиз, выход по току, анодное растворение, бромид калия, серная кислота.

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ABOUT MODERN RESEARCH IN THE FIELD OF COMPLEX SULFIDE COMPOUNDS (STATE AND TRENDS)

Abstract. The article provides an overview of the most significant scientific papers (from more than 600 literature sources), devoted to the studies of complex sulfides, some of which are given in this research. There are examples of research in the field of the most promising complex sulfides CdZnS, AgInS, CuInS, ZnInS and the predicted scope of their practical application in the article. The tendencies in the research for physicochemical properties of complex metal sulphides are revealed.

Key words: complex metal sulfides, doping, quantum dot, quantum transition, photoluminescence, electrochemical properties, phase transitions, traps, optical properties, solar cells, LEDs.

There are extensive series of creating new materials research based on the synthesis of complex complex sulfide compounds has been conducted over the past 3 years. It will be presented examples of research in the field of the most promising complex sulfides CdZnS, AgInS, CuInS, ZnInS.

1. Research in the field of complex sulfide CdZnS.

«Structural, optical and photovoltaic properties of Co (3%): CdZnS nanoparticles» [37]. In the present study, CdZnS and Co (3%): CdZnS nanoparticles (NPs) have been synthesized via wet chemical method at room temperature using 1-thioglycerol as a capping agent. The incident photon-to-current conversion efficiency (IPCE) measurement has been carried out for Co (5%): CdZnS for the first time in this study. The results show that Co (3%): CdZnS can be utilized as sensitizers to improve the performance of solar cells. In addition to the photovoltaic properties; structural, optical and morphological properties of Co (3%): CdZnS NPs have been investigated. The results indicate that Co (3%): CdZnS NPs can be suitable material for photovoltaic applications.

«Influence of Ce^{3+} doping on the optical and photocatalytic properties of $Zn_{0.8}Cd_{0.2}S$-ethylenediamine hybrid nanosheets» [8]. The Ce^{3+}-doped $Zn_{0.8}Cd_{0.2}S$-ethylenediamine (En) hybrid nanosheets were successfully synthesized by a simple solvothermal method and characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), UV-vis diffusion reflectance spectroscopy (UV-vis DRS) and room-temperature photoluminescence spectra (PL). The effects of Ce^{3+} doping amount on the photo-absorption properties and photocatalytic H-2 evolution rates under visible light irradiation over $Zn_{0.8}Cd_{0.2}S$-En hybrid nanosheets were also investigated. The results show that the incorporation of Ce^{3+}, existing in the form of Ce_2S_3 with uniformly distribution in sample can narrow the band gap, enhance the photo-absorption and extend the photo-absorption range of the $Zn_{0.8}Cd_{0.2}S$-En hybrid nanosheets. The photocatalytic activity tests prove that Ce^{3+}-doped $Zn_{0.8}Cd_{0.2}S$-En nanosheets have much higher photocatalytic hydrogen production activity when compared with the undoped one. Under the irradiation of visible light, the highest photocatalytic hydrogen production rate of 229.2 mu mol h(-1) is observed over 0.1 wt.% Ce^{3+}-doped $Zn_{0.8}Cd_{0.2}S$-En nanosheets, which is about 1.4

times higher than that of the undoped $Zn_{0.8}Cd_{0.2}S$-En nanosheets. The improved photocatalytic activity of Ce-doped samples ascribes to the enhanced photo-response in the visible light region and the efficient separation of electron-hole pairs due to the formation of heterojunction between $Zn_{0.8}Cd_{0.2}S$-En and Ce_2S_3.

«Size-dependent structural phase transitions and their correlation with photoluminescence and optical absorption behavior of annealed $Zn_{0.45}Cd_{0.55}S$ quantum dots» [46]. In this paper, we investigate the effect of thermally induced structural phase transitions on the photoluminescence (PL) and optical absorption behaviour of $Zn_{0.45}Cd_{0.55}S$ nanoparticles (NPs). Analysis of X-ray diffraction (XRD) patterns and high-resolution electron microscope (HRTEM) images reveal that the as-synthesized sample possesses zinc-blende-type cubic structure. In addition, at annealing temperature (T-a) 400 degrees C, the cubic structure transforms completely into the wurtzite-type hexagonal structure. Furthermore, the second phase transition of the as-synthesized sample has observed at 700 degrees C, where the cubic structure has transformed into mixed polycrystalline phases of hexagonal ZnO, cubic CdO, monoclinic CdSO3, and orthorhombic $ZnSO_4$ structures. These new phases have also confirmed from the analysis of Raman and FTIR spectra. Analysis of UV-visible optical absorption spectra demonstrates that Increasing T-a results in the decrease of optical band gap due the improvement in crystallinity accompanied by the increase in the particle size. The PL emission bands at an excitation energy of 3.818 eV exhibit redshift and a decrease in the intensity with increasing T-a up to 500 degrees C. Meanwhile, further increase in T-a up to 700 degrees C results in the enhancement of green emission intensity. On the other hand, PL emission spectra at 3.354 eV and T. 700 degrees C, reveal a dramatic increase in the emission intensity nearly by one-order of magnitude with respect to its value of the as-synthesized sample. This behaviour is ascribed to the incorporation of oxygen-related defects via thermal annealing in air, which act as additive radiative centers. Also, we have interpreted the observed spectral blue shift of PL emission spectrum with increasing excitation energy.

A similar study of this complex sulfide is also reflected in the following works [11, 32] and in earlier studies [38, 23, 29].

2. Research in the field of complex AgInS sulfide.

«Luminescence and photoelectrochemical properties of size-selected aqueous copper-doped Ag-In-S quantum dots» [47]. Ternary luminescent copper and silver indium sulfide quantum dots (QDs) can be an attractive alternative to cadmium and lead chalcogenide QDs. The optical properties of Cu-In-S and Ag-In-S (AIS) QDs vary over a broad range depending on the QD composition and size. The implementation of ternary QDs as emitters in bio-sensing applications can be boosted by the development of mild and reproducible syntheses directly in aqueous solutions as well as the methods of shifting the photoluminescence (PL) bands of such QDs as far as possible into the near IR spectral range. In the present work, the copper-doping of aqueous non-stoichiometric AIS QDs was found to result in a red shift of the PL band maximum from around 630 nm to similar to 780 nm and PL quenching. The deposition of a ZnS shell results in PL intensity recovery with the highest quantum yield of 15%, with almost not change in the PL band position, opposite to the undoped AIS QDs. Size-selective precipitation using 2-propanol as a non-solvent allows discrimination of up to 9 fractions of Cu-doped AIS/ZnS QDs with the average sizes in the fractions varying from around 3 to 2 nm and smaller and with reasonably the same composition irrespective of the QD size. The decrease of the average QD size results in a blue PL shift yielding a series of bright luminophors with the emission color varies from deep-red to bluish-green and the PL efficiency increases from 11% for the first fraction to up to 58% for the smallest Cu-doped AIS/ZnS QDs. The rate constant of the radiative recombination of the size-selected Cu-doped AIS/ZnS QDs revealed a steady growth with the QD size decrease as a result of the size-dependent enhancement of the spatial exciton confinement. The copper doping was found to result in an enhancement of the photoelectrochemical activity of CAIS/ZnS QDs introduced as spectral sensitizers of mesoporous titania photoanodes of liquid-junction solar cells.

«Origin and Dynamics of Highly Efficient Broadband Photoluminescence of Aqueous Glutathione-Capped Size-Selected Ag-In-S Quantum Dots» [51]. The 2-3 nm size-selected glutathione-capped Ag In S (AIS) and core/shell AIS/ZnS quantum dots (QDs) were produced by precipitation/redissolution from an aqueous colloidal ensemble. The QDs reveal broadband photoluminescence (PL) with a quantum yield of up to 60% for the most populated fraction of the core/shell AIS/ZnS QDs. The PL band shape can be described by a self-trapped exciton model implying the PL band being a sequence of phonon replica of a zero-phonon line resulting from strong electron phonon interaction and a partial conversion of the electron excitation energy into lattice vibrations. It can be concluded that the position and shape of the PL bands of MS QDs originate not from energy factors (depth and distribution of trap states) but rather from the dynamics of the electron phonon interaction and the vibrational relaxation in the QDs. The rate of vibrational relaxation of the electron excitation energy in MS QDs is found to be size-dependent, increasing almost twice from the largest to the smallest QDs.

«Synthesis of $AgInS_2$ quantum dots with tunable photoluminescence for sensitized solar cells» [14]. Synthesis of quantum dots (QDs) with high photoluminescence is critical for quantum dot sensitized solar cells (QDSCs). A series of high quality $AgInS_2$ QDs were synthesized under air circumstance by the organometallic high temperature method. Feature of tunable photoluminescence of $AgInS_2$ QDs with long lifetime and quantum yields beyond 40% has been achieved, which was mainly attributed to the donor-acceptor pair recombination, contributed above 91% to the whole emission profiles. After ligand exchange with bifunctional linker, water-soluble $AgInS_2$ QDs were adopted as light harvesters to fabricate QDSCs, achieved best PCE of 2.91% (short-circuit current density of 13.78 mA cm(-2), open-circuit voltage of 0.47 V, and fill factor of 45%) under one full sun illumination. The improved photovoltaic performance of $AgInS_2$ QDs-based QDSCs is mainly originated from broadened optoelectronic response range up to-900 nm, and enhanced photoluminescence with long lifetime and high quantum yield beyond 40%, which provide strong photoresponse similar to 40% over the window below 750 nm. The synthetic approach combined with intrinsic defects created by intentionally composition modulation introduces a new approach towards the goal of high performance QDSCs.

The research results of this complex compound are also reflected in the following works [36, 22] in earlier studies [27].

3. Research in the field of complex $CuInS_2$ sulfide.

«Defect Luminescence from Wurtzite $CuInS_2$ Nanocrystals: Combined Experimental and Theoretical Analysis» [45]. $CuInS_2$ nanocrystals with the wurtzite structure show promise for applications requiring efficient energy transport due to their anisotropic crystal structure. We investigate the source of photoluminescence in the near-infrared spectral region recently observed from these nanocrystals. Spectroscopic studies of both wurtzite $CuInS_2$ itself and samples alloyed with Cd or Zn allow the assignment of this emission to a radiative point defect within the nanocrystal. structure. Further, by varying the organic passivation layer on the material, we are able to determine that the atomic species responsible for nonradiative decay paths on the nanocrystal surface are Cu- or S-based. Density functional theory calculations of defect states within the material allow identification of the likely radiative species. Understanding both the electronic structure and optical properties of wurtzite $CuInS_2$, nanocrystals is necessary for their efficient integration into potential biological, photovoltaic, and photo catalytic applications.

«Interplay between Surface Chemistry, Precursor Reactivity, and Temperature Determines Outcome of ZnS Shelling Reactions on $CuInS_2$ Nanocrystals» [10]. ZnS shelling of I-III-$VI_{(2)}$ nanocrystals (NCs) invariably leads to blue-shifts in both the absorption and photoluminescence spectra. These observations imply that the outcome of ZnS shelling reactions on I-III-VI_2 colloidal NCs results from a complex interplay between several processes taking place in solution, at the surface of, and within the seed NC. However, a fundamental understanding of the factors determining the balance between these different processes is still lacking. In this work, we address this need by investigating the impact of precursor reactivity, reaction temperature, and surface chemistry (due to the washing procedure) on the outcome of ZnS shelling reactions on $CuInS_2$ NCs using a seeded growth approach. We demonstrate that low reaction temperatures (150 degrees C) favor etching, cation exchange, and alloying regardless of the precursors used. Heteroepitaxial shell overgrowth becomes the dominant process only if reactive S- and Zn-precursors (S-ODE/OLAM and ZnI_2) and high reaction temperatures (210 degrees C) are used, although a certain degree of heterointerfacial alloying still occurs. Remarkably, the presence of residual acetate at the surface of CIS seed NCs washed with ethanol is shown to facilitate heteroepitaxial shell overgrowth, yielding for the first time CIS/ZnS core/shell NCs displaying red-shifted absorption spectra, in agreement with the spectral shifts expected for a type-I band alignment. The insights provided by this work pave the way toward the design of improved synthesis strategies to CIS/ZnS core/shell and alloy NCs with tailored elemental distribution profiles, allowing precise tuning of the optoelectronic properties of the resulting materials.

The research results of this complex compound are also reflected in the following works [31] in earlier studies [3, 24, 40, 18, 19, 13, 9, 28, 35, 12].

4. Research in the field of complex ZnInS sulfide.

«Improving the emission of ultrasmall Mn-doped ZnInS quantum dots via Ag-induced trap state energy level» [39]. For ultrasmall Mn-doped quantum dots (QDs), the energy transfer of the exciton to the Mn is the key factor for Mn emission. Herein, the Ag-induced electron trap state energy level, which is an intermediate energy level between the conduction band (CB) and T-4(1) of Mn, is proposed for improving the energy transfer. After doping the Ag and forming Ag&Mn:ZnInS QDs, most excitons will first be captured by the intermediate energy level and then be transferred to Mn d-states, leading to enhanced photoluminescence (PL) quantum yields (QY) of the QDs from the original 17% (Mn:ZnInS QDs) to 30% (Ag&Mn:ZnInS QDs).

«Dopant-controlled photoluminescence of Ag-doped Zn-In-S nanocrystals» [50]. In this work, we reported the growth of cadmium-free Ag-doped Zn-In-S nanocrystals (NCs) with effective photoluminescence (PL) via a hot-injection strategy. The effects of the nucleation temperatures, reaction times, and Ag-doping concentrations on the PL properties of Ag-doped Zn-In-S NCs were investigated systematically. The as-synthesized NCs exhibit color-tunable PL emissions covering a broad visible range of 472-585 nm. After being passivated by a protective ZnS shell, the PL quantum yield (QY) of the resultant NCs was greatly improved up to 33%. With the increase of the Ag-doping level, the PL is significantly intensified due to the improved concentration of Ag ions which provides more holes to recombine with electrons from the bottom of the conduction band. This also makes the emission via the dopant energy level become a powerful, competitive advantage for the NCs with higher Ag-doping levels, resulting in a longer lifetime and higher PL QY. These results suggest that tailoring the Ag-doping level can be a powerful strategy to control the optical properties of Ag-doped Zn-In-S NCs.

«Highly bright and stable white-light-emitting cadmium-free Ag, Mn co-doped Zn-In-S / ZnS quantum dots and their electroluminescence» [55]. Optimized white light emitting Ag, Mn:Zn-In-S quantum dots (QDs) were synthesized via a simple, scalable, reproducible, and low-cost one-pot non-injection synthetic approach. After coating a thick ZnS shell (similar to 12 monolayers) on the core QDs, high photoluminescence (PL) quantum yield (QY) up to 76% was achieved and high emission efficiency was retained even when the initially oil-soluble QDs were transferred into aqueous media by ligand replacement. Moreover, both thermal stability and photostability of thick shell-Ag, Mn:Zn-In-S/ZnS QDs were significantly enhanced as compared with those of Ag, Mn:Zn-In-S core QDs due to the suppressed surface defects resulting from the passivation of the dense ZnS layers. White quantum dot light-emitting diodes (QD-LEDs) were fabricated using thick shell Ag, Mn:Zn-In-S/ZnS QDs as single QDs emitter, showing good performance with maximum current efficiency of 1.86 cd A(-1)corresponding to external quantum efficiency (EQE) of 0.82% at a current density of 0.065 mA cm(-2), color rendering indices (CRI) of 83, Commission International d'Eclairage (CIE) coordinates of (0.344, 0.393) and correlated color temperature (CCT) of 5156 K.

«Doping concentration-dependent photoluminescence properties of Mn-doped Zn-In-S quantum dots» [15]. In this report, doping concentration-dependent photoluminescence (PL) properties of Mn-doped ternary Zn-In-S quantum dots (QDs) were studied by using steady-state and time-resolved PL spectroscopy. The QDs PL was firstly significantly intensified with the increasing Mn doping concentration and then decreased after the doping concentration increased up to 7.5 at.%. However, their decay lifetimes exhibit a monotone decrease with Mn doping concentration ranged from 0 to 10 at.%. It can be concluded that the PL intensity was mainly determined by two factors: one was the increased efficiency of energy transfer from host excitons to Mn^{2+} ion accepter, and the other was the decreased efficiency of the emission from a Mn^{2+} ion, which was caused by the increased component of exposed Mn^{2+} ions on QDs surface and the accelerated interaction between adjacent dopants. The competition of above two exciton relaxation dynamics processes determined the trend of the PL intensity, while the latter was responsible for the monotonously decreased lifetime of the Mn^{2+} ion emission with the increasing Mn doping concentration.

The research results of this complex compound are also reflected in the following works [16, 17] in earlier studies [25, 26, 34,1, 2].

Note that other complex compounds of complex ternary sulfides such as CdPbS [7], HgPbS [20], BaPbS [21], CdCoS [4], PbZnS [5], PbCoS [6], HgCdS [30], CdSnS [33], PbCaS [49], CdPbS [52], PbSnS [53], ZnMnS [41], CdMnS [43], ZnCoS [42], CdFeS [54], CdNiS [44], MnZnS [48] were studyed.

Research in the field of sulfides was also carried out by domestic scientists. For example, studies for ZnS sulfides are reflected in [56, 57], and the study for the physicochemical properties of CdS sulfides is described in [58, 59]. Practical applications of complex sulfides are described in [60].

Findings

There a clear tendency of doping the basic sulfide material with various chemical elements that are not part of them is followed from the analysis of the vast majority of modern works (on the synthesis and study of complex sulfides) shown in the literature review. This operation significantly changes the physico - chemical properties of complex sulfide, which, as a result, leads to a significant expansion of their practical application in science and technology.

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КҮРДЕЛІ СУЛЬФИДТІ ҚОСЫЛЫСТАР САЛАСЫНДАҒЫ ЗАМАНАУИ ЗЕРТТЕУЛЕР ТУРАЛЫ (ЖАҒДАЙЫ ЖӘНЕ БЕТАЛЫСЫ)

Аннотация. Мақалада күрделі сульфидтерді зерттеу бойынша бір бөлігі мақалада келтірілген 600 аса әдебиеттік көздердің ең маңызды ғылыми еңбектеріне шолу жасалынды. Ең перспективалы күрделі сульфидтер CdZnS, AgInS, CuInS, ZnInS саласына мысалдар және олардың тәжірибелік қолданылатын болжамды ауқымы келтірілді.

Осылайша, CdZnS күрделі сульфид саласындағы зерттеулер бойынша жарық энергиясын электр тогына түрлендіру тиімділігі анықталды, бұл осы қосылысты күн элементтерінің сипаттамаларын жақсарту үшін сенсибилизатор ретінде пайдалану туралы айтуға мүмкіндік береді. Ce_2S_3 түріндегі Ce^{3+}-ді тегіс бөліп қосу тыйым салынған аймақтың енін тарылтып, $Zn_{0.8}Cd_{0.2}S$ гибридті наножапырақтардың фото сіңіру диапазонын ұлғайтуы және кеңейтуі мүмкін. $Zn_{0.45}Cd_{0.55}S$ нанобөлшектерді оптикалық сіңіру және фотолюминесценциясына термиялық индукцияланған құрылымдық фазалық ауысулардың әсері зерттелді.

AgInS аралас сульфид саласындағы зерттеулерде мыспен легирленуі сұйық өтумен күн элементтеріндегі титан диоксидінің мезокеуекті фотоанодтардың спектрлік сенсибилизаторлары ретінде енгізілген CAIS/ZnS кванттық нүктелерінің фотоэлектрохимиялық белсенділігінің жоғарылауына алып келетіні байқалған. Кванттық нүктелердің фотолюминесценция жолақтарының орналасуы мен пішіні энергетикалық факторлармен емес (тұзақтардың тереңдігімен және жай-күйінің таралуымен), электрондардың фонондармен өзара әрекеттесу динамикасымен және кванттық нүктелерде тербелмелі релаксациямен байланысты екендігі туралы қорытынды жасалады. Жоғары фотолюминесценциялы кванттық нүктелердің синтезі күн элементтері үшін шешуші мәнге ие болатыны атап көрсетілді.

$CuInS_2$ күрделі сульфид саласындағы зерттеулер бойынша жұмыстарда $CuInS_2$ вюрциттің өзін және Cd немесе легирленген Zn үлгілердің спектроскопиялық зерттеулері бұл сәулелenуді нанокристаллдағы радиациялық нүктелік ақауға жатқызуға мүмкіндік беретіні дәлелденген. Өңдеу әдісімен $CuInS_2$ нанокристаллдарындағы ZnS қабыршықтану реакцияларының қорытынды мәселесі прекурсордың реакциялық қабілеттілігінің, реакция температурасының және беттің химиялық құрамының әсерлерін зерттеу арқылы шешіледі.

ZnInS аралас сульфидті зерттеу кезінде легирленген Mn аса аз кванттық нүктелер үшін экситонмен энергияны Mn-ге тасымалдау негізгі фактор болып табылады. Ыстық инжекция әдісімен тиімді фотолюминесценциясы бар, құрамында кадмий жоқ легирленген Ag-ң ZnInS нанокристаллдарының өсуі зерттелді. Ақ жарық сәуле шығаратын оңтайландырылған кванттық нүктелер Ag, Mn белгіленді: ZnInS инжекциясыз қарапайым, масштабталған, жаңғыртылған және қымбат емес синтетикалық тәсіл арқылы синтезделді. Спектроскопияны пайдалана отырып, Mn легирленген ZnInS-ң фотолюминесцентті қасиеттері, үштік кванттық нүктелері зерттелді.

Шолуда келтірілген әдеби көздерді талдаудан, күрделі сульфидтерді синтездеу және зерттеу жөніндегі қазіргі заманғы жұмыстардың басым көпшілігінде сульфидтің негізгі материалын олардың құрамына кірмейтін әртүрлі химиялық элементтермен қоспалау үрдісі айқын байқалады. Бұл операция өз кезегінде ғылым мен техникада практикалық қолдану аясын айтарлықтай кеңейтуге әкелетін күрделі сульфидтің физика-химиялық қасиеттерін айтарлықтай өзгертеді.

Түйін сөздер: металдардың күрделі сульфидтері, қоспалау, кванттық нүкте, кванттық ауысу, фотолюминесценция, электрохимиялық қасиеттері, фазалық ауысулар, тұтқыштар, оптикалық қасиеттері, күн батареялары, жарық диодтары.

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О СОВРЕМЕННЫХ ИССЛЕДОВАНИЯХ В ОБЛАСТИ СЛОЖНЫХ СУЛЬФИДНЫХ СОЕДИНЕНИЙ (СОСТОЯНИЕ И ТЕНДЕНЦИИ)

Аннотация. В статье сделан обзор наиболее значимых научных работ по исследованию сложных сульфидов из более 600 литературных источников, часть которых приведена в статье. Приведены примеры исследований в области наиболее перспективных сложных сульфидов CdZnS, AgInS, CuInS, ZnInS и прогнозируемая сфера их практического применения.

Так, по исследованиям в области сложного сульфида CdZnS выявлена эффективность преобразования световой энергии в электрический ток, что позволяет судить об использовании этого соединения в качестве сенсибилизатора для улучшения характеристик солнечных элементов. Отмечается, что включение Ce^{3+}, существующего в форме Ce_2S_3 с равномерным распределением в образце может сузить ширину запрещенной зоны, увеличить и расширить диапазон фотопоглощения гибридных нанолистов $Zn_{0.8}Cd_{0.2}S$. Исследовано влияние термически индуцированных структурных фазовых переходов на фотолюминесценцию и оптическое поглощение наночастиц $Zn_{0.45}Cd_{0.55}S$.

В исследованиях в области смешанного сульфида AgInS отмечается, что легирование медью приводит к повышению фотоэлектрохимической активности квантовых точек CAIS / ZnS, введенных в качестве спектральных сенсибилизаторов мезопористых фотоанодов диоксида титана в солнечных элементах с жидким переходом. Делается вывод о том, что положение и форма полос фотолюминесценции квантовых точек обусловлены не энергетическими факторами (глубиной и распределением состояний ловушек), а, скорее, динамикой взаимодействия электронов с фононами и колебательной релаксацией в квантовых точках. Отмечено, что синтез квантовых точек с высокой фотолюминесценцией имеет решающее значение для солнечных элементов.

В работах по исследованиям в области сложного сульфида $CuInS_2$ доказано, что спектроскопические исследования как самого вюрцита $CuInS_2$, так и образцов, легированных Cd или Zn, позволяют отнести это излучение к радиационному точечному дефекту в нанокристалле. Проблема исхода реакций шелушения ZnS на нанокристаллах $CuInS_2$ методом травления решается исследованием влияния взаимодействий реакционной способности прекурсора, температуры реакции и химического состава поверхности.

При исследованиях смешанного сульфида ZnInS выявлено, что для сверхмалых квантовых точек, легированных Mn, передача энергии экситоном в Mn является ключевым фактором. Исследован рост нанокристаллов ZnInS, легированных Ag, не содержащих кадмия с эффективной фотолюминесценцией методом горячей инжекции. Отмечено, что оптимизированные излучающие белый свет квантовые точки Ag, Mn: ZnInS были синтезированы с помощью простого, масштабируемого, воспроизводимого и недорогого синтетического подхода без инжекции. Изучены фотолюминесцентные свойства, тройных квантовых точек ZnInS, легированных Mn, с использованием спектроскопии.

Из анализа литературных источников, приведённых в обзоре, следует, что в подавляющем большинстве современных работ по синтезу и исследованию сложных сульфидов явно прослеживается тенденция легирования основного материала сульфида различными химическими элементами, не входящих в их состав. Эта операция заметно изменяет физико-химические свойства сложного сульфида, что, как следствие, в свою очередь приводит к значительному расширению сферы их практического применения в науке и технике.

Ключевые слова: сложные сульфиды металлов, легирование, квантовая точка, квантовый переход, фотолюминесценция, электрохимические свойства, фазовые переходы, ловушки, оптические свойства, солнечные батареи, светодиоды.

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CONVERSION OF PROPANE-PROPYLENE FRACTION INTO AROMATIC HYDROCARBONS ON MODIFIED ZEOLITE CATALYSTS

Abstract. The process of transformation of propane-propylene fraction into aromatic hydrocarbons on zeolite-containing catalysts modified Zn, La, Cr, Zr and P was discovered. The process was carried out in an installation in a flow installation at atmospheric pressure with a temperature variation from 350 to 600°C and a volumetric feed rate of 150-1020 h^{-1}. The catalysts were prepared by impregnation of aluminum hydroxide and zeolite ZSM-5 with aqueous solutions of nitric acid salts of metals and phosphoric acid. The physical and chemical characteristics of the developed catalysts are studied. The BET method established that the surface of the developed catalysts fluctuates within 211.0-274.0 m^2 / g of the catalyst. Catalysts are predominantly mesoporous: pores with $d \approx 2.0$-3.0 nm predominate.

It is shown that the developed modified zeolite-containing catalysts have high catalytic activity and selectivity in the process of processing the propane-propylene fraction into aromatic hydrocarbons. The predominant products formed during the processing of C2-C4 alkanes are toluene and benzene. It was found that the highest yield of aromatic hydrocarbons is 52.8% (550°C, 150 h^{-1}) on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3 with a conversion rate of 100.0%, selectivity for aromatic compounds - 52.8%.

Modified zeolite-containing catalysts have multifunctional properties. The composition of liquefied petroleum gas processing products shows that the formation of aromatic hydrocarbons occurs in one stage as a result of cracking, dehydrogenation, oligomerization, dehydrocyclization, alkylation reactions.

Keywords: zeolite-containing catalysts, propane-propylene fraction, aromatic hydrocarbons.

INTRODUCTION

Kazakhstan has large reserves of light hydrocarbon raw materials: gas condensate, natural and petroleum gases, catalytic processing of which is very limited. Efficient processing of light hydrocarbon raw materials to obtain important products of petrochemical synthesis remains one of the important problems in petrochemistry. To date, light hydrocarbons are used as raw materials in only a small number of technological processes.

Catalytic processing of light hydrocarbons into practically important products is one of the ways aimed at their effective use. These products include olefins and aromatic hydrocarbons, important starting products in the basic organic synthesis industry. On their basis, plastics, synthetic fibers, resins, rubbers for various purposes, dyes, surfactants, pharmaceutical and agricultural products are obtained.

Currently, in the petrochemical and oil refining industry, zeolite-containing catalysts based on highly silica zeolites of the pentasil family are widely used, having a unique micro porous structure and acid-base properties, capable of converting light alkanes into valuable products of petrochemical synthesis. Zeolite-containing catalysts can efficiently process low molecular weight alkanes into aromatic hydrocarbons. At present, interest in high silica zeolites of pentasil type as catalysts for aromatization of low molecular weight hydrocarbons has grown [1-21].

Experimental part

In this paper, the process of processing propane-propylene fractions on zeolite-containing catalysts modified with zinc, phosphorus and metals of variable valence: Zn-La-ZSM-Al_2O_3, Zn- La - P-ZSM-Al_2O_3 Zn-La- Zr -ZSM-Al_2O_3, Zn-Zr-ZSM-Al_2O_3, Zn-La-P-Cr-ZSM-AI_2O_3. The catalysts were prepared by impregnation of a mixture of aluminum hydroxide and zeolite HZSM-5 with aqueous solutions of metal salts followed by drying at 150°C and calcination at 550°C. The catalysts were tested in the process of processing propane-propylene fractions in a flowing quartz reactor with a stationary catalyst bed at varying reaction temperature in the range 350-600°C and atmospheric pressure, volume velocity 150-1020 h^{-1}. The reaction products were analyzed on “Crystal-5000M” and “Agilent chromatographs”.

Results and discussion

When processing propane-propylene fraction on modified zeolite catalyst Zn- La-ZSM-Al_2O_3 (table 1), aromatic hydrocarbons and gaseous products are formed. Benzene, toluene, ethylbenzene, xylenes and C_{8+} - hydrocarbons are found in the liquid phase, and C1-C4 hydrocarbons are found in the gas phase. With an increase in the process temperature from 400 to 650°C, the conversion rate increases from 1.4 to 100.0%. The yield of aromatic hydrocarbons in these conditions increases from 8.9 to 29.2 -28.9%. The maximum selectivity is observed at 600°C and is 29.2%. The quantitative composition of the resulting aromatic hydrocarbons depends significantly on the temperature of the process. Toluene yield in the range of 400 - 650°C varies extremely, reaching a maximum value at 450°C, and is 46.9%. The yield of benzene with increasing temperature increases from 4.1 (400°C) to 39.2% (650°C). The content of xylene in the liquid catalyzate-1,6-7,2%. The yield of ethylbenzene and C5-C6 hydrocarbons decreases with an increase in temperature in the range of 400-650°C from 24.8 to 4.8% and from 21.8 to 4.6 %, respectively. With increasing temperature, cracking increases with the formation of C1-C2 hydrocarbons: the amount of methane increases from 0.1 to 53.1%, ethane-from 1.0 to 44.2%.

Table 1 - Processing of propane-propylene fraction on catalyst Zn-La-ZSM-Al_2O_3

T, °C	400	450	500	550	600	650
Conversion, %	1,4	38,6	97,2	99,5	100	100
The yield of liquid phase, %	8,9	12,4	18,4	26,2	29,2	28,9
Select. ArC, C_4%	-	32,1	18,9	26,3	29,2	28,9
Liquid phase,%						
Benzene	4,1	10,1	16,5	20,7	32,2	39,2
Toluene	31,8	46,9	44,5	32,1	37,2	32,6
Ethylbenzene	24,8	22,2	21,0	8,8	6,6	4,8
Xylene	7,2	6,6	6,6	2,8	2,2	1,6
C_{5-6}	21,8	1,5	0,3	27,2	9,1	4,6
C_{8+}	10,3	12,7	11,1	8,4	12,7	17,2

The process of processing propane-propylene fraction on the catalyst Zn-La-P-ZSM-Al_2O_3 was investigated. From the data presented in table 2, it can be seen that with an increase in temperature from 350 to 600°C, the conversion increases from 27.8 to 98.9%. With an increase in temperature from 350 to 550°C, the yield of aromatic hydrocarbons increases from 19.3 to 38.1%, but at a higher temperature (600°C), there is a decrease in the yield of ArC to 27.1%. In the interval 350-600°C toluene yield is 27.4-39.1%, and benzene-0.5-23.0%. The content of xylene in the liquid catalyzate - 1,6-4,3%. The yield of ethylbenzene decreases with temperature increase in the range of 400-600°C from 22.9 to 5.9%. The yield of C_5-C_6 hydrocarbons decreases with increasing temperature in the range 350-550°C from 37.2 to 17.0%, then increases to 32.0 (600°C). The maximum selectivity for ArC is observed at 500°C and is 54.0%. At higher temperatures, the ArC selectivity is slightly lower-38.7-27.4%. With increasing temperature, cracking with the formation of C_1-C_2 hydrocarbons is observed.

In the process of processing the propane-propylene fraction on the catalyst Zn-La- Zr -ZSM-Al_2O_3 with an increase in temperature from 350 to 600°C, the conversion increases from 7.0 to 100.0%. With an increase in temperature from 350 to 550°C, the yield of aromatic hydrocarbons increases from 4.6 to 28.8%, at 600°C there is a decrease in the yield of aromatic hydrocarbons to 23.2%. With increasing temperature, the selectivity of the formation of target products decreases: the maximum selectivity for

ArC is observed at 350°C and is 65.7%. At higher temperatures, ArC selectivity is lower. Toluene and ethylbenzene prevail in the liquid catalysate. Toluene yield grows from 14.4 to 43.9% in the range 350-550°C, at 600°C toluene yield is slightly lower-40.9%. The yield of ethylbenzene monotonically decreases from 24.0 to10, 6%. The amount of benzene in these conditions increases from 1.7 to 27.2%. The content of xylene ranges from 3,1 to 7,9%. With increasing temperature, cracking with the formation of C_1-C_2 hydrocarbons is observed (table 3).

Table 2 - Processing of propane-propylene fraction on catalyst Zn-La- P-ZSM-Al_2O_3

T, °C	350	400	450	500	550	600
Conversion, %	27,8	36,7	58,6	69,5	98,5	98,9
The yield of liquid phase, %	18,7	19,3	30,6	37,5	38,1	27,1
Select. ArC, %	18,8	52,6	52,2	54,0	38,7	27,4
Liquid phase, %						
Benzene	2,6	3,9	9,2	14,7	23,0	19,1
Toluene	27,4	27,9	31,9	39,1	34,3	28,2
Ethylbenzene	22,9	16,2	15,9	17,5	9,4	5,9
Xylene	4,3	3,8	3,9	4,2	2,5	1,6
C_{5-6}	26,8	37,2	30,7	17,0	17,0	32,0
C_{8+}	16,0	11,0	8,4	7,5	13,8	13,2

Table 3 - Effect of temperature on the process of processing propane-propylene fraction Zn-La-Zr-ZSM-Al_2O_3

T,°C	350	400	450	500	550	600
Conversion, %	7,0	52,2	63,8	92,3	100	100
The yield of liquid phase , %	4,6	10,5	23,0	26,9	28,2	23,2
Select. ArC, %	65,7	20,1	24,5	29,1	28,2	23,2
состав жидкой фазы, % мас						
Benzene	1,7	4,7	9,7	13,6	21,9	27,2
Toluene	14,4	35,0	40,3	42,3	43,9	40,9
Ethylbenzene	24,0	27,7	23,1	21,5	15,0	10,6
Xylene	3,9	7,9	6,6	6,3	4,7	3,1
C_{5-6}	15,8	3,1	7,2	3,1	0,2	1,4
C_{8+}	40,2	21,6	13,1	13,2	14,3	16,8

The influence of the bulk feed rate on the activity and selectivity of the catalyst Zn-La-Zr-ZSM-Al_2O_3 in the processing of propane-propylene fraction was studied (table 4). At 550°C and volume feed rate of 150 h^{-1} conversion is 100%, yield of aromatic hydrocarbons-37,9%. With an increase in the volume feed rate of raw materials up to 825 h^{-1} conversion does not change and is equal to 100%, but the output of the liquid phase is reduced to 10.8%. The qualitative and quantitative composition of the liquid catalyzate does not change much when the volumetric feed rate of the raw material changes. The yield of benzene is in the range of 21.9 to 25.1%, of toluene, from 42.8 to 46.4%. The yield of ethylbenzene is in the range of 13,2 - 15,0%. The maximum selectivity of aromatic hydrocarbons formation reaches 37.9% at V=150 h^{-1}.

Table 4 - Effect of volumetric feed rate on the process
of processing propane-propylene fraction on the catalyst Zn-La-Zr-ZSM-Al_2O_3

V, h^{-1}	150	300	470	675	825
Conversion, %	100	100	97,9	100	100
The yield of liquid phase, %	37,9	28,2	19,4	11,3	10,8
Select. ArC, %	37,9	28,2	19,8	11,3	10,8
Liquid phase, %					
Benzene	23,4	21,9	25,1	23,7	24,9
Toluene	43,2	43,9	42,8	44,9	46,4
Ethylbenzene	13,3	15,0	13,6	14,9	15,0
Xylene	4,0	4,7	4,2	4,7	4,6
C_{5-6}	2,4	0,2	1,3	0,9	0,2
C_{8+}	13,7	14,3	13,0	10,9	8,9

The stability of the modified zeolite-containing catalyst Zn-La-Zr-ZSM-Al_2O_3 in the process of processing gaseous hydrocarbons formed during catalytic cracking was studied. Studies were carried out at 550°C and V=300h^{-1} (table 5). From the data presented in table 5, it can be seen that during 11 hours of operation of the catalyst, the conversion does not change and is 100%. The yield of the liquid phase in the first 5 hours of operation changes little-20.6-17.9%, then after 11 hours of operation, it decreases to 10,8%.

Under these conditions, the yield of benzene varies in the redistribution of 25.0 to 28.9%. The yield of toluene is higher than benzene – 40.9 - of 44.4%. The yield of ethylbenzene-10.9-13.0%, xylene-3.4-6.0%. C_1-C_4 hydrocarbons were found in the gas phase.

Table 5 - Stability of the modified zeolite-containing catalyst Zn-La-Zr-ZSM-Al_2O_3
in the process of processing propane-propylene fraction

Time, h	1	2	3	4	5	6	7	8	9	10	11
Conversion,%	100	100	100	100	100	100	100	100	100	100	100
The yield of liquid phase, %	20,6	20,4	19,0	18,0	17,9	15,7	12,5	12,7	12,3	11,1	10,8
Select. ArC, C_3%	64,2	55,0	44,1	35,4	88,6	-	-	35,8	26,2	64,5	54,8
Select. ArC, C_4%	20,6	20,4	90,0	18,0	17,9	15,7	12,5	12,7	12,3	11,1	10,8
	Liquid phase, %										
Benzene	26,3	27,7	28,7	28,9	26,7	25,9	26,9	24,0	25,0	25,9	26,4
Toluene	42,7	40,9	42,2	41,3	42,9	42,0	43,3	43,2	40,4	44,4	44,2
Ethylbenzene	12,8	11,8	10,9	11,3	12,4	12,1	12,3	13,0	11,6	11,1	12,3
Xylene	4,1	3,7	3,4	3,6	3,9	4,7	3,9	6,0	3,6	4,3	3,9
$C_{5\text{-}6}$	1,4	0,6	1,7	0,8	0,9	2,4	2,0	3,0	8,0	1,0	1,8
C_{8+}	12,7	15,3	13,1	14,1	13,2	12,9	11,6	10,8	11,4	12,3	11,4

When processing the propane-propylene fraction on the catalyst Zn-Zr-ZSM-Al_2O_3, the conversion rate increases from 6.3 to 100% with an increase in temperature from 400 to 600°C. From the data of table 6 it can be seen that the products of processing of propane-propylene fraction contain aromatic hydrocarbons, mainly benzene, toluene, ethylbenzene and xylenes. The total yield of aromatic hydrocarbons (ArC) increases from 8.8 (350°C) to 21.3% (600°C). Maximum ArC selectivity is 29.2% at 450^0C. With an increase in temperature from 400 to 600°C, there is an increase in the content of benzene from 1.0 to 33.3%. Toluene yield varies, increasing from 30.2% (350°C) to 44.3% (500°C) and decreasing to 37.6% (600°C). The content of xylene is small-2,3-5,2%. Ethylbenzene yields vary from 30.3 (400°C) to 7.6% (600°C). Product composition the temperature in the gas phase indicates that as the temperature increases, the cracking direction increases with the formation of methane and ethane.

Table 6 - Processing of propane-propylene fraction on catalyst Zn -Zr -ZSM-Al_2O_3

T, °C	350	400	450	500	550	600
Conversion, %	-	6,3	68,8	95,5	100	100
The yield of liquid phase, %	8,8	10,8	20,1	21,8	20,6	21,3
Select. ArC, %	-	-	29,2	22,8	20,6	21,3
Liquid phase, %						
Benzene	1,0	4,0	9,8	14,6	25,1	33,3
Toluene	36,2	31,2	41,7	44,3	43,4	37,6
Ethylbenzene	30,0	28,0	22,6	19,9	12,3	7,6
Xylene	2,8	5,2	3,6	2,3	3,8	2,5
$C_{5\text{-}6}$	8,0	9,6	3,6	3,5	1,4	0,6
C_{8+}	22,0	22,0	18,7	15,4	14,0	18,4

Table 7 presents the results obtained during the processing of propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-AI_2O_3 (KTK -15).

When processing propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3 at a volumetric rate of 350 h^{-1} with a temperature increase from 400 to 600°C, an increase in the conversion rate from 85.2 % (450°C) to 100% at 600°C is observed (table 7). Under these conditions, the highest yield of aromatic hydrocarbons is 34.5% at 550°C. the Selectivity for aromatic hydrocarbons for C3 is maximum at 400°C and is 64.3%, and for C_4 is maximum at 450°C-38.6%.

With increasing temperature, there is an increase in the yield of benzene and toluene from 4.3% (400°C) to 24.1% (550°C) and from 41.5% (400°C) to 44.1% (550°C), with a further increase in temperature to 600°C, the yield of these products decreases to 12.3 and 18.2%, respectively.

As with most of the catalysts studied (tables 1-6), on Zn-La-P-Cr-ZSM-Al_2O_3 in the range 400 - 600°C toluene yield is higher than benzene.

Yields of ethylbenzene and xylenes with increasing temperature decrease from 29.5 and 4.5% (400°C) to 4.1 and 1.0% (600°C), respectively. During processing of propane-propylene fraction on Zn-La-P-Cr-ZSM-Al_2O_3 cracking of alkanes with formation of methane and ethane is observed.

Table 7 - effect of temperature on the process of processing
propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3

T, °C	400	450	500	550	600
Conversion, %		85,2	100	100	100
The yield of liquid phase, %	25,0	32,9	32,1	34,5	27,0
Select. ArC, %		38,6	32,1	34,5	27,0
Liquid phase, %					
Benzene	4,3	9,4	19,8	24,1	12,3
Toluene	41,5	35,1	40,3	44,1	18,2
Ethylbenzene	29,5	16,9	13,3	12,3	4,1
Xylene	4,5	3,1	2,8	3,0	1,0
C_{5-6}	5,0	25,0	16,3	5,7	47,0
C_{8+}	15,2	10,5	7,5		17,4

At a temperature of 550°C, the effect of the volumetric feed rate on the processing of propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3 was studied (table 8). At 550°C and a volume feed rate of 150h-1, the conversion of software is 100.0%, the output of ArC is 52.8% with selectivity-52.8%. With an increase in the volumetric feed rate to 1020 h^{-1} conversion is reduced to 52.4%, the yield of aromatic hydrocarbons is reduced to 17.2%. Under these conditions, the yield of benzene varies from 30, 8 to 17.9%, toluene – from 40.5 to 47.4%, ethylbenzene - from 7.0 to 20.2%. The yield of xylene is in the range of 1.8 to 3.0%.

Table 8 - effect of volumetric feed rate on the process
of processing propane-propylene fraction on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3

T, °C	150	300	470	675	825	1020
Conversion, %	100	100	100	65,7	90,4	52,4
The yield of liquid phase, %	52,8	34,5	20,4	21,2	20,5	17,2
Select. ArC, %	52,8	34,5	20,4	32,3	22,6	32,8
Liquid phase, %						
Benzene	30,8	24,1	20,0	24,4	21,4	17,9
Toluene	40,5	44,1	46,0	42,5	43,4	47,4
Ethylbenzene	7,0	12,3	15,1	12,1	16,5	20,2
Xylene	1,9	3,0	2,4	1,8	1,8	2,2
C_{5-6}	3,9	5,7	8,8	12,4	5,5	6,0
C_{8+}	15,9		7,7	6,8	11,4	

The developed modified zeolite-containing catalysts have high catalytic activity and selectivity in the process of processing the propane-propylene fraction into aromatic hydrocarbons. It was found that the highest yield of aromatic hydrocarbons is 52.8% (550°C, 150 h^{-1}) on the catalyst Zn-La-P-Cr-ZSM-Al_2O_3 with a conversion rate of 100.0%, selectivity for aromatic compounds-52.8%.

Physical and chemical characteristics of the developed catalysts were studied using various methods (EM, BET, TPD of ammonia). By the BET method it was established that the surface of the developed catalysts fluctuates within 211,0-274,0 m^2/g of cat. Catalysts are predominantly mesoporous: pores with d

≈ 2.0-3.0 nm predominate. The total pore volume of catalysts depends little on their composition and does not exceed 0.13-0.21 ml/g of catalyst. According to electron microscopy data, there are active centers on the surface of catalysts, which include metals - components of the active phase and Lewis and Bronsted acid centers, the presence of which is mainly due to the presence of zeolite ZSM in the catalysts. The active phase particles on the surface of the developed catalysts are highly dispersed. Metals of the active phase are predominantly in the oxidized state, forming clusters on the surface-associates, dispersion, structure and condition of which is determined by the nature of the catalyst components.

The composition of the products formed during the processing of propane-propylene fraction on the developed modified zeolite-containing catalysts indicates that the synthesized catalysts have multifunctional properties. On the developed modified zeolite-containing catalysts, several reactions occur simultaneously and in parallel: cracking, dehydrogenation, isomerization, dehydrocyclization, alkylation.

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ПРОПАН-ПРОПИЛЕН ФРАКЦИЯСЫНАН МОДИФИЦИРЛЕНГЕН ЦЕОЛИТТІ КАТАЛИЗАТОРЛАРДА АРОМАТТЫ КӨМІРСУТЕКТЕР АЛУ

Аннотация. Zn, La, Cr Zr, және P модифицирленген цеолиті бар катализаторларда пропан-пропилен фракциясын өңдеп ароматты көмірсутектер алу процесі зерттелді. Процесс ағынды қондырғыда атмосфералық қысымда 350 – 600°С температурада және шикізатты берудің көлемдік жылдамдығы 150-1020 сағ$^{-1}$-де жүргізілді. Катализаторлар алюминий гидроксидін және ZSM-5 цеолитін металдардың азот қышқылды тұздарының және фосфор қышқылының судағы ерітінділерін сіңіру әдісімен дайындалды. Катализаторлардың физика-химиялық сипаттамалары зерттелді.БЭТ әдісімен катализаторлардың беті 211,0-274,0 м^2/г мөлшерінде болатындығы анықталды. Катализаторлар негізінен мезокеуекті:басым кеуектер d ≈ 2,0-3,0 нм.

Дайындалған модифицирленген құрамында цеолиті бар катализаторлардың ароматты көмірсутектерге пропан-пропилен фракциясын өңдеу процесінде жоғары каталитикалық белсенділікке және селективтілікке ие екендігі көрсетілді. C_2-C_4 алкандарды өңдеу кезінде пайда болатын басым өнімдер толуол және бензол болып табылады. Модифицирленген цеолитті катализаторда Zn-La-ZSM-Al_2O_3пропан-пропилен фракциясын өңдеу кезінде ароматты көмірсутектер (АрК)және газ тәрізді өнімдер пайда болды.

Процесс температурасының 400-ден 650°С-қа дейінөскенде конверсия дәрежесі 1,4-тен 100,0%-ға дейін көтерілді. Бұл жағдайда ароматты көмірсутектердің шығымы 8,9-дан 29,2-28,9%-ға дейін өседі. АрК бойынша ең жоғары селективтілік 600°С-та байқалады және 29,2% құрайды. Түзілгенароматты көмірсутектердің сандық құрамы процестің температурасына байланысты. 400-650°С аралығында толуолдың шығымы экстремальды түрде өзгереді, 450°С-та ең жоғарғы мәнге жетеді және 46,9% құрайды. Температураның өсуімен бензолдың шығымы 4,1 (400°С) бастап 39,2% (650°С)дейін артады. Сұйық катализаттағы ксилолдың мөлшері - 1,6-7,2%. Этилбензол мен C_5-C_6көмірсутегінің шығымы температура 400-650°С аралығында өскенде тиісінше 24,8-ден 4,8%-ға дейін және 21,8-ден 4,6%-ға дейін төмендейді. Zn-La-P-ZSM-Al_2O_3 катализаторында пропан-пропилен фракциясын өңдеу процесі зерттелді. 2-кестеде ұсынылған деректерден температура 350-ден 600°С-қа дейін өсуімен конверсия 27,8-ден 98,9%-ға дейін артқанын көруге болады. Температураның 350-ден 550°С-қа дейін артуы кезінде ароматты көмірсутектердің шығымы 19,3-тен 38,1%-ға дейін өседі, бірақ жоғары температурада (600°С) АрК шығымының 27,1%-ға дейін төмендеуі байқалады. 350-600°С аралығында толуолдың шығымы 27,4-39,1%, ал бензолдың шығымы 0,5 - 23,0% құрайды. Сұйық катализаттағы ксилолдың мөлшері–1,6-4,3%-ке тең. Этилбензолдың шығымы температураның 400 - 600°С аралығында артқанда 22,9-ден 5,9%-ға дейін төмендейді. C_5-C_6 көмірсутектерінің шығымы 37,2-ден 17,0%-ға дейін 350- 550°С аралығында температураның өскенде төмендейді де, содан кейін 32,0% (600°С) дейін артады. АрК бойынша ең жоғары селективтілік 500ºС кезінде байқалады және 54,0% құрайды. Жоғары температураларда АрК бойынша селективтілік біршама төмен–38,7-27,4%.Zn-La-Zr-ZSM-Al_2O_3 катализаторында пропан-пропилен фракциясын өңдеу процесінде температураның 350-ден 600°С-қадейінөсуімен конверсия 7,0-ден 100,0%-ға дейін көтеріледі. Температураның 350-ден 550°С-қа дейін артуы кезінде ароматты көмірсутектердің шығымы 4,6-дан 28,2%-ға дейін өседі, 600°С кезінде ароматты көмірсутектердің шығымының 23,2% - ға дейін төмендеуі байқалады. Температура жоғарылағанда мақсатты өнімдердің түзілу селективтілігі төмендейді: АрК бойынша ең жоғары селективтілік 350°С кезінде байқалады және 65,7%-ды құрайды.Жоғары температураларда АрК бойынша селективтілік төмен. Сұйық катализатта толуол мен этилбензол басым. Толуолдың шығымы 14,4 -тен 43,9% - ға дейін 350- 550°С аралығындаөседі, 600°С-татолуолдың шығымы біршаматөмен - 40,9%. Этилбензолдың мөлшері монотонды түрде 24,0-ден 10,6% - ға дейін төмендейді. Бұл жағдайда бензолдың шығымы 1,7-ден 27,2% - ға дейін өседі.Ксилол мөлшері – 3,1-7,9% аралығында ауытқиды.

Ароматты көмірсутектердің ең жоғары шығымы Zn-La-P-Cr-ZSM-AI_2O_3катализаторында байқалып 52,8%-ға (550°С, 150 сағ$^{-1}$) тең болып конверсия дәрежесі 100%-ға жетеді. Модифицирленген цеолиті бар катализаторлар көп функционалды қасиеттергеие. Пропан пропилен фракциясын өңдеу өнімдерінің құрамы ароматты көмірсутектердің түзілуі крекинг, дегидрлеу, олигомеризациялау, дегидроциклдеу, алкилдеу реакцияларының жүруі нәтижесінде бір сатыда жүретінін көрсетеді.

Түйін сөздер: катализатор, цеолит, пропан-пропилен фракциясы, ароматты көмірсутектер

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ПРЕВРАЩЕНИЕ ПРОПАН - ПРОПИЛЕНОВОЙ ФРАКЦИИ В В АРОМАТИЧЕСКИЕ УГЛЕВОДОРОДЫ НА МОДИФИЦИРОВАННЫХ ЦЕОЛИТНЫХ КАТАЛИЗАТОРАХ

Аннотация. Исследован процесс превращения пропан-пропиленовой фракции в ароматические углеводороды на цеолитсодержащих катализаторах модифицированных Zn, La, Cr Zr, и P. Процесс проводили в установке в проточной установке при атмосферном давлении при варьировании температуры от 350 до 600^{0}С и объемной скорости подачи сырья 150-1020 ч$^{-1}$. Катализаторы готовили методом пропитки гидроксида алюминия и цеолита ZSM-5 водными растворами азотнокислых солей металлов и фосфорной кислоты. Изучены физико-химические характеристики разработанных катализаторов. Методом БЭТ установлено, что поверхность разработанных катализаторов колеблется в пределах 211,0-274,0 м^2/г к-ра. Катализаторы преимущественно мезопористые: преобладают поры с $d \approx 2{,}0$-3,0нм.

Показано, что разработанные модифицированные цеолитсодержащие катализаторы обладают высокой каталитической активностью и селективностью в процессе переработки пропан-пропиленовой фракции в ароматические углеводороды. Преобладающими продуктами, образующимся при переработке C_2-C_4 алканов, являются толуол и бензол.

При переработке пропан-пропиленовой фракции на модифицированном цеолитном катализаторе Zn- La-ZSM-Al_2O_3 образуются ароматические углеводороды (АрУ) и газообразные продукты. В жидкой фазе обнаружены бензол, толуол, этилбензол, ксилолы и C_{8+}-углеводороды, а в газовой фазе содержатся C_1-C_4 углеводороды. С увеличением температуры процесса от 400 до 650^{o}С степень конверсии повышается от 1,4 до 100,0%. Выход ароматических углеводородов в этих условиях растет от 8,9 до 29,2 -28,9%. Максимальная селективность по АрУ наблюдается при 600^{o}С и составляет 29,2%. Количественный состав образующихся ароматических углеводородов существенно зависит от температуры процесса. Выход толуола в интервале 400- 650^{o}С меняется экстремально, достигая максимального значения при 450^{o}С, и составляет 46,9%. Выход бензола с ростом температуры возрастает от 4,1 (400^{o}С) до 39,2% (650 ^{o}С). Содержание ксилола в жидком катализате - 1,6-7,2%. Выход этилбензола и C_5-C_6 углеводородов снижается с ростом температуры в интервале 400- 650^{o}С от 24,8 до 4,8% и от 21,8 до 4,6 % соответственно

Исследован процесс переработки пропан-пропиленовой фракции на катализаторе Zn-La-P-ZSM-Al_2O_3 С ростом температуры от 350 до 600^{o}С конверсия повышается с 27,8 до 98,9%. При увеличении температуры от 350 до 550 ^{o}С выход ароматических углеводородов растет от 19,3 до 38,1%, но при более высокой температуре (600 ^{o}С) наблюдается снижение выхода АрУ до 27,1%. В интервале 350 - 600^{0}С выход толуола составляет 27,4-39,1%, а бензола - 0,5 - 23,0%. Содержание ксилола в жидком катализате - 1,6-4,3%. Выход этилбензола снижается с ростом температуры в интервале 400- 600^{o}С от 22,9 до 5,9%. Выход C_5-C_6 углеводородов снижается с ростом температуры в интервале 350- 550^{o}С от 37,2 до 17,0%, затем увеличивается до 32,0 (600 ^{o}С). Максимальная селективность по АрУ наблюдается при 500^{o}С и составляет 54,0%. При более высоких температурах селективность по АрУ несколько ниже – 38,7-27,4%.

В процессе переработки пропан-пропиленовой фракции на катализаторе Zn-La- Zr -ZSM-Al_2O_3 с увеличением температуры от 350 до 600^{o}С конверсия повышается с 7,0 до 100,0%. При повышении температуры от 350 до 550^{o}С выход ароматических углеводородов растет от 4,6 до 28,8%, при 600^{o}С наблюдается снижение выхода ароматических углеводородов до 23, 2%. Установлено, что наибольший выход ароматических углеводородов составляет 52,8% (550^{o}С, 150 ч$^{-1}$) на катализаторе Zn-La-P-Cr-ZSM-AI_2O_3 при степени конверсии 100,0%. Модифицированные цеолитсодержащие катализаторы обладают полифункциональными свойствами. Состав продуктов переработки пропан-пропиленовой фракции показывает, что образование ароматических углеводородов происходит в одну стадию в результате протекания реакций крекинга, дегидрирования, олигомеризации, дегидроциклизации, алкилирования

Ключевые слова: цеолитсодержащие катализаторы пропан-пропиленовая фракция ароматические углеводороды.

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COMPARATIVE EVALUATION OF DIETHANOLAMINE SOLUTION PURIFICATION TECHNOLOGIES FROM HEAT-STABLE SALTS AND BONDED AMINE

Abstract. The article presents the comparative tests results of the purification of diethanolamine (DEA) aqueous solution by distillation method under reduced pressure and ion exchange from heat-stable salts (HSS) and a bound amine. It was shown that regardless of the cleaning method, there is a significant improvement in organoleptic characteristics (color, smell), but also in the foamy characteristics of solution. For industrial implementation, the vacuum distillation method can be described as mid-complexity, it requires the cost of solution's heating, but its actualization does not require additional reagents. The addition of alkali could lead to extra increasing of amine concentration due to the return of the bound amine; however, distillation in the alkali presence is difficult due to its crystallization upon distillation of a significant part of the water. The distillation was carried out in two ways at a temperature of 130-150^{0}C: with the addition of alkali and without it, with the return of the first fractions to an additional extraction of ethanolamine. Distillation by the first method allowed you to extract about 2.5% of the amine and was not of practical interest. The distillation by the second method allowed to recover up to 88.2% of diethanolamine, at the same time, there was a complete purification from heat-stable salts and bound amine, foam characteristics also returned to normal. Various types of anion exchangers were tested: gel and several macroporous, of different alkalinity. A comprehensive assessment of anion exchangers of various manufacturers by several parameters was performed. Purification by ion exchange method allows you to increase the amine concentration in the purified solution due to its regeneration from the protonated form. The presented research work was carried out with a solution of regenerated diethanolamine from one of the oil refineries in Kazakhstan.

Key words: diethanolamine, heat-stable salt, bound amine, distillation, ion exchange, foaming.

Introduction. Gas and condensates conversion process necessarily includes their purification from acidic components that cause corrosion of manufacturing facilities and are undesirable impurities in commercial products. According to the technological regulations, operating at sulfur removal units, two indicators of desulfurized gas are normalized: the content of hydrogen sulfide and carbon dioxide. The choice of purification technology depends on the acidic components contained in them, however, leading place in world practice in desulfurization field is occupied by absorption purification using alkanolamines, among which monoethanolamine, diethanolamine, methyldiethanolamine and others are used [1-4].

The logic of the alkanolamine desulfurization units provides for main processes reversibility, and the relative simplicity of their implementation and high efficiency explains wide-spread occurrence. Apart from advantages, the process has several disadvantages. Experience has proven that the main cause of problems encountered during operation is the thermochemical decomposition of alkanolamines when interacting with carbon dioxide contained in purifield gas, during which various disrupture products are formed [5-9].

Amount of formed compounds is large, but additively this leads to bound amine formation or protonated amine, which is ballast and is not involved in the main process. In parallel, HSS are formed - residues of various acids that are not removed by thermal desorption of the compound. In general, aqueous solutions of alkanolamines do not exhibit corrosive activity, but in the presence of impurities, corrosion becomes noticeable and mechanical impurities appear in the solution [10, 11]. Along with this, the foamy characteristics of solutions noticeably deteriorate.

Obviously, it is necessary to take measures to combat the negative consequences. Some researchers propose to reduce corrosion using coatings [12], use anti-foaming agents to fight foam [13-15]. Finding ways to purify amine solutions seems more rational than dealing with the consequences.

To date, several technologies have found application to purify amine solutions [16]. Distillation purification at atmospheric or reduced pressure, based on distillation, as a result of which two fractions are formed: amine and still bottoms [17]. This technology is widely used; however, its disadvantage is the large loss of the amine with a still residue, which also needs to be disposed of. Sorption technology using activated carbon has not been widely used due to low efficiency.

The ion exchange method of amine solutions purification has been successfully using by a number of western companies over the past 20-25 years. Currently the most well-known companies distributing this technology are MPR Services, Inc (USA) with HSSX® technology **(**Ion Exchange Heat Stable Salt Removal Process) and Eco-Tec, Inc (Canada) with AmiPur™ technology. Works in this direction are being carried out at the present time [18–20], although the industries for metals mining remain traditional for resins application [21].

Experimental procedure. To determine the concentration of free amine, bound amine, and heat-stable salts, the conductometric titration method was used, which gives more accurate results compared to potentiometric titration [22, 23].

Excess alkali in the absorbing solution, free amine content, amine content, bound to anions of weak acid (HSS) were determined by titration of aliquot with hydrochloric acid.

Titration of solution's sample with sodium hydroxide gives results regarding amine bound content in both thermostable and thermolabile salts. By the sum of free and bound amine content, the total amine content in the solution is calculated, the content of heat-stable salts is determined by the difference in bound amine content and the amine bound to anions of weak acids.

The calculation of amine concentration in % was calculated according to the formula 1:

$$W = \frac{V*N*105}{m*10}, \tag{1}$$

where V – the amount of acid or alkali used for titration, N – concentration, m – weight of sample taken for titration, 105 – molar mass of diethanolamine.

Determination of the foamy characteristics of the amine solution was carried out according to the methodology «Absorbents for natural gases purification from H_2S and CO_2. Determination of foamy characteristics» P51-00158623-11-95.

To select the resin, a laboratory setup was used, the basis of which is a B3-V PER peristaltic pump with a capacity of up to 1 l/h and an ion-exchange column with a volume of 240 ml.

Result and discussion. Testings were carried out with diethanolamine solution with the following indicators: *the concentration of free amine is 14.99%, the content of heat-stable salts is 1.78%, the bound amine is 1.10%.*

In this work, distillation at a residual pressure of 2 kPa was carried out in two ways:

1) With the addition of sodium hydroxide to a concentration of 2.3% with four times working solution resupply, residual distillation was carried out by adding more diluted primary fractions.

2) Without sodium hydroxide addition, with distilling off the first fraction with a volume of 50-70% of parent solution, with its subsequent recycling to distill off the residue.

In view of distillation results of according to method 1, a total 2.64% of the initial amine content was recovered, which is extremely small. This low yield is explained by the impossibility of continuing distillation due to salt incrustation formation on solution's surface as a result of the addition of alkali, which leads to difficulty in boiling, which is accompanied by sharp emissions, polluting the clean solution. Also, boiling point exceeds 150^0C, as a result of which the distillation had to be stopped.

For distilling over in the second method, 100 ml of solution was used. Initially, 50, 60 and 70 ml were distilled off as the primary fraction, which were then returned to the distillation flask. Temperature of distillation was maintained in the range of 130-150^{0}C so that when reaching 150^{0}C a new portion of the primary fraction was added to the flask. Table 1 shows the data obtained by the specified method.

Table 1 – Volumes and compositions of solutions after distillation according to method 2

Ratio of the primary fraction to the total volume,%	The volume of solution taken for rectification, ml	Outlet volume of solution, ml	Amine concentration, %	Degree of extraction,%
50.0	100.0	92.0	12.6	70.6
60.0	100.0	93.0	13.7	77.6
70.0	100.0	94.0	15.4	88.2

Data verification of the obtained samples for foaming are shown in table 2.

Table 2 – Foaming test results after distillation

Indicator	50/50	60/40	70/30
Height of foam, mm	5	5	5
Foam formation	low	low	low
Destruction time of foam, s	4	4	3
Foam stability	low	low	low

Figure 1 shows primary amine samples and samples after distilling over.

Figure 1 – Diethanolamine samples

Selection of anion exchange resin was carried out from the following range of resins: macroporous weakly base anion exchanger Lewatit A365, macroporous strongly base anion exchanger Lewatit TP107, gel strongly base anion exchange resin Tokem-840 and macroporous strongly base Purolite A500Plus anion exchange resin. The best results were achieved with Tokem-840 resin, table 3 shows the test results. According to the table, specified resin copes with heat-stable salts and neutralizes the bound amine by exchanging the anions present in the solution for hydroxide ion, which in turn neutralizes the acidic form of the amine to free amine and water, as a result, there is an increase in free amine concentration relative to the state before purification.

Table 3 – The composition of DEA solution after purification

Volume of solution, ml	C amine, %	C HSS calculated as amine, %	C bound amine,%	Cycle number	Volume of solution, ml	C HSS calculated as amine, %	C bound amine,%
240	13.23	0	0	1440	17.20	0	0
480	17.40	0	0	1680	17.50	0	0
720	17.60	0	0	1920	17.46	0	0.
960	17.20	0	0	2160	17.10	0	0.30
1200	17.20	0	0	2400	17.00	0	0.97

According to the results shown in table 4, purification of DEA by ion exchange on Tokem-840 resin has the most positive effect on the foaming of amine solution. Foamy characteristics are in accordance with the standards.

Table 4 – Foaming test results after Tokem-840

Indicator	Cycle number									
	1	2	3	4	5	6	7	8	9	10
Height of foam, mm	2	3	3	6	8	12	13	13	13	14
Foam formation	L	L	L	L	L	L	L	L	L	L
Destruction time of foam, s	3	3	3	4	4	5	5	6	6	7
Foam stability	L	L	L	L	L	L	L	L	L	L
L – low										

Table 5 includes the integral estimation of work of the tested resins on a five-point scale. Considering the different significance of the criteria for HSS, bound amine and foamability, a factor of 1 is adopted, and for a color index of 0.5.

Table 5 – Comparative performances of resins exposure

Resin	HSS	Bound amine	Foaming	Color	Sum
Lewatit A365	5	2	1	1*0.5	8.5
Lewatit TP107	5	1	1	2*0.5	8.0
Purolite A500Plus	2	2	5	5*0.5	11.5
Tokem-840	5	5	5	5*0.5	17.5

Conclusion. The vacuum distillation method allows the amine to be completely purified from mechanical impurities, heat-stable salts and foaming agents. Under these circumstances, the loss of amine is 11.8-29.4%. Distillation flashing should be carried out at the boiling point of the solution no more than 150^0C. Colority of the solution depends on the ratio of the first fraction to the total amount of the distilled solution. Altogether the method is characterized by medium complexities of the implementation, but requires significant energy costs for solution heating, as well as the consumption of back water for cooling the condensate.

Usage of anion-exchange resins allows, with correct selection, to purify the regenerated solution from heat-stable salts and a bound amine, while the foamy characteristics return to normal and the color index improves. Various types of anion exchangers were tested: gel and several macroporous, of different alkalinity. By indicators sum, the best results were obtained using gel strongly base anion exchange resin. In general, the ion exchange method seems to be more efficient and less costly than vacuum distillation.

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ЫСТЫҚҚА ТӨЗІМДІ ТҰЗДАРДАН ЖӘНЕ БАЙЛАНЫСТЫ АМИНДЕРДЕН ДИЭТАНТОЛАМИН ЕРІТІНДІСІН ТАЗАРТУҒА АРНАЛҒАН ТЕХНОЛОГИЯЛАРДЫ САЛЫСТЫРМАЛЫ ТҮРДЕ БАҒАЛАУ

Аннотация. Аминдік процестің пайда болуынан бастап газды қышқыл компоненттерден тазарту процесінде алканоламин ерітінділері коррозиялық белсенділігі бар қосылыстар түзетіні белгілі. Әр түрлі авторлар жүргізген зертханалық зерттеулер абсорбенттің жұмыс ерітіндісіндегі жағымсыз компоненттер тек әр түрлі шыққан механикалық қоспалар (құм, металл сульфидтері және т.б.) ғана емес, сонымен қатар аминді термиялық деструкция өнімі (диэтанолпиперазин, N(гидроксиэтил) имидазолидон, трис(гидроксиэтил) этилендиамин, N,N' бис(гидроксиэтил) имидазолидон, N(гидроксиэтил) пиперазин, N(гидроксиэтил) оксазолидон) болып табылатындығын көрсетті. Қазіргі уақытта этаноламиндердің жылу және химиялық ыдырауы нәтижесінде түзілген қосылыстар туралы ақпарат едәуір үлкен көлемде жинақталған. Бұл процестер көмірқышқыл газы мен күкірторганикалық қосылыстарының, оттегі, қышқылдар және т.б. әсерінен жүзеге асырылады. Деградацияның ең көп таралған түрлері: 1. Көмірқышқыл газының бастапқы және қайталама аминдердің деградациясы. CO_2-ны газдан шығару кезінде онымен карбамат түзілуімен кері реакцияға түседі. Карбаматтар өз кезегінде сол немесе басқа қайтымсыз реакцияға түседі; 2. Тазартылатын газда оттегінің болуына байланысты оттектік деградациясы; 3. Аминдердің термиялық жойылуы. Бұл негізінен жұмыс ерітінділерінің жалпы және (немесе) жергілікті қызып кетуінен болады; 4. Газмен енгізілген қышқыл сипаттағы ұшпа қоспалар: құмырсқа қышқылы мен сірке қышқылы, формальдегид, көгертетін қышқыл; 5. COS және CS_2 деградациясы - бастапқы аминдерге тән; 6. Металдармен катализделген СО гидролизімен байланысты деградация; 7. Күшті қышқылдар аниондарының әсерінен деградация (хлоридтер, сульфаттар, фосфаттар); 8. Беттік белсенді заттарды енгізу (ББЗ). Бүгінгі таңда амин ерітінділерін тазартуға арналған бірнеше технологиялар қосымшаны тапты. Айыру негізінде атмосфералық немесе төмендетілген қысым кезінде дистилляция, нәтижесінде екі фракция пайда болады: амин және әлі де түб. Бұл технология кеңінен қолданылады, бірақ оның кемшілігі - түбіндегі қалдық бар аминнің үлкен жоғалуы, оны жою керек. Белсендірілген көмірді қолдану арқылы сорбциялық технология төмен тиімділікке байланысты кең қолданылмады. Вакуумдық дистилляция вакуум астында жұмсалған амин ерітіндісін айдау арқылы жүзеге асырылады. Бұл МДЭА өте жоғары қайнау температурасына байланысты, және одан да жоғары және ДЭА үшін одан да жоғары. Нәтижесінде, бұл аминдер ерітіндіден су буымен «ұшып кетпейді». КөрсетілгенМЭА-мен салыстырғанда дистилляция арқылы МДЭА және ДЭА қалпына келтіру процесінің едәуір қиындауын тудырады. Алдымен, өте терең емес вакууммен су бөлінеді, содан кейін вакуум тереңдеген сайын бас фракциясы алынады, содан кейін тотықсызданған амин бөлінеді. Айыру өнімдері арнайы вакуумдық конденсаторға конденсацияланады. Жоғары қайнаған қоспалар, ұшпайтын ЫТТ және шайырлау өнімдері сұйық затты қайнататын ыдыста қалады. Бұл энергияны көп қажет ететін әдіс. Бұл әдіс барлық ұшпайтын қоспаларды (ЫТТ және жоғары молекулалы қосылыстардан) алып тастауға кепілдік береді, сонымен қатар ұшпа қоспаларды өте жақсы кетіреді, олардың қайнау температурасы аминнің қайнау температурасынан өзгеше болады.Алайда, қоспаның қайнау температурасы мақсатты жұмыс аминнің қайнау температурасына қаншалықты жақын болса, соғұрлым қоспаның бөлінуі нашар болады. Алканоламин ерітінділерін тазартудың ең перспективті әдісі - ион алмасу. Бұл термостабельді тұздардан, ал жақсартылған сүзгілеу кезінде термиялық және химиялық деструкцияның жоғары молекулалық салмақ өнімдерінен, қарамайлаудан құтылуға мүмкіндік береді. МДЭА және ДЭА тікелей сулы ерітіндіде азаяды, аздап шоғырланған болуы мүмкін. Сондықтан артықшылығы - қалпына келтіру кезінде суды бөлудің қажеті жоқ. Тағы бір артықшылығы - (ион алмастырғыш элементтерді дұрыс таңдау арқылы) бициннен (ең коррозиялық қоспалардың бірі) толықтай арылуға мүмкіндік береді. Мақалада диэтаноламиннің (ДЭА) сулы ерітіндісін тазартуға арналған салыстырмалы зерттеулердің нәтижелері келтірілген: төмендетілген қысымда дистилляция әдісі және ыстыққа төзімді тұздардан (ЫТТ), байланысты аминдерден ион алмасуы. Тазарту әдісіне қарамастан, органолептикалық сипаттамалардың (түс, иіс) айтарлықтай жақсару байқалады, сонымен қатар ерітіндінің көбік сипаттамалары жақсарады. Өнеркәсіптік енгізу үшін вакуумдық дистилляция әдісін орташа күрделі деп сипаттауға болады, ол ерітіндіні жылыту құнын талап етеді, бірақ оны жүзеге асыру үшін қосымша реагенттер қажет емес. Байланысты аминнің қайтарылуы есебінен, сілтінің қосылуы амин концентрациясының қосымша артуына әкелуі мүмкін, алайда сілтінің қатысуымен тазарту судың едәуір бөлігін айдау кезінде оның кристалдануына байланысты қиын болады. Дистилляция екі жолмен 130-150^{0}С температурада жүргізілді: сілтінің қосылуымен және онсыз, этаноламиннің қосымша экстракциясы үшін алғашқы фракциялардың қайтарылуымен. Бірінші әдіс бойынша айдау шамамен 2,5% аминді алуға мүмкіндік береді және практикалық қызығушылық тудырмайды. Екінші әдіспен дистилляция 88,2% диэтаноламинді қалпына келтіруге мүмкіндік берді, ал ыстыққа төзімді тұздардан және байланысқан аминдерден толық тазарту жүргізілді, көбік сипаттамалары да қалпына келтірілді. Анион алмастырғыштардың әр түрлі түрлері сыналды: гель және бірнеше ірі кеуекті анионитгер, әртүрлі сілтілігі. Әр түрлі өндірушілердің анион алмастырғыштарын кешенді бағалау бірнеше параметрлер бойынша жүргізілді. Ион алмасу әдісімен тазарту протондалған формадан қалпына келуіне байланысты тазартылған ерітіндідегі амин концентрациясын арттыруға мүмкіндік береді. Ұсынылған жұмыс Қазақстандағы мұнай өңдеу зауыттарының бірінен қалпына келтірілген диэтаноламин ерітіндісімен жүргізілді.

Түйін сөздер: диэтаноламин, ыстыққа төзімді тұз, байланысты амин, вспениваедистилляция, ион алмасу, көпіршіктену.

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СРАВНИТЕЛЬНАЯ ОЦЕНКА ТЕХНОЛОГИЙ ОЧИСТКИ РАСТВОРА ДИЭТАНОЛАМИНА ОТ ТЕРМОСТОЙКИХ СОЛЕЙ И СВЯЗАННОГО АМИНА

Аннотация. О том, что растворы алканоламинов в процессе очистки газов от кислых компонентов образуют соединения, обладающие коррозионной активностью, известно с начала появления аминового процесса. Лабораторные исследования, проведенные разными авторами, показали, что нежелательными компонентами в рабочем растворе абсорбента являются не только механические примеси различного

происхождения (песок, сульфиды металлов и т.д.), но и продукты термической деструкции амина (диэтанолпиперазин, N(гидроксиэтил) имидазолидон, трис(гидроксиэтил) этилендиамин, N,N' бис(гидроксиэтил) имидазолидон, N(гидроксиэтил) пиперазин, N(гидроксиэтил) оксазолидон и т.д. К настоящему времени сведений о соединениях, образующихся в результате термического и химического разложения этаноламинов под действием углекислого газа и сероорганических соединений, кислорода, кислот и др., накопилось в достаточно большом объеме. К наиболее распространенным типам деградации можно отнести: 1. Углекислотная деградация первичных и вторичных аминов, которые в процессе удаления CO_2 из газа обратимо реагируют с ним с образованием карбаматов, которые, в свою очередь, вступают в те или иные необратимые реакции. 2. Кислородная деградация, обусловленная присутствием кислорода в очищаемом газе. 3. Термическая деструкция аминов. Вызывается, в основном, общими и (или) локальными перегревами рабочих растворов. 4. Привнесенные с газом летучие примеси кислотного характера: муравьиная и уксусная кислоты, формальдегид, синильная кислота. 5. COS и CS_2 деградация - характерна для первичных аминов. 6. Деградация, связанная с гидролизом CO, катализированного металлами. 7. Деградация под воздействием анионов сильных кислот (хлоридов, сульфатов, фосфатов). 8. Привнесенные поверхностно активные вещества (ПАВ).

На сегодняшний день для очистки аминовых растворов нашли применение несколько технологий. Дистилляционная очистка при атмосферном или пониженном давлении, основанная на перегонке, в результате чего образуется две фракции: аминовая и кубовый остаток. Данная технология широко применяется, однако ее недостатком являются большие потери амина с кубовым остатком, который также необходимо утилизировать. Сорбционная технология использующая активированный уголь не нашла широкого применения в виду низкой эффективности. Вакуумная дистилляция осуществляется путем перегонки отработанного раствора амина под вакуумом, что обусловлено достаточно высокой температурой кипения у МДЭА, и еще большей у ДЭА. В результате указанные амины практически не «улетают» из раствора с парами воды. Указанное обуславливает существенное усложнение процесса восстановления МДЭА и ДЭА дистилляцией по сравнению с МЭА. Вначале при не очень глубоком вакууме отделяется вода, далее, по мере углубления вакуума – снимается головная фракция, а затем – восстановленный амин. Продукты перегонки конденсируются в специальном вакуумном конденсаторе. Высококипящие примеси, а также нелетучие ТСС и продукты осмоления остаются в перегонном кубе. Метод является достаточно энергозатратным. Данный метод гарантированно удаляет все нелетучие примеси (ТСС и высокомолекулярные), а также достаточно хорошо удаляет летучие примеси, у которых температура кипения сильно отличается от температуры кипения амина. Но, чем ближе температура кипения примеси к температуре кипения целевого рабочего амина, тем хуже отделяется примесь. Наиболее перспективным способом очистки растворов алканоламинов представляется ионный обмен. Он позволяет избавиться от термостабильных солей, а при усиленной фильтрации и от высокомолекулярных продуктов термической и химической деструкции и осмоления. МДЭА и ДЭА подвергаются восстановлению прямо в водном растворе, может быть слегка сконцентрированном. Отсюда преимущество – не нужно отделять воду при восстановлении. Также преимущество – возможность (при правильном подборе ионообменных элементов) практически полностью избавится от бицина - наиболее коррозионно-активной примеси.

В статье приведены результаты сравнительных испытаний очистки водного раствора диэтаноламина (ДЭА) методами дистилляции при пониженном давлении и ионного обмена от термостойких солей (ТСС) и связанного амина. Показано, что независимо от способа очистки происходит значительное улучшение органолептических показателей (цвет, запах), но и пенных характеристик раствора. Для промышленной реализации метод вакуумной дистилляции можно охарактеризовать как средне-сложный, он требует затрат на подогрев раствора, но для его реализации не требуется дополнительных реагентов. Добавление щелочи могло бы привести к дополнительному повышению концентрации амина за счет возврата связанного амина, однако перегонка в присутствии щелочи затруднительна в виду ее кристаллизации при отгонке значительной части воды. Разгонку производили двумя способами при температуре 130-150^{0}С: с добавлением щелочи и без нее с возвратом первых фракций на дополнительное извлечение этаноламина. Дистилляция по первому способу позволяет извлечь около 2,5% амина и не представляет практического интереса. Разгонка по второму способу позволила извлечь до 88,2% диэтаноламина, при этом произошла полная очистка от термостойких солей и связанного амина, пенные характеристики также пришли в норму. Были испытаны различные виды анионитов: гелевый и несколько макропористых, разной щелочности. Произведена комплексная оценка анионитов различных производителей по нескольким параметрам. Очистка методом ионного обмена позволяет повысить концентрацию амина в очищенном растворе за счет регенерации его из протонированной формы. Работа проводилась с раствором регенерированного диэтаноламина с одного из нефтеперерабатывающих предприятий Казахстана.

Ключевые слова: диэтаноламин, термостойкая соль, связанный амин, дистилляция, ионный обмен, вспениваемость.

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ACCELERATED LOW-TEMPERATURE PHOSPHATING FROM SOLUTIONS OF RUST CONVERTERS

Abstract. Along with phosphating solutions, rust converters are widely used to obtain anti-corrosion coatings, the use of which does not require preliminary treatment of the metal surface, as is the case with traditional phosphating solutions. However, methods for accelerating phosphating in solutions of rust converters have not found proper application and remain little studied. The aim of this work was to use organic nitro compounds as accelerators in solutions of rust converters for accelerated low-temperature phosphating of the iron samplessurface. Phosphomet and Tsinkar solutions manufactured in industry were used as rust converters, and sodium nitrophenol and sodium m-sodium nitrobenzosulfonate (m-NBS) were used as accelerators.The corrosion resistance of the formed coatings (ZCA), determined by the drop method of Akimov, is compared with the corrosion resistance of coatings deposited from traditional phosphating solutions. The deposition of phosphate coatings was carried out at a temperature of 40°C, a deposition time of 10 minutes, a solution stirring speed of 500 rpm.A study of the effect of phosphate accelerators on the change in the surface structure of deposited coatings, roughness, thickness, and adhesion is carried out.

Keywords: phosphate coatings, rust converters, nitrophenol, corrosion resistance, adhesion.

Introduction. Corrosion resistance of cold rolled steel depends on the type of conversion coating.The most widely used conversion coatings for surface treatment of ferrous and non-ferrous metals are phosphate coatings providing excellent corrosion resistance, wear resistance and adhesion [1-8]. The main disadvantage of existing phosphating solutions is the high energy intensity due to high operating temperatures - 70-90°C. The disadvantage associated with working at high temperatures is the high demand for energy, which is a serious problem in modern conditions.One of the possible ways to reduce energy costs and eliminate difficulties arising from the formation of scale on the heating elements and overheating of the phosphating bath is the use of low-temperature phosphating [9-12]. The processes of low temperature phosphating are very slow and should be accelerated using special accelerators [13-16]. Organic nitro compounds are most widely used to accelerate phosphating processes [17-24]. These compounds, along with the acceleration of phosphate processes, contribute to an increase in the protective ability of formed coatings. The main objective of this study is the development of phosphating solutions based on rust converters using organic nitro compounds as accelerators, which make it possible to obtain low-temperature coatings with high corrosion resistance.

Experimental

The formation of protective anti-corrosion coatings on steel samples (St.3) was carried out using phosphating solutions (1-3) having the following compositions:

FR-1(1): ZnO – 0,145 г/л; $MnSO_4{\cdot}H_2O$ – 0,061г/л; HNO_3 – 0,083 мл; H_3PO_4 – 0,184 мл; $NaOH$ – 0,0315 г/л
FR-1(2): ZnO – 0,58 г/л; $NiNO_3{\cdot}6H_2O$ – 0,26г/л; HNO_3 – 0,332 мл; H_3PO_4 – 0,73 мл; $NaOH$ – 0,126 г/л
FR-1(3). ZnO – 0,725 г/л; $NiNO_3{\cdot}6H_2O$ – 0,33г/л; HNO_3 – 0,415 мл; H_3PO_4 – 0,92 мл; $NaOH$ – 0,1575 г/л
FR-1(4). ZnO – 1,16 г/л; $NiNO_3{\cdot}6H_2O$ – 0, 5208г/л; HNO_3 – 0,614 мл; H_3PO_4 – 1,472 мл; $NaOH$ – 0,252 г/л
FR-2 – ZnO - 0,0263г/л, $Ni(NO_3)_2$ $6H_2O$-0,062г/л $Mn(NO_3)_2 6H_2O$ - 0,025г, HNO_3-0,083мл, H_3PO_4 - 0,23мл, $NaOH$-0,0604 г/л
FR-3 - ZnO - 0,0677 г/л, $Ni(NO_3)_2{*}6H_2O$ - 0,0408 г/л, $Mn(NO_3)_2{*}6H_2O$ – 0,127г/л, H_3PO_4 - 0,226 мл, $NaOH$ - 0,0376 г/л

To deposition phosphate coatings, rust precursors Phosphomet and Tsinkar were also used. Nitrophenol and sodium m-nitrobenzosulfonate were employed as phosphate accelerators. The reagents used in the work had the mark "х.ч" and "ос.ч" and distilled water was used to prepare the solutions.

The surface of metal samples (Art. 3) was cleaned with abrasive material on a mechanical rotating machine, followed by washing with distilled water. Microphotographs and the surface structure of iron samples with phosphate coatings were studied using an OLYMPUSLEXTOLS 4100 microscope. The thickness of the coatings was determined using a thickness gauge of galvanic coatings Constant K6C. Coating strength was determined on a PosiTestAT digital adhesiometer by measuring the minimum tensile stress required to separate the coating from the surface of an iron sample. The corrosion resistance of phosphate coatings was studied by the drop method of Akimov [25].

Results and discussion

The effect of nitrophenol on the corrosion resistance of phosphate coatings obtained from solutions of rust converters Phosphomet, Tsinkar and phosphatizing solution FR-1 (4) using the Akimov drop method on iron samples was studied (Fig. 1).The deposition of phosphate coatings was carried out at a temperature of 40 ° C, a deposition time of 10 minutes, a solution stirring speed of 500 rpm. The concentration of nitrophenol in the phosphate solution was varied from 0.1 to 5 g/L.

Thus, it was shown that the deposition of phosphate coatings from the solution of Phosphomet in the presence of an accelerator of 5 g / l nirofenol leads to the formation of a uniform, firmly bonded to the surface of the iron sample (6 MPa) coating, 2 μm thick. With a degree of roughness (Ra-1,731 and Rz - 11.612) and corrosion resistance of 330 s., which is much higher than the corrosion resistance of coatings obtained in the absence of an accelerator.

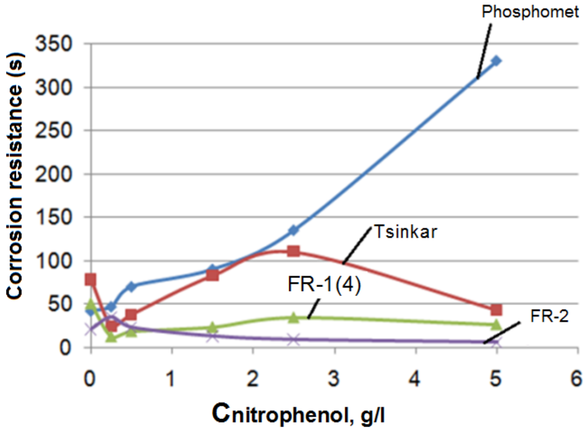


Figure 1 - Effect of nitrophenol on the corrosion resistance of phosphate coatings
from phosphating solutions Phosphomet, Tsinkar, FR-1 (4), FR -2

According to Fig. 1, the greatest increase in the anticorrosion resistance of the resulting coatings on iron samples under the conditions described above occurs when using the Phosphomet rust converter. Under similar conditions, when using the Tzinkar rust converter (Fig. 1, curve 2), with an increase in the concentration of nitrophenol from 0 to 2.5 g/L, an increase in the corrosion resistance of the phosphate coating is observed, however, at higher nitrophenol concentrations, a decrease in the corrosion resistance of the coatings under study is observed. The presence of nitrophenol in traditional phosphating solutions (Fig. 1, curves 3,4) does not cause noticeable changes in the protective ability.

Another dependence of the phosphate coatings protective ability formed on an iron sample is observed when sodium 3-nitrobenzosulfonate (m-NBS) is used as a phosphatization accelerator.

Fig. 2 shows the dependence of changes in the protective ability of coatings obtained from phosphating solutions of FR (1-4) and rust converters Phosphomet and Tsinkar at different concentrations of sodium 3-nitrobenzene sulfate.The concentration of m-NBS was varied from 0 to 50 g/l.

According to Fig.2, the highest corrosion resistance of phosphate coatings obtained from various phosphate solutions in the presence of sodium 3-nitrobenzene sulfonate is observed in a Tsinkar phosphate solution - 180 s. In Phosphomet solution with an increase in the concentration of sodium 3-nitrobenzosulfonate, an increase in the corrosion resistance of the formed coatings occurs to a lesser extent compared to Tsinkar solution.At a concentration of sodium 3-nitrobenzosulfonate of 50 g/l, the corrosion resistance of the coating in Phosphomet solution is 104 s. In phosphating solutions of FR – 1 (1,2,3,4), the effect of sodium 3-nitrobenzosulfonate is observed to a much lesser extent.

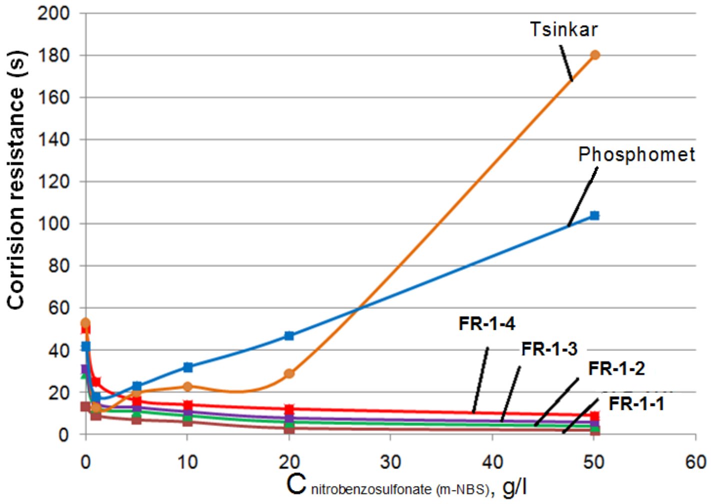
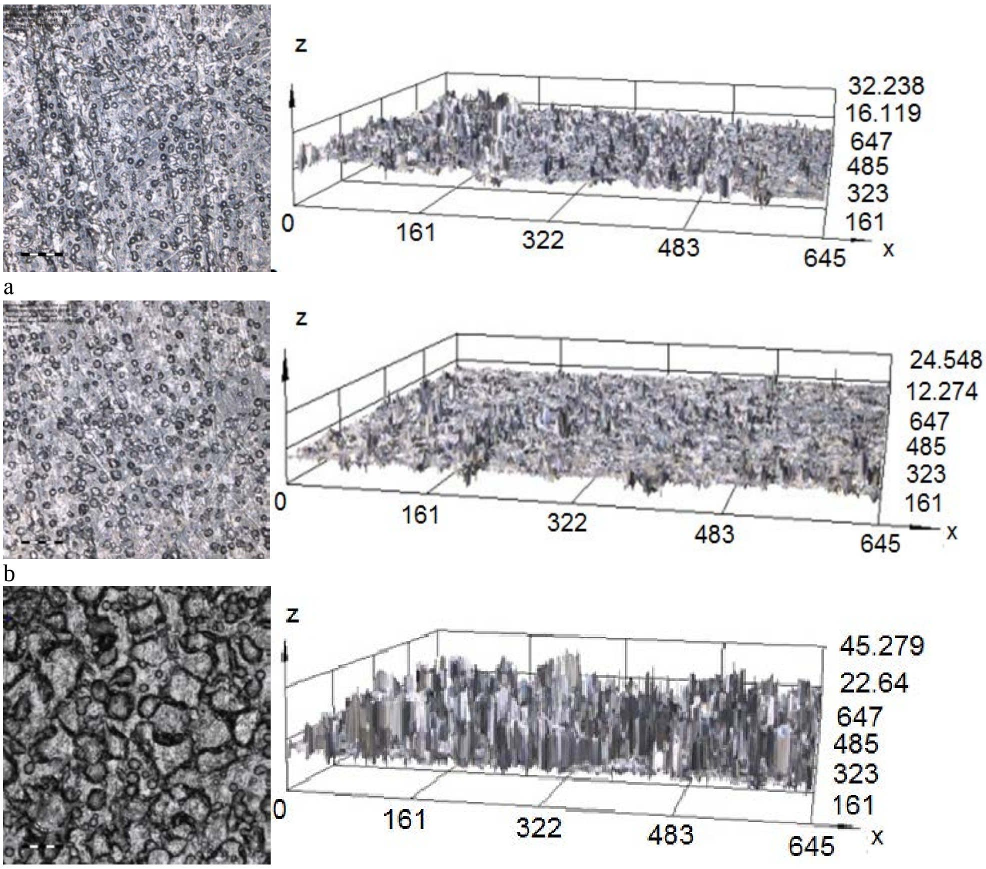


Figure 2 - Effect of the sodium 3-nitrobenzosulfonate concentration on the corrosion resistance of phosphate coatings from various phosphate solutions on steel samples

The microstructure of the iron samples surface with deposited protective coatings from Fosfomet solution with different concentrations of nitrophenol was studied.Fig. 3 shows the effect of nitrophenol on the 2d and 3d structure of the formed coating from Phosphomet solution.The concentration of nitrophenol was varied from 0.5 to 5 g/l. According to Fig. 2, the addition of nitrophenol 0.5 g/l to the solution of Phosphomet results to formation of a uniform fine crystalline precipitate with an average degree of filling and a roughness of Ra - 0.965 and Rz - 6457.An increase in the concentration of nitrophenol to 2.5 g/l contributes to an increase in surface filling, a slight increase in grain size and a decrease in roughness Ra - 0.691 and Rz - 4.420.A further increase in the concentration of nitrophenol to 5 g/l leads to a complete filling of the surface, a significant increase in grain size and an increase in roughness Ra-1.731 and Rz - 11.612.

The thickness of the formed phosphate coatings deposited from the solution of Phosphomet at different concentrations of nitrophenol was determined using a thickness gauge of galvanic coatings. Fig. 4 shows the dependence of the thickness of the phosphate coating from the Phosphomet solution on the concentration of nitrophenol at a deposition temperature of 40 ° C and a deposition time of 10 min. According to Fig. 4, with an increase in the concentration of nitrophenol in the phosphate deposition solution, an increase in the thickness of the formed phosphate coating is observed. At a nitrophenol concentration of 5 g/l, the coating thickness is 2 μm.



a

b

c

Figure 3 - 2d and 3d micrographs of iron samples with precipitated phosphate coatings from a solution of Phosphomet in the presence of various concentrations of nitrophenol (g/l): a – 0,5; b - 2,5; c - 5

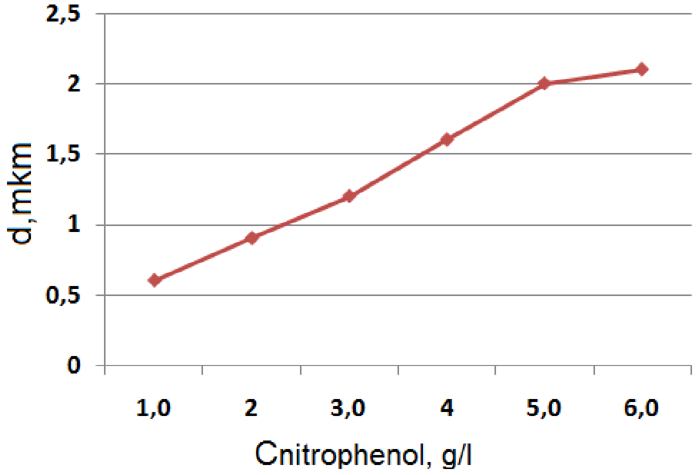


Figure 4 - Dependence of the thickness of the phosphate coating formed in the solution of Phosphomet on the concentration of nitrophenol (g/l): 1 - 0.5; 2 - 2.5; 3 –3,5; 4 – 4,6; 5 – 5,0; 6 – 6,5

The adhesion of the phosphate coating to the surface of the iron sample was determined from the concentration of nitrophenol in the phosphate deposition solution Fig. 5 shows the dependence of the minimum breaking stress required to separate the coating from the iron surface at different concentrations of nitrophenol in the deposition solution.

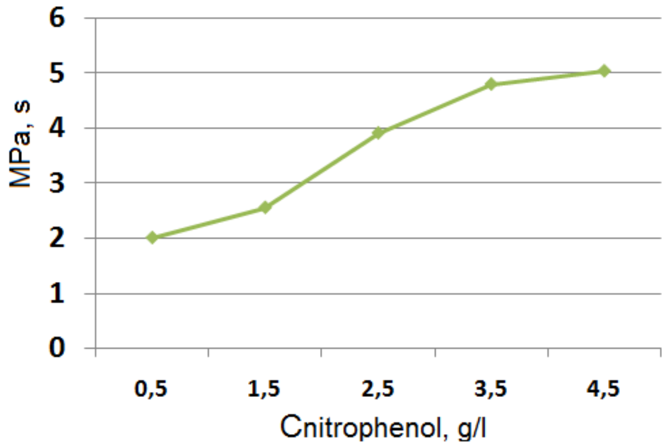


Figure 5 - Dependence of the rate of the phosphate coating separation on the surface of the iron sample at different concentrations of nitrophenol in Phosphomet solution

According to Fig. 5, with an increase in the concentration of nitrophenol in Fosfomet solution, an increase in the adhesion strength of the formed coating to the surface of iron samples is observed.

The greatest adhesion to the surface of the iron sample is observed for coatings deposited from a Phosphometsolution with a nitrophenol concentration of 5 g/l.

Conclusion

Thus, it was shown that the deposition of phosphate coatings from the Phosphomet solution in the presence of an accelerator nirophenol of 5 g/l leads to the formation of a uniform, firmly bonded to the surface of the iron sample (6 MPa) coating, 2 µm thick, with a degree of roughness (Ra-1,731 and Rz - 11.612) and corrosion resistance of 330 s., which is much higher than the corrosion resistance of coatings obtained in the absence of an accelerator.

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ТОТТАРДЫ ТҮРЛЕНІРГІШ ЕРІТІНДІЛЕРДЕГІ ЖЫЛДАМДАТЫЛҒАН ТӨМЕН ТЕМПЕРАТУРАЛЫ ФОСФАТТАУ

Аннотация. Фосфаттаушы ерітінділермен қатар қазіргі кезде коррозияға қарсы қаптама алу үшін дәстүрлі фосфаттаушы ерітінділердегідей метал бетін алдын ала өңдеуді қажет етпейтін тоттарды түрлендіргіш ерітінділер кең қолданыс тапты. Алайда тоттарды түрлендіргіш ерітінділерде фосфаттау процесін жылдамдату жолы аз зерттелініп қажетті қолданыс таппады. Бұл жұмыстың мақсаты темір үлгілерінің бетін төмен температурада жылдам фосфаттау үшін тоттарды түрлендіргіш ерітінділерде органикалық нитроқосылыстарды жылдамдатқыштар ретінде пайдалану болып табылады. Тоттарды түрлендіргіш ретінде өндірісте шығарылатын Фосфомет және Цинкарь қолданылса ал жылдамдатқыштар ретінде нитрофенол мен натрийдің м- нитробензосульфонаты (м-НБС) қолданылды. Түзілетін қаптаманың Акимовтың тамшылы әдісімен анықталынған коррозиялық тұрақтылығы дәстүрлі фосфаттаушы ерітінділерден алынған қаптамалардың коррозиялық тұрақтылығымен салыстырылды. Фосфатты қаптамаларды қондыру 40°С температурада, 10 мин қондыру уақытында және 500 айналым/мин ерітіндіні араластыру жылдамдығында жүргізілді. Құрамында нитрофенол болмаған фосфатты қаптаманың коррозиялық тұрақтылығы 42 с болатындығы көрсетілді. Ерітіндіде нитрофенолдың концентрациясының артуымен, концентрациясы 5 г/л болғанда түзілетін фосфатты қаптаманың қорғағыштық қабілеті 330 с-қа дейін артады. Цинкарь ерітіндісінде нитрофенолдың концентрациясы 0,1 ден 2,5 мл ге дейін артқанда фосфатты қаптаманың коррозияға тұрақтылығы 78с-тан 110с-қа дейін артады. Нитрофенолдың концентрациясының жалғасты артқанда коррозияға тұрақтылығы 43с - қа дейін төмендейді. Нитрофенолдың ФР-1(4) фосфаттаушы ерітіндіден алынатын фосфатты қаптамалардың коррозиялық тұрақтылығына әсері анағұрлым аз. Сондықтан, нитрофенол фосфомет ерітіндісінде түзілетін фосфатты қаптамалардың коррозиялық тұрақтылығына анағұрлым әсерін тигізеді. м-НБС - ты қосқан кезде цинкарь ерітіндісінде алынған фосфатты қаптаманың коррозиялық тұрақтылығына 180 с –тан көбірек әсер ететіндігі көрсетілді. Цинкарьмен салыстырғанда түзілетін қаптаманың коррозиялық тұрақтылығы фосфомет ерітіндісінде (м-НБС)-ның концентрациясының өсуіне байланысты артуы аз болады. М - нитробензосульфонатының (м-НБС) 50 г/л концентрациясында фосфомет ерітіндісінде коррозиялық тұрақтылық 104 с - ты құрайды. ФР–1 (1,2,3,4) ерітінділерінде (м-НБС)-ның әсері аз байқалады. Электрондық микроскоптің көмегімен фосфаттау процесінің жылдамдатқыштары (м-НБС) мен нитрофенолдың түзілген қаптаманың құрылысына әсері зерттелінді. Микрофотолар жылдамдатқыштардың түзілген қаптаманың максималды тұрақтылық көрсететін оңтайлы коцентрациясында алынды. Темірдің бетінде фосфомет ерітіндісінде м-НБС-ның (50) г/л концентрациясында ине тәрізді фосфатты қаптамалар түзілетіндігі көрсетілді. Аталған қаптаманың кедір-бұдырлығы R_a = 1,597 и R_z = 8,731, коррозиялық тұрақтылығы 104 с-ты құрайды. Жылдамдатқыш ретінде нитрофенолды (5 г/л) пайдаланғанда кедір-бұдырлығы R_a = 5,731, R_z = 11,62 болатын және коррозиялық тұрақтылығы 330 с-ты құрайтын тегіс ірі кристалды қаптамалар түзіледі. М – нитробензосульфонатының (50 г/л) цинкарьға қосқанда түзілетін қаптаманың беті тегісірек болады. Кедір - бұдырлығы R_a = 1,795 и R_z = 10,527 құрайды. Тоттарды түрлендіргіш цинкарь ерітіндісінде нитрофенол (2,5 г/л) болғанда түйіршіктерінің өлшемі бірдей болатын ұсақ түйіршікті қаптамалар түзілетіндігі байқалады. Кедір - бұдырлығы R_a = 1,026 и R_z = 7,691 құрайды. Физикалық әдістерді пайдаланып түзілетін қаптаманы зерттелінді: фосфомет және цинкарь ерітінділерінен нитрофенолдың (2,5 г/л) бірдей концентрациясында алынған қаптаманың қалыңдығы мен темір үлгілерінің бетіне адгезиясын зерттеу, қаптамалардың темір үлгілерінің бетімен байланысу беріктігін зерттеу барысында фосфатты қаптаманың темір бетімен байланысу беріктігі фосфометте 4 МПа/с, ал цинкарьда 3,5 МПа/с-ты құрайтындығы көрсетілді.

ФР-фосфаттаушы ерітінділерінде натрийдің м-нитробензосуфонатын жылдамдатқыш ретінде пайдалану темір үлгілерінің бетімен байланысу беріктігінің артуына айтарлықтай әсер етпейді. Кедір-бұдырлығы анағұрлым аз және үлгінің бетімен жақсы адгезияланатын қаптама нитрофенол қатысындағы фосфомет ерітіндісінен алынатындығы анықталынды. Түзілетін қаптаманың қалыңдығына фосфаттау процесінің жылдамдатқыштарының әсері зерттелінді. Қаптманың қалыңдығын Константа К6Ц аппаратында анықталынды. Анағұрлым қалың қаптама жылдамдатқыш қосылмаған цинкарь ерітіндісінде (5 мкм) және м-м-нитробензосульфонатын қосқанда 5,2 мкм-де байқалады. Нитрофенол қатысында түзілген қаптамалардың қалыңдығы 2,5 тен 2 мкм-ді құрайды. Сонымен, жылдамдатқыш нитрофенол 5 г/л қатысындағы фосфомет ерітіндісінен фосфатты қаптамалар алу темір үлгісінің бетімен берік байланысатын (6 мПа), қалыңдығы 2 мкм, кедір - бұдырлығы (Ra-1,731 и Rz – 11,612) болатын және коррозиялық тұрақтылығы 330 с - ты құрайтын қаптамалардың түзілуіне әкелетіндігі көрсетілді.

Түйін сөздер: фосфатты қаптама, тоттарды түрлендіргіш, нитрофенол, коррозиялық тұрақтылық, адгезия

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УСКОРЕННОЕ НИЗКОТЕМПЕРАТУРНОЕ ФОСФАТИРОВАНИЕ ИЗ РАСТВОРОВ ПРЕОБРАЗОВАТЕЛЕЙ РЖАВЧИНЫ

Аннотация. Наряду с фосфатирующими растворами ФР, для получения антикоррозионных покрытий широкое распространение получили преобразователи ржавчины, использование которых не требует предварительной обработки поверхности металла, как это имеет место при использовании традиционных растворов. Однако, способы ускорения фосфатирования в растворах преобразователей ржавчины не нашли должного применения и остаются малоисследованными. Целью настоящей работы являлось использование органических нитросоединений в качестве ускорителей в растворах преобразователей ржавчины для ускоренного низкотемпературного фосфатирования на поверхности железных образцов. В качестве преобразователей ржавчины были применены выпускаемые в промышленности растворы Фосфомет и Цинкарь, а в качестве ускорителей – нитрофенол и м-нитробензосульфонат натрия (м-НБС). Коррозионная стойкость формируемых покрытий (ЗСА), определенная капельным методом Акимова, сопоставлена с коррозионной стойкостью покрытий, осажденных из традиционных фосфатирующих растворов ФР. Осаждение фосфатных покрытий проводили при температуре 40°C, времени осаждения 10 мин., скорости перемешивания раствора 500 об/мин. Показано, что коррозионная стойкость фосфатного покрытия в отсутствии нитрофенола составляет 42 с. С увеличением концентрации нитрофенола в растворе защитная способность формируемого фосфатного покрытия значительно возрастает, достигая 330 с. при концентрации нитрофенола 5 г/л. В растворе Цинкарь с ростом концентрации нитрофенола от 0,1 до 2,5 мл наблюдается увеличение коррозионной стойкости фосфатного покрытия от 78 до 110 с. При дальнейшем увеличении концентрации нитрофенола коррозионная стойкость покрытия уменьшается до 43 с. Влияние нитрофенола на коррозионную стойкость фосфатных покрытий, формируемых из растворов фосфатирования ФР-1(4) проявляется в значительно меньшей степени. Таким образом, наибольшее влияние на коррозионную стойкость формируемых фосфатных покрытий нитрофенол оказывает в растворе Фосфомет. Исследование влияния добавок (м-НБС) показало, что наибольшая коррозионная стойкость фосфатных покрытий наблюдается в растворе фосфатирования Цинкарь – 180 с. В растворе фосфатирования Фосфомет с ростом концентрации(м-НБС) увеличение коррозионной стойкости формируемых покрытий происходит в меньшей степени по сравнению с раствором Цинкарь. При концентрации (м-НБС) 50 г/л коррозионная стойкость покрытия в растворе (Фосфомет) составляет 104 с. В растворах фосфатирования ФР–1(1,2,3,4) влияние (м-НБС) наблюдается в значительно меньшей степени. Проведено исследование воздействия ускорителей фосфатирования м-НБС и нитрофенола на изменение структуры осажденных покрытий с использованием электронной микроскопии. Микрофотографии были получены при оптимальных концентрациях ускорителей, при которых наблюдалась максимальная коррозионная стойкость образующихся покрытий. Показано, что на поверхности железного образца с фосфатным покрытием, полученным из раствора Фосфомет в присутствии м-НБС (50) г/л формируется покрытие с игольчатой структурой. Шероховатость такого покрытия составляет: R_a = 1,597 и R_z = 8,731 с коррозионной стойкостью 104 с. При использовании в качестве ускорителя нитрофенола (5 г/л) формируется равномерный крупнокристаллический осадок с более высокой шерохотоватостью R_a = 5,731, R_z = 11,62 и коррозионной стойкостью 330 с. С добавлением к раствору Цинкарь м-НБС (50 г) поверхность формируемого покрытия становится более равномерной. Профили шерохотоватости составляют R_a = 1,795 и R_z = 10,527. В присутствии ускорителя фосфатирования нитрофенола (2,5 г/л) в растворе преобразователя ржавчины Цинкарь наблюдается формирование мелкозернистого покрытия, характеризующегося одинаковым размером зерен. Профили шероховатости составляет: R_a = 1,026 и R_z = 7,691. Проведено исследование формируемых антикоррозионных покрытий с использованием физических методов: определение адгезии и толщины полученных покрытий с поверхностью стальных образцов. Определение прочности сцепления фосфатных покрытий с поверхностью железных образцов, полученных из раствора Фосфомет и из раствора Цинкарь в присутствии одинаковой концентрации ускорителя фосфатирования нитрофенола (2,5 г/л) показало, что прочность сцепления фосфатного покрытия с поверхностью железного образца, полученного из раствора Фосфомет + 2,5 г/л нитрофенола составляет 4 МПа/с, тогда как прочность сцепления фосфатного покрытия, образующегося из раствора Цинкарь + 2,5 г/л нитрофенола составляет только 3,5 МПа/с. В растворах фосфатирования ФР использование ускорителей Фосфомета и м-нитробензосуфоната натрия не приводит к заметному увеличению прочности сцепления с поверхностью железных образцов. Установлено, что наименьшей шероховатостью и наибольшей адгезией с поверхностью подложки обладают покрытия, полученные из раствора преобразователя ржавчины Фосфомет с ускорителем фосфатирования нитрофенолом. Проведено исследование влияния добавок ускорителей процесса фосфатирования на толщину формируемых покрытий. Толщину покрытий определяли в толщинометре Константа К6Ц. Показано, что наибольшая толщина покрытия наблюдается в растворе Цинкарь без добавок ускорителя (5 мкм), а также покрытия, осажденного в присутствии м-НБС – 5,2 мкм. Покрытия, осажденные в присутствии нитрофенола, имеют толщину 2,5 до 2 мкм. Таким образом, показано, что осаждение фосфатных покрытий из раствора Фосфомет в присутствии ускорителя 5 г/л нирофенола, приводит к формированию равномерного, прочно связанного с поверхностью железного образца (6 мПа) покрытия, толщиной 2 мкм со степенью шероховатости (Ra-1,731 и Rz – 11,612) и коррозионной стойкостью 330 с.

Ключевые слова: фосфатные покрытия, преобразователи ржавчины, нитрофенол, коррозионная стойкость, адгезия.

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KINETICS OF THE HYDROGENATION PROCESS OF THE COAL AT MAMYT DEPOSIT

Abstract. For the first time, the kinetics of hydrogenation of the Mamyt coal in the presence of an oil pasting agent was studied by the method of equilibrium kinetic analysis. The developed program for calculating the rate constants allows to calculate kinetic dependences under given initial conditions and to carry out automated selection by the gradient method of optimal values of the rate constants $_{k1\text{-}k7}$. The rate constants were optimized from the condition of minimum squared deviations between the experimental and calculated values of the mass fractions of the products of coal hydrogenation.

The kinetic-thermodynamic picture of the process of coal hydrogenation at the Mamyt coal deposit obtained by us allows not only to get closer to the knowledge of the process mechanism, but also makes it possible to control the speed and selectivity of the process.

Keywords: kinetics, Mamyt, coal, hydrogenation.

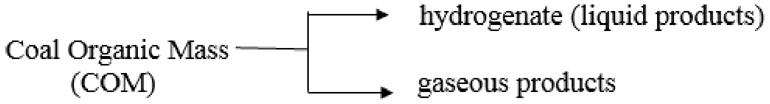
Introduction.

The main and necessary condition for the development of new effective technologies for processing of solid hydrocarbon raw materials, determining the optimal parameters and technical and economic conditions for the process conducting, creating and calculating the hardware design, as well as methods for regulating the process depending on the purpose of the target products is to study the mechanism of transformation of the organic mass of coal, calculation of thermodynamic and kinetic constants of ongoing reactions [1-4].

Coals of various deposits differ in their physicochemical characteristics, properties and composition. All this complicates the study of the kinetics of the processes of hydrogenation processing of coal. A great difficulty in kinetic calculations is caused by multiple simultaneous parallel and sequential reactions in the system [5].

Due to the complexity of the chemical structure of coal, the multicomponent nature of the resulting liquid products, a large number of different kinetic schemes for the process of coal hydrogenation are implemented, which makes it difficult to interpret the results and the uncertainty in the calculation of kinetic parameters. The number of complex reactions occurring in the condensed phase and heterogeneous processes is such that a description of the kinetics of each individual reaction is impossible. Therefore, in a theoretical analysis of the process of coal hydrogenation, it is considered as some single first-order reaction, and some averaged kinetic equations for the dependence of the rate of formation of liquid and gaseous products on temperature are used to describe it [6-8].

At the first stage of solving the kinetic issues of the hydrogenation process, the following scheme for converting the organic mass of coal was used:



Heterogeneous processes are the most difficult for the experimental determination of their kinetic and thermodynamic regularities. The computer simulation of chemical equilibria, which is currently being developed, is related to multicomponent systems and requires complete and reliable a priori information on the properties of each component. We analyse a specific chemical process for which a preliminary knowledge of the properties of the components is optional. All information is extracted from a single series of ordinary temperature and temporary experiments without approaching equilibrium and without strict observance of the set temperature at the beginning of the experiment.

The kinetics of hydrogenation of pyrene, demetallization of heavy oils and asphaltenes, production of boiler fuel, as well as coal hydrogenation in the presence of an oil pasting agent were studied by equilibrium-kinetic analysis (EKA) [9] based on the study [10]. EKA makes it possible to obtain a complex kinetic-thermodynamic picture of the process. Despite a number of advantages, this method has a significant drawback for complex technological processes, since the calculations are carried out for a conditional general reaction scheme, in which parallel and intermediate directions are not taken into account.

Therefore, as already mentioned above, researchers are trying to study the mechanism of the process, drawing up various reaction schemes based on the products obtained.

Experiment.

In this work, for the first time, the kinetics of coal hydrogenation of the Mamyt deposit is studied by the method of equilibrium-kinetic analysis in order to obtain kinetic regularities of the process.

Figures 1, 2 show the kinetic dependences of the conversion of the organic mass of coal into liquid and gaseous products. Analysis of the graphical dependence of the total yield of hydrogenation products (Figure 3) shows that with an increase in the duration of the experiment and the temperature of the process, the conversion of Coal Organic Mass increases from 32.30 to 93.6 wt. % . However, at temperatures above 675–698 K, the yield of gaseous products increases. This, apparently, is explained by adverse reactions, including cracking of hydrocarbon radicals.

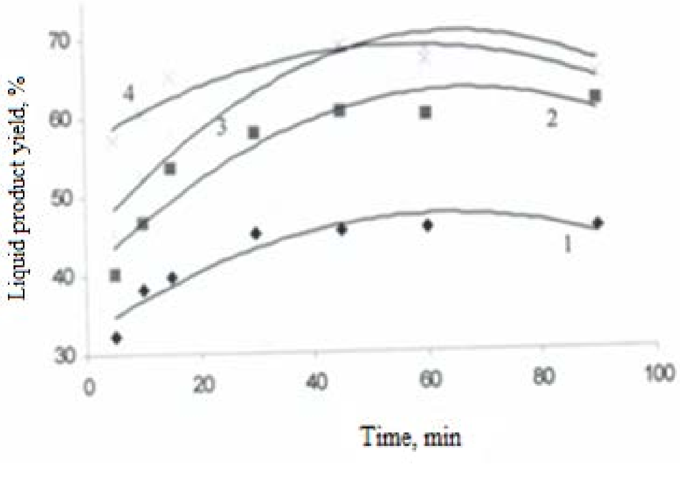


Figure 1 - Kinetic dependences of the conversion of COM into liquid products
1 - fraction up to 653 K; 2 - fraction up to 673 K; 3 - fraction up to 693 K; 4 - fraction up to 71

It is known that at low temperatures, the process of destructive hydrogenation is limited by the diffusion of coal matter across the phase boundary. D.V. Sokolsky and his colleagues [11] established that hydrogen addition processes under certain conditions can occur in the kinetic medium. We experimentally selected the conditions under which the process proceeds in the kinetic medium.

An analysis of the literature data shows [12–20] that information on the kinetics of coal hydrogenation is mainly presented in a hydrogen medium in the presence of molybdenum and cobalt catalysts. However, experimental data show that hydrogenation does not occur with molecular hydrogen, but through the transfer of hydrogen from a molecule of intermediate liquid carbon products to COM, and the catalyst mainly restores the lost H-donor properties of liquid products. The donor abilities of the paste former are sufficient for the hydrogenation of coal, i.e. the absence of molecular hydrogen does not affect the degree of liquefaction of coal. Therefore, in the general reaction, hydrogen, as a separate component, is not taken into account, and the source of hydrogen is the organic mass of the paste.

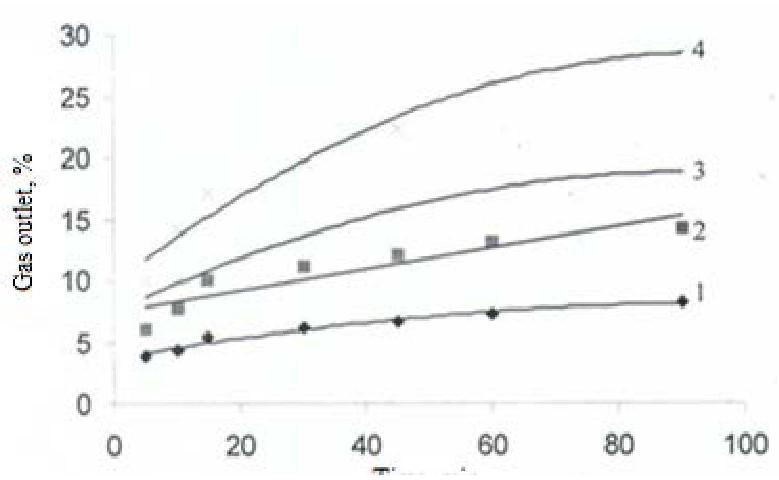


Figure 2– Kinetic dependences of the conversion of COM into gaseous products

fraction up to 653K; 2-fraction up to 673K; 3-fraction up to 693K; 4-fraction up to 713K.

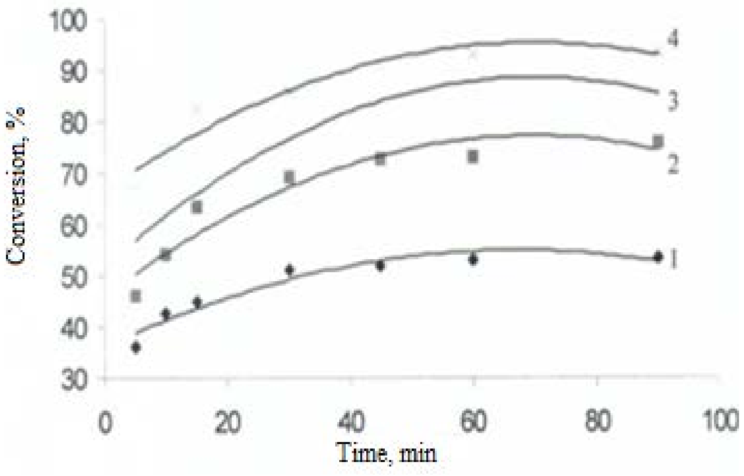


Figure 3 - Kinetic dependences of coal conversion

1 - fraction up to 653 K; 2 - fraction up to 673 K; 3 - fraction up to 693 K; 4 - fraction up to 713 K.

The main disadvantage of the equilibrium-kinetic analysis is the conditional reaction scheme. Of course, in the process of catalytic hydrogenation, several hundred individual compounds are obtained. As mentioned above, this presents the complexity of the calculations. For completeness of kinetic information, we, based on studies of the group composition of liquid products (table 1,) proposed the following scheme of the route for coal liquefaction:

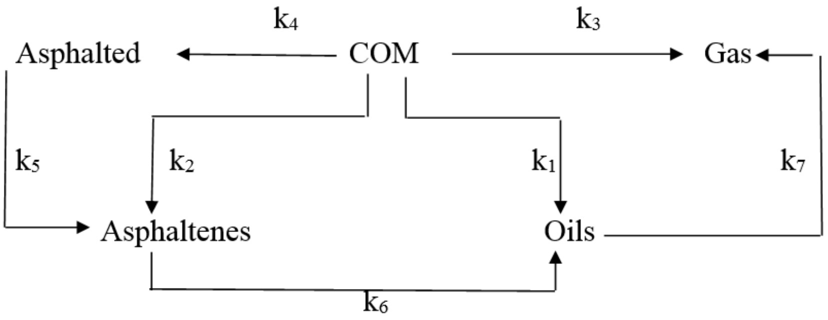


Table 1 - Group composition of products obtained during the hydrogenation of coal of the Mamyt deposit.

T, K	t, min	COM, %	Products, %			
			Asphaltenes	Asphalted	Gas	Oil+water
653	5	60.8	0.94	1.02	3.92	33.32
	10	58.6	0.99	1.08	4.35	34.98
	15	55.0	1.08	1.22	5.35	37.35
	30	50.6	1.23	1.43	6.18	40.56
	45	49.2	1.47	1.57	6.86	40.90
	60	48.8	1.39	1.46	7.15	41.20
	90	48.0	1.25	1.35	8.04	41.36
673	5	52.9	1.41	1.55	6.50	37.64
	10	46.6	1.71	1.87	8.06	41.76
	15	35.7	2.18	2.38	9.64	50.10
	30	31.8	2.45	2.66	11.05	52.04
	45	27.9	2.74	3.03	11.82	54.51
	60	27.0	2.64	2.95	12.07	55.34
	90	24.3	2.48	2.76	14.30	56.16
693	5	47.7	1.94	2.25	7.53	40.58
	10	36.6	2.68	3.25	9.87	47.90
	15	30.1	3.15	4.40	11.74	50.61
	30	23.5	3.83	5.66	13.46	53.55
	45	13.7	4.49	6.90	16.05	58.86
	60	13.4	4.47	6.86	16.51	58.76
	90	12.3	4.29	5.97	19.45	57.99
713	5	33.8	2.71	3.38	10.66	49.45
	10	25.9	3.85	5.11	13.56	51.58
	15	18.6	4.80	6.92	16.44	53.24
	30	13.5	5.54	8.39	19.46	53.11
	45	8.3	6.51	12.10	22.19	50.90
	60	7.0	6.45	12.04	25.33	49.18
	90	6.5	5.89	11.72	28.20	47.69

As was already shown in [21], it can be seen from the straight-line dependence of the graph in the lgC-t coordinates that the hydrogenation reaction is described by a first-order equation. Then, according to the scheme proposals, the process can be described by the following scheme of differential equations:

$$\begin{cases} \frac{\partial C_1}{\partial t} = -(k_1 + k_2 + k_3 + k_4)C_1 \\ \frac{\partial C_2}{\partial t} = k_2 C_1 - k_6 C_2 \\ \frac{\partial C_3}{\partial t} = k_4 C_4 - k_5 C_3 \\ \frac{\partial C_4}{\partial t} = k_3 C_1 + k_7 C_5 \\ \frac{\partial C_5}{\partial t} = k_1 C_1 + k_6 C_2 + k_5 C_5 - k_7 C_5 \end{cases} \tag{1}$$

where, C_1 is the concentration of COM, C_2 is the concentration of asphaltenes in the liquid product, C_3 is the concentration of preasphaltenesin the liquid product, C_4 is the concentration of gaseous products, C_5 is the concentration of oils in the liquid product, k_1 is the reaction rate constant for the conversion of COM into oil, k_2 is the reaction rate constant for converting COM into asphaltene, k_3 is the reaction rate constant for converting COM into gaseous products, k_4 is the reaction rate constant for converting COM into pre-asphaltene, k_5 is the reaction rate constant for converting oil into gaseous products, k_6 is the reaction rate constant of the conversion of asphaltenes into oil, k_7 is the reaction rate constant of the conversion of preasphaltenes into oil.

Using the program “SEARCH” according to equations-1 on a computer, all speed constants were calculated according to this scheme. The calculation results are shown in Table 2.

Table 2 - Kinetics of the hydrogenation process of the Mamyt coal.

Speed constant, min^{-1}	Process stage	Hydrogenation temperature, К			
		653	673	693	713
k_1	COM→oils	1.556	2.501	3.049	4.600
k_2	COM→ asphaltenes	0.0691	0.1620	0.2370	0.4150
k_3	COM→gas	0.229	0.531	0.766	1.354
k_4	COM→ asphalted	0.0779	0.1770	0.2910	0.5860
k_5	asphalted →oils	1.24	1.231	$0.635*10^{-3}$	$0.721*10^{-3}$
k_6	asphaltenes →oils	1.3870	1.2350	0.4200	0.0012
k_7	oils→gas	$0.339*10^{-4}$	$0.507*10^{-4}$	$0.504*10^{-4}$	0.107
$k_\sum$		1.932	3.371	4.343	6.955
F		2.55	1.88	1.63	1.39

F-criterion of minimization:

$$F = \sum_{j=1}^{N} \sum_{i=1}^{N} \left[\frac{V_{\text{ксп}} - V_{\text{расч}}}{V_{\text{расч}}} \right]^2 \tag{2}$$

where, N is the number of measurements, in experiments, V_{exp}, Vc_{alc} are the experimental and calculated values of the content of components in the hydrogenate.

Then, the Arrhenius dependence was constructed for the total rate constant ($k_\sum$) of the process and the main directions of the reaction. In this case, all the points lay in a straight line.

The developed program for calculating the rate constants allows to calculate kinetic dependences under given initial conditions and to carry out automated selection by the gradient method of optimal values of the rate constants. The rate constants were optimized from the condition of minimum squared deviations between the experimental and calculated values of the mass fractions of the products of coal hydrogenation.

From analysis of the results of the rate constants presented in Table 2, we can conclude that the relationship between the rate constants and the yield of coal hydrogenation products is ambiguous. So, the oil yield is mainly due to the value of the rate constant $_{k1}$, as well as $_{k6}$ and k5, $_{\text{and}}$ the probability of the latter sharply decreases with increasing temperature. From table 2 it is seen that the cracking reaction of a liquid product to gaseous increases sharply at a temperature of 713 K. The constant values of the first four phases of the scheme increase with increasing temperature. The fastest phase is the phase of obtaining the target product ($_{k1}$). The total constant of the coal hydrogenation process $k_\sum$ increases with increasing temperature.

Conclusion.

As the result the kinetic-thermodynamic picture of the process of coal hydrogenation at the Mamyt coal deposit obtained by us allows not only to get closer to the knowledge of the process mechanism, but also makes it possible to control the speed and selectivity of the process.

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МАМЫТ КӨМІРІН ГИДРОГЕНИЗАЦИЯЛАУ ҮДЕРІСІНІҢ КИНЕТИКАСЫ

Аннотация. Қатты көмірсутекті шикізатты өңдеудің жаңа тиімді технологияларын жасаудың, үдерістің оңтайлы параметрлері мен техникалық-экономикалық жағдайларын анықтаудың, аппараттық жасақтаманы жасау мен есептеудің, сонымен қатар мақсатты өнімдердің өзара байланысты үдерісті бақылау әдістерінің негізгі және қажетті шарты ретінде көмірдің органикалық массасының өзгеру механизмі, реакциялардың термодинамикалық және кинетикалық константаларын есептеу болып табылады.

Әр түрлі кен орындарының көмірлері физика-химиялық сипаттамалары, қасиеттері мен құрамы бойынша ерекшеленеді. Мұның бәрі көмірді гидрогенизациялау үдерістерінің кинетикасын зерттеуді қиындатады. Кинетикалық есептеулердегі қиындық жүйедегі параллель және тізбектелген көптеген реакцияларға байланысты болады.

Көмірдің химиялық құрылымының күрделілігіне, нәтижесінде алынатын сұйық өнімнің көптеген компоненттеріне байланысты көмірді гидрогенизациялау үдерісіне арналған көптеген кинетикалық сызбалар жүзеге асырылады, яғни нәтижелерді түсінуді қиындатады және кинетикалық параметрлерді есептеудегі белгісіздік тудырады.

Тепе-теңдік-кинетикалық талдау әдісі үдерістің күрделі кинетикалық-термодинамикалық бейнесін алуға мүмкіндік береді. Бірқатар артықшылықтарға қарамастан, бұл әдіс күрделі технологиялық үдерістер үшін айтарлықтай кемшіліктерге ие, себебі есептеулер параллельді және аралық реакцияларды ескермей қарапайым реакцияның сызбасы бойынша жүргізіледі.

Бұл жұмыста алғаш рет үдерістің кинетикалық заңдылықтарын түсіну мақсатында Мамыт кен орны көмірін гидрогенизациялаудың кинетикасы тепе-теңдік-кинетикалық талдау әдісімен зерттелген.

Тепе-теңдік-кинетикалық талдаудың басты кемшілігі - шартты реакция сызбасы. Әрине, каталитикалық гидрогенизациялау үдерісінде бірнеше жүздеген жеке қосылыстар алынады. Бұл есептеулердің күрделілігін тудырады. Сұйық өнімдердің топтық құрамын зерттеу негізінде кинетикалық ақпараттың толықтығы үшін көмірді сұйылту бағытының сызбасы ұсындылды.

Графиктің lgC-t координаттарындағы түзу тәуелділіктен гидрогенизациялау реакциясы бірінші ретті теңдеумен сипатталатындығы көрсетілді. Содан кейін ұсынылған сызбаға сәйкес үдерісті дифференциалдық теңдеулер түрінде сипаттауға болады.

Ұсынылған теңдеулерге сәйкес «ПОИСК» бағдарламасын қолдана отырып, барлық жылдамдық константалары компьютерде есептелінді.

Содан кейін үдерістің жалпы жылдамдығы ($k_{\sum}$) мен реакцияның негізгі бағыттары үшін Аррениус тәуелділігі құрылды. Бұл жағдайда барлық нүктелер түзу сызықта орналасады.

Жылдамдықтың тұрақтылығын есептеуге арналған бағдарлама берілген бастапқы шарттарда кинетикалық тәуелділікті есептеуге және k_1-k_7 жылдамдық константаларының оңтайлы шамаларын градиент әдісімен автоматты таңдауға мүмкіндік береді. Көмірдің гидрогенизациялау өнімдерінің массалық үлестерінің эксперименттік және есептік мәні арасындағы минимумды квадраттық ауытқу жағдайында жылдамдық тұрақтылығы оңтайландырылды.

Талдау нәтижелерінен жылдамдық константалары мен көмір гидрогенизациялау өнімдерінің шығымдылығы арасындағы байланыс бір мәнді емес деген қорытынды жасауға болады. Сонымен, майдың шығымы (k_1) көбінесе k_6 (асфальтендер) және k_5 (преасфальтендер) сияқты тұрақты жылдамдығымен анықталады, ал температура жоғарылағанда оның ықтималдығы күрт төмендейді. Ең жылдам кезең - мақсатты өнімді алу кезеңі (k_1) болып табылады. Көмірді гидрогенизациялау үдерісінің жалпы тұрақтысы $k_{\sum}$ температура жоғарлағанда артады.

Сонымен, Мамыт кен орны көмірін гидрогенизациялау үдерісі туралы алынған кинетикалық-термодинамикалық көрініс бізге технологиялық механизм туралы білім алуға ғана емес, сонымен қатар жылдамдық пен селективтілікті бақылауға мүмкіндік береді.

Түйін сөздер: кинетика, Мамыт, көмір, гидрогенизациялау, жылдамдық константасы, май, асфальтен, преасафальтен, тепе-теңдік кинетикалық талдау.

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КИНЕТИКА ПРОЦЕССА ГИДРОГЕНИЗАЦИИ МАМЫТСКОГО УГЛЯ

Аннотация. Основным и необходимым условием для разработки новых эффективных технологий переработки твердого углеводородного сырья, определения оптимальных параметров и технико-экономических условий проведения процесса, создания и расчета аппаратурного оформления, а также методов регулирования процессом в зависимости от назначения целевых продуктов является изучение механизма превращений органической массы угля, расчет термодинамических и кинетических констант протекающих реакций.

Угли различных месторождений отличаются по своим физико-химическим характеристикам, свойствам и составу. Все это осложняет изучение кинетики процессов гидрогенизационной переработки угля. Большое затруднение в кинетических расчетах вызывает множество одновременно протекающих параллельных и последовательных реакций в системе.

Из-за сложности химического строения угля, многокомпонентности образующихся жидких продуктов реализуется большое количество разнообразных кинетических схем процесса гидрогенизации угля, что обуславливает трудность интерпретации результатов и неопределенность расчета кинетических параметров.

Метод равновесно-кинетического анализа позволяет получить комплексную кинетико-термодинамическую картину процесса. Несмотря на ряд достоинств, этот метод имеет существенный недостаток для сложных технологических процессов, так как расчеты ведутся для условной общей схемы реакции, в которой не учитываются параллельные и промежуточные направления.

В данной работе впервые методом равновесно- кинетического анализа исследована кинетика гидрогенизации угля Мамытского месторождения с целью получения кинетических закономерностей процесса.

Основным недостатком равновесно-кинетического анализа является условная схема реакции. Конечно, в процессе каталитической гидрогенизации получается несколько сотен индивидуальных соединений. В этом и заключается сложность расчётов. Для полноты кинетической информации нами на основании исследований группового состава жидких продуктов предложена схема маршрута ожижения угля.

Из прямолинейной зависимости графика в координатах lgC-t показано, что реакция гидрогенизации описывается уравнением первого порядка. Тогда, согласно предложенной схеме, процесс может быть описан в виде дифференциальных уравнений.

Используя программу «ПОИСК» по предложенным нами уравнениям на ЭВМ были рассчитаны все константы скорости.

Далее была построена аррениусовская зависимость для суммарной константы скорости ($k_{\sum}$) процесса и основных направлений реакции. При этом все точки легли на прямую линию.

Разработанная программа для расчетов констант скоростей позволяет рассчитывать кинетические зависимости при заданных начальных условиях и проводить автоматизированный подбор методом градиента оптимальных значений констант скоростей k_1-k_7. Оптимизация констант скоростей осуществлялась из условия минимума квадратов отклонений между экспериментальными и расчетными значениями массовых долей продуктов гидрогенизации угля.

Из анализа результатов констант скоростей, можно сделать вывод о том, что взаимосвязь констант скоростей и выхода продуктов гидрогенизации угля неоднозначно. Так, выход масел (k_1), в основном, обусловлен величиной константы скорости k_1, а также k_6 (асфальтены) и k_5 (преасфальтены), причем вероятность последних с увеличением температуры резко уменьшается. Самой быстрой стадией является стадия получения целевого продукта (k_1). Суммарная константа процесса гидрогенизации угля $k_{\sum}$ увеличивается с повышением температуры.

Таким образом, полученная нами кинетико-термодинамическая картина процесса гидрогенизации угля Мамытского месторождения позволяет не только приблизиться к знанию механизма процесса, но и дает возможность регулировать скорость и селективность процесса.

Ключевые слова: кинетика, Мамыт, уголь, гидрогенизация, константа скоростей, масла, асфальтен, преасафальтен, равновесно-кинетический анализ.

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RESEARCH OF GOLD EXTRACTION TECHNOLOGY FROM TECHNOGENIC RAW MATERIAL

Abstract. The results of the leaching of the tailings from the heap leaching section with the aim of extracting gold associated with sulfides are presented. A representative sample of the tailings of the heap leaching section was selected and its chemical, phase, and mineralogical composition were studied. It was established that the test sample contains 1.2 g / t Au. According to a rational analysis, by sorption cyanidation at a fineness of 95% class minus 0.071 mm, 76.09% of gold is extracted from a sample of heap leaching tailings, which is mainly (71.74%) represented by intergrowths with ore and rock-forming components. The mass fraction of free (amalgamable noble metal is insignificant (4.35%). The main reason for the persistence to sorption cyanidation is the close association of gold with sulfide minerals. In the optimal mode of cyanidation of oxidation residues, 71.7 % of gold is recovered in 24 hours.

Keywords: gold, heap leaching tailings, phase composition, cyanide.

Introduction

Currently, the state of world mineral resources is characterized by a decrease in the quality of minerals. Due to the depletion of placer gold and silver deposits and the involvement of raw materials with a low content of valuable components and a complex composition, new, more modern and highly efficient technologies for their extraction are required. The intensification technologies currently used make it possible to obtain un-extracted gold from technogenic raw materials. Technogenic wastes are environmentally hazardous, they cause significant harm to the environment, polluting water bodies, soil and air, as dust storms increase the content of toxic elements in the air to a level exceeding the maximum permissible concentrations.

In article [1], dissolution of noble metals by solvents of various types was considered. It should be noted that one of the promising technologies for processing technogenic raw materials is chemical leaching with preliminary oxidation, nitric acid opening, and bacterial leaching [2-4].

Abroad, in particular, South Africa, the tails of gold deposits are involved in recycling, and in Russia example are the tailings of the processing plants of Baleizoloto LLC [5-7].

At present, most gold processing plants process ores in which sulfide minerals are present. Gold in such ores is partially associated with sulfides, and partially is in a free state. In most cases, ores of this type are classified as refractory [8-25].

Technological mineralogy methods allow us to identify useful and harmful minerals and their associations in ores, determine the features of their real composition and structure, the nature of relationships between themselves and with rock-forming phases, control, explain and predict the properties of ores in technological processes.

The raw materials for the re-extraction of gold are heap leach tailings, sorption tailings, flotation ore tailings and substandard raw material reserves. In this regard, the aim of the present research was to develop new methods for additional extraction of gold from the tailings of the heap leaching site.

Experimental methods and results

The object of research was the tailings from the heap leaching section of a gold extraction plant (Kazakhstan). The chemical composition of the studied tailings sample is represented by the following main components, %: 1,385Fe; 0.132 S_{total}; 0.005 Zn; 0.006 Cu; 1.4 g / t Au. A sample of the tailings of the heap leaching area is a finely ground material with a particle size of 90% of the class minus 0.071 mm.

The tail cyanidation products — solution and cake — were subjected to atomic adsorption and assay assays, respectively.

Electron microscopic studies of the main sulfide mineral, arsenopyrite, extracted from the initial tail sample, were performed on a JEOL JXA-8230 scanning electron microscope (Japan) equipped with an energy dispersive analyzer. As can be seen in Figure 1, pyrite, in addition to the main structural elements - iron and sulfur, also contains gold and trace elements of copperand zinc.

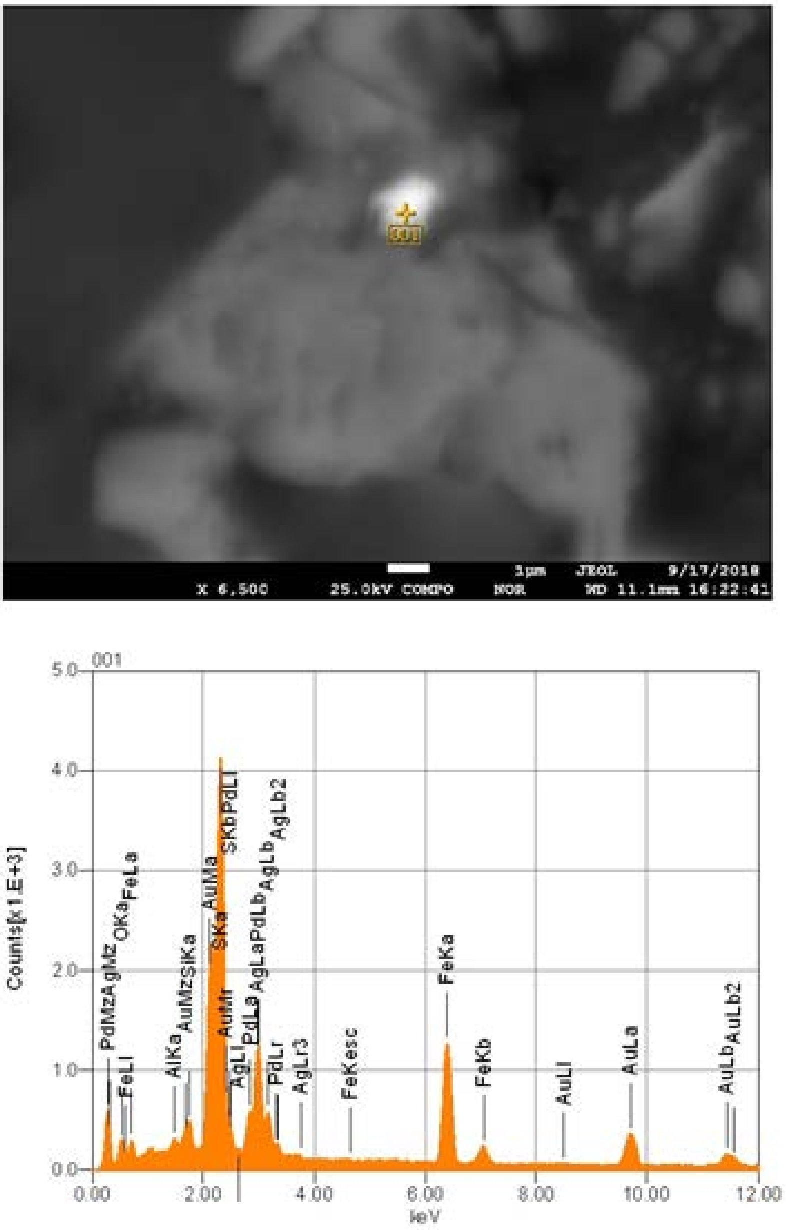

Figure 1 - The microstructure of the initial sample of the tailings (a) and energy dispersive analysis of pyrite (b)

It was established that silver, gold, and silicon are present in the microstructure of the sample. A large part is dominated by non-metallic minerals (quartz more than 30%). According to the electron - probe analysis, we see a particle of gold with a silver content, which develops in sulfides. The shape is gold-plate, irregular, isometric.

X-ray phase analysis showed that the main sulfide mineral in the sample is pyrite (5.8%). In addition, the tail contains a mineral, phyllosilicate of magnesium and aluminum with hydroxyl 7.3% clinochlorine. The mineral composition of the test sample is represented by the following non-metallic components, %: 20.3 albite; 3.2 muscovite; 38.9 quartz; 4.6 calcite. Mineralogical analysis showed that gold is mainly present in finely divided form in quartz and sulfide. The particle size of free finely divided gold is 2.5–3.9 µm, in intergrowths it is 1.2–4.0 µm, and gold grains of irregular isometric shape.

From the results of a rational (phase) analysis of gold in the tails, finely ground to a fineness of 95% class –0.071 mm (table 1), it follows that 76.09% is extracted by sorption cyanidation. Of these, 71.74% fall to intergrowths with ore and rock-forming components, and 4.35% fall to free (amalgamable) metal.

Table 1 - The results of a rational analysis for gold samples of the tailings of the site of heap leaching

The forms of gold and the nature of their association with ore and rock-forming components	Gold allocation	
	g/t	%
Free gold (extractable by amalgamation)	0,040	4,35
In the form of intergrowths with ore and rock-forming components (extracted by sorption cyanidation)	0,660	71,74
Total in possible for cyanidation form	0,700	76,09
Extractable by cyanidation after treatment with alkali (associated with amorphous silica, coated with surface membrane)	0,050	5,62
Extractable by cyanidation after treatment with hydrochloric acid (associated with iron hydroxides, chlorites, carbonates, iron sulfates, sphalerite, etc.)	0,018	1,94
Extractable by cyanidation after treatment with nitric acid (associated with sulfides: pyrite, arsenopyrite, chalcopyrite, etc.)	0,120	13,02
Finely interspersed in rock-forming minerals	0,031	3,33
Total (on balance):	0,920	100,00

The mass fraction of refractory (not extractable by cyanidation) gold is 23.91%. It is mainly associated with sulfides (13.02%), partially - it is coated with surface membranes (5.62%). To a lesser degree, tenacity is affected by the relationship of gold with a complex of minerals soluble in hydrochloric acid — hydroxides, chlorites, and iron carbonates (1.94%).

Determination of the sorption activity of the solid phase was carried out according to the method of JSC Irgiredmet [8]. For this, two parallel cyanidation experiments were carried out on the ground ore sample: in the sorption mode in the presence of activated carbon with a concentration of 10 vol. % and without loading of activated carbon in the following conditions: ratio Liquid: Solid= 2: 1; NaCN concentration - 2.0 g / l; CaO loading - 3 kg / t; cyanidation duration - 24 hours

The relative sorption activity (A, %) was calculated by the formula:

$$A = \left(1 - \frac{R \cdot \mathrm{C}Au}{\beta source\ - \beta cake}\right) \cdot 100\ \%,$$

where R – ratio L:S; C_{Au} – the concentration of gold in solution (in the experiment without a sorbent), mg/l; B_{source} and β_{cake} – accordingly, the gold content in the initial product and cyanide cake in the experiment with the sorbent, g / t

The experimental results are presented in the table 2.

Experimental part

Vat-agitation cyanide leaching of the initial sample of the tailings of the heap leaching site. The results of studies on propaganda cyanide leaching of tailings using an oxidizing agent and a surfactant are presented.

Table 2 - The results of experiments to determine the sorption activity of the tailings from the heap leach plot

Mass fraction of class minus 0.071 mm, %	Experimental conditions	Concentration Au in solution, mg/l	Au content in cake, g/t	Extract Aufrom operations,%	Relative sorption activity,%
95	Without sorbent	0,47	-	-	4,1
	With sorbent	-	0,22	82,1	

* gold content in the initial sample according to the analysis - 1.2 g / t

The results presented in table 2 show that the initial tailings sample does not have sorption activity with respect to the gold cyanide complex.

The optimal parameters for processing the tailings of the heap leaching section were selected by comparing various leaching variants. Taking into account the significant content of carbonates in the tails, in all cases they were pre-treated with acid in order to dissolve the carbonates.

In the process of preparing a sample of the tailings from the heap leaching site for hydrometallurgical studies, it was ground to a particle size of 0.040 mm in a planetary mill. Leaching pulp density is 30% solid. The pH of the pulp during leaching of the tests was maintained at a level of 10.5-11.0. Leaching time is 24 hours (Table 3).

Table 3 - Leaching of the initial sample tailings from the heap leaching section

Variant	The fineness of the material, mm	Gold Content, g / t		Gold extraction,%
		In the original	In cake	
Direct cyanidation				
1	90 % -0,071	1,2	0,54	55,0
2	90 % -0,04	1,2	0,52	56,7
Using calcium hypochlorite $Ca(ClO)_2$				
3	90 % -0,071	1,2	0,47	60,8
4	95 % -0,04	1,2	0,34	71,7

As a result, the following gold recovery indicators were obtained for various options for processing the tailings from the heap leaching samples: variant 1- 55.0%; variant - 56.7 %; variant 3 - 60.8 %; variant 4 - 71.7 %.

The results obtained indicate that in the process of leaching the tailings from the heap leaching section, sulfides are oxidized, resistant gold is opened and its extraction is increased during subsequent cyanidation of oxidation residues. Gold recovery reaches 60.8 and 71.7 %, respectively, in variants 3 and 4 of tailings processing.

Conclusion

It was revealed that the gold content in the test sample is 1.2 g / t. Gold is found in the form of very fine grains in sulfides (arsenopyrite, pyrite), as well as in a finely disseminated state in silicate minerals.

As a result of rational (phase) analysis, the mass fraction of refractory (not extractable by cyanidation) gold is 23.91%. It is mainly associated with sulfides (13.02%), partially - it is coated with surface films (5.62%).

Extraction of gold from the tailings from the heap leaching section with preliminary oxidation is 71.7 %.

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ТЕХНОГЕНДІ ШИКІЗАТТАРДАН АЛТЫН БӨЛІП АЛУДЫҢ ТЕХНОЛОГИЯСЫН ЗЕРТТЕУ

Аннотация. Қазіргі кезеңдегі алтын гидрометаллургиясының маңызды міндеті - оны техногендік шикізаттан бөлудің ұтымды әдістерін табу. Қалдықтарды қайта өңдеуге тарту үшін қалыпты емес әдістер қажет. Техногендік шикізатты өңдеудің перспективті технологияларының бірі - үлкен материалдық шығындарды қажет етпейтін және атмосфераны ластамайтын шаймалау процесінде алдын ала тотығуды қолдану. Бұл әдіс сульфидтердің терең ашылуына байланысты құрамында алтыны бар құрамында шикізаттан алтын алудың тотығу процесін күшейтуге мүмкіндік береді.

Сульфидтермен байланысты алтынды алу мақсатында үйінділерді қалдықтарын шаймалау нәтижелері келтірілген. Үйінділерді қалдықтарынан үлгілері алынып, оның химиялық, фазалық және минералогиялық құрамы зерттелді. Үлгідегі алтынның құрамы 1,2 г/т анықталды. Рационалды талдаудың нәтижесі бойынша, 95% класты 0.071 мм мөлшерінде сорбциялық цианидтендіру арқылы 76,09% алтын алынды, бұл негізінен кен және тау жыныстарын құрайтын өсінділермен ұсынылған (71,74%). Бос (араласатын асыл металдың) үлес салмағы шамалы (4,35%). Сорбциялық цианидтенудің негізгі себебі - алтынның сульфидті минералдармен тығыз байланысы.

Өңделуі қиын (алынбайтын сорбциялық цианизация) түрінде алтынның 23,91% құрайды. Ол келесідей бөлінеді: аморфты кремниймен байланысқан және беттік қабыршақтармен қапталған - 5,62%; тұз қышқылында еритін минералдар кешенімен байланысты (гидроксидтер, карбонаттар, темір хлориттері) - 1,94%; сульфидтермен байланысты: пирит, арсенопирит - 13,02%; тау жыныстары түзілген минералдармен өте жақсы араласады - 3,33%.

Электронды микроскопиялық анализ (SEM) арқылы үйінділерді щаймалау секциясының (жұқа секциялар) қалдықтарының бастапқы үлгісін зерттеу нәтижелері сынаманың микроқұрылымында күміс, алтын және кремний бар екенін көрсетті. Үлкен бөлігін металл емес минералдар құрайды (кварц 30% -дан астам). Электронды-зондтық анализге сәйкес, сульфидтерде дамитын күміс құрамы бар алтын бөлшегін көреміз. Пішіні алтын тәрелке тәрізді, изометриялық.

Бастапқы үлгіні (жіңішке секцияларды) минералогиялық талдау бір жағдайда бос жынысы бар бөлшекке түтікшелі беті бар жұқа дисперсияланған Au (3.6x5.3 mk) таяз шығанақ тәрізді кірістірудің қарапайым жиегі табылғандығын көрсетті. (12x18 мк). Суретте алтынның көкшіл-жасыл реңкі бар, ол бор, ковеллит композицияларының болуы мүмкін екенін көрсетеді (Борнит - Cu5FeS4; Ковеллин - CuS). Мұндай фильмдер цианидтің алтынға қол жеткізуіне кедергі келтіреді. Күміс аз мөлшерде жұқа бөлшектер түрінде болады, мөлшері Ag-да (1-5,7 мк), негізінен еркін. Таралуы бойынша тізімделген ассоциацияланған компоненттер: Арс арсенопириті (FeAsS), пирит (FeS2), халцопирит Сп (CuFeS2) және аз магнитит Mgt (Fe3O4), сфалерит Сл (ZnS); және теннантит tn (Cu12As4S13); бір жағдайда галена га (PbS) бар шоғырланған арсенопирит табылды.

Алынған нәтижелер үйінділерді шаймалау секциясының қалдықтарын сілтілеу процесінде сульфидтер тотығады, өңделуі қиын алтын ашылады және одан кейінгі тотығу қалдықтарын цианизациялау кезінде оның экстракциясы жоғарылайды.

Тотығу қалдықтарын цианидтендірудің оңтайлы жағдайында алтынның 71,7 % -ы 24 сағат ішінде алынады.

Түйін сөздер: алтын, шаймалау аймағының үйінділерінің қалдықтары, фазалық құрамы, цианидтеу.

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ИССЛЕДОВАНИЕ ТЕХНОЛОГИИ ИЗВЛЕЧЕНИЯ ЗОЛОТА ИЗ ТЕХНОГЕННОГО СЫРЬЯ

Аннотация. Важнейшая задача гидрометаллургии золота на современном этапе - изыскание рациональных способов его извлечения из техногенного сырья. Для вовлечения отходов в переработку требуются нетрадиционные методы. Одной из перспективных технологий переработки техногенного сырья является применение в процессе выщелачивания предварительное окисление, которое не требует больших материальных затрат и не загрязняет атмосферу. Этот метод позволяет интенсифицировать процесс окисления извлечения золота из упорного золотосодержащего сырья за счет более глубокого вскрытия сульфидов.

Приведены результаты процесса выщелачивания хвостов участка кучного выщелачивания с целью извлечения золота, ассоциированного с сульфидами. Осуществлен отбор представительной пробы хвостов участка кучного выщелачивания и изучены ее химический, фазовый и минералогический состав. Установлено, что в исследуемой пробе содержится 1,2 г/т Au. По данным рационального анализа сорбционным цианированием при крупности 95 % класса минус 0,071 мм из пробы хвостов кучного выщелачивания извлекается 76,09 % золота, которое в основном (71,74 %) представлено сростками с рудными и породообразующими компонентами. Массовая доля свободного (амальгамируемого благородного металла незначительна (4,35 %). Основной причиной упорности к сорбционному цианированию является тесная ассоциация золота с сульфидными минералами.

В упорной (не извлекаемой сорбционным цианированием) форме находится 23,91 % золота. Оно распределено следующим образом: ассоциированное с аморфным кремнеземом и покрытое поверхностными пленками - 5,62 %; ассоциированное с комплексом минералов, растворимых в соляной кислоте (гидроксидами, карбонатами, хлоритами железа) - 1,94 %; связанное с сульфидами: пиритом, арсенопиритом - 13,02 %; тонко вкрапленное в породообразующие минералы - 3,33 %.

Результаты исследования исходного образца хвосты участка кучного выщелачивания (шлифов) методом электронно-микроскопического анализа (РЭМ) показали, что в микроструктуре пробы присутствуют серебро, золото, кремний. Большую часть преобладает нерудные минералы (кварц более 30%). По данным электро - зондового анализа мы видим частичку золото с содержанием серебра, который развивается в сульфидах. Форма золотинпластинчатая, неправильная, изометричная.

Минералогический анализ исходного образца (шлифов) показали, что в единичном случае обнаружен простой краевой сросток золота, представленный неглубоким заливообразным включением тонкодисперсного Au (3,6х5,3 mk) с бугорчатой поверхностью в частице вмещающей пустой породы п.п. (12х18 mk). На снимке золото имеет синевато-зеленоватый оттенок, свидетельствующий о наличии пленок, вероятно борнит-ковеллинового состава (Борнит – Cu_5FeS_4,; Ковеллин - CuS). Подобные пленки затрудняют доступ цианида к золоту. Серебро присутствует в незначительном количестве в виде тонкодисперсных частиц с вариацией размеров в пределах Ag (1-5,7 mk), преимущественно в свободной форме. Сопутствующие компоненты, перечисленные в порядке их распространенности, представлены: арсенопиритом Ars (FeAsS), пиритом (FeS2), халькопиритом Cp (CuFeS2), и реже магнетитом Mgt (Fe3O4), сфалеритом Sl (ZnS); и теннантитом tn (Cu12As4S13); в единичном случае обнаружен сросток арсенопирита с галенитом ga (PbS)

Полученные результаты свидетельствуют о том, что в процессе выщелачивания хвостов участка кучного выщелачивания происходит окисление сульфидов, вскрытие упорного золота и повышение его извлечения при последующем цианировании остатков окисления.

В оптимальном режиме цианирования остатков окисления за 24 ч извлекается 71,7 % золота.

Ключевые слова: золото, хвосты участка кучного выщелачивания, фазовый состав, цианирование.

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SYNTHESIS OF PILLARED CLAYS FOR USING THEM AS CARRIERS OF CATALYTIC SYSTEMS

Abstract. Natural clays are of particular interest for their rational use as not only adsorbents, but also carriers of new highly selective catalysts. This article presents an overview of the application of pillared clays in catalytic chemistry as catalyst matrix. The physicochemical properties of the synthesized Al-, Zr-, Al / Zr-modified clays were studied by BET, XRF and elemental analysis. The elemental composition of montmorillonite and kaolinite clays was determined. Pillared clays with high specific surface (montmorillonite clay from 20 to 243 m^2/g and kaolinite clay from 5 to 66 m^2/g.) were obtained. The use of pillared clays in catalysis will help to solve the problems of the development of domestic production of catalysts and the replacement of expensive imported analogues.

Key words: natural clays; montmorillonite; kaolinite; mechanical activation; pillared clay; pillarization.

Introduction

Cost-effective and environmentally friendly catalysts are always in demand for synthesis of valuable organic compounds. The main features of a highly efficient catalytic support are: 1) developed surface area for the location of catalytically active centers [1, 2], 2) high thermal stability to prevent sintering and abrasion of the catalyst [3, 4] 3) the presence of various functional groups responsible for stabilization and activation of the catalytically active phase [5, 6].

The presented requirements are fully met by natural clays with a high specific surface. Obtaining of pillared clays and their modification by various transition metal complexes lead to the formation of new porous structures with unique physicochemical properties [7]. In this regard, the urgent task is to develop catalysts based on pillared clay-matrix both for metals and for metal oxides deposited on the surface as catalytically active phases [8].

Therefore the goal of this study is to synthesize new pillared clay samples for the development of highly selective catalysts and to obtain high yields of industrially important gas and petrochemical products, as well as to study the physicochemical properties of columnar structures based on natural clays of the Tagan and Turgay deposits of the East Kazakhstan region.

Materials and methods

Objects of study - synthesized columnar clays for use as a catalyst carrier. Natural clays of the Tagan and Turgay deposits of East Kazakhstan region were used in this work.

Mechanical activation of natural clays

To activate natural kaolinite clays, the AGO-2 high-voltage planetary mill with steel balls with a diameter of 8 mm and a total mass of 200 g, with 150 ml water-cooled steel drums was used. The ratio of the mass of the balls to the mass of the mixture (M) was 20:30. The rotational speed of the drums is 1200 rpm. To ensure a low level of powder contamination in the steel grinding medium, the natural lining of the working surface of the drums and balls, obtained by preliminary processing of a similar mixture, leading to coating the surface of the balls and the inner surface of the drums with the processed composition [9], was used.

Synthesis of pillared clays

Natural clays pre-cleaned and ground to a particle size of 0.25 mm were incubated for 24 hours at room temperature for complete hydration. The aluminum and zirconium hydroxocomplexes obtained by hydrolysis of aqueous solutions of aluminum chloride (0.2 M) and zirconium (0.2 M) in an aqueous solution of NaOH (0.5 M) were used as intercalating solutions [7, 8, 10]. Pillarization was carried out by slowly adding an intercalating agent to clay samples and further washing from chlorine ions. The obtained columnar clays were dried for one day at room temperature and then calcined at a temperature of 500°C for 5 hours [11].

Textural and physico-chemical properties of pillared clays

The texture characteristics of pillared clays were studied via nitrogen adsorption and desorption isotherms using the BET method (Brauner-Emmett-Teller) on SORBTOMETR-M device (Russia). The change in the phase composition of columnar clays was monitored using x-ray phase analysis on a general-purpose diffractometer DRON-4-0.7 with CuKα radiation (Russia).

The elemental composition of the pillared clay samples was analyzed using an INCAENERGY energy dispersive spectrophotometer (OXFORDINSTRUMENTS, UK) combined with Superprobe 733 electron probe microanalyzer at an accelerating voltage of 25 kV and a probe current of 25 nA.

Results and discussion

Montmorillonite is known to be a clay composed of blocks of tetrahedral quartz sheets with a central octahedral aluminum oxide sheet with the chemical formula $(Si_{7.8}Al_{0.2})^{IV}$ $(Al_{3.4}Mg_{0.6})^{VI}O_{20}$ $(OH)_4$, and the theoretical composition without intermediate material is SiO_2 66.7%, Al_2O_3 28.3% and H_2O 5%. Taking into account the speciation of various metals in this formula, the theoretical net surface charge on montmorillonite is 0.8 charge / element, which is responsible for the adsorption of cations [12].

Elemental analysis of the oxide composition of natural montmorillonite and kaolinite clays samples was carried out using quantitative X-ray spectral analysis. The results are presented in table 1.

Table 1 - Elemental composition of natural kaolinite and montmorillonite clay samples

Element / Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	PS
Montmorillonite Clay	Elementcontent, wt. %								
	55,5	19,38	4,4	0,3	1,98	2,18	1,5	1,14	9,5
Element / Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	PS
Kaolinite clay	Elementcontent, wt. %								
	39,33	40,20	17,80	2,01	n.e	0,16	n.e	0,19	0,31

Note: PS –

The data presented in Table 1 indicate that the montmorillonite clay sample contains a large number of alkali and alkaline earth metal cations that can participate cation-exchange reactions, while Ca^{2+} and K^+ ions are absent in the kaolinite clay sample and only small amounts of Mg^{2+} and $Na^+$are detected The results obtained are consistent with published data [13, 14].

Kaolinite is a clay mineral from the group of aqueous aluminum silicates with a chemical composition: Al_4 $[Si_4O_{10}]$ $(OH)_8$. It contains 39.5% Al_2O_3, 46.5% SiO_2 and 14% H_2O. The crystal structure of kaolinite consists of two-layer packets containing one oxygen tetrahedral layer of the composition $[Si_{2n}0_{5n}]^{2n+}$ and one aluminum-hydroxyl octahedral layer of the composition $[Al_{2n}(OH)_{4n}]^{2n+}$. Both layers are combined into a package through common oxygen-silicon-oxygen layer. These layers are interconnected by weak bonds, which determine the very perfect cleavage of kaolinite and the possibility of different overlays of one layer onto another.

Considering the speciation of various metals in this formula, the theoretical net surface charge on kaolinite is zero. However, kaolinite acquires a small total negative charge due to the fact that its surface is not completely inert [12-15].

Thus, mechanical activation of kaolinite clay (Turgay deposit, East Kazakhstan area) was carried out on a high-voltage planetary mill AGO-2. Spectra for natural and mechanically activated kaolinite clay, which are shown in Figures 1 and 2, were obtained by the method of diffraction of the total X-ray radiation (DRON-4-0.7).

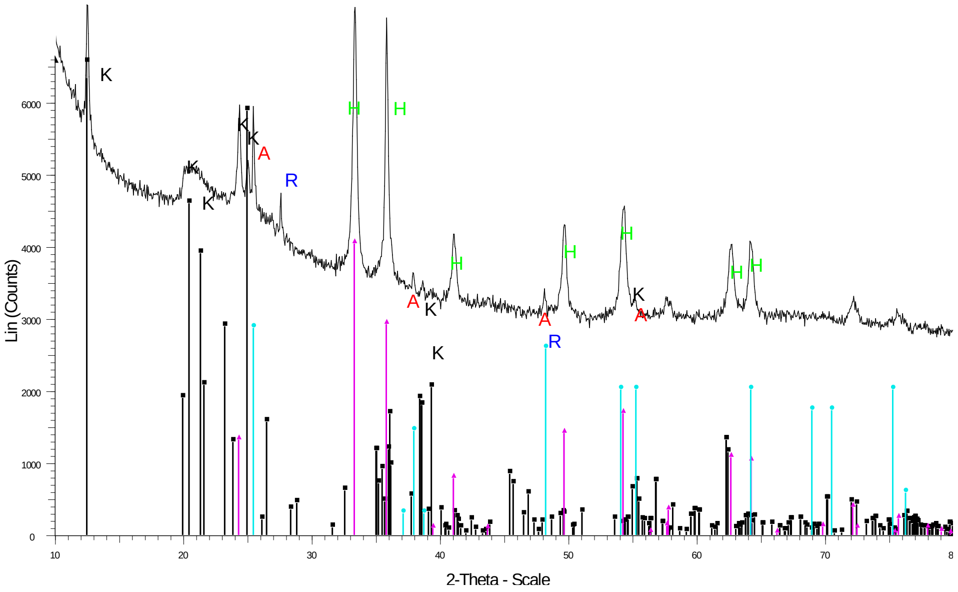

Figure 1 - Diffraction pattern of a sample of the original natural clay: K-kaolinite, A-anatase, R-rutile, H-hematite

When studying the spectrum of a sample of the original natural clay (Figure 1), kaolinite diffraction reflections were recorded (K, PDF-080-0885) with interplanar distances 7.12 (12.40° 2θ), 4.38 (20.35), 4.16 (21.34), 3.56 (24.96) Å; hematite (α-Fe_2O_3, (PDF-089-8103) with interplanar distances 3.661(24.30), 2.69 (33.3), 2.51 (35.78), 2.198 (41.02), 1.834 (49.66), 1.688 (54.30), 1.598 (57.64), 1.481 (62.68), 1.449 (64.18), 1.308 (72.18); (26.85° 2θ); TiO_2 (anatase – 3.502 (25.41), 2.373 (37.88), 1.89 (49.09), 1.664 (55.14); TiO_2 (rutile – 3.240 (27.50) Å ($^{\circ}$ 2θ).

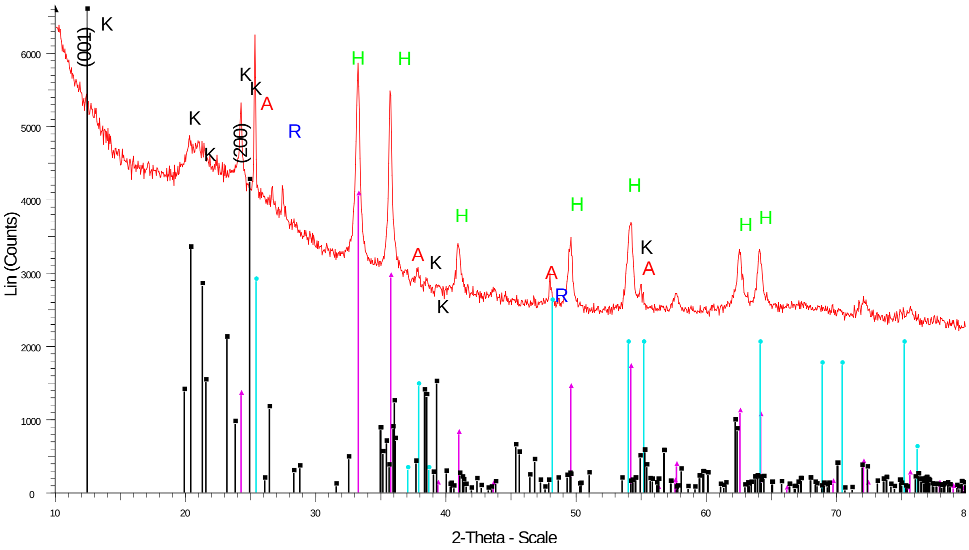

Figure 2 - Diffraction pattern of a sample of modified clay: K-kaolinite, A-anatase, R-rutile, H-hematite

Figure 2 shows the diffraction reflections of mechanically activated kaolinite clay.

According to the literature [15-19], the x-ray spectra of kaolinite clays have nine peaks in the range 1-30^0 (2θ):

- The basal distance is 7,27 Å (2θ = 12,15 °) with intensity 79,4% and tip width 0,20 (2θ = 12,15 °);
- Calcined kaolinite gives 13 peaks in the same range 2. The basal distance is 7,15 Å (2θ = 12,15 °) with intensity 69,7% for kaolinite and tip width 0,10 (2θ = 12,15 °);

- For acid activated kaolinite, the expansion of the basal gap is from 7,27 to 7,30 Å; 2θ = 12,14 °), and the peak intensity is from 23.14% to 21.32% [16].

According to the data obtained, it can be concluded that after mechanical activation, the phase and chemical composition of kaolinite clay has changed, since kaolinite reflections (001) with interplanar spacings of 7.12 Å (12.40 ° 2θ) and (002) 3.56 Å (24.96 ° 2θ) not detected. Hydrogen bonds between the octahedral layer and the oxygen of the tetrahedral layer can serve as a source of interlayer bonds in the structure of kaolinite. [19, 20].

Despite the fact that many works on the general structure of pillared clays have been published, the detailed structure of the columns and the type of connection of the columns with silicate layers are still poorly understood.

Natural clays, including kaolinite and montmorillonite, have a layered structure and high cation exchange capacity. The surface area values vary from 5 to 25 m^2/g for kaolinite and 15.5–82.0 m^2/g for montmorillonite depending on the particle size distribution, particle shape, and pore distribution in the clay material [20, 21].

Changes in the texture characteristics of pillared montmorillonite and kaolinite clays according to the isotherms of low-temperature nitrogen adsorption are presented in table 2.

Table 2 - Structural characteristics of pillared clays

Type of montmorillonite pillared clay	The content of the oxide columns, wt.%	Specific surface area S_{BET}, $м^2/г$	Type of kaolinite pillared clay	The content of the oxide columns, wt.%	Specific surface area S_{BET}, $м^2/г$
МГ-1-Zr/Ba	ZrO_2 – 23%	243	КГ-1-Zr	ZrO_2 – 18%	66
МГ-2-Zr/Sr	ZrO_2 – 22%	240	КГ-2-Al	Al_2O_3 – 15%	55
МГ-3-Zr/Ca	ZrO_2 – 22.5%	240	КГ-3-Zr/Al	Al_2O_3 – 4%, ZrO_2 – 18%	51
Note: The specific area of natural montmorillonite clay is ~ 20 m^2/g.			Note: The specific area of natural kaolinite clay is ~ 5 m^2/g.		

The data in table 2 show that the specific surface area of the initial clay increases with pilling: in montmorillonite clay from 20 to 243 m^2/g and in kaolinite clay from 5 to 66 m^2/g, the content of zirconium reaches 18-23%, aluminum 4 -15%.

The obtained characteristics are in good agreement with the published data that montmorillonite and kaolinite can be used as starting material for modification with the introduction of aluminum and zirconium into the intermediate layers [12–15, 22–24].

The synthesized columnar clays are environmentally friendly and effective for use as carriers in the preparation of heterogeneous catalysts. Also,their use as adsorbents in the production of petrochemical and organic chemicals is not ruled out.

Conclusion

The structure of natural and pillared clays was studied, the relationship between the structure of the pillars and the mechanism of their formation was determined, columnar clays having catalytic properties were obtained.

It is shown that pillared clays synthesized from natural clays of the Tagan and Turgay deposits of the East Kazakhstan region, the Republic of Kazakhstan, can be used as carriers for catalysts. Their specific surface area and catalytic activity are significantly increased by using the pilling process.

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КАТАЛИТИКАЛЫҚ ЖҮЙЕЛЕРДІҢ ТАСЫМАЛДАУШЫСЫ РЕТІНДЕ ҚОЛДАНЫЛАТЫН БАҒАНАЛЫ САЗБАЛШЫҚТАРДЫ СИНТЕЗДЕУ

Аннотация. Табиғи сазбалшықтарды адсорбенттер ретінде ғана емес, сонымен қатар жаңа жоғары селективті катализаторлардың тасымалдаушылары ретінде де ұтымды қолдану үлкен қызығушылық тудырады. Бұл мақалада каталитикалық химия бағытында каталализаторлардың тасымалдаушысы ретінде бағаналы сазбалшықтарды қолдануға шолу жасалған. Al-, Zr-, Al/Zr-модификацияланған сазбалшықтардың физика-химиялық қасиеттері элементтік талдау, БЭТ және РФА әдістері арқылы зерттелген.

Каолинитті сазбалшықты механикалық активтендіру (Торғай кен орны, Шығыс Қазақстан облысы) жоғары кернеулі АГО-2 планеталық диірменінде жүзеге асырылды. Жалпы рентген сәулесінің дифракциясы әдісімен (DRON-4-0.7) табиғи және механикалық активтендірілген каолинит сазбалшықтарына арналған спектрлер зерттелді.

Табиғи сазбалшықтан жасалған үлгінің спектрін зерттеу барысында, каолиниттің (K, PDF-080-0885) дифракциялық шағылыстары: 7.12 (12.40 ° 2θ), 4.38 (20.35), 4.16 (21.34), 3.56 (24.96) Å 3.661 (24.30), 2.69 (33.3), 2.51 (35.78), 2.198 (41.02), 1.834 (49.66), 1.688 (54.30), 1.598 (57.64), гематиттің (α-Fe_2O_3, PDF-089-8103) аралық қабаты: 1.481 (62.68), 1.449 (64.18), 1.308 (72.18); кварц (26,85 ° 2θ); TiO_2 (анатаза - 3.502 (25.41), 2.373 (37.88), 1.89 (49.09), 1.664 (55.14); TiO_2 (рутил - 3.240 (27.50) Å (° 2θ) аралық қабаттары жазылды. Алынған мәліметтер негізінде сазбалшықтың фазалық құрамы туралы қорытынды жасауға болады. Каолинит сазбалшығының механикалық құрамы механикалық активацияға байланысты өзгерді, өйткені 7,12 Å (12.40 °2θ) және (002) 3.56 Å (24.96 °2θ) аралығындағы қабат кеңістігі бар каолинит (001) шағылыстары анықталмады.

Зерттеуга алынған каолинит және монтмориллонит сазбалшықтарының элементтік құрамдары анықталды. Нәтижесінде монтмориллонит үшін ~20-дан 243 м^2/г, каолинит үшін ~5-тен 66 м^2/г дейінгі меншікті беттік қабаты бар бағаналы сазбалшықтар алынды.

Алынған көрсеткіштер монтмориллонит пен каолинитті аралық қабаттарға алюминий мен цирконий енгізумен модификациялау үшін бастапқы материал ретінде қолдануға болатыны әдебиеттерде жақсы келісілген.

Осылайша, жоғарыда келтірілген ақпарат синтезделген бағаналы саздар экологиялық таза және гетерогенді катализаторлардың тасымалдаушысы ретінде пайдалану үшін тиімді екенін көрсетті. Катализде аталған бағаналы сазбалшықтарды қолдану катализаторлардың отандық өндірісін дамыту және қымбат импорттық аналогтарын алмастыру мәселесін шешуге септігін тигізеді.

Түйін сөздер: табиғи сазбалшықтар; монтмориллонит; каолинит; механикалық активтендіру; бағаналы сазбалшықтар; бағаналау.

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СИНТЕЗ СТОЛБЧАТЫХ ГЛИН ДЛЯ ПРИМЕНЕНИЯ ЕГО В КАЧЕСТВЕ НОСИТЕЛЯ КАТАЛИТИЧЕСКИХ СИСТЕМ

Аннотация. Природные глины представляют особый интерес для их рационального использования в качестве не только адсорбентов, но и носителей новых высокоселективных катализаторов. В данной статье представлен обзор сведений использования столбчатых глин в области каталитической химии в качестве носителей катализаторов. Изучены физико-химические свойства синтезированых Al-, Zr-, Al/Zr-модифицированных глин методами БЭТ, РФА и элементного анализа.

Была проведена механическая активация каолинитовой глины (Тургайское месторождение, ВКО) на высоконапряженной планетарной мельнице АГО-2. Методом дифракции общего излучения рентгеновских лучей (ДРОН-4-0.7) были изучены спектры для природной и механически активизированной каолинитовых глин.

При исследовании спектров образца исходной природной глины были зафиксированы дифракционные рефлексы каолинита (K, PDF-080-0885) с межплоскостными расстояниями 7.12 (12.40° 2θ), 4.38 (20.35), 4.16 (21.34), 3.56 (24.96) Å; гематита (α-Fe_2O_3, PDF-089-8103) с межплоскостными расстояниями 3.661(24.30), 2.69 (33.3), 2.51 (35.78), 2.198 (41.02), 1.834 (49.66), 1.688 (54.30), 1.598 (57.64), 1.481 (62.68), 1.449 (64.18), 1.308 (72.18); кварца (26.85° 2θ); TiO_2 (анатаз – 3.502 (25.41), 2.373 (37.88), 1.89 (49.09), 1.664 (55.14); TiO_2 (рутил – 3.240 (27.50) Å (° 2θ). По полученным данным можно сделать выводы о том, что фазовый состав проведения механической активации химический состав каолинитовой глины изменилась, так как, рефлексы каолинита (001) с межплоскостными расстояниями 7.12 Å (12.40° 2θ) и (002) 3.56 Å (24.96 ° 2θ) не обнаружены.

Определены химические элементные составы исследуемых монтмориллонитовой и каолинитовой глины. В результате исследования получены столбчатые глины с высокой удельной поверхностью: у монтмориллонитовой глины от ~20 до 243 м^2/г и у каолинитовой глины от ~5 до 66 м^2/г.

Полученные показатели вполне согласуются с литературными данными о том, что монтмориллонит и каолинит вполне могут быть использованы в качестве исходного материала для модификации с введением алюминия и циркония в промежуточные слои.

Таким образом, выше представленные сведения показали, что синтезированные столбчатые глины являются экологически чистыми и эффективными для применения их в качестве носителя гетерогенных катализаторов. Использование столбчатых глин в катализе поможет решить вопросы развития отечественного производства катализаторов и замены дорогих импортных аналогов.

Ключевые слова: природные глины; монтмориллонит; каолинит; механическая активация; столбчатые глины; пилларирование.

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BIS(2,2,2-TRIFLUOROETHYL)(2-CYANOETHYL) PHOSPHATE – A NEW URANIUM EXTRAGENT

Abstract. Organophosphate compounds are widely used in industrial hydrometallurgical processes as extractants and complexones of non-ferrous, noble, rare-earth metals and transuranic elements. Among these compounds, organic phosphates occupy a special place, as they allow for the extraction processes with good selectivity and efficiency. However, a significant drawback of known organic phosphates is their low extraction capacity, as well as rather good solubility in water and their hydrolysability in aqueous acidic solutions, which leads to both loss of the extractant and contamination of the extracted metal with organophosphorus compounds. Therefore, the search and development of new uranium effective extractants is an important task for the development of modern hydrometallurgical processes.This report describes the successful use of available bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate, which is easily obtained from bis(2,2,2-trifluoroethyl) chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system as an extractant of uranium from uranium-containing acid solutions. For this functional phosphate containing a cyano group, one should expect a synergistic effect of the extraction properties of the phosphates themselves, as well as of the known extractants - contribute to an increase in its incombustibility.The purpose of this research is to develop the optimal conditions for the scaled synthesis of bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate, to accumulate its enlarged batch and to study the extraction properties in the production process of uranium extraction from uranium-containing sulfate and nitric acid solutions.The research results showed that bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate, easily obtained from the available bis(2,2,2-trifluoroethyl) chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system, exhibits pronounced extraction properties with respect to uranium. Thus, the use of this extractant in the production of the extraction of uranium from uranium-containing nitric acid or sulfuric acid solutions was 20.7% and 18.7%; the content of uranium in the extractant was 63.9 g/dm^3 and 49. 7 g/dm^3, respectively.Positive results were also obtained when studying the synergistic properties of the new extractant and the traditional - bis(2-ethylhexyl) phosphate. Using a mixture of these extractants (their weight ratio was 1:1.2) allows you to extract 57% of uranium from the uranium sulphate solution. This is 9% more than in a similar process using only bis(2-ethylhexyl) phosphate as an extractant. The use of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate as a new extractant makes it possible to extract up to 20.7% of uranium from technological nitrate or sulphate of uranium-containing solutions. With the combined use of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate and the known extractant bis(2-ethylhexyl) phosphate in this process, a synergistic effect is observed, which increases the efficiency of uranium extraction and improves the technological indicators of extraction.The extractantbis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate works more efficiently in nitric acid solutions than in sulphate.

Keywords: organic phosphates, polyfluoroalkyl groups, extractant, uranium.

Introduction. Organophosphate compounds are widely used in industrial hydrometallurgical processes as extractants and complexones of non-ferrous, noble, rare-earth metals and transuranic elements [1-7]. Among these compounds, organic phosphates occupy a special place, as they allow for the extraction processes with good selectivity and efficiency [1, 2, 4-8]. For example, tributyl phosphate in most countries, including Russia and Kazakhstan, is used in hydrometallurgy to determine and separate heavy metals (including uranium) [1, 4–10], as well as to separate uranium from nuclear fuel. 2 There are patent data on the use of bis(2-ethylhexyl) phosphate (the trivial name of the extractant is di(2-ethylhexyl) phosphoric acid) in the mixture as an extractant of uranium from industrial ores of Kazakhstan [9]. However, a significant drawback of known organic phosphates is their low extraction capacity, as well as rather good solubility in water and their hydrolysability in aqueous acidic solutions, which leads to both loss of the extractant and contamination of the extracted metal with organophosphorus compounds [2, 12]. Therefore, the search and development of new uranium effective extractants is an important task for the development of modern hydrometallurgical processes.

This report describes the successful use of available bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate, which is easily obtained from bis(2,2,2-trifluoroethyl) chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system [13] as an extractant of uranium from uranium-containing acid solutions. For this functional phosphate containing a cyano group, one should expect a synergistic effect of the extraction properties of the phosphates themselves, as well as of the known extractants - contribute to an increase in its incombustibility [14-19].

The purpose of this research is to develop the optimal conditions for the scaled synthesis of bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate, to accumulate its enlarged batch and to study the extraction properties in the production process of uranium extraction from uranium-containing sulfate and nitric acid solutions.

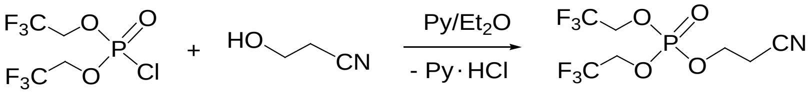
Methods and Materials. As extractants used bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate 1, specially synthesized under the conditions of scaled synthesis (see below), and commercial bis(2-ethylhexyl) phosphate 2 (initial content of the main component 70 %), «Khimprom» (Extragent 57, grade A), TC 2435-337-065763441-2004, density 0.945 g/cm^3.

As a source of raw materials used sulfuric acid solution of marketable desorbate from uranium production with a uranium concentration of 15.0 g/dm^3 (concentration of H_2SO_4 – 26.95 g/dm^3), as well as a nitric acid solution of commercial desorbate with a uranium concentration of 15.0 g/dm^3 (concentrationHNO_3 - 52.50 g/dm^3). As a diluent for extraction, commercial diesel fuel produced by JSC PPCP (Pavlodar Petrochemical Plant), GOST 10227-86, density 0.776 g/cm^3 was used.

The ^{1}H, ^{13}C, ^{19}F, ^{31}PNMR spectra were obtained on a Bruker DPX 400 spectrometer (400.13, 101.61, 376.50 and 161.98 MHz, respectively) in a $CDCl_3$ solution, the internal standard is HMDS (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), the external standard is 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Bruker IFS 25 spectrometer in a thin layer.

The concentration of the main component - uranium in aqueous solutions and the organic phase was determined by the bulk method - titration with ammonium vanadate [20].

*Enlarged synthesis of the extractant bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate 1.*Bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate was obtained in a yield of 80% by the interaction of bis(2,2,2 trifluoroethyl) chlorophosphate with 3-hydroxypropanonitrile in the pyridine (Py)/diethyl ether system (Scheme).



1

Scheme - The reaction for the production of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate

Previously, to obtain this extractant, 30 mmol of the starting chlorophosphate was used [13], in this report the method of scaled (3 times) synthesis of the preparation of the target compound **1** was developed.

The method of integrated synthesis of extractant bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate 1. In a three-necked flask equipped with a reflux condenser and a dropping funnel, a solution of 25.24 g (90 mmol) bis(2,2,2-trifluoroethyl) chlorophosphate in 180 ml of absolute diethyl ether. To the resulting solution was added dropwise with stirring a solution of 6.40 (90 mmol) of 3-hydroxypropanonitrile and 7.12 g (90 mmol) of pyridine in 20 ml of diethyl ether for 1 hour at room temperature, while the formation of a white precipitate of pyridinium hydrochloride was observed.The reaction mixture was stirred at room temperature for an additional 8 hours and left overnight. The pyridinium hydrochloride precipitate was filtered and washed with diethyl ether (3x30 ml). The solvent from the filtrate was distilled off under reduced pressure, the residue was distilled in vacuo. Received 21.5 g (80%) of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate 1, clear liquid, BP 129-130 °C (1 mmHg.), Lit. data 129 °C (1 mmHg) [13], d_4^{20} 1.5191. Found, %: C 26.34; H 2.27; F 36.49; N 4.39; P 10.11. $C_7H_8F_6NO_4P$. Calculated,%: C 26.68; H 2.56; F 36.18; N 4.45; P 9.83. The spectral characteristics are identical to the literary ones [13].

General method of uranium extraction from uranium-containing acid solutions. Tests were carried out under various conditions of the organization of the extraction process in the parameters as close as possible to the production ones. The process of extracting uranium was investigated from uranium sulfate solutions: extractant **1**, a mixture of extractants **1** + **2** and extractant **2**, from uranium nitrate solutions: extractant **1.**

At the first stage of work, an extraction mixture was prepared, which included diesel fuel (diluent) and extractants with a concentration in the extraction mixture of 7%. In the experiment using a mixture of extractants of bis(2,2,2-trifluoroethyl) (2-cyanoethyl) phosphate **1** and bis (2-ethylhexyl) phosphate **2**, a weight ratio of components 1.0:1.2 was taken. The diluent is used to increase the speed of phase separation, stabilize and prevent significant losses of the extractant, as well as to increase the yield and reduce the viscosity of the extractant.

At the second stage of the work, the prepared extraction mixture (diluent and extractant) was added to aqueous solutions of sulphate or nitric acid product strips. The extraction of uranium was carried out by a single contact of the organic and aqueous phases with constant stirring on a magnetic stirrer (the temperature in the production room is 24 °C, the contact time is 20 min). In the case of product sulfate desorbate, the ratio of organic and aqueous phases used (O:B) used in production was selected: 1.0:17.33; in the case of product nitrate desorbate, extraction was carried out at a ratio O:B of 1.0:20.8. Under laboratory conditions, separation funnels were used to separate the phases.

Extraction of uranium from sulfate or uranium-containing nitrate solutions of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate 1 was carried out under the above conditions and showed that extractant **1** is poorly soluble in diesel fuel. As a result, at the final stage of extraction, three phases were obtained with the following uranium content in them: the lower phase — extractant 1, the uranium content 49.7 g/dm^3 (in the case of sulfuric acid solutions) or 63.9 g/dm^3 (using nitric acid solutions); middle phase - extraction mother liquor, uranium content 12.2 g/dm^3 (in the case of sulphate solutions) or 11.9 g/dm^3 (using nitric acid solutions); the upper phase is diesel fuel, the uranium content is 0.0 g/dm^3 (i.e., there was no participation in the extraction process). Extraction of uranium with extractant **1** was: 20.7% (from a nitric acid solution) and 18.7% (from a sulfate solution).

Extraction of uranium from uranium sulfate solutions with a mixture of extractants - bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate 1 and bis(2-ethylhexyl)phosphate 2. As a result of extraction at the final stage, three phases were obtained with the following uranium content in them: the lower phase - extractant **1**, the uranium content 1.7 g/dm^3; middle phase - extraction liquor, uranium content 6.45 g/dm^3; the upper phase is diesel fuel and extractant **2**, the uranium content is 10.6 g/dm^3. Extraction of uranium with a mixture of extractants **1** and **2** was 57%.

Extraction of uranium from uranium sulfate solutions of bis(2-ethylhexyl) phosphate 2. As a result of extraction, at the final stage, two phases were obtained with the following uranium content in them: the lower phase - extraction mother liquor, the uranium content of 7.8 g/dm^3; the upper phase is diesel fuel and extractant **2**, the uranium content is 8.4 g/dm^3. The formation of the third phase in this case did not occur. Extraction of uranium extractant **2** was 48%.

To study the extraction properties of bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate in the process of extracting uranium from marketable desorbates of uranium-containing sulphate and nitrate solutions, an enlarged batch of this extractant from bis(2,2,2-trifluoroethyl) chlorophosphate was accumulated and 3-hydroxypropanonitrile under scaled synthesis conditions. For the synthesis, 3-hydroxypropanonitrile (Alfa Aesar) (purity 97%) was used; the initial bis(2,2,2-trifluoroethyl) chlorophosphate was obtained according to a known procedure [13].

Results and discussion. The research results showed that bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate **1**, easily obtained from the available bis(2,2,2-trifluoroethyl) chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system, exhibits pronounced extraction properties with respect to uranium. Thus, the use of this extractant in the production of the extraction of uranium from uranium-containing nitric acid or sulfuric acid solutions was 20.7% and 18.7%; the content of uranium in the extractant **1** was 63.9 g/dm^3 and 49. 7 g/dm^3, respectively (table, experiments 1 and 2).

Positive results were also obtained when studying the synergistic properties of the new extractant **1** and the traditional [9] - bis(2-ethylhexyl) phosphate **2**. Using a mixture of these extractants (their weight ratio was 1:1.2) allows you to extract 57% of uranium from the uranium sulphate solution. This is 9% more than in a similar process using only bis(2-ethylhexyl) phosphate **2** as an extractant (table, cf. experiments 3 and 4).

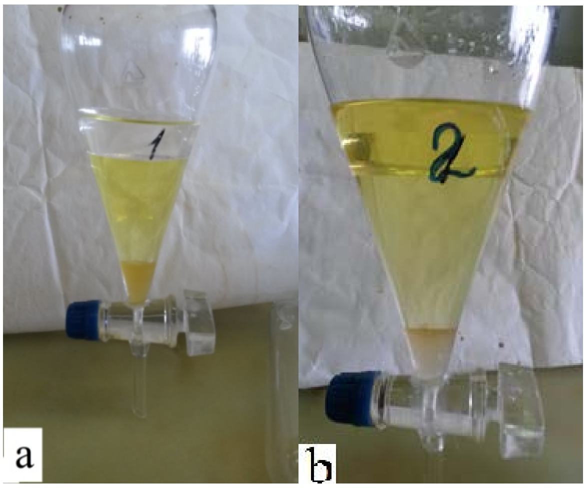


Figure 1 - Extraction of uranium using bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate (a), using the mixture of uranium bis (2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate and bis(2-ethylhexyl) phosphate (b)

Table - The results of determining the content of uranium in the extraction products from acid solutions of commodity desorbate[a]

№ experience	Extragents**1**and**2**	Extraction of uranium from solution, %
1	Extragent**1**	20.7 (63.9)[b]
2	Extragent**1**	18.7 (49.7)[b]
3	Extragent**1** + Extragent**2**[b]	57.0
4	Extragent**2**	48.0

[a]In experiment № 1, uranium-containing nitrate solution was used as a raw material; in experiments № 2-4 - uranium sulfate solutions. [b]In brackets - the uranium content in the extractant 1, g/dm^3. in the weight ratio of extractants**1** and **2** = 1:1.2.

Thus, the conditions for the enhanced synthesis of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate **1** based on the reaction of bis(2,2,2-trifluoroethyl)chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system have been worked out. an experimental batch of phosphate **1** and studied its extraction properties with respect to uranium.

Conclusion

1. The use of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate as a new extractant makes it possible to extract up to 20.7% of uranium from technological nitrate or sulphate of uranium-containing solutions.
2. With the combined use of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate and the known extractant bis(2-ethylhexyl) phosphate in this process, a synergistic effect is observed, which increases the efficiency of uranium extraction and improves the technological indicators of extraction.
3. The extractant bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate works more efficiently in nitric acid solutions than in sulphate.

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БИС(2,2,2-ТРИФТОРЭТИЛ)(2-ЦИАНОЭТИЛ)ФОСФАТ - УРАННЫҢ ЖАҢА ЭКСТРАГЕНТІ

Аннотация. Фосфор органикалық қосылыстар өнеркәсіптік гидрометаллургиялық процестерде түсті, асыл, сирек-жер металдарының және трансурандық элементтердің экстрагенттері және комплексондары ретінде кеңінен қолданылады. Бұл қосылыстардың ішінде органикалық фосфаттар ерекше орын алады, өйткені олар экстракция процестерін жақсы таңдамалықпен және тиімділікпен жүргізуге мүмкіндік береді. Алайда белгілі органикалық фосфаттардың маңызды кемшілігі олардың экстракциялық қабілеттілігінің төмендігі, сонымен қатар суда ерігіштігі және сулы қышқыл ерітінділеріндегі гидролизі болып табылады, бұл экстрагенттің жоғалуына да, алынған металдың фосфор органикалық қосылыстарымен ластануына әкеледі. Сондықтан уранның жаңа тиімді экстрагенттерін іздеу және оны әзірлеу қазіргі гидрометаллургиялық процестерді дамытудың өзекті міндеті болып табылады.Бұл жариялымда қолжетімді бис(2,2,2-трифтороэтил) (2-цианоэтил) фосфатты, бистен(2,2,2-трифторэтил) оңай алынатын хлор фосфатты және пиридин/диэтил эфир жүйесіндегі 3-гидроксипропанонитрилді құрамында уран бар қышқыл ерітінділерінен уран экстрагенті ретінде пайдалану туралы мәліметтер келтірілген. Құрамында тобы бар функционалды фосфат үшін фосфаттардың және олардың белгілі экстрагенттері - цианидтердің экстракциялық қасиеттерінің синергетикалық әсерін күту керек. Сонымен қатар, бұл экстрагентте полифторалкил топтарының болуы оның үйлесімсіздігінің артуына ықпал етуі керек.

Бұл зерттеудің мақсаты - бис (2,2,2-трифлороэтил) (2-цианоэтил) фосфаттың кеңейтілген синтезі үшін оңтайлы жағдайларды жасау, оның үлкейтілген партиясын шығару және уран сульфаты мен азот қышқылының ерітінділерінен уран алудың өндірістік процесінде экстракциялық қасиеттерді зерттеу. Зерттеу нәтижелері қол жетімді жариялымда қолжетімді бис(2,2,2-трифтороэтил) (2-цианоэтил) фосфатты, бистен(2,2,2-трифторэтил) оңай алынатын хлор фосфатты және пиридин/диэтил эфир жүйесіндегі 3-гидроксипропанонитрилді уранға қатысты айқын экстрационды қасиеттер көрсетеді (1а-сурет). Сонымен, бұл экстрагентті құрамында уран бар азот немесе сульфат ерітінділерінен уран алудың өндірістік процесінде қолдану 20,7% және 18,7% құрады; экстрагентте уран мөлшері сәйкесінше 63,9 г/дм^3 және 49,7 г/дм^3 құрады.. Дәстүрлі - бис (2-этилексил) фосфатын және жаңа экстрагенттің синергетикалық қасиеттерін зерттеу кезінде оң нәтижелер алынды. Бұл экстрагенттердің қоспасын қолдану (салмақ коэффициенті 1: 1,2) құрамында уран бар сульфат ерітіндісінен 57% уран алуға мүмкіндік береді. Бұл экстрагент ретінде тек бис (2-этилегексил) қолданған ұқсас процестен 9% артық.

Бис (2,2,2-трифлороэтил) (2-цианоэтил) фосфатын жаңа экстрагент ретінде пайдалану технологиялық азот қышқылы немесе құрамында уран бар сульфат ерітінділерінен 20,7% уран алуға мүмкіндік береді. Осы процессте бис (2,2,2-трифлороэтил) (2-цианоэтил) фосфаты және белгілі экстрагент бис (2-этилгексил) фосфатын қолданған кезде синергетикалық әсер байқалады, бұл уран алудың тиімділігін арттыруды қамтамасыз етеді және өндірудің технологиялық параметрлерін жақсартады. Бис (2,2,2-трифлороэтил) (2-цианоэтил) фосфат экстрагенті күкірт қышқылының ерітінділеріне қарағанда азот қышқылының ерітінділерінде тиімді жұмыс істейді.

Түйін сөздер: органикалық фосфаттар, полифторалкил топтары, экстрагент, уран

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БИС(2,2,2-ТРИФТОРЭТИЛ)(2-ЦИАНОЭТИЛ)ФОСФАТ - НОВЫЙ ЭКСТРАГЕНТ УРАНА

Аннотация. Фосфорорганические соединения широко применяются в промышленных гидрометаллургических процессах как экстрагенты и комплексоны цветных, благородных, редкоземельных металлов и трансурановых элементов. Среди этих соединений органические фосфаты занимают особое место, так как они позволяют проводить экстракционные процессы с хорошей избирательностью и эффективностью. Однако существенным недостатком известных органических фосфатов является их невысокая экстракционная способность, а также довольно хорошая растворимость в воде и их гидролизуемость в водных кислых растворах, что приводит как к потере экстрагента, так и к загрязнению экстрагируемого металла фосфорорганическими соединениями. Поэтому поиск и разработка новых эффективных экстрагентов урана является актуальной задачей развития современных гидрометаллургических процессов.В настоящем сообщении приводятся данные об успешном использовании доступного бис(2,2,2-трифторэтил)(2-цианоэтил)фосфата, легко получаемого из бис(2,2,2-трифторэтил)- хлорфосфата и 3-гидроксипропанонитрила в системе пиридин/диэтиловый эфир в качестве экстрагента урана из урансодержащих кислотных растворов. Для этого функционального фосфата, содержащего цианогруппу, следует ожидать синергизм действия экстракционных свойств самих фосфатов, а также известных экстрагентов – цианидов. Кроме того, наличие полифторалкильных групп в данномэкстрагенте должно способствовать повышению его негорючести.

Цель данного исследования - отработка оптимальных условий масштабированного синтеза бис(2,2,2-трифторэтил)(2-цианоэтил)фосфата, наработка его укрупненной партии и изучение экстракционных свойств в производственном процессе экстракции урана из урансодержащих сернокислых и азотнокислых растворов. Результаты исследования показали, что бис(2,2,2-трифторэтил)(2-цианоэтил)фосфат, легко получаемый из доступных бис(2,2,2-трифторэтил)хлорфосфата и 3-гидроксипропанонитрила в системе пиридин/диэтиловый эфир, проявляет выраженные экстракционные свойства по отношению к урану (рисунок 1а). Так, использование этого экстрагента в производственном процессе экстракции урана из урансодержащих азотнокислых или сернокислых растворов составило 20.7% и 18.7%; при этом содержание урана в экстрагенте было 63.9 г/дм^3 и 49.7 г/дм^3, соответственно. Положительные результаты были получены также при изучении синергетических свойств нового экстрагента и традиционного - бис(2-этилгексил)фосфата. Использование смеси этих экстрагентов (их весовое соотношение составляло 1:1.2) позволяет извлекать 57% урана из сернокислого урансодержащего раствора. Это на 9% больше, чем в аналогичном процессе с применением в качестве экстрагента только бис(2-этилгексил).

Применение бис(2,2,2-трифторэтил)(2-цианоэтил)фосфата в качестве нового экстрагента позволяет извлекать до 20.7% урана из технологических азотнокислых или сернокислых урансодержащих растворов. При комбинированном использовании в этом процессе бис(2,2,2-трифторэтил)(2-цианоэтил)фосфата и известного экстрагента - бис(2-этилгексил)фосфатанаблюдается синергетический эффект, обеспечивающий повышение эффективности извлечения урана и улучшающий технологические показатели экстракции. Экстрагент бис(2,2,2-трифторэтил)(2-цианоэтил)фосфат работает более эффективно в азотнокислых растворах, чем в сернокислых.

Ключевые слова: органические фосфаты, полифторалкильные группы, экстрагент, уран.

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NEW NANOSTRUCTURAL CATALYSTS FOR NEUTRALIZATION OF TOXIC GASES IN INDUSTRY

Abstract. One of the key environmental problems is the protection of the air basin in the cities and industrial zones of the Republic of Kazakhstan. The environmental situation is increasingly affecting the economic well-being of the state, and becoming the most significant factor in the development of the country. The catalytic methods for cleaning exhaust gases from harmful components are a great help in solving these problems. The main advantage of the catalysts is their autonomy, ease of use and accessibility to users. The main indicators of catalysts include such parameters as activity, productivity, resistance to poisons, price, etc. This article shows the presence of active in the complete oxidation reaction of alumina nanoclusters formed during sorption from aqueous solutions of chloroplatinic acid and provides the technological scheme for the production of industrial catalysts.

Keywords: Catalysts, oxidation, carrier, platinum, aluminum.

Introduction

Purification the atmosphere of very toxic exhaust gases from motor vehicles and gas emissions from industrial enterprises is one of the pressing problems of humankind, attracting the attention of the public and scientists of the leading countries of the world.

The level of air pollution of many industrial cities of Kazakhstan exceeds the existing regulatory limits due to emissions of motor vehicles, boiler houses and industrial plants.

Complete catalytic oxidation of organic substances contained in gases to carbon dioxide and water, sulphur dioxide and reduction of nitrogen oxides is one of the most effective ways to utilize and neutralize harmful emissions from industry and vehicles.

We have developed a technology on the basis of which the production of catalytic converters is organized [1,2].

Noble metal catalysts are the most commonly used in solving environmental problems of the sources of emissions of both motor vehicle and stationary pollutants. Typically, the carrier for such catalysts is alumina in pure form or with additives of cerium oxides, lanthanum, zirconium, etc. Alumina during the deposition of platinum from a solution of H_2PtCl_6 $6H_2O$ chloroplatinic acid forms a complex which upon further heating, is converted into nanosized active sites. The early existence of similar complexes with the carrier is shown in a number of works. So, in [3], 2 absorption peaks of H_2 were detected at 200 ^{o}C and 340°C by the TPR method on Pt/Al_2O_3 calcined at 500°C in air. The first peak belongs to the reduction of massive platinum oxides, higher temperature peak is at the most strongly bonded to the oxide surface of the carrier, difficult to reduce forms of platinum oxides [4,5]. In [6], a strong interaction was found with the five-coordinated unsaturated platinum carrier sites, which prevents further sintering of the metal. As shown in [7], the surface platinum atoms may be in two Pt^{o} and Pt^{δ} states. The latter is a low-ligand platinum cluster consisting of several platinum atoms with a degree of oxidation of +1 to +2 and exists due to the presence of electron-negative chlorine and oxygen atoms in its coordination sphere.

Experimental research

We have observed that the order of application of the active components is of great importance when introducing platinum-competing cobalt and manganese cations. Varying the order of application of the active components showed that the initial application of a noble metal, and then a mixture of manganese and cobalt was from their nitrates formed the most active catalyst (Fig.1 curve 1), the least active catalyst was formed in the reverse order of application (Fig.1 curve 3), and the intermediate catalyst was formed from a common solution of chloroplatinic acid and cobalt and manganese nitrates (Fig.1 curve 2). Quantitative data on propane conversion in the complete oxidation reaction are shown in Table 1.

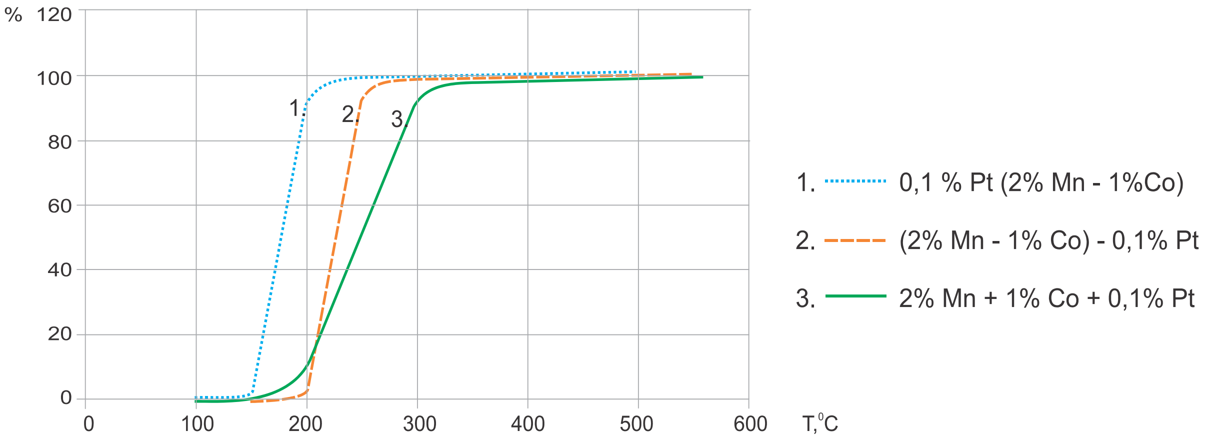

Figure 1 - Temperature dependences of propane conversion in air (1:35) on various catalysts

Table 1 - Effect of varying the order of application of the active components
on the activity of the catalysts in the propane air oxidation reaction (1:35)

T, °C	Propane conversion, %		
	0,1 % Pt (2% Mn – 1% Co)	(2% Mn – 1% Co) – 0,1% Pt	2% Mn +1% Co + 0,1% Pt
50	0	0	0
100	2,40	1,77	0,56
150	3,36	0,45	1,94
200	91,70	1,18	10,91
250	97,79	92,52	59,25
300	98,63	98,74	92,45
350	99,20	99,89	97,82
400	99,30	99,92	99,63
450	100	100	100
500	100	100	100

This indicates the presence of specific stabilization sites on the surface of alumina, as it was shown in [3–8]. They are common to both platinum complexes and other variable valence metals (Mn, Co).

Not only alumina but also chlorine ions in the composition of chloroplatinic acid play a very important role in the formation of nanoscale active sites. In our work [8] catalysts for oxidation of hydrocarbons with platinum-based air applied on oxide Al-Ce-carriers have been investigated. During the study using a transmission electron microscope, chlorine-containing phases were detected in samples of oxidized catalysts. The microdiffraction pattern represented by rows of reflections corresponds to the $AlCl_3 \cdot 6H_2O$ (JCPDS, 8-453) phase, and the ring set to the $Al(ClO_4)_3(ClO_3)_2$ (JCPDS, 28-4) phase. Chlorates and perchlorates are known to be formed by oxidation of chlorides, and the presence of Pt on the catalysts, apparently, contributes to this process. t should be noted that when heated, chlorates ($KClO_3$) and perchlorates ($KClO_4$) decompose in the temperature range 400-620°C with the release of oxygen and the formation of chlorides. In the presence of variable valence metal catalysts, the decomposition temperature can significantly decrease up to 200°C. Chlorates and perchlorates produced by the oxidation of ion chloride appear to contribute to oxygen involvement in oxidation processes due to high reactivity and low thermal stability. Subsequent oxygen evolution upon decomposition or reduction of the chlorate and perchlorate ions retains chlorine ions on the surface of the carrier [8].

One of the components of the active center in addition to platinum and aluminium is chlorine. Earlier, when purchasing platinum- chloroplatinic acid from “Aurat”, we encountered a mismatch in the composition of the compound H_2PtCl_6 $6H_2O$. A mismatch was found in the amount of chlorine in the chloroplatinic acid molecule, which led to insufficient solubility of the compound and a significant deterioration in the activity of the catalysts obtained from this compound. According to stoichiometry, the platinum content corresponding to the chloroplatinic acid compound cannot exceed 37.5-37.6% of the molecule, while the content of the base metal on the chloroplatinic acid market is up to 40%. All specifications indicate only the content of platinum and basic impurities, but no one indicates the chlorine content. An atomic ratio of platinum to chlorine of 4.62 was found in the sample of the purchased preparation according to X-ray fluorescence analysis, instead of 6.00 according to the formula (Table 2). Thus, the compound lacks about 1.4-1.5 chlorine atoms per platinum atom. It is known that in the process of evaporation of the chloroplatinic acid solution to the concentration required by specifications, not only the loss of excess water but also the decomposition with the loss of chlorine atoms in the chloroplatinic acid compound to $PtCl_4$ and even to $PtCl_3$ is possible. Since we cannot change the technology for the production of chloroplatinic acid, after additional correction with hydrochloric acid to stoichiometry or higher, the activity of the catalysts is completely restored.

Table 2 - Platinum to chlorine ratio in standart chloroplatinic acid according to GOST
and chloroplatinic acid from “Aurat” in batches for 2018 and 2019 years

Sample of chloroplatinic acid	Area of peak, conventional units	Chlorine content per 1 platinum atom
Standart (HCI)	4,15	6,0
Sample from 2019	3,18	4,60
Sample from 2018	3,14	4,54
Sample from 2018+1CI	3,36	4,86
Sample from 2018+2CI	4,08	5,90
Sample from 2018+6CI	4,94	10,59

Thus, in order to form the active sites, it is necessary to have an alumina with a developed surface and a chloroplatinic acid with stoichiometric or large amount of chlorine. The absence of one of the components results in a significant decrease in the activity of the catalysts. Base metal blocks coated with secondary carrier in the form of aluminium oxide is the preferred basis for catalysts, because they have a developed surface, have a large choice of design options, high thermal and mechanical stability, low gas-dynamic resistance.

Conclusion

During implementation of the project "Organization of Production of Metal Catalytic Converters of Toxic Components in Gas Emissions of Motor Transport and the Industrial Enterprises", carried out within grant financing of commercialization of the results of scientific and (or) scientific and technical activities and financed from the funds of the State Institution “Science Committee of the Ministry Education and Science of the Republic of Kazakhstan”, JSC “D.V.Sokolskiy Institute of Fuel, Catalysis and Electrochemistry” together with JSC "Science Foundation" organized a workshop for the production of domestic catalysts.

Organization of production and introduction of highly efficient domestic catalysts to reduce toxic gas emissions will ensure import substitution and significantly improve the condition of the air basin.

For this development, the Institute obtained a Patent of the Republic of Kazakhstan for Invention No. 11868 "Block catalyst for exhaust gases of vehicles" dated 02.22.2001 [9].

A certificate of origin of goods “ST-KZ” No. KZ 910500735 dated 05.12.2019 for catalytic converters was obtained as well.

The Institute successfully passed the Prequalification of potential suppliers and is included in the List of pre-qualified potential suppliers of the Sovereign Wealth Fund «Samruk-Kazyna» JSC., pre-qualification No. 826247615 dated 29.08.2019.

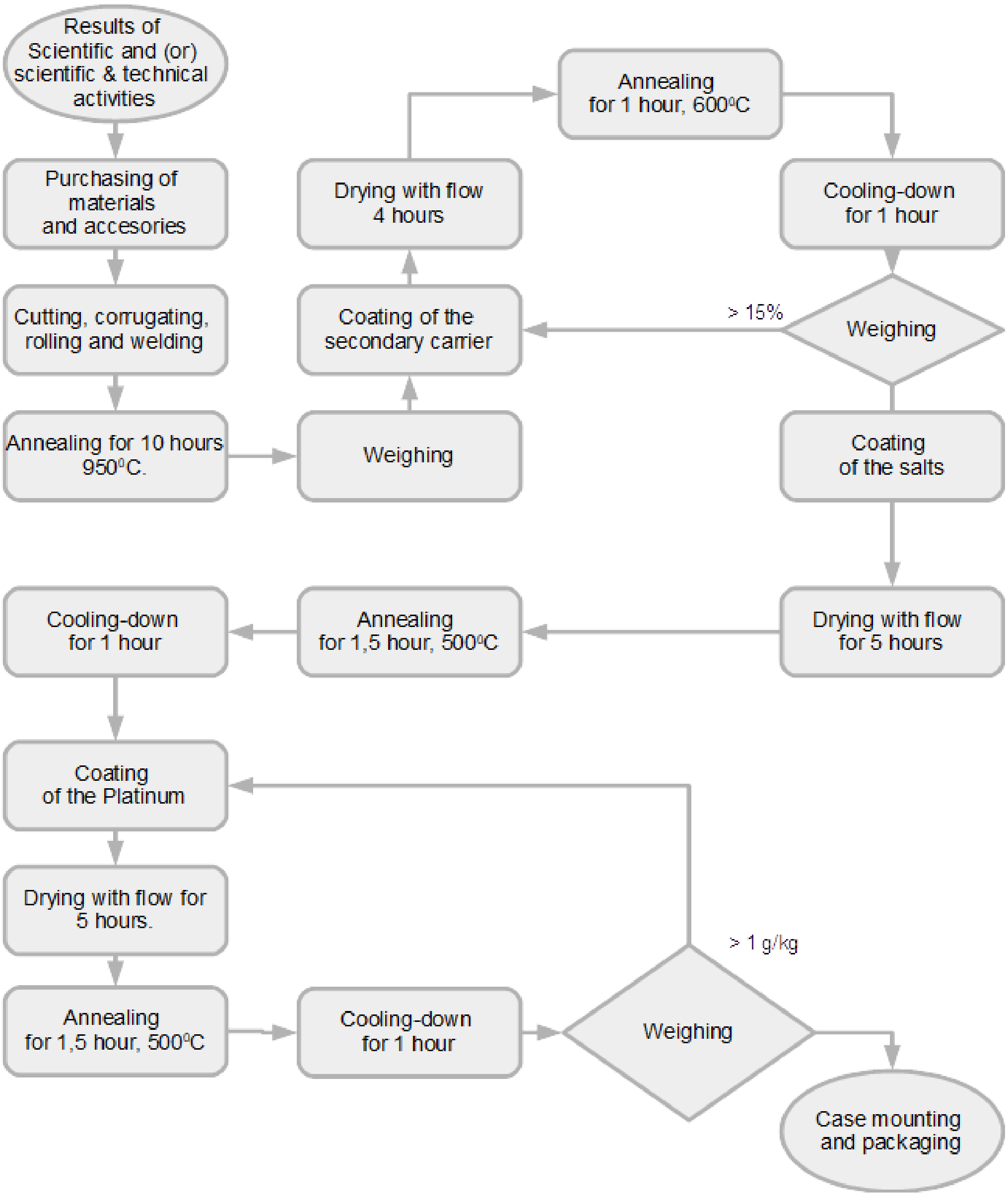

Figure 2 – Catalyst production flow diagram

Figure 3 - Workshop products installed at industrial facilities

At present, the catalysts of the Institute are installed on oil heating furnaces, motor vehicles, diesel and gas generators of subsoil users companies, banks and other enterprises of our Republic (Figure 3).

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ӨНЕРКӘСІПТІК УЛЫ ГАЗДАРДЫ БЕЙТАРАПТАНДЫРУҒА АРНАЛҒАН ЖАҢА НАНОҚҰРЫЛЫМДЫ КАТАЛИЗАТОРЛАР

Аннотация. Қоршаған ортаны өнеркәсіптік және көліктік ластанулардан қорғау күн сайын адамзат алдына бейтараптандыру катализаторларын синтездеу және тастанды газ шығарындыларын зиянды қоспалардан тазарту әдістерін жақсартуға талаптар қойып отыр. Қазақстанда 1 млн.-нан астам автокөлік ауаға күн сайын көміртегі, азот оксидтері, көмірсутектер және тағы да басқа 3 млн. тоннаға жуық зиянды заттарды тастайды. Қазақстанның көптеген өнеркәсіптік қалалары ауасының ластану деңгейі автокөлік, қазандық және өнеркәсіптік қондырғылар шығарындыларынан қолданыстағы нормативтік шектерден 6-10 есе артық. Қазақстан Республикасы экологиясының негізгі проблемаларының бірі қалалар мен өнеркәсіптік аймақтарының әуе бассейнін қорғау болып табылады. Мемлекеттің экономикалық әл-ауқаты деңгейіне экологиялық жағдай көп жағдайда әсер етеді және қазіргі таңда елдің дамуының неғұрлым маңызды факторына айналып отыр. Өнеркәсіптік кәсіпорындар мен автокөлік тастанды шығарындыларына қарсы күрестің бірқатар әдістері бар, олар: сорбциялық тазалау, озон көмегімен тазарту, түрлі электр сүзгілермен қатты бөлшектер мен аэрозольдардан тазарту, қышқыл газдарды сілті және тағы да басқа ерітінділерімен сіңіру болып табылады. Бұл мәселелерді шешу мақсатында тастанды газдарды зиянды компоненттерден тазартудың каталитиздік әдістері қолданылады. Катализаторлардың негізгі артықшылығы олардың дербестігі, қолдану қарапайымдылығы және пайдаланушылар үшін қол жетімділігі болып табылады. Бұл мақалада платинахлорсутекті қышқылдың (ПХСҚ) су ерітінділерінен сорбция кезінде пайда болатын алюминий оксидіндегі нанокластерлердің толық тотығу реакциясында белсенді болуы көрсетілген. Мұндай катализаторларды дайындау үшін бастапқы платинахлорсутекті қышқылында жеткілікті мөлшерде хлор иондарының болуы өте маңызды. Хлор иондарының өзі нақты катализ температурасында тасымалдағыштың бетінде өте тұрақты және алюминий оксидімен платина кластерінің құрамына кіреді. Хлор иондары тасымалдағыштың бетінде перхлораттар мен хлораттарды түзуге және осылайша шығынды газдардың толық тотығу процестері үшін қосымша оттегіні тартып алуға қабілетті. Біз отандық катализаторлар өндіретін цехта жүзеге асырылған өнеркәсіптік катализаторлар өндірісінің технологиялық сызбасын ұсындық. Біздің катализаторлар үшін бастапқы тасымалдағыш ретінде қолдануға Х15Ю5 және Х23Ю5 маркалы фехраль негізіндегі ыстыққа төзімді фольга таңдалды. Металл блоктарды дайындау үшін фольганы алдын ала гофрлайды және қажетті диаметрлі рулонға орайды, одан әрі майсыздандырудан және қыздырудан кейін блокқа бемит суспензиясынан және церий нитратының судағы ерітіндісінің екінші тасымалдағышы отырғызылады. Содан кейін ылғал сыйымдылығы бойынша сіңдіру әдісімен екінші тасымалдағышқа платинохлорды сутегі қышқылының сулы ерітіндісі (ПХСҚ) отырғызылады, әрі қарай кептіргеннен және түпкілікті қыздырғаннан кейін алынған блокты катализатор оралады және қоймаға немесе тапсырыс берушіге жіберіледі. Металл блоктар тапсырыс берушілердің сұранысын қанағаттандыруға, блоктың өлшемін де, каналдардың өлшемін де өзгертуге мүмкіндік береді, жоғары термиялық және механикалық тұрақтылыққа ие, төмен газдинамикалық кедергіге ие және блок массасының оның көлеміне оңтайлы арақатынасы бар. Импорт алмастыруды қамтамасыз ету және әуе бассейнінің жағдайын едәуір жақсарту мақсатында катализатор өндірісін ұйымдастыру және тиімділігі жоғары отандық катализаторларды өнеркәсіпке енгізу біз үшін маңызды жетістік болып табылады.

Түйін сөздер: катализаторлар, тотығу, тасымалдағыш, платина, алюминий

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НОВЫЕ НАНОСТРУКТУРНЫЕ КАТАЛИЗАТОРЫ ДЛЯ НЕЙТРАЛИЗАЦИИ ТОКСИЧНЫХ ГАЗОВ В ПРОМЫШЛЕННОСТИ

Аннотация: Охрана окружающей среды от промышленных и транспортных загрязнений ежедневно ставит перед человечеством требования к улучшению методов синтеза катализаторов нейтрализации и очистки газовых выбросов от вредных примесей. В Казахстане свыше 1 млн. автомобилей ежедневно выбрасывают около 3 млн. т вредных веществ, таких, как оксиды углерода, азота, углеводороды и др. Уровень загрязнения воздуха многих промышленных городов Казахстана более, чем в 6-10 раз выше существующих нормативных пределов из-за выбросов автотранспорта, котельных и промышленных установок. Одной из ключевых проблем экологии является защита воздушного бассейна в городах и промышленных зонах Республики Казахстан. На уровень экономического благополучия государства все в большей степени влияет экологическая ситуация и становится все более значимым фактором развития страны. Существует ряд методов борьбы с выбросами промышленных предприятий и автотранспорта, таких, как сорбционная очистка, очистка озоном, очистка различными электрофильтрами от твердых частиц и аэрозолей, поглощение кислых газов растворами щелочей и т.д. Большим подспорием для решения этих проблем являются каталитические методы очистки отходящих газов от вредных компонентов. Основным преимуществом катализаторов является их автономность, простота применения и доступность для пользователей. К основным показателям катализаторов относятся такие параметры как активность, производительность, устойчивость к ядам, цена и т.д. В данной статье показано наличие активных в реакции полного окисления нанокластеров на оксиде алюминия, образующихся при сорбции из водных растворов платинохлористоводородной кислоты (ПХВК). Отмечена большая важность для приготовления таких катализаторов наличие хлор ионов в достаточных количествах в исходной ПХВК. Сами хлор ионы чрезвычайно устойчивы на поверхности носителя при температурах реального катализа и входят в состав кластера платины с оксидом алюминия. Хлор ионы способны образовывать перхлораты и хлораты на поверхности носителя и вовлекать таким образом дополнительно кислород для процессов полного окисления отходящих газов. Нами представлена технологическая схема производства промышленных катализаторов, которая реализована в цехе по производству отечественных катализаторов.В качестве первичного носителя для наших катализаторов выбрана жаростойкая фольга на основе фехраля марки Х15Ю5 и Х23Ю5. Для изготовления металлических блоков фольгу предварительно гофрируют и сворачивают в рулон нужного диаметра, далее после обезжиривания и прокалки на блок наносится вторичный носитель из суспензии бемита и нитрата церия в воде. Затем на вторичный носитель методом пропитки по влагоемкости наносится водный раствор платинохлористоводородной кислоты (ПХВК), после сушки и окончательного прокаливания полученный блочный катализатор упаковывается и отправляется на склад или заказчику. Металлические блоки позволяют гибко реагировать на запросы заказчиков, менять размеры и как самого блока, так и размеры каналов, имеют высокую термическую и механическую устойчивость, обладают низким газодинамическим сопротивлением и оптимальным соотношением массы блока к его объему. Важным достижением для нас является организация производства и внедрение высокоэффективных отечественных катализаторов с целью обеспечения импортозамещения и значительного улучшения состояние воздушного бассейна.

Ключевые слова: катализаторы, окисление, носитель, платина, алюминий.

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МЕТИЛИРОВАНИЕ ТОЛУОЛА НА МОДИФИЦИРОВАННЫХ ЦЕОЛИТНЫХ КАТАЛИЗАТОРАХ

Реакция метилирования толуола может протекать в двух направлениях: 1 – алкилирование по метильной группе (в боковой цепи) с образованием этилбензола, 2 – алкилирование по атому углерода бензольного кольца с образованием изомерных ксилолов. Обе реакции привлекают внимание возможностью создания промышленного одностадийного экологически чистого, малоэнергоемкого процесса получения ценных мономеров из дешевого и доступного сырья [1-5]. Дегидрированием этилбензола получают стирол, используемый в производстве полистирола, бутадиен-стирольного каучука, пенополистирола и др. А изомерные ксилолы используются как растворители и в синтезе красителей. Самым ценным является п-изомер - п-ксилол применяется как сырьё для синтеза терефталевой кислоты, являющейся полупродуктом для получения полиэтилентерефталата, как самого чистого и благоприятного для здоровья людей материала для изготовления тары для пищевых продуктов и полиэфирной продукции.

В последние годы большой интерес вызывает возможность разработки новых стереоспецифических каталитических процессов получения пара-замещенных ароматических углеводородов на цеолитных катализаторах. Перспективными в этом аспекте являются высококремнезёмные цеолиты типа ZSM, обладающие высокими значениями силикатного модуля (отношение SiO:AlO может варьироваться от 15-20 до 200 и выше) и содержащие в своей структуре регулярную систему каналообразных микропор со средним диаметром менее 0,9 нм.

В процессе синтеза ксилолов из толуола образуется равновесная смесь изомеров: пара – 23 %, мета – 51 % и орто – 26 %. Для достижения высокой селективности по п-ксилолу нужны новые катализаторы на основе цеолитов с регулируемыми параметрами. Благодаря уникальной структуре алюмосиликатного каркаса цеолит ZSM-5 представляется интересным для селективного пара-алкилирования, т.к. внутри микропор замещение в о- и м- положение должно быть стерически затруднено. Огромную роль играют диффузионные ограничения, что благоприятно для образования п-ксилола, т.к. скорость проникновения п-изомера в пористую структуру на 3 порядка выше, чем у о- и м-изомеров. Вследствие этого изомерный состав продуктов метилирования толуола зависит от размеров цеолитных кристаллов – чем больше длина диффузионных путей, тем выше содержание линейного изомера п-ксилола. Показано, что цеолиты типа ZSM, обладают максимальной среди цеолитов электроотрицательностью (~ 4,2) и проявляют максимальную активность в алкилировании толуола в ароматическое кольцо, а именно пара-селективностью [6].

Одним из путей изменения каталитических и молекулярно-ситовых свойств цеолитов является направленное регулирование пор и модифицирование кислотных центров путем изменения количества кислотных центров и их природы [7-8]. Например, модифицирование цеолита ZSM-5 соединениями бора, фосфора, магния и кремния оказывает пара-ориентирующее влияние на его активность в реакциях алкилирования алкилароматических углеводородов [7-9].

В настоящей работе приводятся результаты исследований превращения толуола в процессе метилирования в присутствии модифицированных катализаторов на основе синтетического цеолита ZSM-5 с мольным отношением SiO_2/Al_2O_3 35, 80 и 135, которые модифицировали редкоземельными элементами (РЗЭ) – La, Ce и Sc. Реакцию проводили на проточной установке «Finetech 4000» с загрузкой 5,0 см^3 катализатора при температуре 250–500 °С. Анализ продуктов реакции осуществляли методом газожидкостной хроматографии на хроматографе Кристаллюкс 2000М.

Толуол превращается в ксилолы согласно реакции: $C_6H_5\text{-}CH_3 + CH_3OH \rightarrow C_6H_4\text{-}(CH_3)_2 + H_2O$

Исследовалось влияние величины кремнеземного модуля цеолита HZSM-5, соотношения толуол:метанол, природы модифицирующего металла и температуры в диапазоне 250-500 °С на конверсию толуола, выходы изомерных ксилолов и селективность по п-ксилолу.

С ростом кремнеземного модуля цеолит ZSM-5 от 35 до 135 активность катализаторов возрастает (таблица 1), на самом активном модуле цеолита – 135 наблюдаются максимальные значения конверсии толуола – 65 %, выхода п-ксилола – 38 % и селективность по п-ксилолу – 59 %. Т.е. чем выше модуль цеолита, тем выше его активность в синтезе п-ксилола.

Таблица 1 – Метилирование толуола на HZSM-5 катализаторе с разным модулем при0,86 час$^{-1}$, 300 °С, при соотношении толуол:метанол 1:3

Катализатор	Конверсия толуола, %	Выход, %			Селективность по п-ксилолу, %
		П-ксилол	М-ксилол	О-ксилол	
HZSM-5 (35)	56	32	22	4	57
HZSM-5 (80)	60	35	24	4	58
HZSM-5 (135)	65	38	25	3	59

Варьировался состав реакционной смеси – соотношение толуол:метанол от 2:1 до 1:4 (таблица 2). Конверсия толуола, выход п-ксилола и селективность по п-ксилолу увеличивается с ростом соотношения толуол:метанол от 1:1 до 1:3, а дальнейшее повышение содержания метанола до 1:4 снижает величины этих показателей. Минимальные значения конверсии толуола 65 %, выхода п-ксилола 38 % и селективности по п-ксилолу 59 % наблюдаются при соотношении толуол:метанол 2:1. Оптимальным соотношением толуол:метанол является 1:3.

Таблица 2 – Метилирование толуола на HZSM-5 (135) катализаторе при 0,86 час$^{-1}$, 300 °С с различным соотношением толуол:метанол

Соотношение толуол:метанол	Конверсия толуола, %	Выход, %			Селективность по п-ксилолу, %
		П-ксилол	М-ксилол	О-ксилол	
1:1	58	31	22	5	54
1:2	64	38	23	3	58
1:3	65	38	25	3	59
1:4	63	37	24	2	58
2:1	45	22	19	4	49

Модифицирование цеолита ZSM-5 металлами РЗЭ -La,Ce и Sc увеличивает конверсию толуола, выход основного продукта и селективность по п-ксилолу по сравнению с исходным цеолитом (таблица 3). Выявлен наиболее активный редкоземельный металл – La, на котором наблюдались максимальная конверсия толуола до 85 %, выход п-ксилола до 59 % и селективность по п-ксилолу до 69 %. По активности в пара-метилировании толуола металлы можно расположить в следующий ряд: La > Ce > Sc. Влияние La, Ce и Sc, по сравнению с исходной формой связано, в основном, с двумя факторами: вследствие химического модифицирования происходит сужение каналов цеолита, что приводит к увеличению диффузии молекул п-ксилола и возрастанию стерических препятствий для диффузии о- и м-ксилолов, а также уменьшению доли сильных протонных центров на поверхности цеолита.

Таблица 3 – Метилирование толуола на цеолитных катализаторах, модифицированных различными РЗЭ, при 0,86 час$^{-1}$, 300 ^{o}C, соотношение толуол:метанол 1:3

Катализатор	Конверсия толуола, %	Выход, %			Селективность по п-ксилолу, %
		П-ксилол	М-ксилол	О-ксилол	
HZSM-5	65	38	25	3	59
La-ZSM-5	85	59	24	2	69
Ce-ZSM-5	80	52	24	4	65
Sc-ZSM-5	77	48	26	3	63

Методом порометрии показано, что модифицирование HZSM-5 уменьшает размер пор: если на чистом цеолите размер пор (каналов) составлял 0,6 нм, то при введении La – 0,4 нм, Ce и Sc – 0,5 нм. Этим обусловлено повышение пара-селективности по п-ксилолу модифицированных цеолитов. Кроме того, модифицирование цеолита изменяет его поверхностную кислотность. Результаты термопрограммированной десорбции аммиака показали, что редкоземельные элементы снижают кислотность сильных кислотных центров, а именно уменьшают концентрацию кислотных центров Бренстеда на 35 % и увеличивают количество центров Льюиса на 28 %, что также повышает селективность по п-ксилолу.

Исследования проводили в температурном интервале 250-500 ^{o}C (таблица 4). Выбор данного температурного интервала основан на анализе литературных и собственных экспериментальных данных [4-5]. Селективность метилирования толуола в п-ксилол увеличивается с повышением температуры, что косвенно указывает на необходимость преодоления диффузионных затруднений. Оптимальной температурой выбраны значения 300-400 ^{o}C.

Таблица 4 – Метилирование толуола на La-ZSM-5 катализаторе при 0,86 час$^{-1}$, соотношение толуол: метанол 1:3 при различных температурах

Темпера-тура, ^{o}C	Конверсия толуола, %	Выход, %			Селективность по п-ксилолу, %
		П-ксилол	М-ксилол	О-ксилол	
250	65	40	22	3	61
300	85	59	24	2	69
350	86	60	23	3	70
400	87	60	24	2	69
500	89	55	28	6	62

Методом рентгено-фазового анализа показано, что модифицирование РЗЭ не изменяет кристаллическую структуру цеолита ZSM-5 (рисунок 1).

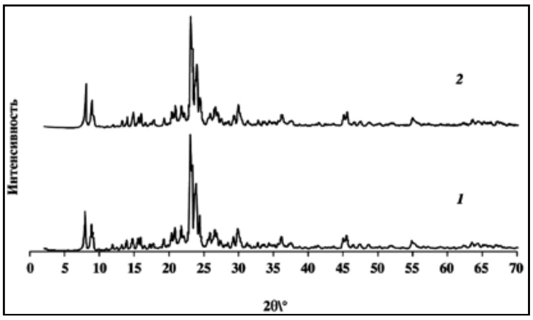

Рисунок 1 – Дифрактограммы HZSM-5 до (1) и после модифицирования La(2)

Таким образом, высокий кремнеземный модуль ZSM-5 и оптимальная температура обеспечивает увеличение пара-селективности. Из использованных модификаторов РЗЭ лантан оказывает наибольшее пара-ориентирующее влияние на активность ZSM-5 в реакции метилирования толуола и показало наилучшие результаты: максимальная конверсия толуола до 85 %, выход п-ксилола до 59 % и селективность по п-ксилолу до 69 %.

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TOLUENE METHYLATION ON THE MODIFIED ZEOLITE CATALYSTS

Abstract. The toluene methylation reaction can proceed in two directions: 1 – alkylation on the methyl group (in the side chain) with the formation of ethylbenzene, 2 – alkylation on the carbon atom of the benzene ring with the formation of isomeric xylenes. Both reactions attracted the attention of researchers by the possibility of creating of industrial one-stage environmentally friendly, low-energy process for producing valuable monomers from cheaper and more affordable raw materials - styrene and p-xylene, used for the synthesis of polystyrenes and polyethylene terephthalate.

During the synthesis of xylenes from toluene, an equilibrium mixture of isomers is formed: para – 23 %, meta – 51 % and ortho – 26 %. To achieve high selectivity for p-xylene, new catalysts based on zeolites with adjustable parameters are needed. Due to the unique structure of the aluminosilicate framework, ZSM-5 zeolite is of great interest for selective para-alkylation, since inside micropores substitution in the o- and m-position should be sterically difficult. A huge role is played by diffusion restrictions, which is favorable for the formation of p-xylene, because the penetration rate of the p-isomer into the porous structure is 3 orders of magnitude higher than that of the o- and m-isomers. As a result of this, the isomeric composition of toluene methylation products depends on the size of zeolite crystals – the longer the diffusion paths, the higher the content of the linear p-xylene isomer. In addition, zeolites of the ZSM type have the highest electronegativity among the zeolites (~ 4.2) and exhibit maximum activity in the alkylation of toluene into the aromatic ring, namely, para-selectivity. One of the ways to change the catalytic and molecular sieve properties of zeolites is directed regulation of pores and modification of acid centers by changing the number of acid centers and their nature.

The paper presents the results of studies of the conversion of toluene during methylation in the presence of modified catalysts based on synthetic zeolite ZSM-5 with different modules SiO_2/Al_2O_3 35, 80, and 135 which were modified with rare-earth elements (REE) – La, Ce, and Sc. The process was carried out under flowing conditions at the installation "Finetech 4000". It has been studied the following parameters of the process: the effect of the silica modulus of zeolite HZSM-5, the ratio of toluene : methanol, the nature of the modifying metal and the temperature in the range of 250-500°C on the conversion of toluene, the yields of isomeric xylenes and selectivity for p-xylene. It was found that, with the growth of the silica module, the zeolite ZSM-5 from 35 to 135 catalyst activity increases. On the most active zeolite module – 135, the maximum values of toluene conversion are observed 65 %, p-xylene yield 38 % and selectivity 59 %. That is, the higher the zeolite modulus, the higher its activity in the synthesis of p-xylene. The optimal composition of the reaction mixture was chosen - the toluene:methanol ratio of 1:3, at which the maximum values of toluene conversion were obtained 65 %, p-xylene yield 38 %, and selectivity for p-xylene 59 %. The selectivity of methylation of toluene to p-xylene increases in the temperature range of 250-500 °C, the maximum values of toluene conversion, yield of p-xylene and selectivity for p-xylene are observed at optimal temperatures of 300-400 °C.

Modification of ZSM-5 zeolite with REE (rare earth elements) – La, Ce and Sc increases toluene conversion, yield of the main product and selectivity for p-xylene compared to the initial zeolite. It was found the most active rare-earth metal – La, on which the maximum conversion of toluene reached to 85 %, the yield of p-xylene – 59 %, and the selectivity for p-xylene to 69 %. By activity in para-methylation, metals can be arranged in the following row: La > Ce > Sc. The effect of La, Ce, and Sc, compared with the initial form, is mainly associated with two factors: due to chemical modification, the zeolite channels are narrowed, which leads to an increase of diffusion of p-xylene molecules and an increase in steric hindrances for the diffusion of o- and m-xylenes, as well as a decrease in the proportion of strong proton centers on the zeolite surface. Using porosimetry, it was shown that the modification of HZSM-5 reduces pore size: while on pure zeolite, the pore (channel) size was 0.6 nm, then with the introduction of La - 0.4 nm, Ce and Sc – 0.5 nm. This caused the increase in para-selectivity for p-xylene of modified zeolites. In addition, the modification of zeolite changes its surface acidity. The results of thermoprogrammed ammonia desorption showed that rare-earth elements reduce the acidity of strong acid centers, namely, they reduce the

concentration of Brønsted acid centers to 35 % and increase the number of Lewis centers to 28 %, which also increases the selectivity for p-xylene. By X-ray phase analysis, it was shown that the modification does not change the crystal structure of ZSM-5 zeolite. Thus, the high silica module ZSM-5 and the optimum temperature provide an increase in para-selectivity. Of the REE modifiers used, lanthanum exerted the largest para-orienting effect on the activity of ZSM-5 in the toluene methylation reaction and showed the best results: maximum toluene conversion up to 85 %, p-xylene yield up to 59 % and p-xylene selectivity up to 69 %.

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ПОПОВА НИНА МИХАЙЛОВНА

(2.06.1930-1.11.2019)

В 2019 году на 90 году ушла из жизни доктор химических наук, профессор лауреат госпремии РК Н.М.Попова, чья научная деятель-ность в течение 50 лет была связана с Институтом органического катализа и электрохимии им. Д.В.Сокольского.

Попова Нина Михайловна родилась 2 июня 1930 года в г. Таш-кенте. После окончания в 1953 г. химического факультета КазГУ им. С.М.Кирова, затем аспирантуры АН КазССР (1953-1956 гг.) работала в Институте химических наук АН КазССР младшим, затем старшим научным сотрудником (1961 г.). В 1961-1962 г.г. по заданию МинВуза КазССР ею была организована лаборатория по катализу в Чим-кентском технологическом институте, которой она руководила. С 1969 по 1996 г.г. Н.М. Попова являлась руководителем лаборатории окисления в Институте органического катализа и электрохимии АН КазССР, затем работала главным научным сотрудником.

Кандидатскую диссертацию защитила в 1958 году, докторскую – в 1971 г., в 1974 г. утверждена в ученом звании профессора. В 1966 году окончила Алма-Атинский университет патентоведения и изобретательства.

Н.М.Попова – известный ученый в области катализа.

Основное направление исследований Н.М.Поповой – разработка низкопроцентных металлических и оксидных катализаторов на носителях для процессов гидрогенизации (жиров, нитросоединений), глубокого и селективного окисления CO, органических соединений, восстановления оксидов азота, комплексной очистки газов, окислительной дегидрогенизации и окисления алканов и выяснения механизма адсорбции и взаимодействия реагирующих компонентов. Н.М. Поповой развиты физико-химические основы нанесения Ni-катализаторов гидрогенизации жиров в растворителях, палладиевых и многокомпонентных оксидных катализаторов для окислительной и комплексной очистки газовых выбросов промышленности и автотранспорта от токсичных компонентов (CO, NO, органические соединения), а также конструирование оксидных катализаторов регулярного строения из перовскитов и гетерополисоединений Mo и W 12 ряда для глубокого селективного окисления метана в целевые продукты (формальдегид, синтез-газ) и окислительной дегидрогенизации алканов в олефины, H_2, формальдегид.

Н.М.Попова – автор 50 изобретений и патентов на катализаторы, способы их получения для различных процессов, методы их регенерации и извлечения благородных металлов из отработанных катализаторов. Технология катализаторов очистки газов освоена на Редкинском опытном заводе (действуют ТУ на катализаторы ШПАК-0,5, П-4, П-5), СКТБ катализаторов (Новосибирск, ШПАК-0,2, П-17), опытно-экспериментальной базе АН РК (П-3, О-5, М-03, ШПАК-0,2), на опытном производстве ИНИХТИМ (О-5, г.Ташкент), изготовлены десятки тонн катализаторов. Катализаторы используются в 40 установках очистки газов различных производств бывшего Союза, были внедрены и в Казахстане (НПО Мерей). За разработку и внедрение катализаторов защиты окружающей среды, монографию «Каталитическая очистка газов» (1970) Н.М.Попова в числе других ученых ИОКЭ удостоена в 1974 году Государственной премии Каз.ССР. Применение комплекса новейших методов исследования катализаторов и процессов, в том числе разработанного в лаборатории метода температурно-программированной десорбции, позволило выявить новые закономерности адсорбции реагирующих в окислительно-восстановительных реакциях веществ (CO, O_2, H_2, SO_2, NO, NH_3) и механизма реакции окисления СО, углеводородов, восстановления окислов азота и разработать теоретические основы действия нанесенных металлических и многокомпонентных оксидных катализаторов в указанных процессах.

Под руководством Н.М.Поповой защищены 2 докторские и 27 кандидатских диссертаций. По результатам исследований ею опубликовано более 500 работ, в том числе 6 монографий, 2 методических руководства, 4 брошюры, ряд обзорных работ в зарубежных изданиях. Она принимала участие и выступала на многих Международных, Всесоюзных и Республиканских научных конференциях по катализу. Н.М. Попова выполняла большую научно-организационную работу в Академии наук РК, являясь руководителем химико-технологической секции Научного совета «Охрана биосферы» при Президиуме АН КазССР, членом РИСО химико-технологического отделения АН РК, зам. Председателя секции ГКНТ Совмина СССР «Каталитические способы защиты атмосферы от загрязнений», заместителем координатора планов совместных работ многостороннего сотрудничества АН Соцстран и координационного центра по катализаторам СЭВ «Экологический катализ», экспертом Научного Совета «Катализ и его промышленное использование».

Результаты работ Н.М.Поповой получили высокую оценку Правительством Казахстана, руководством Академии наук Казахстана и СССР. Она награждена орденом «Знак Почета» (1976 г.), медалями «За доблестный труд», «Ветеран труда». В 1974 году ей присуждена Госпремия КазССР. За разработку катализаторов очистки газов (1975, 1982 г.г.) она награждена бронзовой и серебряной медалями ВДНХ СССР и КазССР.

Н.М. Поповой опубликовано свыше 550 научных работ. По результатам многолетних научно-методических исследований ею опубликована монография «Катализаторы селективного окисления и разложения метана и других алканов» (Н.М.Попова, К.Д.Досумов). Алматы, 2007г., которая привлекла внимание специалистов. На этот труд опубликовано несколько рецензий в России и дальнем зарубежье.

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