ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel, catalysis
and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

2 (440)

MARCH – APRIL 2020

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

Clarivate
Analytics

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.

«ҚР ҰҒА Хабарлары. Химия және технология сериясы».
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.).
Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген **№1089-Ж** мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28; 219, 220 бөл.; тел.: 272-13-19; 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Редакцияның мекенжайы: 050100, Алматы қ., Қонаев к-сі, 142, «Д. В. Сокольский атындағы отын, катализ және электрохимия институты» АҚ, каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Типографияның мекенжайы: «NurNaz GRACE», Алматы қ., Рысқұлов көш., 103.

«Известия НАН РК. Серия химии и технологии».
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы).
Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан **№10893-Ж,** выданное 30.04.2010 г.

Периодичность: 6 раз в год.
Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28; ком. 219, 220; тел. 272-13-19; 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142, АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Адрес типографии: «NurNaz GRACE», г. Алматы, ул. Рыскулова, 103.

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)
Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty).
The certificate of registration of a periodic printed publication in the Committee of Information and Archives of the Ministry of Culture and Information of the Republic of Kazakhstan N 10893-Ж, issued 30.04.2010.

Periodicity: 6 times a year.
Circulation: 300 copies.

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19; 272-13-18,
http://chemistry-technology.kz/index.php/en/arhiv

Editorial address: JSC «D.V. Sokolsky institute of fuel, catalysis and electrochemistry», 142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22, e-mail: orgcat@nursat.kz

Address of printing house: «NurNaz GRACE», 103, Ryskulov str, Almaty.

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.17**
Volume 2, Number 440 (2020), 6 – 13

UDC 661.183 (088.8)

A.Kh. Zhakina[1], O.V. Arnt[1], Ye.P. Vassilets[1], T.S. Zhivotova[1],
Z.M. Muldahmetov[1], A.M. Gazaliev[1], S.A. Semenova[2]

[1]Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan;
[2] Federal Research Center of Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences,
Kemerovo, Russia.
E-mail: alzhakina@mail.ru, oxana230590@mail.ru, vassilets88@mail.ru,
zhts2004@mail.ru, semlight@mail.ru

SYNTHESIS AND PROPERTIES OF A COMPOSITE MATERIAL BASED ON COAL MINING WASTE

Abstract. The article presents the results of a study of the synthesis of composite materials based on coal waste combined with coal and polymer raw materials, using ultrasonic chemistry methods and determining the possibility of their use as an active mineral additive for replacing part of cement in fine-grained concrete. By varying the composition of the matrix and the filler, a composite material is obtained whose properties are quantitatively and qualitatively different from the properties of each of its components. As a filler in the composition of the composite material, burned rock is used - the product of oxidative self-firing of waste rock, extracted together with coal to the surface. Burned rocks contain an organic part (unburned carbonaceous impurities) and a mineral part (calcined clay-sandy part). Features of the material composition of burned rocks, coal industry waste allows us to consider them as secondary mineral raw materials. The binder in the composite material used is thiourea-formaldehyde resin. The resin was obtained by the standard method of polycondensation of thiourea with formaldehyde at a molar ratio of thiocarbamide:formaldehyde = 1:2. The choice of thiourea-formaldehyde resin is due to the availability, water solubility and the presence of a sufficient number of proton acceptor centers capable of complexation with a modifier. The modifier for composite materials used a coal waste product related to promising natural polymers in nanotechnology, sodium humate, extracted by alkaline extraction from oxidized coal from the Shubarkol deposit. Sodium humate refers to polyfunctional polymers with a unique combination of hydrophobic and hydrophilic sites, a variety of oxygen-containing functional groups, aromatic, heterocyclic and other groups. All this suggests a high ability of sodium humate to intermacromolecular interactions with both the burned rock and thiourea-formaldehyde resin. Composite material based on burned rock, sodium humate with thiourea-formaldehyde resin was synthesized by impregnation using ultrasonic treatment. The decisive role of ultrasonic activation is shown and the effectiveness of its application to the process of producing composites is noted. The modern physicochemical and physicomechanical methods have characterized the composition and structure of the obtained composite materials. The mineralogical composition of composite materials was studied using x-ray phase analysis, and surface morphology based on microscopic analysis using a scanning electron microscope. Filling the composite material with burnt rock provides higher physical and mechanical properties. The strength of burnt-filled composites is higher than that of samples of a similar composition without burnt rock. The resulting composite can be used as a building material.

Key words: composite material, filler, binder, burned rock, thiourea-formaldehyde resin.

Introduction

In the industrial zone of the Karaganda region everywhere you can see a lot of stacked dumps and heaps of different shapes and sizes. Storage dumps are products of oxidative self-firing of waste rock, which are extracted together with coal to the surface. Annually, mine heaps occupying large areas of land increase by hundreds of thousands of cubic meters. Like coals, they should be attributed to promising minerals that can be used as raw materials for processing into various products [1-3]. The disposal of such wastes and the development of methods for obtaining important products on their basis are very relevant.

Due to the intensive development of the construction industry in the country, there is a shortage of natural mineral raw materials used for the needs of the construction complex. The use of coal mining waste in the production of building materials allows not only solving environmental problems, but also increasing the raw material base of the construction industry.

Burned rocks of mine heaps (BR) can be attributed to sources of natural mineral raw materials of technogenic origin. They have found the most diverse application in various industries, and, first of all, in the construction industry [2, 4-8]. The importance of burned rocks as raw materials for processing into various products for construction purposes is confirmed by significant foreign experience [5-7].

Among the promising areas is the development of polymer concrete technology. As you know, polymer concrete is a highly filled composition based on synthetic polymer binders, fillers and fillers. The degree of filling can reach 90-95%. With a relatively low consumption of polymer, they have high strength and durability. A review of information in the field of developing technology for producing polymer concrete, theoretical and experimental studies of the laws of their structural formation, physicochemical properties, shows their higher strength and chemical resistance to traditional concrete [8-12]. Most widely used for the manufacture of polymer concrete are available epoxy, polyurethane, furan, polyester, and phenolic resins. The issues of developing a composition based on burned rock with thiocarbamide resins remain poorly understood.

The aim of this work is to synthesize a composition for polymer concrete based on burnt rocks of mine heaps with thiocarbamide resins and to determine the possibility of their use as an active mineral additive in fine-grained concrete.

Experimental part

Materials

In preparing the composition, the thiourea formaldehyde resin (TUFR) was used as the cheapest and most technologically advanced synthetic binder. The choice of thiourea-formaldehyde resin is due to its availability and water solubility. Thiourea with a melting point of 180-182°C and a 37% aqueous formaldehyde solution are the feedstock for the synthesis of TUFR. TUFR was obtained by the standard method of polycondensation of thiourea with formaldehyde at a molar ratio of thiourea:formaldehyde = 1:2. Hardener used phosphoric acid (H_3PO_4). The resin yield was 92%. The composition and structure are proved by the data of IR-spectroscopy and conductometry.

The filler in the composition of the composite materials used burned rock (BR) - a product of oxidative self-firing of waste rock, extracted together with coal to the surface.

The modifier is sodium humate (HNa), isolated by alkaline extraction from oxidized coal from the Shubarkol deposit. Characteristics of HNa: ∑COOH+OH – 4,5 mEq/g, ∑COOH – 3,0-3,5 mEq/g, A - 13-15%, W^a - 10-12%, nitrogen content - less than 1%.

Synthesis of composite material

Composite material of the composition BR+HNa+TUFR (3:1:2 and 2:1:1) was synthesized as follows. The objects of the study were obtained by the traditional method of impregnating the filler (BR) with a solution of modifier (HNa) of a given concentration under the influence of ultrasonic treatment for 10 minutes (ultrasound frequency 22 kHz). Then we leave the mixture for impregnation for 24 hours. After impregnation, the composite was dried in a stream of air at 80°C for 4 hours. The resulting composite material of the composition BR+HNa (3:1 and 2:1) is then impregnated with a hot solution of TUFR at a ratio of BR+HNa+TUFR equal to 3:1:2 and 2:1:1.

Methods

Sample preparation of the burnt rock was carried out by the sieve method using an electrodynamic vibrostand PE-6700 (Russia, St. Petersburg). The vibrostand is an electronic-mechanical device with indexing the time interval until the end of work, and allows the sieving of bulk materials on laboratory sieves.

An ultrasound device IL-100-6/2 with a maximum power of 1200 W and a cylindrical waveguide was used as a source of ultrasound. The unit is equipped with an ultrasonic generator IL-10 with a magnetostrictive transducer with an operating frequency of 22 kHz.

To determine the mineralogical composition of the composite material, X-ray phase analysis (XRD) was used. The phase composition of the composition was studied on a DRON-2.0 diffractometer using Co (Kα) radiation $\lambda = 1,7902$ Å in the range 10°-90° (2θ), with a counter rotation speed of 2 deg/min, I = 10 mA, U = 30 kV.

To study the surface morphology of the synthesized composite, a microscopic analysis was performed using a TESCAN MIRA-3 scanning electron microscope.

The nominal viscosity of the starting resin was determined using a VZ-246 viscometer with a nozzle with a diameter of 4 mm.

Bulk density was determined according to GOST 19440-94, dry residue, mass fraction of free formaldehyde was determined according to GOST 14231-88

Results and discussion.

Burned rocks, depending on their composition and degree of heat treatment, can be used in the construction industry as one of the components in the production of: concrete, concrete products, thinning additives in the manufacture of bricks, filler composite materials, etc. The work used burned rocks from the dumps of the mine them. Gorbachev of the Karaganda region, representing brick-red comminuted stones. The initial BR were crushed in a jaw crusher, where the particle size was reduced to 5 mm. Eliminated and washed with plenty of water to get rid of carbonaceous and other inorganic impurities, then they were screened. The burned rocks used have the following chemical composition: silicon (60%), aluminum (25%), iron (4-5%), potassium, calcium, magnesium up to 2%, sodium, titanium, phosphorus up to 1%. The composition of burned rocks also includes valuable natural cement - the result of calcination of limestone and clay in the process of burning coal. In the course of the study, 0,1 mm fractions were used.

In order to increase the technical parameters and reduce the porosity of the burned rock, it was modified with sodium humate, obtained on the basis of oxidized coals of the Shubarkol deposit. The effectiveness of using sodium humate as chemical and structural modifiers for the filler is due to the peculiarities of its molecular structure, multifunctionality, the ability to various kinds of chemical reactions, as well as to donor-acceptor and hydrophobic interactions. The method is based on the immobilization of humate in the porous structure of a burnt rock using ultrasonic dispersion. Ultrasonic treatment allows you to achieve a uniform distribution of sodium humate throughout the volume of the rock. The results of silicate analysis of burning rock impregnation with a solution of sodium humate of a given concentration under the influence of ultrasonic treatment for 10 minutes showed that ultrasound contributes to a change in the content of silicon and aluminum oxides in the composites. So, under the influence of US in composites, the content of silicon oxides significantly decreases (57%), and the content of aluminum oxides increases (28%), which significantly reduces the silicate module in comparison with the module of the original burned rock. Upon receipt of the BR+HNa composite, the removal of iron, titanium, phosphorus, and calcium oxides into the filtrate is observed. Significantly increases the content of metabolic sodium. At the same time, composites are enriched with calcium and magnesium ions, iron and potassium ions go to the filtrate. The optimal ratio of the starting components is a 1:1 ratio and the optimal ultrasonic processing time is 10 minutes.

The main disadvantage of composite material (BR+HNa) when using it is poor chemical resistance during operation in real conditions, when the material is influenced by numerous factors: temperature difference, aggressive environment, mechanical stress, and more. One way to increase the life cycle of composites is to impregnate the surface of the material with resins. As a resin in the matrix of the composite material used TUFR (table 1).

Table 1 - the Effect of various factors on the yield of the composites

Composite	Ratio (L:S:S)	US, min	Yield, %
BR+HNa+TUFR	2:1:1	0	81,3
		10	84,0
	3:1:2	0	82,2
		10	81,3

Among the composites BR+HNa+TUFR (3:1:2 and 2:1:1), the most promising is the composite of BR+HNa+TUFR (2:1:1).

The X-ray phase composition of the composite material, BR+HNa+TUFR (2:1:1), was studied on a DRON-2.0 diffractometer using Co(Kα) radiation. Figure 1 shows X-ray diffraction patterns for a change in the composition of the composite.

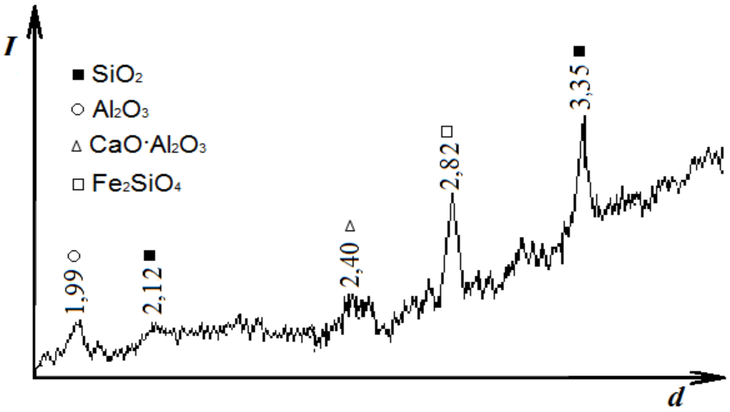
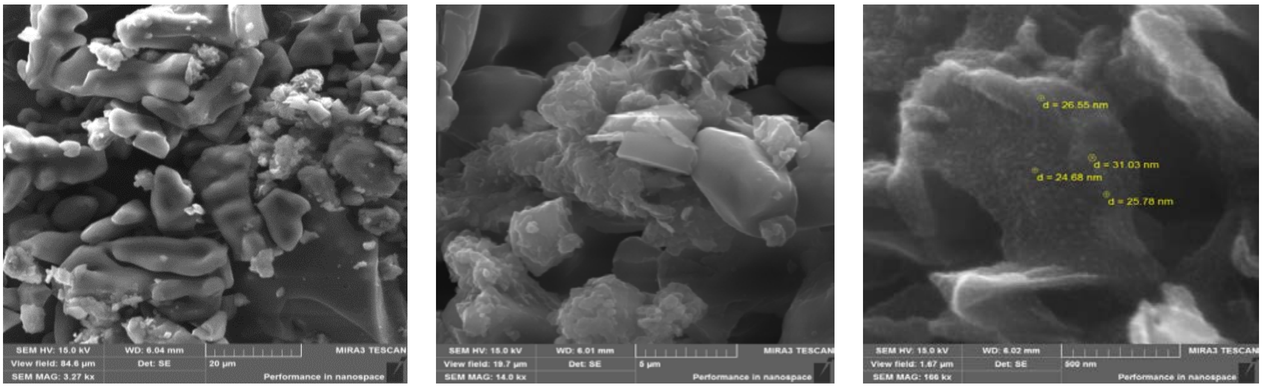


Figure 1 - X-ray diffraction pattern of the obtained composite BR+HNa+TUFR (2:1:1)

As the results of the study showed, heights are indexed in the region of interplanar spacing: d=1,99 Å (γ-Al_2O_3), d=2,12 Å (α-quartz SiO_2), d=2,40 Å ($CaO{\cdot}Al_2O_3$), d=2,82 Å (Fe_2SiO_4 - fayalite), d=3,35 Å (α-quartz SiO_2).

One of the main methods for studying the structure of substances is electron microscopy. The current level of development of this direction allows us to increase objects by several thousand times and consider micron-sized particles. The results of studying the surface morphology of the synthesized composite BR+HNa+TUFR (2:1:1) are shown in Figure 2.



a - × 3 270 b - × 14 000 c - × 166 000

figure 2 - Electron microscopic images of BR+HNa+TUFR (2:1:1)

In the micrograph you can see the loose surface of the sample, on which there are both small and large grains, you can also see particles that have the form of thin plates. An increase of 166 000 times (figure 2 c) shows smooth and uniform growths with fine-grained particles and aggregates with sizes from 24,68 to 31,03 nm. The elemental composition and the multilayer EDS-map of the composite composition are presented in figure 3.

The result of mapping the elemental composition of BR+HNa+TUFR (2:1:1) fully confirms the composition of the product, and the distribution of chemical elements on the microstructure confirms the presence of elements that are both part of the resin and elements that make up the burned rock, such as carbon, oxygen, silicon, aluminum, iron, potassium, magnesium.

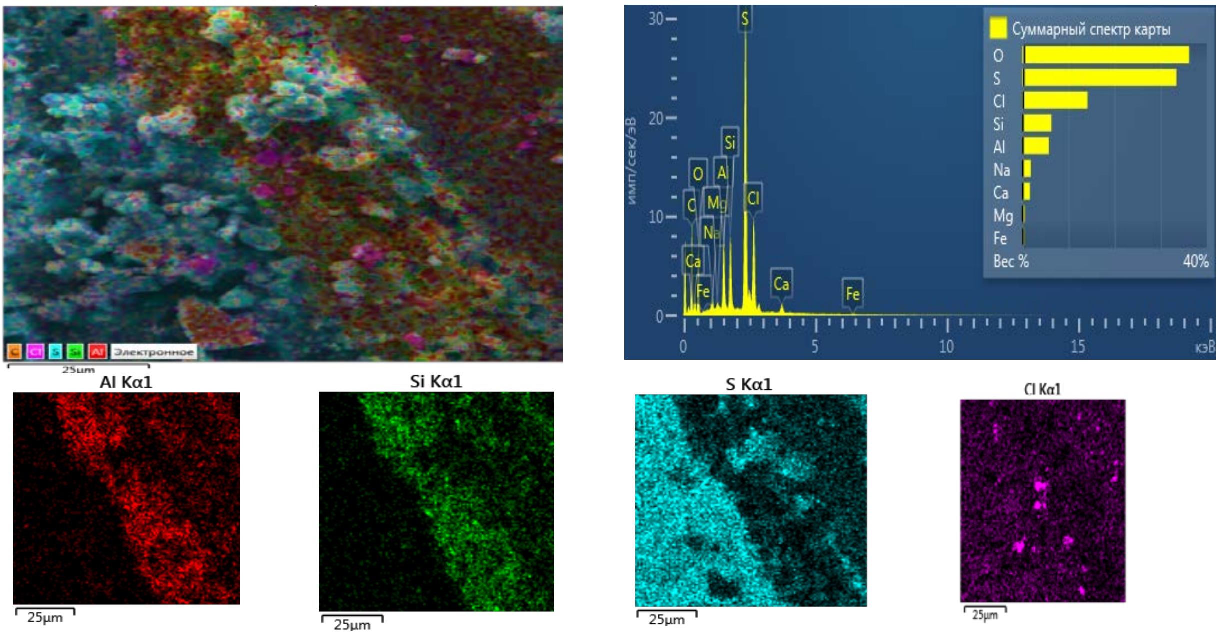


Figure 3 – EDS-map of the composite BR+HNa+TUFR = 2:1:1

Table 2 shows the physicomechanical characteristics of the obtained composites.

Table 2 - Physico-mechanical characteristics of the obtained composites

Composite	Conditional viscosity, sec	Curing time, sec (20°C, H_3PO_4)	Dry residue, %	The content of free formaldehyde, %	Bulk density, g/cm^3	Breaking point	
						R_{bend}, MPa	R_{compr}, MPa
TUFR	30	60	55,4	0,9	0,45		
BR+HNa+TUFR (2:1:1)	62	120	94,2	0,6	0,92	3,1	4,0
BR+HNa+TUFR (3:1:1)	70	128	83,8	0,5	0,95	2,5	2,7

As can be seen from table 2, the curing time for composites based on burned rock with sodium humate in combination with thiourea-formaldehyde resin increases compared with the original resin. However, the addition of filler to the resin leads to a decrease in the formaldehyde content in the composite, thereby reducing its toxicity. The bulk density of thiourea-formaldehyde resin is 0,45 g/cm^3, and for composites based on it, the value ranges from 0,92-0,95 g/cm^3.

Based on the results obtained, it can be assumed that the mechanism of the formation of a composite of the composition BR+HNa+TUFR flows through a series of stages of series-parallel reactions and leads to the formation of a composite, the composition of which is determined by the ratio of the starting reagents, as well as the order of their mixing. The resulting composites are complex complexes and when they are poured onto glass substrates, sufficiently strong composites.

In order to identify the possibility of using BR as an active mineral filler of an additive in the composition of a composite material, tests were carried out on the compressive strength of samples. The test results are shown in table 2. It follows from the table that the student criterion is higher than 2,07, the additive is considered to have passed the strength test. Based on the test data, it follows that the addition of burned rocks as a filler is considered to have passed the strength test.

Conclusion

Thus, a new composite material was developed. By varying the composition of the matrix and filler, the mechanical strength of the composite is increased and toxicity is reduced. The composition of the composite obtained is confirmed by elemental and x-ray phase analysis. A microscopic analysis was performed to study the surface morphology of the synthesized composite. The physicomechanical characteristics of composites are studied. A decrease in the content of free formaldehyde in the composite indicates a decrease in toxicity. The resulting composite can be used as a building material.

Acknowledgement

This work was financially supported by the Ministry of Education and Science of the Republic of Kazakhstan on the theme of target program №BR05236438 «Development of the scientific foundations of science-intensive and resource-saving technologies for producing multifunctional materials based on natural, synthetic raw materials and coal processing wastes».

А.Х. Жакина[1], О.В. Арнт[1], Е.П. Василец[1], Т.С. Животова[1],
З.М. Мулдахметов[1], А.М. Газалиев[1], С.А. Семенова[2]

[1]ҚР ЖШС Органикалық синтез және көмірхимиясы институты, Қарағанды, Қазақстан;
[2]Ресей ғылым академиясының Сібір бөлімінің көмір және көмір химиясы федералды зерттеу орталығы,
Федералдық мемлекеттік бюджеттік ғылыми мекемесі, Кемерово, Ресей

КӨМІР ӨНДІРУ ҚАЛДЫҚТАРЫ НЕГІЗІНДЕГІ КОМПОЗИТТІК МАТЕРИАЛДЫҢ СИНТЕЗІ МЕН ҚАСИЕТТЕРІ

Аннотация. Мақалада ультрадыбыстық химия әдістерін пайдалану арқылы көмір және полимерлі шикізатпен ұштастыра отырып, көмір өндіру қалдықтары негізінде композитті материалдар синтезін зерттеу нәтижелері және ұсақ түйіршікті бетондардағы цемент бөлігін ауыстыруға арналған белсенді минералды қоспа ретінде қолдану мүмкіндігін анықтау ұсынылған. Матрица мен толтырғыштың құрамын өзгертіп, оның қасиеттері әрбір құрамдас қасиеттерінен сандық және сапалық жағынан ерекшеленетін композитті материал алынды. Композитті материал құрамында толтырғыш ретінде жанғыш қазбалар – көмірмен бірге жер бетіне шығарылатын бос жыныстарды тотықтырғыш өздігінен күйдіру өнімі қолданылған. Жанған жыныстардың құрамында органикалық бөлігі (жанбаған көмірлі қоспалар) және минералды (күйдірілген сазды-құмды) бөлігібар. Жанғыш қазбалардың заттық құрамының, көмір өнеркәсібі қалдықтарының ерекшеліктері оларды қайталама минералдық шикізат ретінде қарастыруға мүмкіндік береді. Композиттік материалда байланыстырушы тиомочевиноформальдегид шайыры қолданылған. Шайыр тиокарбамид: формальдегид = 1:2 молярлық қатынаста формальдегидпен тиомочевина поликонденсациясының стандартты әдісі бойынша алынған. Тиомочевиноформальдегид шайырын таңдау қол жетімділігімен, суда ерігіштігімен және модификатормен кешенді түзуге қабілетті протоноакцепторлы орталықтар санының жеткілікті болуымен байланысты. Композиттік материалдар үшін модификатор Шұбаркөл кен орнының тотыққан көмірінен сілтілі экстракция әдісімен бөлінген нанотехнологиядағы перспективалы табиғи полимерлерге жататын көмір өңдеу қалдықтары өнімі, натрий гуматы қолданылған. Натрий гуматы гидрофобты және гидрофильді учаскелердің бірегей үйлесімі, құрамында оттегі бар функционалдық топтардың, хош иісті, гетероциклді және басқа да топтардың алуан түрлілігі бар полифункционалды полимерлерге жатады. Техникалық параметрлерді арттыру және жанғыш қазбалардың кеуектілігін төмендету мақсатында Шұбаркөл кен орнының тотыққан көмірі негізінде алынған натрий гуматымен модификациялау жүргізілді. Толтырғышқа арналған химиялық және құрылымдық модификаторлар ретінде натрий гуматын қолданудың тиімділігі оның молекулалық құры-лысының ерекшеліктерімен, полифункционалдылығымен, әртүрлі химиялық реакцияларға қабілеттілігімен, сондай-ақ донорлық-акцепторлық және гидрофобтық өзара әрекеттесулерге негізделген. Мұның бәрі натрий гуматының макромолекулааралық сипатына қарай, өртенген жыныспен де, тиомочевиноформальдегидді шайырмен де өзара әрекеттесуге жоғары қабілеттілігін көрсетеді. Күйдірілген жыныстар, тиомочевиноформальдегидті шайыры бар натрий гуматы негізіндегі композициялық материал ультрадыбыстық әсерді қолдану арқылы сіңдіру әдісімен синтезделген. Әдіс ультрадыбыстық диспергирлеуді пайдалана отырып, жанғыш қазбалардың кеуекті құрылымына гуматты иммобилизациялауға негізделген. Ультрадыбыстық өңдеу жыныстың барлық көлемі бойынша натрий гуматының біркелкі таралуына қол жеткізуге мүмкіндік береді. Ультрадыбыстық активтендірудің анықтаушы рөлі және оны композиттерді алу процесіне қолданудың тиімділігі көрсетілген.

Қазіргі заманғы физика-химиялық және физика-механикалық әдістермен алынған композиттік материалдардың құрамы мен құрылымы сипатталған. Композиттік материалдардың минералогиялық құрамы Co(Kα)-сәулеленуді пайдалана отырып, ДРОН-2,0 надифрактометрінде рентгенофазды талдау көмегімен зерттелген, ал TESCAN фирмасының MIRA-3 растрлық электрондық микроскопты пайдалана отырып, микроскопиялық талдау негізінде бетінің морфологиясы зерттелген. Элементтік құрамды карталау нәтижесі өнімнің құрамын растайды. Композициялық материалды жанғыш қазбалармен толтыру жоғары физика-механикалық көрсеткіштерді қамтамасыз етеді. Жанғыш қазбалармен толтырылған композиттердің беріктігі жанған жыныссыз ұқсас құрам үлгілеріне қарағанда жоғары. Алынған композит құрылыс материалы ретінде пайдаланылуы мүмкін.

Түйін сөздер: композитті материал, толтырғыш, байланыстырушы, жанғыш қазбалар, тиомочевиноформальдегид шайыры.

А.Х. Жакина[1], О.В. Арнт[1], Е.П. Василец[1], Т.С. Животова[1],
З.М. Мулдахметов[1], А.М. Газалиев[1], С.А. Семенова[2]

[1] ТОО Институт органического синтеза и углехимии РК, Караганда, Казахстан;
[2] Федеральный научно-исследовательский центр угольной и химической промышленности
Сибирского отделения Российской академии наук, Кемерово, Россия

СИНТЕЗ И СВОЙСТВА КОМПОЗИТНОГО МАТЕРИАЛА НА ОСНОВЕ ОТХОДОВ УГЛЕДОБЫЧИ

Аннотация. В статье представлены результаты исследования синтеза композитных материалов на основе отходов угледобычи в сочетании угольным и полимерным сырьем, с использованием методов ультразвуковой химии и определение возможности их применения в качестве активной минеральной добавки для замены части цемента в мелкозернистых бетонах. Варьируя состав матрицы и наполнителя, получен композитный материал, свойства которого количественно и качественно отличаются от свойств каждого из его составляющих. В качестве наполнителя в составе композиционного материала использована горелая порода – продукт окислительного самообжига пустых пород, извлекаемых вместе с углем на поверхность. Горелые породы содержат органическую часть (несгоревшие углистые примеси) и минеральную (обожженную глинисто-песчанистую часть). Особенности вещественного состава горелых пород, отходов углепромышленности позволяет рассматривать их как вторичное минеральное сырье. Связующим в композитном материале использована тиомочевиноформальдегидная смола. Смола получена по стандартной методике поликонденсации тиомочевины с формальдегидом при молярном соотношении тиокарбамид:формальдегид = 1:2. Выбор тиомочевиноформальдегидной смолы обусловлен доступностью, водорастворимостью и наличием достаточного количества протоноакцепторных центров, способных к комплексообразованию с модификатором. Модификатором для композитных материалов использован продукт отхода углепереработки, относящийся к перспективным природным полимерам в нанотехнологии, гумат натрия, выделенный методом щелочной экстракции из окисленных углей Шубаркольского месторождения. Гумат натрия относится к полифункциональным полимерам с уникальным сочетанием гидрофобных и гидрофильных участков, разнообразием кислородсодержащих функциональных групп, ароматических, гетероциклических и других группировок. С целью повышения технических параметров и снижения пористости горелой породы проведено ее модифицирование гуматом натрия, полученного на основе окисленных углей Шубаркольского месторождения. Эффективность использования гумата натрия в качестве химических и структурных модификаторов для наполнителя обусловлена особенностями его молекулярного строения, полифункциональностью, способностью к разного рода химическим реакциям, а также к донорно-акцепторным и гидрофобным взаимодействиям. Все это предполагает высокую способность гумата натрия к межмакромолекулярным взаимодействиям с как с горелой породой, так и тиомочевиноформальдегидной смолой. Композиционный материал на основе горелой породы, гумата натрия с тиомочевиноформальдегидной смолой синтезирован методом пропитки с использованием ультразвукового воздействия. Метод основан на иммобилизации гумата в пористую структуру горелой породы с использованием ультразвукового диспергирования. Ультразвуковая обработка позволяет добиться равномерного распределения гумата натрия по всему объёму породы. Показана определяющая роль ультразвуковой активации и отмечена эффективность его применения на процесс получения композитов.

Современными физико-химическими и физико-механическими методами охарактеризованы состав и структура полученных композитных материалов. Минералогический состав композитных материалов изучен с помощью рентгенофазового анализа на дифрактометре ДРОН-2,0 с использованием Co(Kα)-излучения, а морфология поверхности на основании микроскопического анализа с использованием растрового электронного микроскопа MIRA-3 фирмы TESCAN. Результат картирования элементного состава полностью подтверждают состав продукта. Наполнение композиционного материала горелой породой обеспечивает более высокие физико-механические показатели. Прочность, наполненных горелой породой, композитов выше, чем у образцов аналогичного состава без горелой породы. Полученный композит может быть использован в качестве строительного материала.

Ключевые слова: композитный материал, наполнитель, связующий, горелая порода, тиомочевиноформальдегидная смола.

Information about authors:

Zhakina Alma Khasenovna – Candidate of Chemical Sciences, docent, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, e-mail: alzhakina@mail.ru, https://orcid.org/0000-0001-5724-2279;

Arnt Oxana Vasilyevna–Master of Technical Sciences, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, t-mail:oxana230590@mail.ru, https://orcid.org/0000-0002-8996-4572;

Vassilets Yevgeniy Petrovich – Master of Pedagogical Sciences, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, e-mail: vassilets88@mail.ru, https://orcid.org/0000-0003-2242-486X;

Zhivotova Tatyana Sergeevna – Doctor of Chemical Sciences, professor, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, e-mail:zhts2004@mail.ru, https://orcid.org/0000-0002-0793-4653;

Muldahmetov Zeynulla Muldahmetovich – academic NAN RK, Doctor of Chemical Sciences, professor, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan. https://orcid.org/0000-0001-9497-2545;

Gazaliev Arstan Maulenovich – academic NAN RK, Doctor of Chemical Sciences, professor, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, https://orcid.org/0000-0003-2161-0329;

Semenova Svetlana Alexandrovna – Candidate of Chemical Sciences, docent, Federal Research Center of Coal Chemistry, Siberian Branch, Russian Academy of Sciences, https://orcid.org/0000-0002-2373-4993

REFERENCES

[1] Scrivener K.L. (2008) Innovation in use and research on cementitious material. Cement and Concrete Research. Volume 38(2) (2008), PP. 128-136. https://doi.org/10.1016/j.cemconres. 2007.09.025

[2] Kuzmin M.P., Larionov L.M., Kondratiev V.V., Kuzmina M.Yu., Grigoriev V.G., Kuzmina A.S. (2017). Burned coal deposits in the production of concrete products. Engineering and Construction Journal. Volume 8(76) (2017), PP. 169-180. DOI: 10.18720/MCE.76.15.

[3] Gamaliy E.A. (2008) Burned rocks as an active mineral additive in concrete. Bulletin of SUSU. Ser. Construction and architecture. Volume 25 (2008), PP. 22-27.

[4] Patil S.B., Vyas A.K., Gupta A.B., Patil R.S. (2016) Imperial smelting furnace slag as fine aggregate in cemrnt concrete mixes, Journal of solid waste technology and management, Volume 42(2) (2016), PP. 128-136. DOI:10.5276/JSWTM.2016.128

[5] Kulikov V.A., Abdrahimov V.Z., Kovkov I.V. (2010). The use of burned rocks in the production of semi-dry pressed bricks. Bashkir Chemical Journal. Volume 17, Number 4 (2010), PP. 82-84.

[6] Panova V.F., Panov S.A. (2015) Coal preparation waste as raw material for building materials. Bulletin of the Siberian State Industrial University. Volume 2 (12) (2015), PP. 71-75. ISSN 2304-4497 (Online)

[7] Chernyshov E.M., Potamoshneva N.D., Monastyrev P.V., Yartsev V.P. (2016). Construction and technological recycling of industrial waste as a complex system of environmental and economic development of territories and urban development. Issues of modern science and practice. University named after V.I. Vernadsky. Volume 4 (62) (2016), PP. 67-86. DOI:10.17277/VOPROSY.2016.04.PP.067-086

[8] Oxama Y. (2008) Developments in the Formulation and Reinforcement of Concrete. Elsevier, Japan. https:// doi.org/10.1533/9781845694685.256

[9] Raman B., Rakesh C., Singh S.P. (2013) Mechanical Properties of Polymer Concrete. Journal of Composites. 2013, PP. 1-12. http://dx.doi.org/10.1155/2013/948745

[10] Asif A., Anis A.A. (2013) Polymer Concrete as Innovative Material for Development of Sustainable Architecture. 2nd International Conference on Emerging Trends in Engineering & Technology. College of Engineering, Teerthanker Mahaveer University. PP. 1-4. DOI: 10.13140/2.1.4761.5040

[11] Momtazi A.S., Khoshkbijari R.K., Mogharab S.S. (2015) Polymers in Concrete: Applications and Specifications. European Online Journal of Natural and Social Sciences. Volume 3, Nunmer 3 (2015), PP. 62-72. ISSN 1805-3602. http://www.european-science.com

[12] Hameed A. M., Hamza M.T. (2019) Characteristics of polymer concrete produced from wasted construction materials. Energy Procedia. Volume 157 (2019), PP. 45-50. https://doi.org/10.1016/j.egypro.2018.11.162

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.18**
Volume 2, Number 440 (2020), 14 – 22

UDC 544.23.057
IRSTI 31.25.19

A.N. Nurlybayeva, E.I. Rustem, H.R. Sadiyeva, G.A. Seitbekova,
A.S. Darmenbayeva, M.S. Kalmakhanova, A.M. Egisinova, U.T. Otinshieva

Taraz state University named after M.Kh. Dulati, Kazakhstan

SYNTHESIS AND APPLICATION OF ACRYLIC FILMS IN PAINT AND VARNISH MATERIALS

Abstract. Copolymerizations of unsaturated compounds with different ratios of acrylic monomers were synthesized. The synthesized copolymers exhibit good adhesion, flexibility and waterproofing performance may be used in the paint industry. The behavior of the copolymers of MMA and BuMA and proven by IR spectroscopy. This paper describes the synthesis, structure and properties of certain block copolymers. The practical application of scanning electron microscopy used for investigation of materials.

Keywords: methyl methacrylate, butyl methacrylate, copolymers, paint, films, tensile strength, elongation at break, shore hardness.

Introduction. Polymers based on methacrylic monomers have optical, mechanical properties, they are biocompatible, easy to functionalize, that causes a wide application in various fields ranging from coatings and ending medicine. This explains the need for controlled synthesis of polymers based on [1] of the class of monomers.

Methyl methacrylate and butyl methacrylate copolymers are widely used adhesive compositions, paint, varnish, materials for restoration work, due to its transparency, good film-forming properties, high adhesion to various substrates, increased bio and weather. Block copolymers of the structure is used to improve the compatibility of the polymer components in the solutions and the mixtures.

In this paper, the synthesis of new hydrophobic copolymers based on butyl methacrylate (BuMA) and methyl methacrylate (MMA) investigated their physicochemical and surface properties. Methyl methacrylate as a monomer contains a highly polar ester group, which confirms the hydrophilic nature while the methylene and methane groups in the main chain and side chain support the hydrophobic nature, respectively.

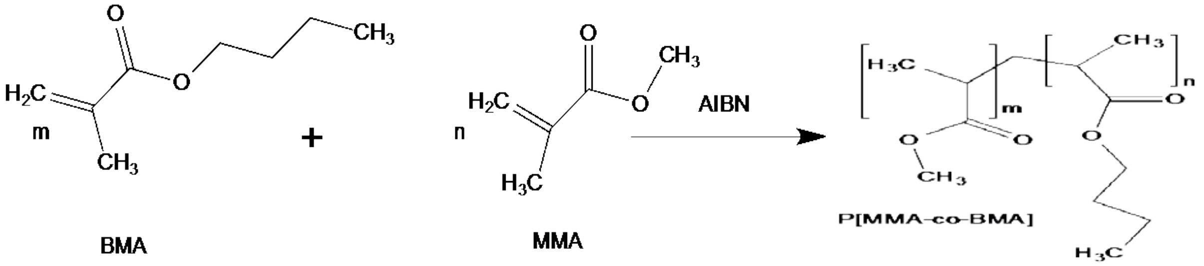
This work relates to paints and can be used to protect various surfaces in the home and in industry. Methacrylic paint composition according to the first embodiment comprises a film-forming methacrylate - acrylic organic soluble copolymer of butyl methacrylate with methyl methacrylate. This relates to the production of coatings and can be used to generate protection against various external surfaces aggressive action and giving the appearance of the corresponding products. Paints and coatings based on methacrylic copolymers such as a copolymer of butyl methacrylate and methyl methacrylate are highly weather- and light resistance [2]. This elastic coating resistant to shock, have good adhesion to the surface.

The structure of the copolymers block of is used to improve the compatibility of the polymer components in the solutions and the mixtures. The thermal behavior of the copolymers is important to predict the lifetime of materials. The aim of this work is to study of methyl methacrylate (MMA) with butyl methacrylate (BuMA) by IR spectroscopy, SEM and physical-mechanical properties.

Experimental (Materials and apparatus). Methyl methacrylate, butyl methacrylate, Azobisisobutyronitrile acid production company «Aldrich Chemical Co.» USA was used without further purification and other chemicals as ethanol and acetone used in this experiment. Benzoyl peroxide (BPO) (supplied by Melbourne), N,N-dimethyl-p-toluidine (DMPT) (supplied by Fluka) and hydroquinone (HQ) (supplied by Merck) were used as purchased.

Synthesis of copolymers. In the ground-glass prepared monomer mixture of 450g methyl methacrylate (MMA) mixed with 50g butyl methacrylate (BuMA) and a molar ratio of 90:10 after assembly of the device in a three-necked reaction flask was charged with a stirred mixture of 100 g and the reaction mixture was stirred for 10 minutes at stirring heated air bath to 800S. When the temperature reached 500C, the supply of nitrogen or argon that extends almost to the surface of the reaction mass. Gas flow rate was controlled clamp so that the bottle was held through an intermediate air bubbles. To the residue was added a mixture of the dinitrile 0,5gr azobisisobutyronitrile acid (AIBN) and the stirrer and dissolve with vigorous stirring. After dissolving the mixture and stirring the cooling slowly drop wise over 1 hr through the addition funnel administered initiator (Scheme 1).

Methyl methacrylate Poly methyl radical obtained by reacting a copolymer of methyl methacrylate with methyl methacrylate according to the following scheme:



Scheme 1 - General reaction for the synthesis of MMA/BMA copolymer

Copolymerization is carried out to syrup state. The mixture was then cooled in cold water, carefully opened, and dissolved in acetone. Copolymers transferred to a beaker dissolved in acetone, the contents of the solution was purified by precipitation in ethanol. This occurs because the copolymer is not soluble in ethanol. Then they were dried in a pre-weighed Petri dish, first in air and then vacuum circuit drier.

Tests. This paper was carried out by IR spectroscopy on 65 Spectrum FT-IR spectral range between 4000 – 4500 cm^{-1} and a scanning electron microscope "EVO 50 XVP" (Carl Zeiss) (Wolverhampton Instruments) synthesized copolymers were filmed in different proportions. Experimental part [The tensile properties of the copolymers and terpolymers cast films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least four measurements was taken, and the 1-kN load cell was used. Shore A, D hardness was measured using an indentation hardness tester according to ASTM D2240-75.]

Results and discussion FT-IR spectra. Infrared spectroscopy method was used to solve the problem in our research. It is one of the most informative methods for optical investigation of solids as well as allows you to record the vibrations of the structure of molecules and surface groups of atoms, as well as to observe the change in the chemical bonds in the process of adsorption of the reactants. With the help of IR - spectroscopy we can determine the structure of molecules, as in the infrared region contains the majority of the vibrational and rotational spectra of molecules.

For the determination of [3] components in the copolymers there should have a spectrum characteristic, easily identifiable intense absorption bands by IR spectroscopy (see table 1).

Table 1 - The compositions of the copolymers obtained by IR - spectroscopy

IR - spectra, the oscillation frequency	MMA: BuMA 90:10, cm^{-1}	MMA: BuMA 50:50, cm^{-1}	MMA: BuMA 10:90, cm^{-1}
1	2	3	4
CH_2 tension	2930	2955	2957
CH, CH_2 и CH_3 tension	–	2874	2873
C=O tension	1722	1722	1722
C=C bending	1434	1447	1464
CH_3 bending	1386	1385	1384
C-O-C tension	–	1267	1267

Continuation of table 1

1	2	3	4
C-O-C tension	1237	1238	1239
O=C–O– tension	1142	1142	1143
–C–O–C– tension	1061	1063	1063
–C–O–C– tension	–	–	1019
–C–C– tension	985	964	945
–C–C– tension	840	844	844
C–H bending	749	748	748
O–C–O shears	–	–	517
O–C–O shears	478	482	438

If any, by comparing the value of this peak with the gauge dependence of the peak intensity - concentration of the component, it is possible to determine the content of the copolymer. The copolymers synthesized based on MMA: BuMA were recorded IR spectra (figure 1).

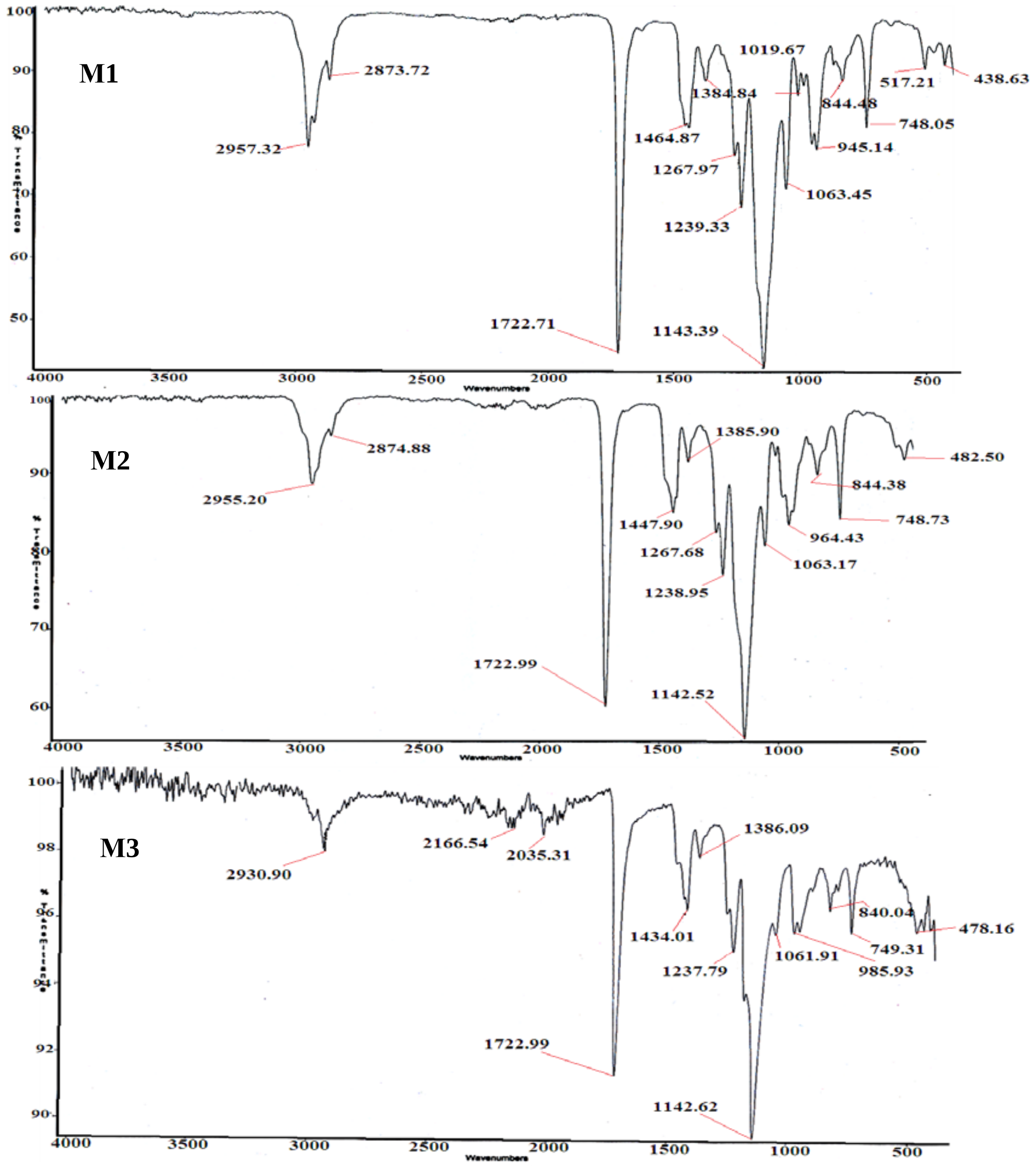


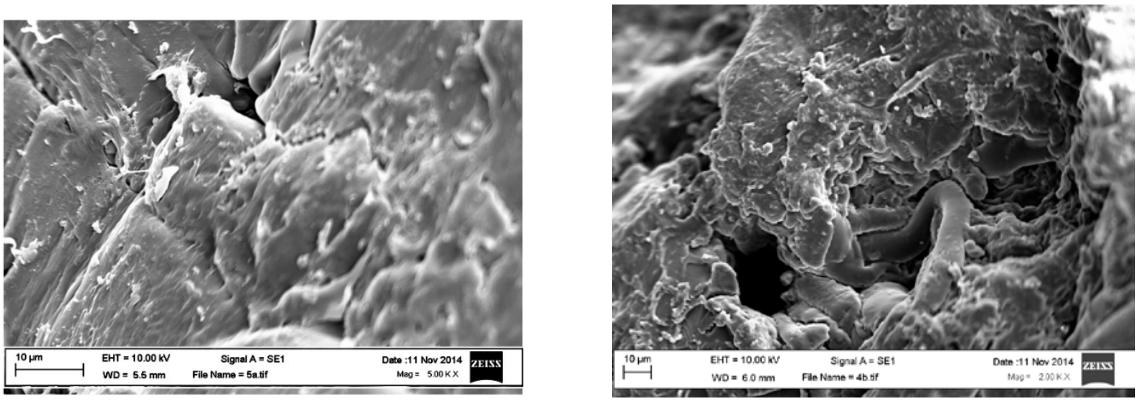
Figure 1 - IR spectra of copolymers based on MMA: BuMA
Composition [MMA]: [BuMA] mol.%: 90:10 (M1), 50:50 (M2), 10:90 (M3)

The spectra of copolymers based on MMA: BuMA are characterized by an absorption band in the band range 2874cm^{-1} – 2873cm^{-1} can be attributed to the stretching vibrations of aliphatic and by the presence of methyl groups CH, CH_2 and CH_3 bonds.

Meanwhile, the signal can be seen in 2957cm^{-1} – 2930cm^{-1} is the result sp^3 carbonyl monomer butyl methacrylate and most intensive absorption bands esters [4] are in 1723cm^{-1} – 1722cm^{-1} stretching vibrations of unsaturated carbonyl groups C=O.

Absorption band at 1434 cm^{-1} – 1464 cm^{-1} monomer spectrum [5] due to the presence of a double bond C = C stretching vibrations and vibrations = CH - groups, with absorption bands in the region 1267cm^{-1} - 1237cm^{-1}, 1142cm^{-1} -1143cm^{-1} и 1061cm^{-1} - 1063cm^{-1} -C-O-C- ester group, indicating the formation of a copolymer of MMA: BuMA. In the 1019 cm^{-1} there is a series of four absorption bands, which together with the strip in 790 см$^{-1}$ are characteristic of methacrylate structure. Intensive pass band frequency range 1019 cm^{-1} - 790 cm^{-1} and 2957cm^{-1} – 2930cm^{-1} traced in the spectra of all the samples. The IR spectra of different ratios of copolymers were observed changes in the intensity of transmission bands of carbonyl functional groups in all the samples, which allowed us to estimate the degree of polymerization of MMA and BuMA [6]. The composition of the copolymers MMA: BuMA identified by IR - spectra, which are stretching vibrations of the respective functional groups. The intensity of the bands corresponding to the characteristic depends on the composition of the starting monomeric mixture. It is clearly seen that the copolymer consists of units of different amounts of methyl methacrylate and butyl methacrylate [7].

Scanning electron microscope (SEM). Scanning electron microscopy (SEM) to analyze the materials have been widely used to solve specific scientific and technological problems due to their high information content and reliability of the results of the study. The physical and mechanical properties of the materials are determined by their microstructure which depends on the electronic structure, chemical composition, and their fabrication technology [8].



1. MMA:BuMA 10:90

2. MMA:BuMA 50:50

3. MMA:BuMA 90:10

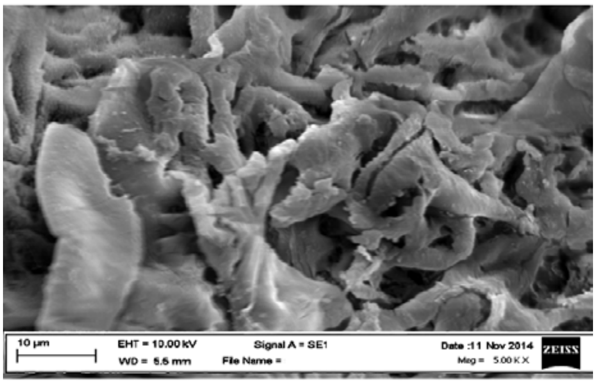


Figure 2 - Images of copolymers based on MMA: BuMA obtained by the SEM method

Different ratios of copolymers were evaluated by scanning electron microscopy. From figure 2 the copolymers of MMA: BuMA are porous, and swelling due to a large capacity of the copolymers.

SEM images showed copolymers, species such as a structure that provides a large surface area for improved adsorption. Structure existed small pores and is indicated for the better solubility. For the copolymerization reaction of MMA: BuMA in different proportions structure was porous and irregular look strong and changed the structure is not uniform.

Filler and fine aggregate. In this work, fine - dispersed calcium carbonate was used as a filler in paint products, and fine quartz sand was used as a fine filler. Before using these fillers, they were dried at 105 ° C for 48 hours to remove moisture at least 0.1%. Table 2 presents the characteristics of the filler and the fine aggregate [9].

Table 2 - Properties of filler and fine aggregate

Filler or fine aggregate	Size (μm)	Density (20 ^{o}C, g/cm^3)	Water content (%)	Organic impurities
Calcium carbonate	<2.5	2.7	<0.1	Nil
Silica sand	106-121	2.61	<0.1	Nil

Preparation of copolymer syrups. Copolymer syrup was produced by dissolving copolymer (MMA/BuMA) and BPO into MMA monomer at normal temperature (25^{0}C). Then, a liquid component was produced using MMA monomer, DMPT and HQ. BPO and DMPT were added at 1.5 and 0.75 parts per hundred (pph) to syrup to act as initiator and accelerator, respectively. HQ was added in the syrup as an inhibitor. Paraffin wax was as added 1% wt. of syrups. This copolymer syrup was then placed into the liquid component mixed with ratio 10/90 % wt/wt to maintain the mixing ratio at 100% as shown in table 3.

Table 3 - Formulation of copolymer syrup for acrylic paint

Group	Syrups	Copolymer (Powder, gm)	MMA (Liquid, gm)
Group 1	Syp10/M1	10	90
	Syp10/M2	10	90
	Syp10/M3	10	90

Film preparation. Films were prepared by casting the acryl syrups on leveled surfaces and allowing them to dry at room temperature for 3 hours. The films were stored in a desiccator at room temperature for further characterization and measurements [10-11].

Mechanical Properties of polymer films. The mechanical properties of the copolymer films with respect to the amount of MMA and BuMA are shown in figures 3-5.

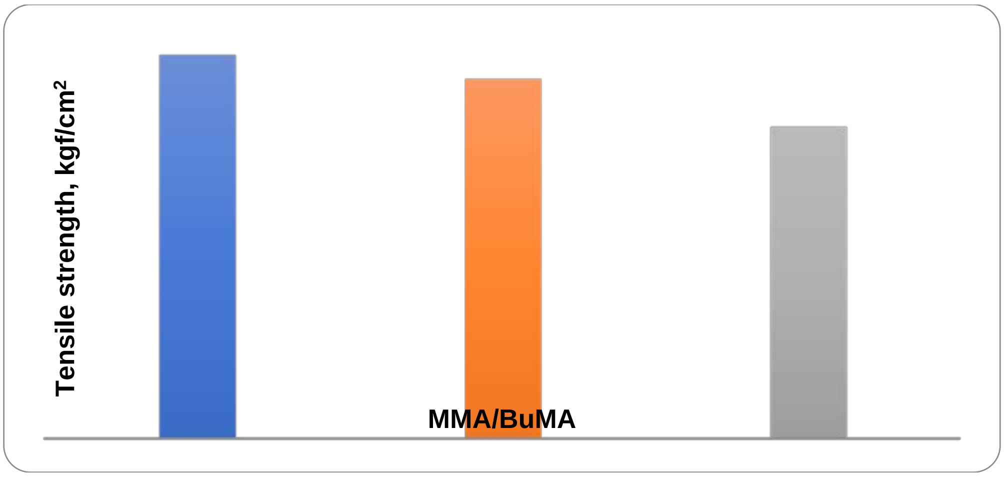


Figure 3 - Tensile strength of copolymer films as a function of MMA/BuMA content

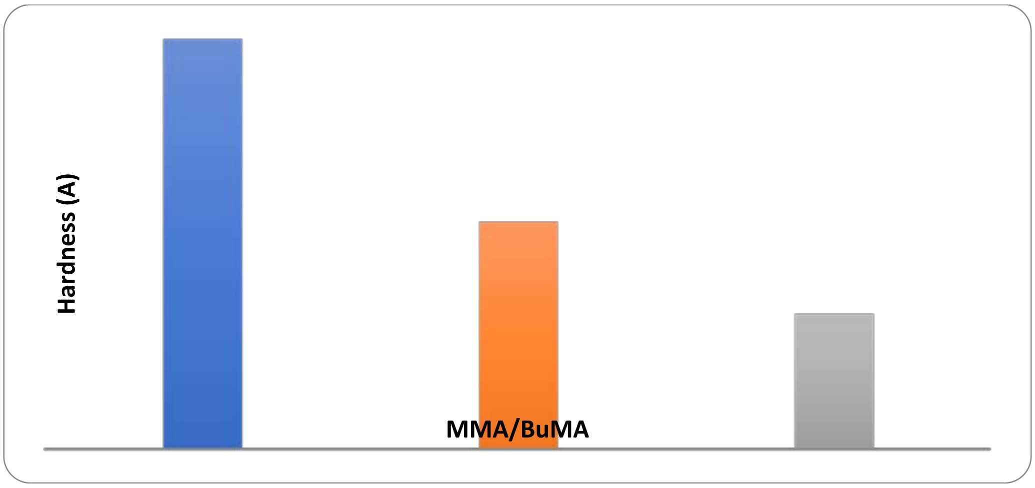


Figure 4 - Hardness of copolymer films as a function of MMA/BuMA content

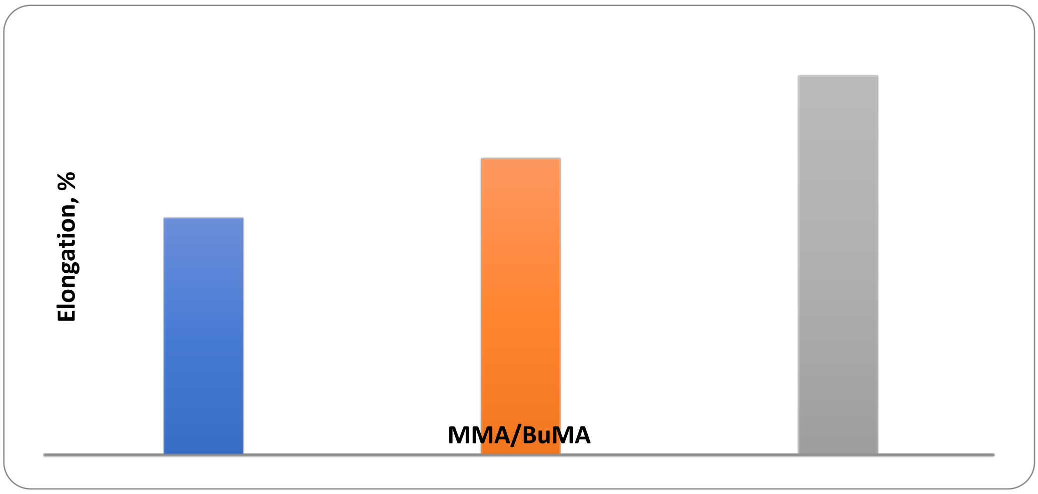


Figure 5 - Elongation at break of copolymer films as a function of MMA/BuMA content

It can be seen that tensile strength increased with increasing amounts of MMA in the copolymer (figure 1). MMA/BuMA (90/10) showed the largest tensile compared with MMA/BuMA (50/50). This is presumably due to the increased hard segment contents (MMA) in the copolymer film. The elongation at break was increased with increasing amount of BuMA as shown in figure 2. It may be due to the increased in chain flexibility (BuMA). Similarly, hardness shore (A) was found to increase with increasing of MMA content in the copolymer films as shown in figure 3 [12].

Conclusion. We have obtained a new synthetic copolymers based on methyl methacrylate (MMA) and butyl methacrylate (BuMA), with use of the dinitrile as an initiator of Azobisisobutyronitrile acid (AIBN).

The result of research, the molecular interaction with the MMA: BuMA liquid phase methacrylic copolymer dispersions, which had a significant impact on the protective properties of the coatings. Polyampholytic properties of cross linked copolymers of MMA: BuMA, partly due to the presence of unsaturated groups and carboxyl methacrylate structure characteristic for which presence confirmed also that by decreasing the content of the hydrophobic monomer MMA copolymers are obtained which are insoluble in water. Ionization of the carboxyl groups is a major contributor to the process of swelling and aspirations to the distribution of solvent throughout the volume of the polymer network.

Studies have confirmed the effectiveness of dispersion paints using MMA: BuMA staff 50:50 mole. %, can improve water repellency, resilient flooring, as well as to reduce the drying time of coatings to touch on various mineral substrates [13].

Study waterproofing properties of the films showed that the higher content of the copolymer composed of MMA contributes to obtaining films with lower adsorption capacity and hence higher waterproofing properties.

А.Н. Нурлыбаева, Е.И. Рустем, Г.Р. Садиева, Г.А. Сейтбекова,
А.С. Дарменбаева, М.С. Калмаханова, А.М. Егисинова, У.Т. Отыншиева

М.Х. Дулати атындағы Тараз мемлекеттік университеті, Казахстан

АКРИЛ ҮЛДІРЛЕРІН СИНТЕЗДЕУ ЖӘНЕ ЛАК-БОЯУ МАТЕРИАЛДАРЫНА ҚОЛДАНУ

Аннотация. Берілген мақалада метилметакрилат (ММА) пен бутилметакрилат (БМА) және тігуші агент АИБН инициаторын қосу арқылы жаңа полимерлерді синтездеп алу және олардың негізгі заңдылықтары қарастырылды. Осыған байланысты сыр-бояу материалдары саласындағы өзекті мәселенің бірі – өнеркәсіпте қолдану үшін қасиеттері жақсартылған, жылдам кебетін, экологиялық таза, сольвентсіз бояулар алу. Әлемде сольвентсіз бояулар ретінде эпоксидті және полиуретанды бояулар ұсынылған. Акрил бояуларының құрамында судың және органикалық еріткіштердің болмауы сольвентсіз бояулар деп аталатын, құрамында ұшпа органикалық қосылыстар өте төмен болатын бояуларды синтездеп алуға және физика-механикалық қасиеттері мен экологиялық сипаты жағынан таза, жақсы өнім алуға мүмкіндік береді.

Зерттеу тақырыбының өзектілігі. Қазақстанның құрлықтық климат түрінің тез өзгергіштігіне және күрделі гидрогеологиялық жағдайына байланысты, ғимараттар мен құрылыстарды гидроизоляциялық қорғау маңызды болып саналады. Осыған байланысты, Қазақстанда бояу жабындыларын дайындау, олармен қамту және осындай өндірісті дамыту – өзекті мәселелердің бірі.

Өнеркәсіп әрқашан өте жоғары эксплуатациялық қасиеттерге ие жаңа сыр-бояу материалдарын өндіруге талпынады. Акрильді сыр-бояу материалдары (СБМ) бірқатар баға жетпес қасиеттерге ие, оның ішінде атмосфераға және жарыққа тұрақтылығы және су мен сілтілерге төзімділігі бар.

Жұмыс мақсаты – әртүрлі мономерлермен қаныққан метакрильді шайырлар – метил метакрилаты негізінде жаңа сополимерлер алу. Жаңа сополимерлер негізінде метилметакрилат пен бутилметакрилат синтездеу және оның физика-химиялық қасиеттерін зерттеу. Гидроизоляциялық қасиеттері бар акрилат бояуларын қолданудағы полимерлі акрилаттар негізін алудың технологиясын құру.

Әртүрлі қатынастағы жаңа сополимерлер – ММА және БМА синтезделді, сондай-ақ физика-химиялық қасиеттері зерттелді. Үлдірлер, сірнелер дайындау үшін сополимер қолданылды, олардың физика-механикалық қасиеттері зерттелді және бояудың құрамына әсері қарастырылды.

Негізгі нәтижелері:

– алғаш рет ММА-БМА негізінде сополимерлер бастапқы қоспадағы мономердің әртүрлі қатынастағы массада бос радикалды сополимерлену әдісі арқылы синтезделді;

– алынған сополимер ИҚ спектроскопия әдісімен сипатталды. Осы алынған мәліметтер негізінде, сополимерлер құрылымы ұсынылды;

– алынған сополимердің беткі қабатының морфологиясын зерттеу үшін сканерлеуші электрондық микроскоп әдісі қолданылды;

– алынған сополимерлердің үлгілері СЭМ әдісімен талдау арқылы мономердің әртүрлі қатынастарына байланысты, беткі қабатының морфологиясында айтарлықтай айырмашылықтар бар екенін көрсетеді. Бутил метакрилатымен метил метакрилат негізінде жаңа сополимерлердің физика-химиялық қасиеттерін синтездеу және зерттеу. Бутил метакрилатымен метил метакрилат негізінде жаңа сополимерлердің физика-химиялық қасиеттерін синтездеу және зерттеу. Мономердің әртүрлі қатынастары полимер бөлшектерінің морфологиясына әсер ететіні зерттелді;

– синтезделген сополимерлер үлдірлер, акрилат сірнелері, бояу жабындыларын алуда қоданылды;

– акрилат бояуларын алу үшін катализаторлар, толтырғыштар қолданылды. Катализаторлар айтарлықтай жабындарлардың кептіру уақытын қысқартатыны, ал толтырғыштар, бояу кепкен кезде, ондағы полимердің көп отырмауына себепші болатыны, әртүрлі ортаның әсеріне тұрақтылығын арттыратыны, полимерлік композиттік материалдардың механикалық қасиеттерін жақсартатыны және полимерлік материалдардың өзіндік құнын төмендететіні анықталды;

– заманауи физика-механикалық зерттеу әдістері көмегімен полимер үлдірлерінің және акрильді сірнелерінің физика-механикалық қасиеттері анықталды, оның ішінде созылу беріктілігі, ажырау кезіндегі салыстырмалы ұзаруы, Шор тәсілі бойынша қаттылығы зерттелді.

Түйін сөздер: метилметакрилат, бутилметакрилат, сополимерлер, бояу, үлдірлер, созылу беріктілігі, ажырау кезіндегі салыстырмалы ұзаруы, Шор тәсілі бойынша қаттылығы.

А.Н. Нурлыбаева, Е.И. Рустем, Г.Р. Садиева, Г.А. Сейтбекова,
А.С. Дарменбаева, М.С. Калмаханова, А.М. Егисинова, У.Т. Отыншиева

Таразский государственный университет им. М.Х. Дулати, Казахстан

СИНТЕЗ И ПРИМЕНЕНИЕ АКРИЛОВЫХ ПЛЕНОК В ЛАКОКРАСОЧНЫХ МАТЕРИАЛАХ

Аннотация. Данная статья посвящена синтезу новых полимеров, установлению основных закономерностей получения сополимеров на основе метилметакрилата (ММА) с бутилметакрилатом (БМА) с 2,2-азобис-изобутиронитрил (АИБН). В связи с этим, решение задачи получения экологически безопасных быстросохнущих красок (не содержащие органические растворители) с улучшенными эксплуатационными характеристиками промышленного назначения является актуальной в области создания лакокрасочных материалов. В мире безсольвентные краски в основном представлены эпоксидными и полиуретановыми лакокрасочными покрытыми. Предлагается создание акрилатных лакокрасочных материалов, не содержащих органические и водные растворители, так называемые безсольвентные краски с очень низким содержанием летучих органических соединений, что позволяет сочетать отличные физико-механические и эксплуатационные характеристики и экологичность.

В Казахстане в связи с резко континентальным типом климата и сложной гидрогеологической обстановкой, гидроизоляционная защита зданий и сооружений является необходимой мерой. В связи с этим разработка гидроизоляционных лакокрасочных покрытий является актуальным.

Промышленность непрерывно стремится производить новые лакокрасочные материалы с лучшими эксплуатационными свойствами. Акриловые лакокрасочные материалы обладают рядом ценных свойств, в том числе атмосфер- и светостойкостью, устойчивостью к воздействию воды и щелочей.

Целью работы является создание новых сополимеров на основе ненасыщенных метакриловых смол – метилметакрилата с различными мономерами. Синтезирование и исследование физико-химических свойств новых сополимеров на основе метилметакрилата с бутилметакрилатом. Получение полимерной акрилатной основы для применения в акрилатных красках с гидроизоляционными свойствами.

Синтезирование новых полимерных связующих и реагентов при различных соотношениях мономеров ММА-БМА и исследование их физико-химических свойств. Сополимеры были использованы для приготовления пленок, сиропов, затем были изучены их физико-механические свойства и влияние их на свойства красок.

Основные результаты:

- Впервые получены сополимеры на основе ММА и БМА методом радикальной полимеризации в массе с различным содержанием мономеров в исходной смеси.
- Полученные сополимеры охарактеризованы методами ИК-спектроскопии. На основании полученных данных предложена структура полимеров.
- Для исследования морфологии поверхности полученных сополимеров был использован метод сканирующей электронной микроскопии (СЭМ).
- СЭМ-анализ образцов сополимеров четко показывают, что существуют заметные различия в количестве мономеров в зависимости от стадии эксперимента. Разные составы мономеров влияет на морфологию частиц полимера.
- Синтезированные новые сополимерные пленки, акрилатные сиропы можно использовать в лакокрасочных покрытиях.
- Для получения акрилатных красок были использованы катализаторы и наполнители. Выявлено, что катализаторы значительно сокращают время высыхания лакокрасочного покрытия, когда краска высыхает, то наполнитель не дает полимеру осаждаться, повышают устойчивость к воздействию различной среды, улучшают механические свойства полимерных композиционных материалов и снижают стоимость полимерных материалов.
- С помощью современных физико-механических методов были определены физико-механические свойства акриловых сиропов и полимерных пленок, в том числе прочность на растяжение, относительное удлинение при разрыве, твердость по Шору.

Ключевые слова: метилметакрилат, бутилметакрилат, сополимеры, краска, пленка, прочность на растяжение, относительное удлинение при разрыве, твердость по Шору.

Information about the authors:

Nurlybayeva Aisha Nurlybayevna – PhD doctor of chemical Sciences, associate Professor, Taraz University named after M.Kh. Dulati, rustem_ergali@mail.ru, https://orcid.org/0000-0001-9904-9979;

Rustem Ergali Ilesbekuly – 2 year doctoral student Taraz University named after M.Kh. Dulati, rustem_ergali@mail.ru;

Sadiyeva Khalipa Ryskulovna – candidate of technical Sciences, associate Professor, Taraz University named after M.Kh. Dulati, xalipa71@mail.ru, https://orcid.org/0000-0002-8925-8053;

Seitbekova Gulnazia Atashbekovna – candidate of technical Sciences, associate Professor, Taraz University named after M.Kh. Dulati, gul1970naz@mail.ru, https://orcid.org/0000-0001-7087-7180;

Darmenbayeva Akmaral Sabetbekovna – PhD doctor of chemical Sciences, associate Professor, Taraz University named after M.Kh. Dulati, maral88@mail.ru, https://orcid.org/0000-0003-2974-0398;

Kalmakhanova Marzhan Seitovna – PhD of chemical Sciences, M.Kh.Dulati Taraz State University, marjanseitovna@mail.ru, https://orcid.org/0000-0002-8635-463X;

Egisinova Ayazhan Masatovna – мaster of Chemistry 2 courses, M.Kh.Dulati Taraz State University, maral88@mail.ru, https://orcid.org/0000-0001-7067-2468;

Otinshieva Uldana Tanysbekovna – мaster of Nanomaterials and nanotechnology 2 courses, M.Kh.Dulati Taraz State University otynshieva.uldana@mail.ru, https://orcid.org/0000-0001-6889-2912

REFERENCES

[1] Spectroscopic study of intermolecular interactions of acrylates and methacrylates with a proton donor solvent // Mat. X All-Union. Soveshch on the physics of fluids. Samarkand, 1974. p 157.

[2] Infrared spectroscopy polymers, ed. I. Dehanta GDR. 1972. Trans. with it. Ed. EF Oleynik. M.: Chemistry, 1976. p.174.

[3] Koenig J.L., Spectroscopy of Polymers, Elsevier, 1999.

[4] Koenig J.L., Infrared and Raman spectroscopy of polymers, Smithers Rapra Publishing, 2001.

[5] Peter Wilhelm, Modern Polymer Spectroscopy, John Wiley & Sons, 2009.

[6] Krishtal, MM Scanning electron microscopy and microanalysis in the examples of practical application / MM Krishtal, IS Yasnikov, VI Polunin et al. M.: Technosphere, 2009. 208 p.

[7] Bryk MT Destruction of filled polymers. M.: Chemistry, 1989. 192 p. 2. Nikitin MK, Melnikova EP Chemistry of restoration. L.: Chemistry, 1990. 304 p.

[8] Kumar, M.N. V.R.; Muzzarelli, R.A.; Muzzarelli C.; Sashiwa, H.; Domb, A. J., Chemical Reviews, 104, 12, (2004), 6017–6084.

[9] Appelhans D., Ferse D., H. Adler J. P., Plieth W., Fikus A., Grundke K., Schmitt F. J., Bayer T., Adolphi B., Colloids and Surfaces // New York. 2000. P.161-203.

[10] Wu S., Polymer Interface and Adhesion // New York: Marcel Dekker Inc.1982. P. 130.

[11] Mittal K.L. and Lee K.W. Polymer Surfaces and Interfaces–Netherlands: Characterization, Modification and Application // CRC Press, Utrecht. 1997. P. 120.

[12] Huang F.L., Wang Q.Q., Wei Q.F., Gao W.D., Shou H.Y.,and Jiang S.D., Dynamic wettability and contact angles of poly(vinylidene fluoride) nanofiber membranes grafted with acrylic acid // Express Polymer Letters. 2011. Vol. 4. №9. P. 551-558.

[13] Dzhakipbekova N.O., Eshenko L.S., Isayeva A.N., Dzhakipbekov E.O., Issa A.B. Physical-chemical and colloidmechanical methods of research of modified polymer reagents of THE M-PAA series and their application for obtaining of ointment // News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology. 2019. Vol. 2(434), P. 44-49.

NEWS
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.19**
Volume 2, Number 440 (2020), 23 – 30

UDC 661.724.4

N. Fayzullayev[1], K. Akmalaiuly[2], A. Karjavov[3]

[1]Samarkand State University, Samarkand, Uzbekistan;
[2]Satbayev University, Almaty, Kazakhstan;
[3]Tashkent Chemical-Technological Research Institute, Tashkent, Uzbekistan.
E-mail: kakmalaev@mail.ru; fayzullayev72@inbox.ru; asadjon2515@mail.ru

CATALYTIC SYNTHESIS OF A LINE BY ACETYLENE HYDRATION

Abstract. Acetone is a valuable chemical product. It can be obtained by oxidative dehydrogenation of isopropyl alcohol, oxidation of propylene, decomposition of acetic acid and ethyl alcohol, oxidation of cymene and others. Among the known processes for the production of acetone, the most promising is the synthesis by hydration of acetylene in the presence of catalysts. The advantage of this method is the possibility of carrying out the process in existing plants for the production of acetic aldehyde. On the other hand, the process of simultaneously producing acetaldehyde and acetone under the influence of multifunctional catalysts and carrying out the process using flexible technology is promising. The vapor-phase hydration of acetylene with the formation of acetone on polyfunctional catalysts was studied. Process parameters are found that provide acetone with high selectivity and acetylene conversion. At present, acetic aldehyde is mainly obtained by two methods - hydration of acetylene and oxidation of ethylene. The process of hydration of acetylene to acetic aldehyde in the presence of catalysts has been studied quite well. Numerous catalysts have been proposed for this process. Among the known catalysts for hydration of acetylene to acetic aldehyde, the most active was the cadmium calcium phosphate catalyst (CCF), which is recommended for industrial use. However, cadmium calcium phosphate catalyst is not without drawbacks. The average yield of acetaldehyde in one pass of acetylene does not exceed 7.0%. The CCF catalyst is very sensitive to temperature changes, its service life before regeneration does not exceed 72-76 hours.

Keywords: acetone, propylene, hydration process, catalyst, crosslinking, multifunctional properties.

Introduction. Acetylene hydration in the presence of a catalyst can be carried out in order to obtain aceton. The advantage of this method is the possibility of carrying out the process in existing plants for the production of acetic aldehyde. Replacing cadmium calcium phosphate catalyst with a zinc-containing catalyst allows obtaining acetone with a good yield with minor changes in technology [1-5]. Recently, the sol-gel method has been intensively used for the synthesis of inorganic and oregano-inorganic matrices at low temperatures.

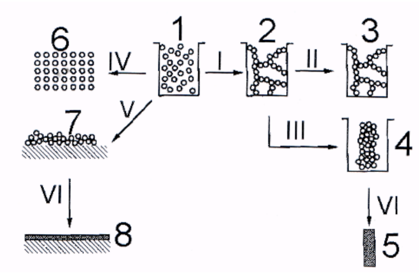


Figure 1 - General scheme for the production of nano catalysts by the sol-gel technology

This method has a number of advantages: the simplicity of the equipment used, efficiency, environmental safety, low cost, adaptability of technology and others. Figure 1 shows the general scheme for the preparation of Nano catalysts by the sol-gel technology.

The main processes that occur in the sol-gel transition and the products that can be obtained by the sol-gel method are shown in figure 1. I-maturing of the sol and gel formation: sol (1) → gel (2); II-drying under super critical conditions or washing the gel with solvents: gel (2) → airgel (3); III-drying under normal conditions: gel (2) → xerogel (4); IV-deposition of nano particles: sol (1) → powder (6); V-absorption of a sol by a rod substance: sol (1) → a thin layer xerogel (7); VI - tempering (cooking): xerogel (4) or a thin layer of xerogel (7) → monolithic glass and ceramics (5) or a thin layer and shell. Nano catalysts exhibit high catalytic activity, selectivity, as well as stability (stability).

Firstly, with decreasing particle sizes, most of the atoms are located on the surface; therefore, a catalyst consisting of nano particles has a large surface and becomes very active in heterogeneous reactions.

Secondly, most of the properties of nano particles are related to their size (size efficiency), therefore, by changing the size of nano particles one can control not only activity, but also selectivity. With a decrease in the particle size of the catalyst, the reaction rate sharply increases.

Based on the foregoing, it follows that the study of the possibility of using nano-catalysts obtained on the basis of metals Zn, Mn, Fe, V and other elements with multifunctional properties for the hydration reaction of acetylene and its derivatives is an urgent task [6-9].

Methods. The experiments on the catalytic hydration of acetylene and its derivatives in the gas phase were carried out in a reactor with a diameter of 25 mm, a height of 1000 mm, made of stainless steel under stationary conditions. The qualitative and quantitative composition of the reaction products was studied by gas-liquid chromatography under the following conditions: stationary phase 15% Apiezon-M in Color chromium, column thermostat temperature 80 0C, carrier gas flow rate helium 60 cm^3/min., DIP detector. Quantitative analysis was carried out using the internal standards method.

The specific surface area, crushing strength, total pore volume and ash content of the samples were determined.

The specific surface area was determined by thermal desorption of nitrogen in a carrier gas flow - helium at the boiling point of liquid nitrogen, the experimental data were processed using the BET equation [10-13].

The mechanical strength of the granules for crushing was measured on a device “Durably measures PK-1”, designed to test granular materials for mechanical strength under static conditions by compression. The arithmetic average of 25 individual tests was taken as the result of the analysis.

The total pore volume of the granules was calculated by the formula:

$$V = \frac{1}{p_k} - \frac{1}{p_n}$$

where, pk, pn are the apparent and psychometric density of the granules, g/ml, respectively.

The apparent density of the granules was determined by measuring their volume without taking into account the internal pores. The volume of the granules was found by immersing them in solid powder (silica sand with a particle size of 0.063-1.1 mm).

The phase composition of the samples was determined by x-ray diffractometry, the survey was carried out on a DRON-3M diffract meter using CuKα radiation with a Ni filter, and the length of the x-ray radiation.

The specific surface area of the obtained catalyst was calculated by the BET method, the average mesopore size by the VUA method. The dispersed properties of the catalyst were studied using a scanning electron microscope (JSM-6510 LV). The catalytic activity of the obtained sample was studied on the hydration reaction of acetylene [14-17].

Acetaldehyde and acetone were synthesized as follows. Acetylene was saturated with water at a temperature of 70-80 ^{0}C and at a ratio of water: acetylene = (1: 3) - (1: 5) moll was passed through a catalyst bed at 360 ^{0}C with a space velocity of 180-200 h-1.

The gas-vapor mixture leaving the reactor was cooled in the refrigerator. The reaction products were captured in water. Catalysis contains acetaldehyde, acetone, cretonne aldehyde, steam aldehyde and others. In order to maintain the degree of acetylene conversion not lower than 80%, every 20 hours the reaction temperature was raised by 10 ^{0}C. After 96-120 hours, the degree of conversion of acetylene is reduced to 75-70%. Then the reaction was stopped and the catalyst was regenerated in a known manner [18-21].

Further, the effect of various parameters (temperature, space velocity, acetylene-water ratio) on the conversion of acetylene and the yield of acetone was studied.

Results. Because of studying the effect of temperature on the acetone yield, it was found that in the temperature range 360-500 ^{0}C the dependence between the reaction yield, temperature is extreme, and at 450 ^{0}C, the yield was considered maximal.

Based on the results on the qualitative and quantitative composition of the reaction products on this catalyst, we propose the following acetone formation mechanism:

In the reaction of acetone formation, acetaldehyde is first formed then 3-hydroxybutanal is formed as a result of aldol condensation.

$$CH{\equiv}CH + H_2O \rightarrow CH_3CHO,$$

$$2CH_3CHO \rightarrow CH_3CHOHCH_2CHO.$$

Upon hydration of 3-hydroxybutanal, a dihydric alcohol is formed and upon further dehydrogenation, acetoacetic acid is formed:

$$CH_3CHOHCH_2CHO + H_2O \rightarrow CH_3CHOHCH_2CH(OH)_2$$

$$CH_3CHOHCH_2CH(OH)_2 \rightarrow CH_3COCH_2COOH + 2H_2$$

In turn, acetoacetic acid under these conditions is decarboxylase and acetone is formed.

$$CH_3COCH_2COOH \rightarrow CH_3COCH_3 + CO_2$$

We have proposed a technological scheme for producing acetaldehyde, acetone (or a mixture thereof) is shown in figure 2.

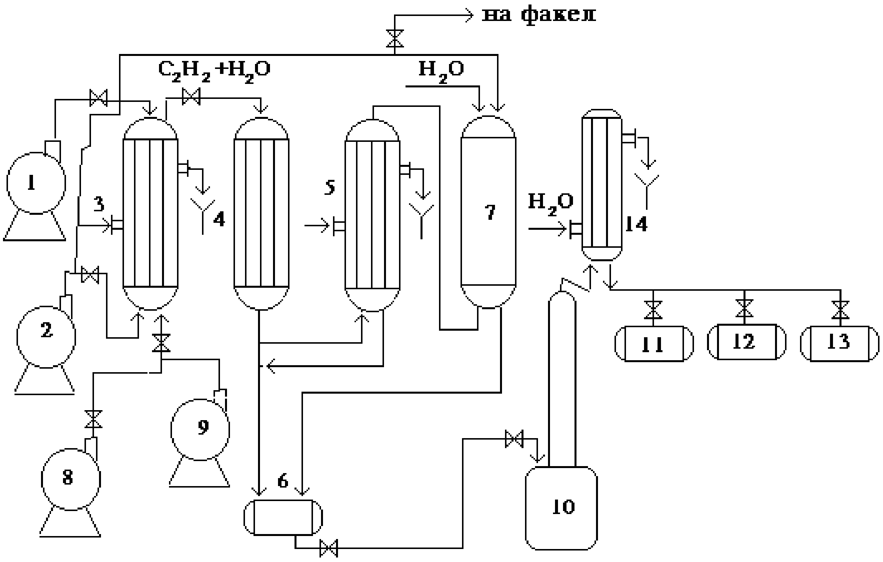


Figure 2 - Technological scheme of hydration of acetylene:
1-pump; 2-acetylene gas holder; 3-heat exchanger; 4-reactor; 5-heat exchanger; 6-capacity for catalysis; 7-absorption column; 8-blower; 9-gas holder for nitrogen; 10-distillation column; 11-container for acetaldehyde; 12-capacity for acetone; 13-tank for bottoms; 14-heat exchanger

We have studied the process of catalytic vapor-phase hydration of acetylene and its derivatives in the presence of complex mixed polyfunctional catalysts. In the process of producing acetaldehyde, cadmium fluoride on alumina promoted by aluminum fluoride was used as a catalyst. In the synthesis of acetone, zinc oxide supported on alumina, promoted with cadmium fluoride and aluminum, of the following composition, % weight: ZnO-20.0-25.0 was used as a catalyst; CoF_2-3.0-5.0; $A1F_3$-3.0-5.0; Al_2O_3-60.0-84.0.

The composition and properties of the synthesized catalysts for the synthesis of acetaldehyde and acetone are shown in table 1.

Table 1 - The composition and properties of the synthesized catalysts

№	Composition, mass %	Legend	Specific surface, m^2/g	Operating time before regeneration, hour	The yield of the target product, %	
					acetaldehyde	acetone
1	ZnO-20.0; AlF_3– 3.0 Al_2O_3 -77.0	ЦХ-1	135,0	72,0	10,0	82,0
2	CdF_2 – 20.0 Al_2O_3 – 80.0	КА-1	186,0	96,0	75,0	5,0
3	CdF_2 -18.0; AlF_3-3.0 Al_2O_3 – 79.0	КА-2	210,0	96,0	82,0	3,0
4	CdF_2-18.0; AlF_3-2.0 Cr_2O_3-5.0; Al_2O_3-75.0	КХА-1	225,0	120,0	83,0	1,5
5	ZnO-18.0; CdF_2-2.0 Cr_2O_3-5.0; Al_2O_3-80.0	ЦКХА-1	165,0	120,0	3,0	86,0

As can be seen from the table, catalyst No. 5 stably works for 120 hours (if the temperature rises by 100 ^{0}C every 20 hours), ensuring the degree of conversion of acetylene at the level of 91-95% and the yield of acetone is 86.0%.

The following is the dependence of the degree of conversion, the stability of the catalyst (catalyst No. 5) and the yield of the target product on the ratio of water: acetylene (table 2).

From the presented data, it follows that with an increase in the water: acetylene ratio, a gradual increase in the stability and selectivity of the catalyst, yield of the target product, and acetylene conversion are observed.

Table 2 - The dependence of the degree of conversion, the stability of the catalyst
and the yield of the target product on the ratio of water: acetylene

The ratio of water: acetylene, mol	The average mileage of the catalyst before regeneration	The yield of the target product, on the reacted acetylene, %		Acetylene conversion, %
		acetaldehyde	acetone	
1	32,0	4,6	55,0	70,2
2	54,0	3,4	66,0	80,4
3	96,0	2,2	76,0	86,0
4	125	1,5	80,0	91,0
5	144	1,2	82,0	95,0
6	132	1,1	76,0	94,0

We also studied the effect of temperature, space velocity, the ratio of methyl acetylene-allen fraction: water and others on the yield of acetone. Under optimal conditions, acetone was obtained with a yield of 86.0% upon conversion of the methyl acetylene-allene fraction 92.0-94.0%.

The hydration reaction of acetylene to acetaldehyde was carried out in the presence of cadmium chromium aluminum catalyst - KHA in the temperature range 360-460 ^{0}C.

The effect of the ratio of acetylene: water on the selectivity of acetaldehyde formation in the range of acetylene: water = 1: 1-6 mol was studied. Moreover, it was found that in the range of the ratio of acetylene: water = 1: 1-1: 3, an increase in the proportion of side products is observed.

The yield of acetaldehyde does not exceed 26.0% of the reacted acetylene. At a ratio of -1: 4-1: 6, the yield of acetaldehyde and the conversion of acetylene reaches a maximum. A further increase in the ratio of acetylene water has no significant effect.

It was experimentally established that the yield of acetaldehyde and the conversion of acetylene substantially depends on the space velocity of acetylene.

The effect of the space velocity of acetylene on the acetaldehyde yield and its conversion was studied in the range of the space velocity from 50 to 120 hours (figure 3).

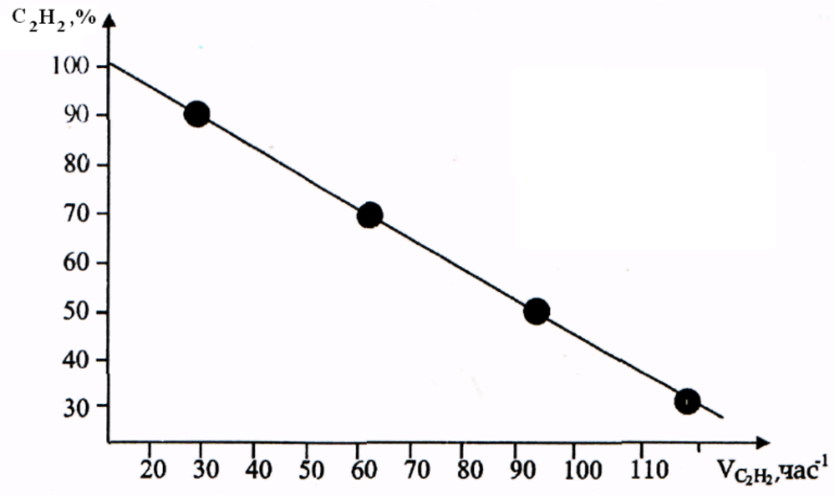


Figure 3 - The effect of the space velocity of acetylene on its conversion

The effect of temperature, grain size of the catalyst, reactor parameters, and catalyst bed height on the process parameters was studied. It was found that the reaction for the synthesis of acetaldehyde begins at 350 ^{0}C. In order to maintain the acetylene conversion at a level of 70-75%, the temperature of the reactor was raised by 10 ^{0}C every 10 hours. It was found that the optimum ratio of the height of the catalyst layer to the diameter of the reactor equal to 50-60, the space velocity of acetylene is 50-60 hours Under these conditions, the KXA-1 catalyst with constant activity lasts up to 120 hours and during regeneration within 16-24 hours completely restores its activity.

Replacing cadmium chromium aluminum catalyst with zinc alumina fluoride or zinc cadmium chromium aluminum catalyst leads to the formation of acetone as the main product in the process of hydration of acetylene.

In order to establish technological parameters of the process for producing acetone by direct hydration of acetylene, we studied the effect of space velocity, temperature, the ratio of acetylene: water and others on the yield of acetone,

The effect of temperature was studied in the range of 250-500 ^{0}C in the presence of CCA-1 catalyst, with a ratio of acetylene water = 1: 4 moll, with a space velocity of acetylene of 80 hours1 (table 3).

Table 3 - The effect of temperature on the conversion of acetylene

Temperature, ^{0}C	Acetone yield on reacted acetylene, %	Acetylene conversion, %
250	15,2	18,0
300	20,6	26,0
325	33,4	34,0
350	63,0	62,0
375	70,6	80,0
400	82,0	84,0
425	84,0	90,0
450	65,0	94,0
500	52,0	98,0

As can be seen from the table, TsKKA-1 catalyst is inefficient up to 350 ^{0}C. Starting from 350 ^{0}C to 425 ^{0}C, there is a gradual increase in acetone yield and acetylene conversion. A further increase in temperature leads to a significant decrease in the yield of acetone due to the flow of side products.

Conclusion. The reactions of acetone synthesis were studied by direct hydration of acetylene on catalysts prepared from oxides and fluorides of zinc, cadmium, iron, chromium and aluminum, using a solution of acetic acid as a peptizing agent. The main texture and operational characteristics of the synthesized catalysts are determined.

Based on the study of the dependence of the degree of conversion, the stability of the catalyst and the yield of the target product on the water: acetylene ratio, it was revealed that catalyst No. 5 worked stably for 125-144 hours (provided that the temperature rose by 100 ^{0}C every 20 hours), ensuring the degree of conversion of acetylene at the level of 91-95% and the yield of acetone - 90-92%.

A technological scheme for producing acetaldehyde, acetone by catalytic hydration of acetylene is proposed.

Н. Файзуллаев[1], К. Акмалайұлы[1], А. Каржавов[3]

[1]Самарқанд мемлекеттік университеті, Узбекистан;
[2]Satbayev Unibersity, Алматы, Қазақстан;
[3]Ташкент химия-технологиялық ғылыми-зерттеу институты, Узбекистан

АЦЕТОН ЛИНИЯСЫНЫҢ КАТЕТИКАЛЫҚ СИНТЕЗІ

Аннотация. Ацетон – маңызды химиялық өнім. Оны изопропил спиртін тотығу арқылы дегидрлеу, пропиленнің тотығуы, сірке қышқылы мен этил спиртінің ыдырауы, куменнің тотығуы және басқалары арқылы алуға болады.

Ацетон өндірудің белгілі процестерінің ішінде катализаторлардың қатысуымен ацетиленнің гидратациясы арқылы синтездеу перспективалы сипатта болып келеді. Бұл әдістің артықшылығы қолданыстағы өсімдіктерде сірке альдегидін өндіру процесін жүргізу мүмкіндігімен байланысты. Екінші жағынан, көпфункционалды катализаторлардың әсерінен ацетальдегид пен ацетонды бір уақытта өндіру және икемді технологияны қолдану арқылы процесті жүргізу перспективалы сипатта болып келеді.

Ацетиленнің көпфункционалды катализаторларда түзілуімен бу фазалы гидратациясы зерттелді. Процесс параметрлері ацетонды жоғары селективтілікпен және ацетилен түрлендірумен қамтамасыз етеді.

Қазіргі уақытта сірке альдегиді негізінен екі әдіспен шығарылады: ацетиленнің гидратациясы және этиленнің тотығуы.

Катализаторлардың қатысуымен ацетиленді сірке альдегидіне дейін ылғалдандыру процесі жақсы зерттелген. Бұл процесс үшін көптеген катализаторлар ұсынылды. Ацетиленді сірке альдегидіне дейін ылғалдандыруға арналған белгілі катализаторлардың ішінде өнеркәсіптік қолдануға ұсынылған кадмий-кальций фосфатының катализаторы (CCF) белсенді болды. Алайда кадмий кальций фосфатының катализаторы кемшіліктерсіз болмайды. Ацетиленнің бір жолындағы ацетальдегидтің орташа шығымдылығы 7,0 %-дан аспайды. CCF катализаторы температураның өзгеруіне өте сезімтал, оны қалпына келтіруге дейінгі қызмет мерзімі 72-76 сағаттан аспайды.

Катализатордың қатысуымен ацетилен гидратациясын ацетон алу үшін жүргізуге болады. Бұл әдістің артықшылығы – қолданыстағы өсімдіктерде сірке альдегидін өндіру процесін жүргізу мүмкіндігінде. Кадмий-кальций фосфатының катализаторын цинк бар катализатормен алмастыру технологиядағы аздаған өзгерістермен жақсы шығымды ацетон алуға мүмкіндік береді.

Жақында бейорганикалық және органикалық-бейорганикалық матрицаларды төмен температурада синтездеу үшін сол-гель әдісі қарқынды қолданыла бастады. Бұл әдіс бірқатар артықшылықтарға ие: қолданылатын жабдықтың қарапайымдылығы, үнемділік, экологиялық қауіпсіздік, арзан баға, технологиялардың бейімділігі және басқалары.

Н. Файзуллаев[1], К. Акмалайұлы[1], Б. Каржавов[3]

[1]Самаркандский государственный университет, Узбекистан;
[2]Satbayev Unibersity, Алматы, Казахстан;
[3]Ташкентский химико-технологический институт, Узбекистан

КАТАЛИТИЧЕСКИЙ СИНТЕЗ ЛИНИИ ГИДРАТАЦИЕЙ АЦЕТИЛЕНА

Аннотация. Ацетон является ценным продуктом химической промышленности. Он может быть получен окислительным дегидрированием изопропилового спирта, окислением пропилена, разложением уксусной кислоты и этилового спирта, окислением кумола и др.

Среди известных процессов производства ацетона наиболее перспективным является синтез гидратацией ацетилена в присутствии катализаторов. Преимуществом данного метода является возможность проведения процесса в существующих установках производства уксусного альдегида. С другой стороны,

многообещающим является процесс одновременного получения ацетальдегида и ацетона под действием полифункциональных катализаторов и проведение процесса по гибкой технологии.

Изучена парофазная гидратация ацетилена с образованием ацетона на полифункциональных катализаторах. Найдены параметры процесса, обеспечивающие получение ацетона с высокой селективностью и конверсией ацетилена.

В настоящее время уксусный альдегид в основном получают двумя методами - гидратацией ацетилена и окислением этилена.

Процесс гидратации ацетилена до уксусного альдегида в присутствии катализаторов изучен достаточно хорошо. Для этого процесса предложены многочисленные катализаторы. Среди известных катализаторов гидратации ацетилена до уксусного альдегида наиболее активным оказался кадмийкальций-фосфатный катализатор (ККФ), который рекомендован для промышленного применения. Однако кадмийкальцийфосфатный катализатор не лишен недостатков. Средний выход ацетальдегида за один проход ацетилена не превышает 7,0 %. ККФ катализатор очень чувствителен к изменению температуры, его срок службы до регенерации не превышает 72-76 часов.

Гидратация ацетилена в присутствии катализатора может быть проведена с целью получения ацетона. Достоинством данного метода является возможность проведения процесса в существующих установках производства уксусного альдегида. Замена кадмийкальцийфосфатного катализатора на цинксодержащий катализатор позволяет получить ацетон с хорошим выходом при незначительных изменениях в технологии.

В последнее время золь-гель метод интенсивно используется для синтезирования неорганических и органо-неорганических матриц при низких температурах. Этот метод обладает целым рядом преимуществ: простотой используемого оборудования приборов, экономичностью, экологической безопасностью, низкой себестоимостью, приспособляемостью технологий и другие. На Рис.1 приведена общая схема получения нанокатализаторов методом золь-гель технологии.

Information about authors:

Fayzullayev N., professor, Samarkand State University, Samarkand, Uzbekistan; fayzullayev72@inbox.ru; http://orcid.org/0000-0001-5838-3743

Akmalaiuly K., doctor of technical sciences, professor, Satpayev University, Almaty, Kazakhstan; kakmalaev@mail.ru; https://orcid.org/0000-0002-9796-8813

Karjavov A., Tashkent Chemical-Technological Research Institute, Tashkent, Uzbekistan; fayzullayev72@inbox.ru

REFERENCES

[1] Fayzullaev N.I., Yusupov D., Umirzakov R.R. Catalytic synthesis of acetone by direct hydration of acetylene // Uzbekistan kimyo magazines. (2001). N5. P. 68-71.

[2] Fayzullaev N.I., Yusupov D., Umirzakov R.R. Acetone VA acetaldehyde birhalikda catalyst synthesis // Composition materiallar journals. (2002). N4. 7-8 betlar.

[3] Fayzullaev NI, Yusupov D., Shirinov X. Sh., Korotoev A.V., Umirzakov R.R. Catalytic vapor-phase hydration of acetylene and its derivatives // Chemical Industry. (2002). N7. S. 1-33.

[4] Fayzullaev N.I., Yusupov D., Mirkomilov T. M. // Dokl.akad.nauk. Rep. Uzbekistan. (2002). №5. 47-50.

[5] Fayzullaev N.I., Yusupov D., Umirzakov R.R. Catalytic synthesis of acetone by direct hydration of acetylene // Uzbekistan kimyo magazines. (2001). N5. P. 68-71.

[6] Fayzullayev N. I. Optimization process of synthesis of acetone from acetylene // 224th ACS national meeting, Boston, MA August 18-22. (2002). P.80.

[7] Fayzullayev N.I., Umirzakov R.R. Kinetics and mechanism of hydratation of acetylene // Turkey. Kars, 06. (2004)

[8] Fayzullaev N.I., Turabzhonov S.M., Korotoev A.V.. Catalytic vapor-phase hydration of acetylene // Technique of fanlary VA XXI ASR global muammolari. Res.Mikoshidagi Professor-Kituvchilarning ilmiy amaliy konferentsi. Marusular tўplami, 4-қism. Tashkent: Tash DTI, (2001). 24-25 betlar.

[9] Tangyarikov N.S., Musulmanov N. Kh., Turobzhonov S.M., Ikramov A., Prokofiev V.Yu. Catalytic hydration of acetylene and its derivatives. Moscow, Lenand, (2014).150 P.

[10]Turabzhanov S.M., Tangyarikov N.S., Yusupov D., Ikramov A., Yusupov B.D. Development and study of the properties of new catalysts for the synthesis of acetaldehyde.// Vestnik TSTU. Tashkent, (2006). No. 3. P.114-118. (02.00.00.№11).

[11]Musulmonov N.Kh., Ikromov A., Tangyarikov N.S. Technology for producing cadmium zinc catalysts and their x-ray phase and derivatographic analysis. // Kimyovy technology. Nazorat WA bosharuv // Ilmiy technician magazine. (2010). No. 3. P. 9-12. (02.00.00.№10).

[12]Zhurinov M.Zh., Kassymbekov Zh.K, Kassymbekov G.Zh. Mastering and development hydropower in Kazakhstan // Of the national academy of sciences of the republic of Kazakhstan series of geology and technical sciences, (2019),Volume 3, Number 435 219 – 224 https://doi.org/10.32014/2019.2518-170X.88

[13]Tangyarikov N.S. Catalytic vapor-phase hydration of acetylene. // Scientific and technical journal. Chemistry and chemical technology // Ivanovo, (2010) Volume 53 Issue 5, P.56-58. (02.00.00.№24).

[14]Tangyarikov N.S., Turabzhanov S.M., Ikramov A., Musulmanov N.Kh. Mathematical description of the reactor for the synthesis of acetaldehyde and acetone. // Scientific and technical journal. Chemistry and chemical technology // Ivanovo, (2015) Volume 58 Issue 9, P.68-69. (02.00.00.№24).

[15]Turabzhanov S.M., Kadirov H.I., Ikramov A., Gafurov B.B. Heterogeneous composite catalysts for acetone synthesis // International Conference. -Tashkent. (2013). P 108-109.

[16]Turabzhonov S.M., Ikramov A., Kadirov H.I., Ruziev D.U., Gafurov B.B. Some aspects of the selection of catalysts for heterogeneous addition of HX molecules to acetylene // International Conference. Tashkent. (2013). P. 29-30.

[17][Ikramov A., Khalikova S., Khamdamov D.A., Dushanov O.J. Joint production of acetone, acetaldehyde and acetic acid // Materials of the international scientific-practical conference. Buhara. (2015). P. 21-23.

[18]Ikramov A., Mukhitdinov B.F., Ten A.V., Halikova S.D., Ruziev D.U., Dushanov O.J. Bentonite-based catalysts for acetylene hydration. // Materials of the VIII-th International Scientific and Technical Conference. Navoi, (2015). 316 p.

[19]Massenova A.T., Kalykberdiyev M.K., Sass A.S., Kenzin N.R., Abilmagzhanov A.Z., Kanatbayev E.T., Kassenova D.S. // CATALYTIC HYDRODEAROMATIZATION OF MOTOR FUELS AS A METHOD OF PRODUCING ECO-FRIENDLY FUELS, (2019), Volume 5, Number 437 (2019), 37–45. https://doi.org/10.32014/2019.2518-1491.51

[20]Ikramov A., Tangyarikov N.S., Kadirov H.I., Ruziev D.U.,. Saidov Sh.A, Khakimova G.R. Catalytic vapor-phase hydrate of acetylene and its derivatives // Materials of the VIII-International scientific and technical conference. Navoi. (2015). P. 320-3321.

[21]Ikromov A., Musulmanov N.Kh., Tangyarikov N.S., Turabzhanov S.M., Mathematical description of the synthesis reactor of acetaldehyde and acetone // Chemistry and Chemical Technology. Izv. Universities, (2015), Vol. 58, No. 9. S.68-69.

[22]Temkin O.N. Chemistry of acetylene "Acetylene tree" in organic chemistry of the XXI century //. Soros educational journal. (2001). №6. P. 32-41.

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.20**
Volume 2, Number 440 (2020), 31 – 38

UDC 541.13:546.5
IRSTI 31.15.33

A.B. Bayeshov[1], E.Zh. Tuleshova[2], A.K. Baeshova[3], M.A. Ozler[4]

[1]Institute of Fuel, Catalysis and Electrochemistry named after D. V. Sokolsky, Almaty, Kazakhstan;
[2]Khoja Akhmet Yessevi Kazakh-Turkish University, Turkestan, Kazakhstan;
[3]Al-Farabi National University, Almaty, Kazakhstan;
[4]Mugla Sitki Kocman University, Mugla, Turkey.
E-mail: bayeshov@mail.ru, elmira.tuleshova@ayu.edu.kz, azhar_b@bk.ru, aozler@mu.edu.tr

ELECTROCHEMICAL BEHAVIOR OF SILVER IN A POTASSIUM FERROCYANIDE SOLUTION

Abstract. One of the main priorities of the innovative industrialization of the country is the development of metallurgy and the production of finished products. In this regard, the application of new methods for producing metals and their compounds or extracting them from solutions is an important task of our time. One of the promising methods applied currently is the polarization by alternating current of industrial frequency, which arouses the interest of researchers both from the point of view of oxidation and destruction of the passivating film. The peculiarity of the processes occurring under the action of industrial alternating current is that, by changing the direction of the current, it is possible to remove the oxide film and create conditions for the metal to further dissolve.

The work shows the distinctive features of electrochemical processes occurring on a silver electrode during electrolysis by industrial alternating current in a solution of ferrosyne-sintered potassium by the method of rational mathematical planning. The optimal conditions for the dissolution of silver are determined by studying the effect of current density at the electrodes, the concentration and temperature of the electrolyte, the duration of the electrolysis and the frequency of the alternating current. It is shown that when polarized with an alternating current of silver in a pair with a titanium electrode, the passivation process of the silver electrode is eliminated and the dissolution rate of the metal increases.

Keywords: alternating current, silver, electrode, electrolysis, closeness of current, current output.

Recently in electrochemical researches special attention is paid to the processes proceeding with an electrode involvement by superimposed a. c. technique [1-7].

Use of the nonstationary mode of electrolyzing expands the possibilities of a research of the mechanism of the cathode and anode processes, opens essentially new opportunities of using them for the solution of different technological questions.

Electrochemical processes are used to solve various topical issues in the field of production. Rather than direct current, alternating current allows to create simple, yet rational technological processes [8].

In the works [9-13] is provided this to polarization of a silver electrode by an industrial alternating current with a frequency of 50 Hz. It was set that in sulfate solution silver is dissolved with a high efficiency in case of low current densities, and in solution of hydrochloric acid the efficiency of dilution of silver makes only 10,4%.

It is necessary to mark that the detail researches carried out by us on a silver electrode and other researchers studying titanium, chrome, molybdenum, lead, etc. in case of polarization by an alternating current of industrial frequency, showed that the electrode processes proceeding with an electrode involvement by superimposed a. c. technique, sharply differ both on the mechanism, and according to the quantitative characteristics [14-17].

Electrochemical processes involving noble metals are interesting, especially silver, in connection with the increasing need for it in various branches of technology and industry. The most valuable properties of silver are its high electrical conductivity, reflectivity and beautiful decorative appearance of polished sediments. Silver plating is widely used in electronics, electrical engineering and other industries to improve surface conductivity and minimize transition resistance at the points of contact, as well as to impart optical properties to the surface of a product. Technical-economic and quality indicators of the silvering process depend on the nature and composition of the electrolyte. Cyanide solutions are the most widespread ones, but they are toxic and dangerous to the environment.

The most common substitute for cyanide silvering electrolytes is a solution of ferrous sulphide potassium. This is explained by the fact that it is less toxic than cyanide electrolyte, cheaper than iodide and sulphite, and, according to [18,19], it has the best scattering ability. In this regard, it is interesting to question of the behavior of silver in a ferrosynetosuronic solution during polarization with industrial alternating current and the possibility of the formation of the corresponding complex compound of silver.

Systemic studies, which allow to establish the laws of the silver electro-oxidation with the subsequent synthesis of its compounds, can lead to both the intensification of its production and the solution of resource-saving problems.

In this regard, the study of the processes of silver ionization discharge under the action of industrial alternating current seems relevant and timely.

The purpose of this work is to study the electrochemical behavior of silver during the polarization of unsteady currents in a solution of ferrocyanide syngas potassium.

To study the electrochemical behavior of silver in a potassium ferrocyanide syrup solution, the main experiments were carried out in a 100 ml cell. A titanium wire and a silver plate were used as electrodes.

Electrodes before experiments were thoroughly cleaned, degreased and washed with distilled water.

Results and discussion

The study of the electrochemical behavior of silver in a neutral medium was carried out by the method of rational mathematical planning [20]. In accordance with the planning for the six factors, and in each factor of five levels 25 experiments were conducted. The studied factors and their levels are presented in table 1.

Table 1 – Levels of factors under study

Factor	Level				
	1	2	3	4	5
X_1, current density on the silver electrode, A/m^2	200	400	600	800	1000
X_2, current density on the titanium electrode, kA / m^2	20	40	60	80	100
X_3, solution concentration, M	0,5	1,0	1,5	2,0	2,5
X_4, duration of electrolysis, min	15	30	45	60	75
X_5, electrolyte temperature, ° C	20	30	40	50	60
X_6, frequency of alternating current, Hz	50	100	150	200	250

The experiments results after mathematical processing are shown in Table 2, in which Y_1,Y_2, etc. - particular functions, respectively, of factors X_1, X_2, etc.

Based on table 2, the graphs were plotted (figure 1). To describe point data, it is necessary to choose the right empirical formulas. The dependence $Y_1=f(X_1)$ is described by the equation of a straight line. The equation of a line is:

$$Y_1 = aX \qquad (1)$$

Table 2 – Experimental values of private functions.

Function	Level					Average value
	1	2	3	4	5	
Y_1	70,6	73,7	61,5	55,2	49,0	62
Y_2	52,5	65,5	70,6	63,2	58,3	62
Y_3	73,7	64,5	60,2	54,1	46,65	62
Y_4	73,7	68,5	63,3	55,8	49,4	62
Y_5	73,7	67,8	60,8	56,4	51,3	62
Y_6	73,7	68,6	59,7	55,6	52,5	62

It can be considered that the straight line drawn on the graph goes out from some point, taken arbitrarily on the left side of the straight line, with coordinates X_1, Y_1. The offset of the origin to this point is fixed as follows:

$$Y - Y_1 = a\,(X - X_1) \tag{2}$$

Selecting on the right side of the line any point with coordinates X_2, Y_2 and substituting them into this equation, we get:

$$Y_2 - Y_1 = a\,(X_2 - X_1) \tag{3}$$

After the final transformation, the equation has the form:

$$Y = Y_1 + \frac{Y_2 - Y_1}{X_2 - X_1}(X - X_1) \tag{4}$$

Some graphs have the form of a parabola, we enter the extremum values into the parabola equation. In the parabola equation ($Y = aX^2$), we enter the values X_1, $Y_1$with the offset of the origin:

$$Y = Y_1 - a\,(X - X_1)^2 \tag{5}$$

Then we select the second point with coordinates X_2, Y_2 approximately in the middle of the section of the branch passing through the experimental points, and substitute all four numbers into the final equation:

$$Y = Y_1 + \frac{Y_2 - Y_1}{(X_2 - X_1)^2}(X - X_1)^2 \tag{6}$$

The calculated values at the matrix levels of the arguments are given in table 3.

Table 3 – Calculated values of functions at matrix levels

Function	Level					Average value
	1	2	3	4	5	
$Y_1 = 93\text{-}0{,}018\ (X\text{-}300)$	71,17	74,83	67,60	64,00	60,40	67,60
$Y_2 = 91\text{-}0{,}0037\ (X\text{-}70)^2$	65,00	70,63	71,63	66,67	61,75	67,13
$Y_3 = 91 – 4{,}6666\ (X\text{-}0{,}75)$	72,16	69,83	67,5	65,17	62,83	67,49
$Y_4 = 95 - 0{,}29\ (X\text{-}22{,}5)$	77,17	72,82	68,47	64,12	59,77	68,47
$Y_5 = 92 - 0{,}2666\ (X\text{-}25)$	73,33	70,67	68,01	65,33	62,67	68,00
$Y_6 = 93 - 0{,}0029\ (X\text{-}40)^2$	72,70	72,70	70,39	65,75	58,79	68,06

The significance or insignificance of the function can be established without repeated experiments using the nonlinear multiple correlation coefficient:

$$R = \sqrt{1} - \frac{(N-1)\sum (Y_T - Y_Э)^2}{(N-K-1)\sum (Y_Э - Y_{cp})^2} \tag{7}$$

$$t_R = \frac{R\sqrt{N-K-1}}{1-R^2} \rangle 2$$

where N is the number of points described, K is the number of active factors, $Y_Э$ is the experimental result, Y_T is the theoretical (calculated) result, Y_{cp} is the average experimental value.

The nonlinear multiple correlation coefficient for the 5% level and the value of its significance is $t_R > 2$, which indicates the significance of the functions.

The correlation coefficient and the significance of the corresponding particular functions are listed in table 4. As can be seen, all the considered functions influence the silver dissolution.

To describe the statistical multifactor dependencies, the particular functions generalized M.M.Protodyakonov’s equation [21]:

$$Y_n = \prod_{i=1}^{n} Y_i;$$

$$Y_n = \frac{[93-0{,}018(X_1-300)]\cdot[91-0{,}0037(X_2-70)^2]\cdot[91-4{,}6666(X_3-0{,}75)]}{88{,}85^5\cdot[95-0{,}29(X_4-22{,}5)]\cdot[92-0{,}2666(X_5-25)]\cdot[93-0{,}0029(X_6-40)^2]} \qquad (8)$$

Table 4 – Correlation coefficient R and its significance t_R for particular functions

Function	R	t_R	Function significance
Y_1	0,92	19,08	Significant
Y_2	0,75	2,72	Significant
Y_3	0,88	5,65	Significant
Y_4	0,95	85,64	Significant
Y_5	0,96	14,38	Significant
Y_6	0,94	10,15	Significant

Based on the equation, we find the correlation coefficient for N = 25 and K = 6. It is equal to 0.4956 and the significance is $t_R = 3.02 > 2$, which indicates the adequacy of the generalized equation.

Based on the equation, 8 was determined as the optimal conditions for the electrochemical dissolution of silver: the density on the silver electrode was 200 A/m^2, the density on the titanium electrode was 60 kA/m^2, the electrolyte concentration was 0.5-1.0 mol/l, the electrolyte temperature was 20-40 °C, electrolysis duration - 15-30 minutes, frequency of alternating current - 50 Hz.

As the research results have shown, during the silver polarization by industrial alternating current, silver ions, silver dicyanoferrate are formed.

In the cathode half-period, gaseous hydrogen is released on the titanium electrode and silver ions are reduced. At this point, the silver electrode is in the anodic half-period and dissolves to form silver ions, dicyanoargentate and silver oxide.

With an increase in the current density at the silver electrode, the current output (CO) of silver dissolution decreases (Fig. 1a). This is due to the fact that at high current densities, the proportion of electricity affected by a side process - oxygen evolution - increases compared to the amount of electricity affected by the dissolution process of silver.

The effect of current density on the titanium electrode on the CO dissolution of silver was studied in the range of 20-100 kA/m^2. The maximum CO value is observed at i_{Ti} = 60 kA/m^2 (Fig. 1b).

When studying the electrolytes concentration effect on the results of electrolysis, it was found that the maximum value of the current efficiency is achieved at a concentration of 0.5 mol/l (Fig. 1c).

Studying the effect of the electrolysis duration on the dissolution process of silver during polarization with industrial alternating current showed that with an increase in the electrolysis duration, the current dissolution rate of silver naturally decreases. It should be noted that on the electrode during prolonged experiments the electrode surface is covered with a layer of dark color.

The study results of the temperature effect on the electrically dissolving the silver electrode showed that the behavior of silver in the electrolyte solution under study has a similar character with the above data (Fig. 1e). An increase in temperature adversely affects the electrochemical activity of silver. Apparently, with increasing temperature, electrode processes become more reversible, that is, compounds formed in the anodic half-period can be restored back to the cathode.

Figure 1f shows the dependence of CO dissolution of silver on the alternating current frequency. With an increase in frequency, the W of metal dissolution decreases. The decrease in the electrolytic silver dissolution with increasing frequency of the current, apparently, is due to the decrease in the duration of the anode half-period.

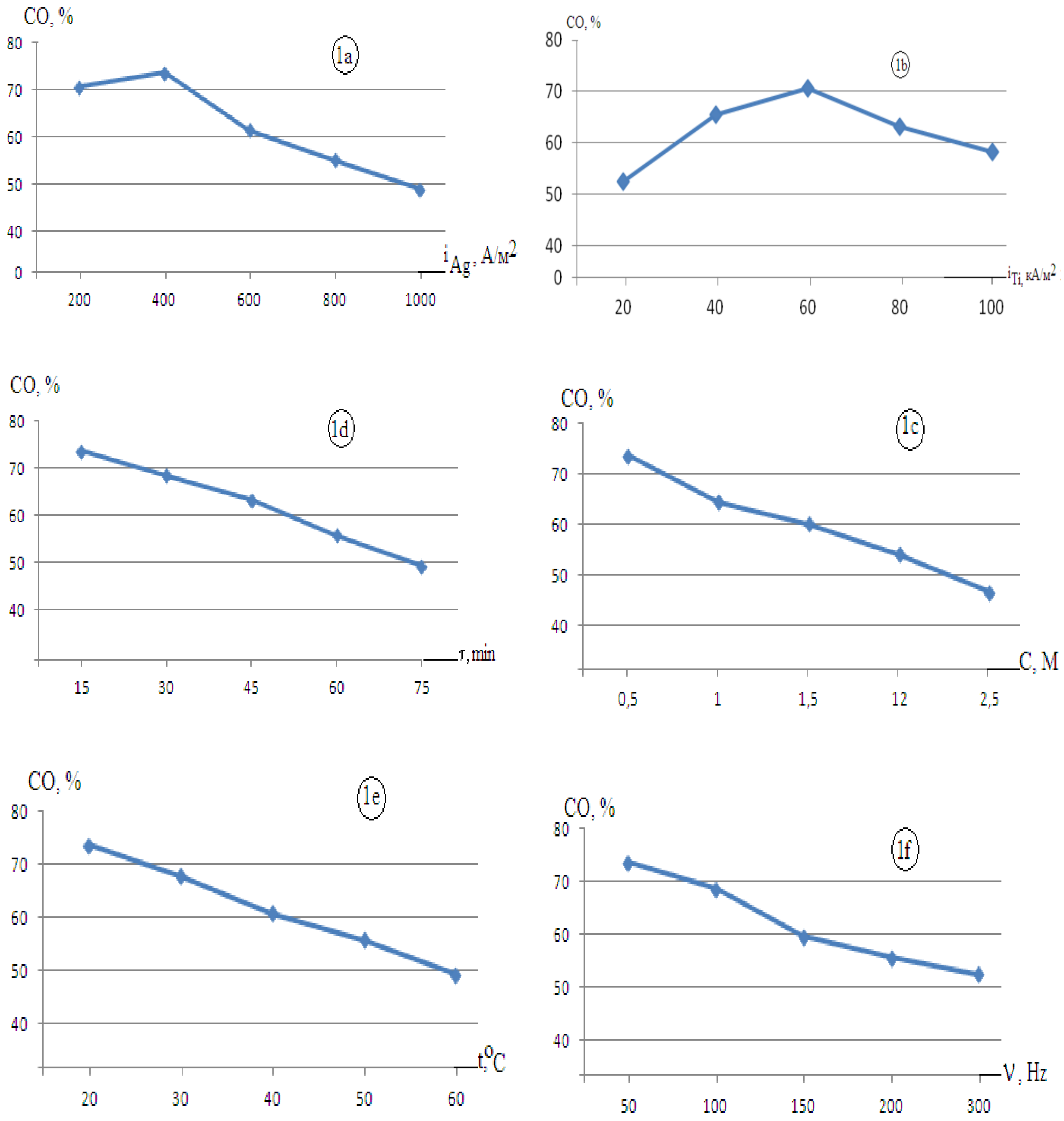


Figure 1 – Point graphs and curve approximation effect on W silver dissolution:
a – current density on a silver electrode, b – current density on a titanium electrode, c – electrolyte concentration,
d – electrolysis duration, e – electrolyte temperature, f – AC frequency

Thus, we studied the electrochemical behavior of silver during polarization of industrial alternating current in a potassium ferrocyanide potassium solution by rational mathematical planning, it is shown that when the system of silver-titanium electrodes is polarized by an alternating current, the silver electrode dissolves to form potassium dicyanoargentate, and it has been established that the parameters studied have a significant influence on the silver dissolution.

А.Б. Баешов[1], Э.Ж. Тулешова[2], А.К. Баешова[3], М. Өзлер[4]

[1] Д.В. Сокольский атындағы Жанармай, катализ және электрохимия институты, Алматы, Қазақстан;
[2] Қожа Ахмет Ясауи атындағы Халықаралық қазақ-түрік унверситеті, Түркістан, Қазақстан;
[3] Аль-Фараби атындағы Қазақ Ұлттық Университеті, Алматы, Қазақстан;
[4]Мугла Сыткы Кочман университеті, Түркия

КАЛИЙ ФЕРРОЦИАНИДІ ЕРІТІНДІСІНДЕГІ КҮМІСТІҢ ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТІ

Аннотация. Еліміздің инновациялық индустрияландыруының негізгі басымдықтарының бірі – металлургия мен дайын бұйымдарды өндіру. Осыған байланысты, металдарды және олардың қосылыстарын өндірудің жаңа әдістерін қолдану немесе оларды ерітінділерден бөліп алу өте маңызды. Қазіргі кезде қолданылатын перспективалық әдістердің бірі – өндірістік жиіліктегі айнымалы токпен поляризация. Өнеркәсіптік айнымалы токтың әсерінен өтетін процестердің ерекшеліктері ток бағытын ауыстырған кезде, оксидті пленканы алып тастауға және металды әрі қарай үздіксіз еріту үшін жағдай жасауға болады.

Бағалы металдардың, әсіресе, күмістің қатысуымен жүретін электрохимиялық процестер машина жасау мен өнеркәсіптің әртүрлі салаларында, сұраныстың өсуіне байланысты, қызықты болып отыр. Күмістің ең құнды қасиеттері – оның жоғары электр өткізгіштігі, шағылысу қабілеті және жылтыратылған тұнбаның әдемі сәндік түрі.

Калийдің ферроцианид ерітіндісі күмістендіруде цианды электролиттердің ең көп таралған алмастырғышы болып саналады. Күмістің электртотығу заңдылықтарын анықтауға мүмкіндік беретін, оның қосылыстарын синтездеуге жүргізілген жүйелі зерттеулер оның өндірісін қарқындатуға да, сондай-ақ ресурсты үнемдеу мәселелерін шешуге де әкелуі мүмкін.

Жұмыста айнымалы токпен поляризацияланған күміс электродында калий гексацианоферраты ерітіндісінде жүретін электрохимиялық үрдістердің ерекшеліктері рационалды математикалық жоспарлау әдісі бойынша көрсетілген. Жоспарға сәйкес алты фактор үшін және әрбір фактор бес деңгейге ие 25 эксперимент жүргізілді. Статистикалық көпөлшемді тәуелділіктерді сипаттау үшін жеке функциялар – М.М. Протодьяконовтың теңдеуі қолданылды. Осы теңдеудің негізінде біз n = 25 және K = 6 үшін корреляция коэффициентін анықтадық. Оның мәні 0,4956 және t_r = 3,02>2 және бұл жалпыланған теңдеудің сәйкестігін көрсетеді.

Күмістің электрохимиялық еруінің оңтайлы шаралары анықталды: күміс электродының тығыздығы – 200 А/м^2, титан электродының тығыздығы – 60 кА/м^2, электролит концентрациясы – 0,5-1,0 моль/л, электролит температурасы – 20-40 °С, электролиз ұзақтығы – 15-30 мин., айнымалы ток жиілігі – 50 Гц.

Титан электродымен жұптасқанда, күміс электродында пассивтену процесі жойылып, металдың еру жылдамдығы артатыны анықталды. Катодты жартылай периодта титан электродында газ тәрізді сутегі бөлінеді және күміс иондарының тотықсыздануы байқалады. Осы сәтте күміс электроды анодты жартылай периодта болады және күміс иондарының, дицианоаргентаттың және күміс оксидінің пайда болуымен ериді. Зерттелген параметрлер күмісті еріту процесіне елеулі әсер ететіні анықталды.

Түйін сөздер: айнымалы ток, күміс, электролиз, айнымалы ток жиілігі, ток тығыздығы, ток бойынша шығым.

А.Б. Баешов[1], Э.Ж. Тулешова[2], А.К. Баешова[3], М. Өзлер[4]

[1]АО «Институт топлива, органического катализа
и электрохимии имени Д.В.Сокольского», Алматы, Казахстан;
[2]Международный казахско-турецкий университет имени Ходжи Ахмеда Ясави, Туркестан, Казахстан;
[3] Казахский Национальный университет имени аль-Фараби, Алматы, Казахстан;
[4] Университет Муглы имени Сыткы Кочман, Турция

ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ СЕРЕБРА В РАСТВОРЕ ФЕРРОЦИАНИДА КАЛИЯ

Аннотация. Одним из основных приоритетов инновационной индустриализации страны является развитие металлургии и производство готовых продуктов. В этой связи применение новых способов получения металлов и их соединений или извлечения их из растворов является актуальной задачей современности. Одним из перспективных способов, применяющихся в настоящее время, является поляризация переменным током промышленной частоты, которая вызывает интерес исследователей как с точки зрения оксидообразования, так и разрушения пассивирующей пленки. Особенность процессов, протекающих под действием промышленного переменного тока, заключается в том, что при смене направления тока удается снять оксидную пленку и создать условия для беспрепятственного дальнейшего растворения металла.

Интересным представляются электрохимические процессы с участием благородных металлов, в особенности серебра, в связи с возрастающей потребностью в нем различных отраслей техники и промышленности. Наиболее ценными свойствами серебра является его высокая электропроводность, отражательная способность и красивый декоративный вид полированных осадков.

Наиболее распространенным заменителем цианидных электролитов серебрения является раствор железистосинеродистого калия. Системные исследования, позволяющие установить закономерности электроокисления серебра с последующим синтезом его соединений, могут приводить как к интенсификации его производства, так и решать проблемы ресурсосбережения.

В работе показаны отличительные особенности электрохимических процессов, протекающих на серебряном электроде при электролизе промышленным переменным током в растворе железистосинеродистого калия методом рационального математического планирования. В соответствии с планированием для шести факторов, а в каждом факторе пять уровней было проведено 25 опытов. Для описания статистических многофакторных зависимостей частные функции обобщили уравнение М.М.Протодьяконова. На основании уравнения нашли коэффициент корреляции при N = 25 и K = 6. Он равен 0,4956 и значимость $t_R = 3{,}02 > 2$, что указывает на адекватность обобщенного уравнения.

Определены оптимальные условия электрохимического растворения серебра: плотность на серебряном электроде – 200 А/м^2, плотность на титановом электроде – 60 кА/м^2, концентрация электролита – 0,5-1,0 моль/л, температура электролита – 20-40 °С, продолжительность электролиза – 15-30 мин., частота переменного тока – 50 Гц.

Показано, что при поляризации переменным током серебра в паре с титановым электродом, устраняется процесс пассивации серебряного электрода, и скорость растворения металла возрастает. В катодном полупериоде на титановом электроде выделяется газообразный водород и наблюдается восстановление ионов серебра. В этот момент серебряный электрод находится в анодном полупериоде и растворяется с образованием ионов серебра, дицианоаргентата и оксида серебра. Установлено, что изученные параметры оказывают заметное влияние на процесс растворения серебра.

Ключевые слова: переменный ток, серебро, электролиз, частота тока, плотность тока, выход по току.

Information about the authors:

Baeshov Abduali Baeshovich – «D.V.Sokolsky Institute of Fuel, Catalysis and Electrochemistry», Doctor of Chemistry Science, Professor, E-mail: bayeshov@mail.ru, https://orcid.org/0000-0003-0745-039X;

Tuleshova Elmira Zhanbirbayevna – Khoja Akhmet Yassawi International Kazakh-Turkish University, Candidate of Chemistry Science (PhD), Associate Professor, E-mail: elmira.tuleshova@ayu.edu.kz, https://orcid.org/0000-0003-2249-9570;

Baeshova Azhar Kospanovna – [3]Al-Farabi National University, Doctor of technical sciences, E-mail: azhar_b@bk.ru

Ozler Mehmet Ali – Mugla Sitki Kocman University. Doctor, professor, Phone, e-mail: +90 555 984 65 15, aozler@mu.edu.tr

REFERENCES

[1] Kostin N.A., Kublanovskiy V.S., Zabludovsky V.A. Impulse electrolysis. [Impul'snyj jelektroliz] - Kiev: Naukova Dumka, **1989**. 166 p. (in Russ).

[2] Didenko A.N., Lebedev V.A., Obraztsov S.V. Intensification of electrochemical processes on the basis of asymmetrical alternating current [Intensifikacija jelektrohimicheskih processov na osnove nesimmetrichnogo peremennogo toka] // V.Sc.: Intensification of electrochemical processes in hydrometallurgy [Intensifikacija jelektrohimicheskih processov v gidrometallurgii]. Moscow: Nauka, **1988**. P. 189-213. (in Russ).

[3] Chernenko V.I., Snezhkov L.A., Popanov I.I. Obtaining coatings with anodic-spark electrolysis. [Poluchenie pokrytij anodno-iskrovym jelektrolizom]. L .: Chemistry, **1991**. 126 p. (in Russ).

[4] Vagramyan A.T. Electrodeposition of metals. [Jelektroosazhdenie metallov]. Moscow: Publishing House of the Academy of Sciences of the USSR, **1950**. 200 p. (in Russ).

[5] Kostin N.A., Labyak O.V. Elektrochemistry [Jelektrohimija]. **1995**, 31, 5. P. 510-516 (in Russ).

[6] Zhylisbaeva G.N., Baeshov A.B., Khamitova M.M., Myrzabekov B.E. News of the National Academy Of Science RK, **2016**, 2. P.71 - 76 (in Kaz).

[7] Sarbayeva G.T., Baeshov A.B., Matenova M., Sarbayeva K.T., Abdualieva U.A., Tuleshova E.Zh. News of the National Academy Of Science RK, **2017**, 2. P. 73–78 (in Kaz).

[8] Bayeshov A.B., Bayeshova A.K., Bayeshova C.A. (2014) Electrochemistry (theory and practice). [Electrokhimiya (teoriyasi men koldaniui)]. Almaty: Kazakh university. P. 316. ISBN 978-601-04-0671-1. (In Kazakh).

[9] Baeshov A.B., Tuleshova E.Zh., Baeshova A.K. Bulletin of KazNU. [Vestnik KazNU], 2005, 4 (40). P.170-175 (in Russ).

[10] Baeshov A.B, Tuleshova E.Zh., Baeshova A.K. Reports of NAS RK, **2005**, 4. P.103-107 (in Russ).

[11] Tuleshova E.Zh., Baeshov A.B, Baeshova A.K. 1st International Forum "Actual Problems of Modern Science" [1-j Mezhdunarodnyj forum «Aktual'nye problemy sovremennoj nauki»], Samara, **2005**. P.132-135 (in Russ).

[12] Tuleshova E.Zh. Bayeshov A., Tukibayeva A. Oriental journal of chemistry, **2013**, 29, 1. P.33-37 (in Eng).

[13] Tuleshova E.Zh. Bayeshov A., Tukibayeva A., Aibolova G. Baineyeva F. Oriental journal of Chemistry, **2015**, 31, 4. P.1867 – 1872. DOI: 10.13005/ojc/310403 (in Eng}.

[14] Baeshov A., Junusbekov M., Baeshova A., Zharmenov A. Industry of Kazakhstan [Prom. Kazahstana], **2001**, 1. P.113-116 (in Russ).

[15] Baeshova S.A., Revenko S., Baeshov A.B Chemical Journal of Kazakhstan [Himicheskij zhurnal Kazahstana], **2005**, 2. P.121-126 (in Russ).

[16] Bayeshov A.B., Nurdillayeva R.N., Khabibullayeva Sh.H. (2019) Effect of the bromide ions on the titanium electrode dissolution polarized by alternating current in aqueous solutions. News of the Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. №2. (In Eng) https://doi.org/10.32014/2019.2518-1491.21

[17] Nurdillayeva R.N., Bayeshov A.B., Sunatullayeva L.A., Zhylysbayeva G.N. Dissolution behavior of brass polarized by alternating current in sodium phosphate aqueous solution. News of the Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. №3. (In Eng) https://doi.org/10.32014/2019.2518-1491.33

[18] Fedotev N.P., Ilin V.A., Chernozatonskaya I.N. (1962) Elektroosazhdenie serebra iz rastvorov netsianistyih kompleksnyih soley [*Electrodeposition of silver from solutions of non-cyanic complex salts*].– Leningrad: Dom nauch-tehn. Propagandyi.

[19] Yampolsky A.M. (1961) Pokryitiya blagorodnyimi metallami [*Coating noble metals*].– Moscow: Mashgiz.

[20] Malyshev V.P. (1977) Matematicheskoe planirovanie metallurgicheskogo i himicheskogo jeksperimenta [*Mathematical Planning of Metallurgical and Chemical Experiments*] Alma-Ata: Nauka.

[21] Protod'jakonov M.M., Teder R.I. (1970) Metodika racional'nogo planirovanija jeksperimenta [*The method of rational experiment planning*] Moscow: Nauka.

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.21**
Volume 2, Number 440 (2020), 39 – 46

UDC 547.99
IRSTI 31.23.23

A.B. Tashimbetova[1], A.K. Umbetova[1], Z.B. Halmenova[1],
Y.S. Ikhsanov[1] , M.I. Choudhary[2], Zh.A. Abilov[1], G.Sh. Burasheva[1]

[1]Al-Farabi Kazakh National University Research Institute
of New Technologies and Materials Republic of Kazakhstan, Almaty, Kazakhstan;
[2]International Center for Chemical and Biological Sciences,
Karachi University, Karachi, Pakistan.
E-mail: erbol.ih@gmail.com, alma_0875@mail.ru, zaure.halmenova@mail.ru, akniyettashimbetova@mail.ru,
abilovs51@mail.ru, iqbal.choudhary@iccs.edu, gauharbur@mail.ru

CHEMICAL STUDY OF *LAVANDULA FERTILIZER*

Abstract. Genus *Lavandula* – specially grown as an aromatic and medicinal plant. In inflorescences, the content of essential oil is from 0.8 % to 2.6 %, in leaves up to 0.3 %. The main components of the essential oil are linalool (10-30 %) in the free state and its esters with acetic, butyric, valerianic, caproic acids (30-60 %), as well as geraniol, citral, borneolen, bisabolene, α-pinene and others.

Currently, the plant is used as an ornamental, as a spice in cooking, as well as for medicinal purposes. In traditional medicine, flowers, leaves and branches of lavender are used.

In Bulgaria, lavender is used as a means of calming the nervous system, relaxing baths and for skin diseases.

In Germany, ointments are made from lavender petals. In Austria, lavender leaves are collected before flowering and are used as soothing and anti-inflammatory drugs. In Poland, in combination with a pharmacy chamomile flower, the flowers of a lavender plant are used in the healing of a fresh voice and bronchial disease.

In France, an infusion of lavender flowers is used as an urolithic substance.

The object of the study is raw materials *L.angustifolia* of individual collection at the experimental site of the laboratory of medicinal plants of the Institute of Phyto-Introduction and Botany at the Ministry of Science and Education of the Republic of Kazakhstan of Almaty.

The technology for producing a biologically active complex from the plant species under study has been developed by varying the nature of the extractant, its ratio with raw materials, time and extraction ratio.

The optimal condition for obtaining a biologically active complex from a plant is: extractant – 50 % ethyl alcohol, the ratio of extractant to raw material – 1: 9, the time of double extraction – 72 hours, temperature – 25 ºC.

The fractional composition of the aerial mass of *L.angustifolia*, which is represented by water-soluble and water-insoluble fractions, was studied.

The article presents for the first time the data of a qualitative and quantitative analysis of the lipophilic components of the aerial mass of *L.angustifolia*, determined by gas-liquid chromatography with mass spectrometry (GC / MS).

Analyzes were carried out in a laboratory of chemistry of natural coefficients, University of Karachi, Karachi, Pakistan, the structure and quantitative content of 16 compounds were established in the aerial mass of the plant *L.angustifolia*.

The identification of the components was carried out by analogy with the known mass spectra of the samples embedded in the computer data bank and relative retention times. Quantitative determination of the composition of the analyzed mixture was carried out by the method of normalization by peak areas.

Keywords: *Lavandula (L. angustifolia),* GC-MS, extraction, BAS, aerial parts.

Introduction

Lavandula root is a rod, a tree, and strongly branched on its support. When the new bushes are stretched to the surface, the obsolete bumps bend over. The leaves are rectangular, oval greens, bearded or rectangular, with the edges. The young leaves of the lavanta plant are gray, aged leaves – green [1-3].

Lavandula was specially crafted as aromatic and medicinal plant in the year 2000. Today *Lavandula* plant is used in many different spheres. It is widely used as lavender in lavender, as a spice in culinary, as well for therapeutic purposes, lavender flowers, leaves and branches are used in folk medicine. Collect lavender flowers at the time of flowering and dry it on a sunny day. Then, prepare the flowers, leaves and sprays separately for use in the pots [4-6].

Flowers of *Lavandula* contain uric acid, cinnamic and garnarin. Essential oils will be 0.8-2.6 % in the bouquet, 0.3 % in the leaves and 0.19 % in the class. The main components of the essential oils are linoleum (10-30 %) in vacuum and its esters (30-60 %) with acetic, oily, valerian and caproic acids, as well as alumina, citral, borneol, bisabolene, α-pinene, dihydrochrylophyllene epoxy, as healing.

It is known that the composition of plant extracts is directly related to various factors such as the temperature of the extraction process, the extraction time, the plant raw material and the nature of the solvent or solvent system used.

Depending on the tasks to be solved, a wide array of organic solvents such as hexane, chloroform or benzene is used to extract biologically active substances.

However, most organic solvents are highly toxic compounds, have a build-up effect in tissues or are carcinogens, whereby it is requireв to include additional steps for drug substance purifi cation and additional methods for quality control of such preparations. These measures lead to an imminent increase in the cost of end product [7-11].

This article analyzes the lipophilic composition of the ethanol extract Lavandula with various alcohol / water content. The aim of the study was to compare the chemical composition of the extracts from Lavandula using two solvents, which are different in polar type, to allow the two systems to be used as a basis for the medicinal forms.

Materials and Methods

The selection of the optimal technological parameters of raw plant materials ting aimed at the identification of those affecting directly the composition and the quality of the final complex of biologically active substances (BAS) [12]:

1) the nature of the solvents;
2) raw material:solvent ratio;
3) the temperature;
4) the duration of the extraction;
5) the extraction frequency.

The selection of the optimal solvent was carried out on the basis of the qualitative analysis of the main BAS groups and the quantitative extraction of extractive substances by pharmacopocial methods [13].

Determination of lipophilic components of a substance by chromatography spectrometry. The extracted extrudate is extracted with hexane (1: 2) for 72 hours at 20-24 °C. The extract is enriched in a rotary evaporator in a soft case.

A Perkin-Elemer Autosystem gas chromatograph with an XL mass-selective detector – TurboMass is used with a flare quartz capillary column (30 x 2.5 mm, 0.25 μm thick), PE-5 coating and a 99.9 % helium-filled phase. It starts at a temperature of 60 °C (works for 5 minutes), from 20 °C / min to 180 °C, from 3.5 °C/min to 290 °C. The final temperature is maintained for 40 minutes.

Mass spectra are ionized with an emission of 70 eV and a full scan in the range of 40-350 a.m. The injector temperature was 310 °C, and the RA-TiO sample was divided by 1:60 according to the model [14-20].

Methods for determining the qualitative composition of the ground part of plants and roots, determining the composition of fractions, as well as determining the structure and purity of the separation of compounds in raw materials:

– extraction of various polar solvents;

– two-dimensional and one-dimensional chromatography on FN3 paper (Germany) and with a system of solutions.

As the main method for studying chemical composition, the authors opted for the method of high performance gas chromatography with mass-selective detector as the most accurate and universal, which allows for identification of the widest possible spectrum of compounds.

When selecting the optimal extractant, the following solvents are used: ethyl alcohol (50 %, 70 %, 90 %) water solution. 5 g of *Lavandula* (*L. angustifolia*) of the ground part of the plant, 50 ml capacity, packaged in sausages. The raw material and the solvent obtained in a ratio of 1:6 are kept for 24 hours at room temperature. After 24 hours, the resulting extract can be filtered through a Buchner filter and a vacuum pump. The resulting extract is measured with a measuring cylinder, poured into a porcelain dish, evaporated in a water bath, and the substance is removed.

In the technology of substance separation, the main parameter is the ratio of raw materials and extractant. In order to determine the optimal volume, the selected extractant changes the ratio of raw material and solvent from a ratio of 1:4 to a ratio of 1:10. 5 g crushed (*L. angustifolia*) – ground part of plants of various sizes (20, 30, 40, 45, 50) 50 % extraction with ethyl alcohol. In addition, during the extraction process as a stable factor: extraction time (24 hours) and temperature (20-25 °C).

Determination of technological parameters for obtaining substances

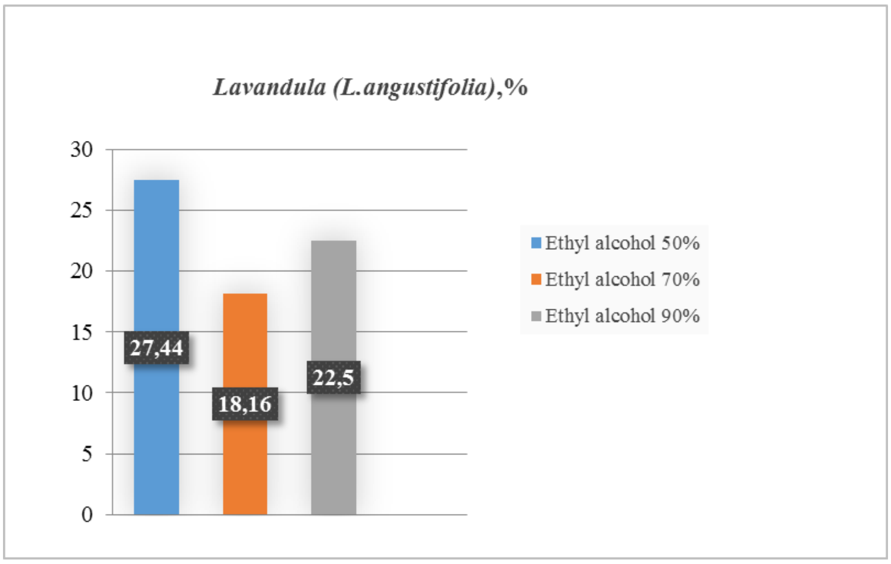
Selecting the extraction state: Obtaining the substance was carried out according to the following scheme:

50-100 g vegetable raw materials *Lavandula* (*L. angustifolia*) 250-500 ml of 50 % water-ethyl alcohol, preparation of raw materials and extractant in a ratio of 1:9 and settling at room temperature for 72 hours. The contents of the flask are thoroughly mixed, and the paper is filtered into a dry flask through a filter. This extraction process is repeated 2 times using the high-temperature method.

The resulting extracts are added and filtered with paper used at the beginning of the filter.

Results and discussion

According to the results obtained (*L. angustifolia*), during 72 hours of extraction at a temperature of 24-28 ºC.the time and multiplicity of extraction are the same. 100 g of dried and standardized plant raw materials were obtained for extraction.



Picture 1 - General provisions of *Lavandula* using various extractants origin of the substance from the ground part of the plant , %

Using the obtained extracts of *Lavandula* (L. from the aboveground part of the angustifolia plant, a substance of 50 % ethyl alcohol was taken in large quantities.

Table 1 - *Lavandula* is related to the relationship between" raw material-extractant» %

Ratio of raw material (g) and extractant (ml)	*Lavandula (L.angustifolia),%*
1:4	–
1:6	27,44
1:8	31,96
1:9	55,94
1:10	55,36

Using the selected extractant, the optimal raw material – extractant ratio is 1: 9. if you choose the right ratio of raw materials and extractant, you can save time by knowing the content and ratio of extractant in the industrial industry.

Table 2 - General provisions depending on the time of the extraction process *Lavandula* %

Time of extraction	*Lavandula (L.angustifolia),%*
12	27,24
24	55,94
48	75,52
72	88,66

Table 3 - General provisions depending on the multiplicity of extraction of *Lavandula*, %

Number of extractions	*Lavandula (L.angustifolia),%*
1 extraction	28,01
2 extraction	28,14

As the next step, the extract was examined by high-performance gas chromatography with mass selective detector Aligent Technologies 6400 Series Triple Quadrupole LC/MS under the following conditions: Poroshell 120 EC-C18 column (50 mm long, 3 mm in diameter, with the coating substance particle size of 4.0, 2.7 and 1.9 μm) was used, with 10 % aqueous solution of methanol as mother solvent and 90 % methanol as final solvent at the pressure of 11.5 mPa and the temperature of 40 °C. Components were identified by mass spectra and retention times using the NIST library and Wiley LC/MS.

Based on the research of the studied plant raw materials, it was found that there are 16 compounds. Plant raw materials contain the amount of methyl ester of linoleic acid (29.34 %) and hexahydrofarrenal acetone (0.41 %). *Lavandula* plant raw material contains methyl ester of linoleic acid (29.34 %), ethyl ether of palmitic acid (21.48 %) and methyl ester of palmitic acid (15.42 %). The Lavandula plant contains β-santalol (0.41 %), which contains very small amounts of Sesquitersenoid compounds.

It is obvious that with in case of an unchanged amount of the plant material, the increase of the extragent amount in the extraction process results in increase of the substance dissolved and transported from the cell to the intercellular space. At the same time, the increase of the volume of the extragent Jeads to decrease of BAS concentration in the extract.

The ground raw material is introduced to a five-, seven-. nine- and twelve-fold amount of the solvent for studying the dependence of the raw material solvent ratio on the BAS amount in the plants studies. The results are shown in Fig. 1, The raw material solvent ratio has a positive effect. In fact, the solvent in the ratio considered brings about a greater amount of the extractive substances obtained despite the solvent used. This is consistent with the mass transfer principle as the concentration gradient between the solid and most of the liquid is the driving force.

In accordance with the mass transfer law the difference between the concentration of the extract and thesolvent increases the transition of the soluble substances into the solvent and continues until the establishment of equilibrium. It is so because the concentration difference is the driving force of the diffusion process.

However, the increase of the solvent consumption is limited by the cost of concentrating the extract obtained.

It follows that the cost of the extract evaporation is an important factor requiring consideration. Therefore, the smaller the raw material: solvent ratio, the more efficient from an economic pint of view is the extraction process.

The effect of the extraction temperature on the process of maximum extraction of BAS complex is studied. The temperature increase leads to an increase of the solubility of the various polyphenolic constituents,as well as to an increase of the rate of their diffusion. Since the boiling point of the solvents used does not exceed 80 °C no significant change of the composition of the extracted substances is expected.

Table 4 - Lipofil composition of *Lavandula angustifolia* plant

No	Connection name	RT (min)	Amount,%	Molecular formula
1	Methyl 4-propan-2-yl benzoate	17.021	0.59	$C_{11}H_{14}O_2$
2	α - terpene	19.403	1.88	$C_{10}H_{16}$
3	Caryophyllene oxide	20.427	7.87	$C_{15}H_{24}O$
4	δ - zedrol	21.173	4.03	$C_{15}H_{26}O$
5	Lancel	21.635	0.73	$C_{15}H_{24}O$
6	Caryophylline oxide	21.895	2.41	$C_{15}H_{24}O$
7	2,6,8- trimethylbicyclo [4.2.0] oct-2-en-1,8-diol	22.02	0.88	$C_{11}H_{18}O_2$
8	β - santalol	22.222	0.7	$C_{15}H_{24}O$
9	Hexahydropharnesyl acetone	24.369	0.41	$C_{18}H_{36}O$
10	8-Oxo-2' – deoxyguanosine	25.963	0.63	$C_{15}H_{22}O$
11	Palmettic acid methyl ester	26.24	15.42	$C_{17}H_{34}O_2$
12	Palmettinic acid ethyl ester	28.253	21.48	$C_{18}H36O2$
13	Linoleic acid methyl ester	31.516	29.34	$C_{19}H32O2$
14	Phytol	31.709	4.25	$C_{20}H_{40}$
15	Stearic acid methyl ester	31.902	3.98	$C_{19}H_{38}O_2$
16	Linoleic Acid Ethyl Ester	32.506	1.4	$C_{20}H_{3}4O_2$

Conclusion

The lipophilic composition of the surface of the angustifolia *Lavandula* plant was determined by gas chromatography using an ion detector and an Agilent HP-5MC device at Karatekin University, Chancara, Turkey. The studied plant material contains linoleic acid methyl ether (29.34 %), palmitic acid ethyl ether (21.48 %) and palmitic acid methyl ether (15.42 %). *Lavandula* (contains a very small amount of β-santalol (0.41 %), which is part of sesquitrepenoid.

16 compounds were identified using the chromatogram shown in table 4.(methyl-4-propane-2-yl benzoate, α – terpinene, caryophyllene oxide, δ – cedrol, Lancel, 2,6,8 – trimethylbicyclo [4.2.0]Oct-2-EN-1,8-diol, β – santalol, hexahydrofarnesylacetone, 8-Oxo-2'-deoxyguanosine, methyl palmitic acid ester, ethyl palmitic acid ester, methyl ether linolenic acid, phytol, stearic acid methyl ester, linoleic acid ethyl ester). The resulting lavender essential oil contains 70-80 % saturated C6-c44 hydrocarbons. Quantitative quantities are: docosan (2.8779 %), genacosan (2.4896 %), non-docosan z-14 (2.2156 %), tetracosan (2.3894 %). Butyl-1-methylpropyl ether (4.4067 %) and cyclochloroctane (3.0660 %), 1,2-Benzenesulfonic acid. Test essential oil contains from 10 to 15 esters. In addition, korneol found in essential oils (0,0287 %) and caryophyllia (0,0123 %).

А.Б. Ташимбетова[1], А.К. Умбетова[1], З.Б. Халменова[1],
Е.С. Ихсанов, М.И. Чоудхари[2], Ж.А. Абилов[1], Г.Ш. Бурашева[1]

[1] әл-Фараби атындағы Қазақ ұлттық университеті,
Жаңа технологиялар мен материалдар ғылыми-зерттеу институты
Қазақстан Республикасы, Алматы, Қазақстан;
[2] Халықаралық химиялық және биологиялық ғылымдар орталығы,
Карачи университеті, Карачи, Пәкістан

LAVANDULA FERTILIZER-ДІҢ ХИМИЯЛЫҚ ЗЕРТТЕУІ

Аннотация. Лаванда (*Lavandula*) біздің дәуірімізге дейін хош иісті және дәрілік өсімдік ретінде арнайы өсірілген. Эфир майы құрамы гүл шоғырында – 0,8 %-дан 2,6 %-ға дейін, жапырақтарында 0,3 %-ға дейін болады. Эфир майының негізгі компоненттерінде еркін жағдайдағы линалоол (10-30 %) және сірке суы, май, валериян, капрон қышқылы (30-60 %) бар, сондай-ақ оның эфирлері – гераниол, цитраль, борнеолен, бисаболен, α-пинен. Қазіргі уақытта өсімдік сәндік өнімдерде, дәмдеуіш ретінде аспаздық үшін, сондай-ақ емдік үшін де пайдаланылады. Халықтық медицинада дәрілік мақсаттармен лаванданың гүлдері, жапырақтары мен бұтақтары қолданылады, бұтақтарын бөлек бөтелкелерге жинап, пайдалануға дайындайды. Болгарияда лаванда жүйке жүйесін тыныштандыратын, ванналар мен тері ауруларын емдейтін дәрі ретінде қолданылады. Германияда лаванда жапырақтарынан жақпа жасайды. Австрияда лаванда жапырақтары гүлденгенге дейін жиналады, олар тыныштандыратын және қабынуға қарсы препараттар ретінде пайдаланылады. Польшада дәріханалық түймедақ гүлімен бірге, лаванда өсімдіктерінің гүлдері жаңа дауыс пен бронх ауруын емдеуде қолданылады. Францияда лаванда гүлінің тұнбасы несеп айдайтын зат ретінде пайдаланылады.

Зерттеу объектісі – Қазақстан Республикасы Ғылым және Білім Министрлігі жанындағы фитоинтродукция және ботаника институты дәрілік өсімдіктер зертханасының эксперименталдық бөлімінде жеке жиналған *Lavandula (l.angustifolia)* шикізаты.

Зерттеліп жатқан өсімдік түрлерінен биологиялық белсенді кешен алу технологиясы экстракция затының табиғатын, шикізатқа қатынасын, уақытты және экстракция коэффициентін өзгерте отырып жасалды.

Өсімдіктен биологиялық белсенді кешен алудың оңтайлы шарты: экстрагент – 50 % этил спирті, экстракцияның шикізатқа қатынасы – 1: 9, қосарланған экстракция уақыты – 72 сағат, температура – 250 °С.

L.angustifolia жер үсті массасының фракциялық құрамы зерттелді, ол суда еритін және суда ерімейтін фракциялардан тұрады.

Мақалада алғаш рет *L.angustifolia* жер үсті массасының липофильді компоненттерінің сапалық және сандық талдауының деректері келтірілді, масс-спектрометриясы (GC/MS) бар газ сұйықтықты хроматография әдісімен анықталған.

Талдаулар табиғи қосылыстар химиясы зертханасында, Карачи қаласының университетінде, Пәкістан қаласында *L.angustifolia* өсімдігінің жер үсті массасында 16 қосылыстың құрылымы мен сандық құрамы орнатылды.

Компоненттерді сәйкестендіру компьютердің деректер банкіне салынған үлгілердің белгілі масс-спектрлеріне және ұстап қалу уақытына ұқсас жүзеге асырылады. Талданатын қоспаның құрамын сандық анықтау шыңдар ауданы бойынша қалыпқа келтіру әдісімен жүзеге асырылды.

А.Б. Ташимбетова[1], А.К. Умбетова[1], З.Б. Халменова[1],
Е.С. Ихсанов, М.И. Чоудхари[2], Ж.А. Абилов[1], Г.Ш. Бурашева[1]

[1] Казахский национальный университет имени аль-Фараби
Научно-исследовательский институт новых технологий и материалов
Республика Казахстан, Алматы, Казахстан;
[2]Международный цент химических и биологических наук университета Карачи,
г. Карачи, Пакистан

ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ *LAVANDULA FERTILIZER*

Аннотация. Род Лаванда (*Lavandula*) – специально выращенный как ароматное и лекарственное растение. В соцветиях содержание эфирного масло от 0,8 % до 2,6%, в листьях до 0,3 %. Основными компонентами эфирного масла являются линалоол (10–30%) в свободном состоянии и его эфиры с уксусной,

масляной, валерияновой, капроновой кислотами (30–60 %), а также гераниол, цитраль, борнеолен, бисаболен, α-пинен и другие.

В настоящее время растение используется как декоративное, в качестве специй в кулинарии, а также в лечебных целях. В народной медицине используются цветы, листья и ветви лаванды.

В Болгарии лаванду используют как средство, успокаивающее нервную систему, расслабляющие ванны и при кожных заболеваниях.

В Германии делают мази из лепестков лаванды. В Австрии собраны листья лаванды до цветения и используются в качестве успокаивающих и противовоспалительных препаратов. В Польше, в сочетании с аптечным цветком ромашки, цветки лавандового растения применяются при заживлении свежей раны и бронхиальной болезни.

Во Франции настой цветков лаванды используют как мочегонное вещество.

Объектом исследования является сырье *Lavandula* (*L.angustifolia*) индивидуального сбора на экспериментальном участке лаборатории лекарственных растений Института фитоинтродукции и ботаники при Министерстве науки и образования Республики Казахстан города Алматы.

Отработана технология получения биологически активного комплекса из исследуемого вида растения варьированием природы экстрагента, его соотношением с сырьем, времени и кратности экстракции.

Оптимальным условием для получения биологически активного комплекса из растения является: экстрагент – 50 % этиловый спирт, соотношение экстрагента и сырья – 1:9, время двухкратной экстракции – 72 часа, температура – 25^0C.

Изучен фракционный состав надземной массы *L.angustifolia*, который представлен водорастворимыми и нерастворимыми в воде фракциями.

В статье впервые приведены данные качественного и количественного анализа липофильных компонентов надземной массы *L.angustifolia*, определены методом газожидкостной хроматографией с масс-спектрометрией (GC/MS).

Анализы проведены в лаборатории химии природных соединений, Университета города Карачи, г. Карачи, Пакистан, в надземной массе растения *L.angustifolia* установлены структуры и количественное содержание 16 соединений.

Идентификация компонентов осуществлена по аналогии с известными масс-спектрами образцов, заложенных в банк данных компьютера и относительным временем удерживания. Количественное определение состава анализируемой смеси осуществлено методом нормализации по площадям пиков.

Ключевые слова: *Lavandula (L. angustifolia),* ГХ-МС, экстракция, БАВ, надземная часть.

Information about authors:

Ikhsanov Yerbol Saginovich - PhD Department of Chemistry and Chemical Technology of the Al-Farabi Kazakh National University Kazakh National University, e-mail: erbol.ih@gmail.com, https://orcid.org/0000-0003-4640-9584;

Umbetova Almagul Kengebaeva - Candidate of chemical Sciences, faculty of chemistry and chemical technology, al-Farabi Kazakh national University, El. mail: alma_0875@mail.ru, https://orcid.org/0000-0001-9879-5398;

Khalmenova Zaure Bisentaeva - Candidate of technical Sciences, faculty of chemistry and chemical technology, al-Farabi Kazakh national University, El. mail: zaure.halmenova@mail.ru, https://orcid.org/0000-0002-6991-560X;

Tashimbetova Akniyet Bakytbekkyzy - faculty of chemistry and chemical technology, al-Farabi Kazakh national University, Эл. почта: akniyettashimbetova@mail.ru, https://orcid.org/0000-0002-0010-805X;

Abilov Zharylkasyn Abduahitovich - Doctor of Chemical Sciences, Professor of the Department of Chemistry and Chemical Technology of Al-Farabi Kazakh National University, Email mail: abilovs51@mail.ru, https://orcid.org/0000-0002-2665-2539

Muhammad Ihbal Chowdhari - Doctor of Chemical Sciences, Professor, Karachi University, Email mail: iqbal.choudhary@iccs.edu, https://orcid.org/0000-0001-5356-3585;

Burasheva Gauhar Shahmanovna - Doctor of Science professor, Department of Chemistry and Chemical Technology of the Al-Farabi Kazakh National University, e-mail: gauharbur@mail.ru, https://orcid.org/0000-0003-2935-3531

REFERENCES

[1] Pavlov N.B. (1961) Flora Of Kazakhstan. 5th ed. Alma-ATA: an KazSSR. 70-72 p. 3. Beklemishev N.D. Drugs from plants. Almaty, 2002. 208 p.

[2] Bajtenov M.S. (2001) Flora Kazahstana. Rodovoj kompleks flory. Almaty: Gylym. ISBN 9965-07-036-9

[3] Mahmedova.M.(1991) Labiatae Central Asia. Tashkent. 54-55.

[4] Uzakbay S.A., Khalmenova V.D., Umbetova A.K. (2016) Investigation of chemical composition of plants *Ogidapim vulgare* in Almaty region. Izvestiya NAS RK. No. 6 (420). P 99-102.

[5] Ishmuratova M., Tleukenov S.U. (2007) To the study of plants of the family Labiatae of the flora of Central Kazakhstan // Proceedings of int.science. Conf. The plant world and its protection. Almaty. P. 352-354.

[6] Kurgan S.A. (1995) Useful herbs and rare flowers in the garden. Moscow: Nauka. p.128.

[7] Wulf E.V., Pigulevsky G.V., Albrecht E.A.(1999) Culture of plants giving essential oils on the southern coast of Crimea. Yalta. 126 p.

[8] Voronina E. P.(1993) introduction of lavender In the main Botanical garden of the Russian Academy of Sciences.GL. Botan.garden's. Vol.168. P. 3-8.

[9] Romanenko L. G.(1992) Improvement and development of methods of selection of narrow-leaved lavender (Lavandula angustifolia Mill.). Auto-Ref-Doct.SEL.sciences'. Moscow, 44 p.

[10] Buyukli M.V.(1990) Lavender and its culture in the USSR. Chisinau: Carta Moldoveneasca p-327.

[11] Karasavidis A.O. (2005) Some types of odoriferous raw material in medical practice// Vestnik of VSU.No. 1. p. 205-211.

[12] Trellakis S, et al.(2012) Subconscious olfactory influences of stimulant and relaxant odors on immune function. Eur Arch Otorhinolaryngol.

[13] Kim, N.-S., & Lee, D.-S. (2002). Comparison of different extraction methods for the analysis of fragrances from Lavandula species by gas chromatography–mass spectrometry. Journal of Chromatography A, 982(1), 31-47. doi:10.1016/s0021-9673(02)01445-0.

[14] Lu Huil,2, Li He 2, Lu Huan 1, Li XiaoLan3* and Zhou Ai Guo (2010) Chemical composition of laverder essential oil and its andioxidant activity and inhidition against rhinitisrelated bacteria. African Journal of icrobiology. Vol. 4. №4. P. 309-313.

[15] Tabopda, T., Ngoupayo, J., Khan Tanoli, S., Mitaine-Offer, A.-C., Ngadjui, B., Ali, M., Lacaille-Dubois, M.-A. (2009). Antimicrobial Pentacyclic Triterpenoids fromTerminalia superba. Planta Medica, 75(05), 522–527. doi:10.1055/s-0029-1185328

[16] Beens J., Brinkman U.A.T. Analyst (Cambrigde, UK), 2005. Vol. 130. P. 123.

[17] Aitkulova RE, Abubakirova AA, Kudasova DE, Kaldybekova GM (2016) Role of medicinal plants from south-kazakhstan region for addition into livestock’s fodder. News of the national academy of sciences of the republic of kazakhstan series of biological and medical 314: 155–158. (in Eng). https://doi.org/10.32014/2018.2518-1629

[18] Tursynova A., Sunnenova N.S., Erezhepova N, Sarsenbayeva N.B., Kalekeshov A.M., Makashev E.K. (2016) Effect of the feed additive based on bentonite and chlorella body of agricultural animals and birds, News of the national academy of sciences of the republic of Kazakhstan series of biological and medical. 3: 27–33. https://doi.org/10.32014/2018.2224-526 (in Eng).

[19] Oscanov B.S., Ikhsanov Y.S. , Litvinenko Yu.A., Adekenov S.M., Burasheva G.Sh., Biologically active substances from plant sudaeda vera and their anestizing activity News of the national academy of sciences of the republic of kazakhstan series of biological and medical ISSN 2224-5308.Volume 5, Number 329 (2018), 63 – 66. https://doi.org/10.32014/2018.2518-1629.8

[20] Aitkulova R.E., Abubakirova A.A., Kudasova D.E., Kaldybekova G.M. (2016) Role of medicinal plants from south-kazakhstan region for addition into livestock’s fodder. News of the national academy of sciences of the republic of kazakhstan series of biological and medical 314: 155 – 158. (in Eng). https://doi.org/10.32014/2018.2518-1629

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.22**
Volume 2, Number 440 (2020), 47 – 55

UDC 658.567; 691.33

Z.A. Estemesov[1], P.I. Sadykov[1], A.V. Barvinov[1], N. B. Sarsenbaev[1],
M.Z. Estemesov[1], A.U. Uralkhanova[1], A. A.Tulaganov[2]

[1]TseLSIM LLP, the Central Laboratory for Certification of Building Materials Tests, Almaty, Kazakhstan;
[2]Tashkent Architectural-Constructional Institute, Tashkent, Uzbekistan.
E-mail: tselsim@mail.ru, pernekhan.sadykov@inbox.ru, barvinov00@inbox.ru,
sarsenbayev_n@inbox.ru, myestemesov@inbox.ru, uralkhanova@inbox.ru, a_tulaganov@inbox.ru

PHYSICAL AND CHEMICAL PROCESSES OCCURRING IN THE GRANULATED PHOSPHORUS SLAG DUMPS

Abstract. One of the most dangerous man-made mineral formations located in the territory of Kazakhstan is disposal areas for granulated phosphorus slag, since its shells contain initially the dangerous gases such as PH_3, H_2S, HF, etc. Permanent sources of such gases are also Ca_3P_2 (intrinsically poisonous gas), CaS and CaF_2. In the structures of phosphorous ash disposal areas, the chemical and physical-chemical processes contain initially gases, which may be in different modifications. For example:

- Phosphene (PH_3) in the form: $PH_3 \rightarrow P_2O_5 \rightarrow HPO_3 \rightarrow H_3PO_4$;
- Hydrogen sulfide (H_2S): $H_2S \rightarrow H_2SO_3 \rightarrow H_2SO_4$;
- Hydrogen fluoride and silicon tetrafluoride: $HF \rightarrow SiF_4 \rightarrow H_2SiF_6 \rightarrow H_2SiO_3$;
- Carbon oxide (CO): $CO \rightarrow CO_2 \rightarrow COCl_2$.

Such chemical processes intensify greatly the anthropogenic effect of phosphorous ash disposal areas on the environment – biogeocoenosis.

In addition to the processes related to gas components, in the phosphorous ash disposal areas, the hydration processes occur as a result of interaction of slag with water. Thereat, sub-microcrystalline CSH(I) and calcium are generated. Depth of slag hydration reaches 1…3 μm. Such processes form a thin layer on the surface of slag particles resulting in linking of separate grains into a whole. Therefore, the surface of phosphorous ash disposal areas has the certain strength with cracks, through which water, air, snow, etc. are penetrating into the disposal area.

It is evident that granulated phosphorus slag in the form of disposal areas has very adverse impact on the biogeocoenosis, causing the pressing need for their disposal; moreover, such slags are valuable raw material for the construction industry and agriculture only after their decontamination from dangerous gases.

Keywords. Granular phosphorus slag, dumps, hazardous gases, chemical reactions.

Introduction. One of the most dangerous technogenic mineral formations located on the territory of Kazakhstan is the granular phosphorus slag dumps (hereinafter referred to as GPS or GPD), (figure 1), formed as by-products in the production of phosphorus and its compounds [1].

Near Shymkent and Taraz there dumps have more than 20 million tons of granular phosphorus slag where chemical and physicochemical processes constantly occur, due to which hazardous gases derivatives in the dump structures such as phosphine (PH_3), hydrogen fluoride (HF), hydrogen sulfide (H_2S) and others, previously occurring during the sublimation of elemental phosphorus from phosphorite [2.3], are formed.

In addition, under certain conditions, phosphide (poisonous in itself), calcium sulfide and fluoride, which are part of the slag can serve as these gases sources, which while interacting with water, form a hydration phase of type CSH (I), generating a crust of certain strength with cracks on the surface of the dumps [4-6].

Figure 1 – The dump of granular phosphorus slag near the city of Taraz

Consequently, slag dumps are the same hazardous objects as emissions of the same gases during production processes. At the same time, emissions are controlled, and phosphate slag dumps are uncontrolled, constant, and therefore their danger is significantly higher.

The utilized phosphate slag dumps through the neutralization of granular phosphorus slag, which is environmentally friendly can be an excellent raw material used for construction and agriculture.

The phosphorus and GPS generation technology is the following: in electric furnaces at temperatures of 1450 ... 1500°C in mixtures consisting of phosphorite ($3CaO \cdot P_2O_5$) of the Karatau deposit, quartz sand (SiO_2) and carbon (C), the reaction occurs according to the following formula:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3\,(CaO \cdot SiO_2) + 2P\uparrow + 5CO\uparrow \qquad (1)$$

From this formula it follows that P and CO are released as gases, and $CaO \cdot SiO_2$ – as a melt, at rapid cooling the GPS is generated.

In addition, as a result of complex physical and chemical processes, dangerous gas-dust-like impurities arise - in the form of phosphine (PH_3), fluoride (HF) and hydrogen sulfide (H_2S), slag (and other) dust that are released into the atmosphere, in production and other premises concentrated in the GPS shells located in dumps [7.8].

Emission of harmful dust and gas substances into the atmosphere and their presence in production facilities are well studied [7.8]. For example, at slag production and bucket discharge sites, the content of PH_3 reaches 0.3 ... 3.5 g / m^3, and HF – 1.25 ... 6.9 mg / m^3 [8]. At four phosphorus production plants (before 1990) in Shymkent and Zhambul, the emission of harmful gas-dust-like substances into the atmosphere reached 150 billion m^3, the content of phosphine, hydrogen fluoride and hydrogen sulfide, dust up to 200 thousand tons per year (currently, “Kazphosphate” LLP pay special attention to labor protection and safety) . There is no such close attention to phosphate slag dumps.

The above mentioned gases are very dangerous and toxic (table 1).

Table 1 – MPC (in mg/$m^{3)}$ gas toxic substances occurring in the composition of phosphorus slag dumps [9]

Substance	Hazard	Maximum permissible concentration (mg/m^3)*		
		MPC_{WA}	MPC_{MS}	MPC_{AD}
H_2S	2	10	0,008	0,008
HF	2	0,5	0,02	0,005
SiF_4	2	0,5	0,02	0,005
PH_3	2	0,5	0,1	0,1
CO	4	20	3 ... 5	1 ... 3
Dust	3	–	0,3	0,1

*****WA - working area, MS – maximum single, AD - average daily

Studies have shown that higher MPC may cause various human diseases (peptic ulcer, chronic gastritis, cirrhosis of the liver, musculoskeletal disorders) and animals’ skull bones and teeth destruction. They are especially dangerous for river and marine animals [7.8].

There are known developments of non-fired and composite binders and concrete on the basis of electrothermophosphorus slags from the Novo-Zhambul phosphoric plant, Kazfosfat LLP with high strength and durability, also physicochemical processes of the products of hydration and structure formation of these binders have been studied [10-12].

An analysis of the literature data shows [7.8] that in the phosphorus industry, particular attention is paid to emissions and production facilities, and phosphorus slag dumps are almost absent. Meanwhile, these dumps have a significant uncontrolled anthropogenic impact on biogeocenosis, i.e. the environment. Therefore, the study of physical and chemical processes associated with GFSD is quite urgent – this is what this work is devoted to.

Research Methodology. The object of the study was granular phosphorus slag from dumps located on the territory of Kazphosphate LLP (Taraz).

The chemical and phase GPS compositions were identified using a DRON-3M X-ray machine (Russia), derivatographic unit Q-1500 D (MOM, Hungary), infrared spectrophotometer Specord M 80, a MIN-8 polarizing microscope, and traditional chemical analysis.

The determination of hazardous gases was done using the ALTAIR PRO gas analyzer (single-channel explosion-proof portable). Sample preparation with a specific surface of 500 m^2/ kg was carried out for physicochemical analyzes at a laboratory vibratory mill with a capacity of 2 kg. In this case, the released gases were measured through holes with a diameter of 2 mm.

The experimental results. The dumps of granular phosphorus slag (GFSD) in Shymkent and Taraz occupy about 1730 hectares of fertile land with the enclosing territory allocated based on the sanitary standards. In addition, chemical enterprises engaged in the production of phosphorus-containing products are located near the rivers Sairam (Shymkent) and Assa (Taraz), which due to location reasons raises many negative issues.

The GFSD storage period has already reached about 30 ... 50 years. The total amount is more than 20 million tons (moreover, the Shymkent GFSD is constantly decreasing, due to the fact that it is constantly used in road construction - without any permits, Taraz plant is growing due to the existing new Zhambul phosphorus plant).

The chemical composition (rounded) GFS, %: SiO_2 - 41 ... 44; CaO – 44 ... 48; Al_2O_3 – 3.2 ... 3.6; Fe_2O_3 – 0.5 ... 0.6; MgO – 2.5 ... 3.2; P_2O_5 – 1.07 ... 2.5; SO_3 – 0.5 ... 0.8; F – 1.2 ... 2.0; calcium phosphide (Ca_3P_2) – 0.2 ... 0.3; calcium fluoride (CaF_2) – 4.0 ... 4.5; calcium sulfide (CaS) – 0.2 ... 0.3.

Such a chemical composition of GFS is obtained as a result of physicochemical processes occurring at a temperature of about 1450°C in electrothermal furnaces in mixtures consisting of phosphate [$Ca_3(PO_4)_2$] from the Karatau deposit, quartz sand (SiO_2) and carbon (C) based on the following formula (1).

When molten slag comes into contact (t = 1450 ... 1500°C) with water vapor and in case of water granulation the chemical pyrohydroline reactions occur (schematically) [13] as follows:

$$\begin{gathered} CaF_2 + H_2O + SiO_2 = 2HF + CaO \cdot SiO_2, \\ Ca_3P_2 + 3H_2O + 3SiO_2 = 2PH_3 + 3\,(CaOSiO_2), \\ CaS + H_2O + SiO_2 = H_2S + CaO \cdot SiO_2. \end{gathered} \tag{2}$$

Elemental phosphorus, interacting with atmospheric oxygen, forms phosphoric anhydrite based on the following formula:

$$4P + 5O_2 \rightarrow 2P_2O_5 \tag{3}$$

With rapid water cooling, the melt does not have time to crystallize and by retaining some of the internal energy, passes into the vitreous state. This state gives GFS a certain astringent property which increased when grinded and activated by various additives. The average GFS density is about 1100 ... 1200 kg / m^3, its soft shell material is easily destroyed by external influences.

The formation of the halo in the X-ray diffraction pattern and the diffusivity of the main maxima of the absorption bands of the IRS confirm its amorphism. The endoeffect in its thermogram at 800 °C shows softening of the glass, and the exoeffect at 920 °C – the crystallization of pseudo-(CaO · SiO_2) (figure 2). From this physical analysis it can be seen that GFS is an excellent material for use in silicate and building materials and products, including road construction and agriculture. However, only if it is neutralized from hazardous impurity gases.

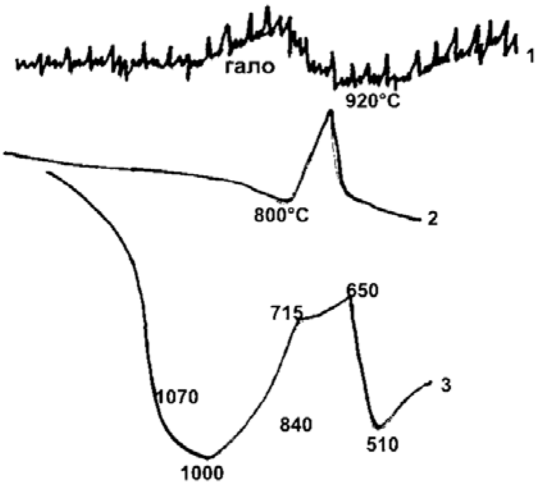


Figure 2 – X-ray diffraction pattern (1), thermogram (2) and a fragment of the infrared spectrum (3) of the GFS

It should be emphasized that the components of the GFS are not inactive but actively interact with the environmental ingredients and themselves, by significantly increasing its anthropogenic impact on biogeocenosis. Gas-dust emissions of the existing phosphorus plant settling on the surface of GFSD will make their negative contribution.

In GFSD structures the main interdependent parallel physical and chemical processes may occur as follows:

- chemicals associated with harmful gases;
- physical and chemical, associated with the hydration of slag and its dust.

a) Chemical reactions associated with gases in GFS shells, for example, with PH_3:

$$PH_3+H_2O\rightarrow PH4++OH^-,$$

$$PH4++H_2O\rightarrow PH_4OH+H^-,$$

or

$$PH4++H_2O\rightarrow PH_3+H_3O^+,$$

$$PH4++OH^-\rightarrow PH_3+H_2O^+,$$

$$2\,PH_3+4O_2\rightarrow P_2O_5+3H_2O, \tag{4}$$

$$P_2O_5+H_2O\rightarrow 2HPO_3,$$

$$HPO_3+H_2O\rightarrow H_3PO_4$$

Therefore, depending on the environment, a phosphine in the ecosystem can exist in the form of compounds as follows: $PH_3\rightarrow P_2O_5\rightarrow NRA_3\rightarrow H_3PO_4$.

The same chemical reactions occur with H_2S, HF + SiF_4 and CO, respectively, with the formation (schematically):

$$H_2S\rightarrow H_2SO_3\rightarrow H_2SO_4;$$

$$HF\rightarrow HF_2;\ SiF_4\rightarrow H_2SiO_3\rightarrow H_2SiF_6 \tag{5}$$

$$CO\rightarrow CO_2\rightarrow COCl_2$$

Furthermore:

- calcium phosphide is poisonous gas – it may under certain conditions be a constant source of formation of a new portion of PH3;
- calcium sulfide turns into H_2S based on the following formula:

$CaS + 2H_2O \xrightarrow{100^\circ C} Ca(OH)_2 + H_2S\uparrow$(under conditions of phosphoric slag binders steaming);

$$CaS + CO_2 + H_2O\rightarrow CaCO_3 + H_2S\uparrow; \tag{6}$$

calcium fluoride - during autoclaving of phosphoric slag binders it can give HF based on the following formula:

$$CaF_2 + H_2SO_4 \xrightarrow{130...200^\circ C} CaSO_4 + 2HF\uparrow \tag{7}$$

As can be seen from the table 2 the content of Ca_3P_2, CaF_2 and CaS in the composition of GFSD in the amount of 20 million tons of solids: 69.3; 2700 and 69.3 respectively, t.

Table 2 – The total content of gas-forming substances in GFSD, the amount of which is 20 million tons

Name of gas-forming substances	Chemical formula	Content of gas-forming substances	
		%	t
Calcium phosphide	Ca_3P_2	0,3	69,3
Calcium fluoride	CaF_2	4,0	2700
Sulfide calcium	CaS	0,3	69,3

b) Physical and chemical processes associated with slag hydration:

A neoplasm is formed on the surface of the slag grains as a result of interaction with water. A physicochemical study showed (figure 3) that this neoplasm consists of a gel- and crystalline CSH (I) and calcite. As can be seen from this figure, peaks appear on the radiograph at d/n = 3.03; 2.84 and 1.82 Å, typical for crystalline CSH (I). Five effects are recorded on the thermogram – three endo and two – exoeffects.

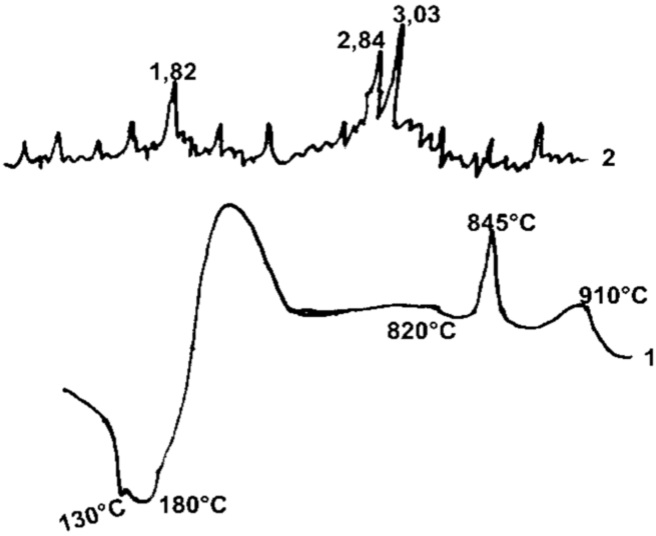


Figure 3 – X-ray diffraction pattern (2) and thermogram (1) of GFSD grains

The endoeffect at 130 °C indicates the presence of gel-like phases in the neoplasm and the endoeffect at 180 °C is apparently a submicrocrystalline part of the hydrosilicate phases.

These processes proceed according to the following schemes:

$$C_2SH_2 \xrightarrow{120-180°C} C_xS_yH_z + CH.$$

The endoeffect at 820°C shows the calcite decarbonization according to the scheme:

$$CaCO_3 \xrightarrow{180°C} CaO + CO_2, \quad (8)$$

which confirms carbonization of previously formed hydrosilicate phases that arose during the surface interaction of slag grains with water.

The exoeffect at 840°C indicates the transition of CSH (I) at elevated temperature to wollastonite by the reaction:

$$CSH \xrightarrow{845°C} \beta\text{–}CS. \quad (9)$$

The exoeffect at 910 °C confirms crystallization of the initial glassy slag with the formation of β–CaO–SiO_2.

Petrographic studies show that the gel-like silicate mass has light refraction in the range n = 1.51 ... 1.53; CSH (I) – n = 1.54 ... 1.56, and $CaCO_3$ – n_0 = 1,658; n_s = 1.485. In this case, CSH (I) has a fibrous structure, and calcite crystals are formed as a rhombohedron and a prism. The depth of hydration of the slag grains is 0.1 ... 0.3 microns.

Thus, in dumps, granular phosphorus slag is hydrated in the presence of water, which leads to its transformation into stone with a certain strength, as a result of which individual grains are crosslinked into a single whole, which is denser than slag, therefore it envelops the slag grains in a dense layer, which prevents further hydration of the slag itself. However, this dense layer in the form of a crust occurs with cracks through which water, gas, snow, etc. penetrate into the dump.

Phosphate slag dumps are a constant source of pollution of the region's ecosystem. In fact, as long as these phosphorus slag dumps exist nearby, there can be no improvement of the environmental situation in the southern region of Kazakhstan.

In preventing environmental pollution caused by phosphorus slag and waste disposal facilities, there are four main options:

– cover them with a thick layer of earth or with a special polymer or concrete mixture;

– liquidate by laying them in mine and other man-made spaces;

– use as fertilizer for agricultural farming and material for land reclamation purposes;

– produce various building materials on their basis.

It is possible, of course, to leave everything as it is. However, this is counterproductive, as discussed above.

Let's briefly consider all the pros and cons of implementing the above in terms of environmental and economic efficiency.

1. The closure of phosphate slag dumps with a total area of 50 hectares with a thick layer of land is unproductive, because:

– removal of this land causes additional anthropogenic environmental pollution and the alienation and desolation of lands;

– huge financial, human and technical costs;

– earth filling of phosphate storage facilities with a height of 50 m each is not so simple based on the technical capabilities of existing machines and mechanisms;

– the main low productivity of this venture is that this work will need to be repeated periodically, since the thickness of the backfill may decrease due to erosion reason;

– when closing the dumps with concrete mix it can be considered that the environmental problem will be solved, however, such work will be more expensive than backfilling option (for example, the cost of 1 ton of land is 2500 tg, cement – 14500 ... 15000 tg) therefore, from an economic point of view such an event is extremely ineffective;

– closing the dumps with a special polymer mixture is the most promising among others, however, the life of the polymer film is relatively short (1-1.5 years), such an expensive mixture will need to be exported, since it is not produced in Kazakhstan, in addition, under certain conditions (for example, in its interaction with acids toxic substances) it creates an environmental problem.

2. Even more inefficient in environmental and economic terms is the liquidation of phosphate slag dumps by laying down mine and other man-made spaces. For example, the cost of one 60-ton wagon reaches 320 thousand tenge. For 20 million tons of phosphorus slag, 333,333 wagons are needed. It is easy to calculate - the transportation of slag dumps by wagons will amount to 106 billion tenge. But in addition to transportation, there are other operations such as loading and unloading, filling, etc. These are additional costs – their cost is equal to 20-30 % of the transportation cost.

3. If slag dumps are used as fertilizer for agricultural farming and as material for land reclamation, then, first of all, a technological line cleaning gaseous substances, especially phosphine, hydrogen fluoride and hydrogen sulfide will be needed. In addition, the technical and economic efficiency of slag dumps as fertilizer used for land reclamation shall be defined since there are conflicting data on this [14].

4. What if to produce various effective building materials on the basis of slag dumps? However, we note the following: with some certainty, it can be argued that there is simply no alternative to processing these dumps into building and silicate materials. In our opinion, this direction is the most promising and environmentally and economically effective, since in this case the problem associated with the slag dumps utilization is solved comprehensively.

The specificity and nature of the phosphate dumps in which the prehistory of their occurrence is associated with the production of phosphate-containing products, determines the increased degree of their anthropogenic impact on the ecosystem, namely, as already mentioned on biogeocenosis.

Summary. 1. In the phosphorus industry, environmental, technological and sanitary safety usually means the measures and technical requirements related to the emission of harmful substances into the atmosphere and hydrosphere, as well as their level of concentration in production facilities without giving the required attention to the granular phosphorus slag dumps.

Meanwhile, the granular phosphorus slag dumps in the amount of 20 million tons have a significant anthropogenic impact on biogeocenosis, i.e. the environment, since hazardous gas-dusty ingredients are accumulated in its structures.

2. Chemical and physico-chemical processes constantly occur in the structures of dumps, as a result of which:

- phosphine (PH_3) can be in the form: $PH_3 \leftrightarrow P_2O_5 \leftrightarrow HPO_3 \leftrightarrow H_3PO_4$;
- hydrogen sulfide (H_2S) – $H_2S \leftrightarrow H_2SO_3 \leftrightarrow H_2SO_4$;
- hydrogen fluoride and silicon tetrafluoride - $HF \leftrightarrow SiF_4 \leftrightarrow H_2SiF_6 \leftrightarrow H_2SiO_3$;
- carbon monoxide (CO) – $CO \rightarrow CO_2 \rightarrow COCl_2$;
- slag → CSH (I).

3. The potential amount of 20 million tons of phosphate and calcium sulfide sludge can reach 69.3 tons, and calcium fluoride – up to 2700 tons, which under certain conditions can be sources of the above-mentioned dangerous gases.

4. Finding granular phosphorus slag in the form of dumps is extremely dangerous for biogeocenosis and the urgent need for their disposal suggests itself, especially since these slags are valuable raw materials for the construction industry and agriculture.

Confirmations. Scientific results were obtained within the framework of TsELSIM LLP work.

З.А. Естемесов, П.И. Садыков, А.В. Барвинов,
Н. Б. Сарсенбаев, М.З. Естемесов, А.У. Уралханова, А.А. Тулаганов

«ЦеЛСИМ» ЖШС Орталық құрылыс материалдарын сертификаттау сынақтары зертханасы,
Алматы қ., Қазақстан

ТІЙІРШІКТЕЛГЕН ФОСФОР ҚОЖДАРЫ ҮЙІНДІЛЕРІНДЕ БОЛАТЫН ФИЗИКАЛЫҚ-ХИМИЯЛЫҚ ПРОЦЕСТЕР

Аннотация. Қазақстан аумағындағы ең қауіпті техногендік минералдық түзілімдердің бірі – түйіршіктелген фосфор қожының үйінділері, өйткені оның қабықтарында бастапқыда PH_3, H_2S, HF және т.б. сияқты қауіпті газдар бар. Бұл газдардың тұрақты көздері – Ca_3P_2 (өзімен өзі улы газ), CaS және CaF_2 де. Фосфор қожы үйінділерінің құрылымдарында үнемі химиялық және физикалық-химиялық процестер орын алып тұрады, нәтижесінде бастапқыда болатын газдар әртүрлі модификацияларда болуы мүмкін. Мысалы:

- Фосфин (PH_3) $PH_3 \rightarrow P_2O_5 \rightarrow HPO_3 \rightarrow H_3PO_4$ түрінде;
- Күкірт сутегі (H_2S): $H_2S \rightarrow H_2SO_3 \rightarrow H_2SO_4$ түрінде;
- Фторлы сутегі және кремний тетрафториді: $HF \rightarrow SiF_4 \rightarrow H_2SiF_6 \rightarrow H_2SiO_3$;
- Көміртегі оксиді (CO): $CO \rightarrow CO_2 \rightarrow COCl_2$.

Мұндай химиялық процестер фосфор қожы үйінділерінің қоршаған ортаға антропогендік әсерін – биогеоценозды айтарлықтай күшейтеді.

Газды құрамдастарға байланысты процестерден басқа, фосфор қожы үйінділерінде қождың сумен өзара әрекеттесуі нәтижесінде гидратациялық процестер орын алады. Бұл ретте субмикрокристалды CSH(I) және кальций түзіледі. Қождың гидратация терендігі 1...3 мкм-ге жетеді. Осы процестердің нәтижесінде қож бөлшектерінің бетінде жұқа қабат пайда болады, соның салдарынан жекелеген түйіршіктердің біртұтас болып бірігуі орын алады. Сондықтан фосфор қожы үйінділерінің беті үйіндінің ішіне су, ауа, қар және т.б. кіретін жарықтармен белгілі бір беріктікке ие.

Түйіршіктелген фосфор қождарының үйінділер түрінде болуы биогеоценозға өте теріс әсер ететіні белгілі, осыған байланысты оларды кәдеге жаратудың аса үлкен қажеттілігі туындайды, әсіресе, бұл қождар, оларды қауіпті газдардан зарарсыздандырғаннан кейін ғана құрылыс индустриясы мен ауыл шаруашылығы үшін бағалы шикізат болып саналады.

Түйін сөздер. Түйіршіктелген фосфор қожы, үйінділер, қауіпті газдар, химиялық реакциялар.

З.А. Естемесов, П.И. Садыков, А.В. Барвинов,
Н. Б. Сарсенбаев, М.З. Естемесов, А.У. Уралханова, А. А. Тулаганов

ТОО «ЦеЛСИМ» Центральная лаборатория сертификационных испытаний строительных материалов,
г. Алматы, Казахстан

ФИЗИКО-ХИМИЧЕСКИЕ ПРОЦЕССЫ, ПРОИСХОДЯЩИЕ В ОТВАЛАХ ГРАНУЛИРОВАННЫХ ФОСФОРНЫХ ШЛАКОВ

Аннотация. Одним из наиболее опасных техногенных минеральных образований, находящихся на территории Казахстана, являются отвалы гранулированного фосфорного шлака, поскольку в его скорлупах изначально присутствуют такие опасные газы как PH_3, H_2S, HF и др. Постоянными источниками этих газов являются также Ca_3P_2 (сам по себе ядовитый газ), CaS и CaF_2. В структурах фосфошлакоотвалов постоянно происходят химические и физико-химические процессы, в результате которых изначально присутствующие газы могут находиться в различных модификациях. Например:

- Фосфин (PH_3) в виде: $PH_3 \rightarrow P_2O_5 \rightarrow HPO_3 \rightarrow H_3PO_4$;
- Сероводород (H_2S): $H_2S \rightarrow H_2SO_3 \rightarrow H_2SO_4$;
- Фтористый водород и тетрафторид кремния: $HF \rightarrow SiF_4 \rightarrow H_2SiF_6 \rightarrow H_2SiO_3$;
- Оксид углерода (CO):$CO \rightarrow CO_2 \rightarrow COCl_2$.

Такие химические процессы существенно усиливают антропогенное влияние фосфошлакоотвалов на окружающую среду – биогеоценоз.

Кроме процессов, связанных с газовыми составляющими, в фосфошлакоотвалах происходят гидратационные процессы в результате взаимодействия самого шлака с водой. При этом образуются субмикрокристаллические CSH(I) и кальций. Глубина гидратации шлака достигает 1…3 мкм. В результате этих процессов на поверхности частиц шлака возникает тонкий слой, вследствие чего происходит сшивание отдельных зерен в единое целое. Поэтому поверхность фосфошлакоотвалов обладает определенной прочностью с трещинами, через которые внутрь отвала проникают вода, воздух, снег и др.

Очевидно, что нахождение гранулированных фосфорных шлаков в виде отвалов чрезвычайно негативно влияет на биогеоценоз, в связи с этим возникает настоятельная необходимость их утилизации, тем более эти шлаки являются ценным сырьем для строительной индустрии и сельского хозяйства, только после их обезвреживания от опасных газов.

Ключевые слова. Гранулированный фосфорный шлак, отвалы, опасные газы, химические реакции.

Information about the authors:

Estemesov Zatkali Ayranbayuly - Director, Doctor of Technical Sciences, professor of TseLSIM LLP, Almaty, Republic of Kazakhstan; tselsim@mail.ru; https://orcid.org/0000-0001-8625-3735;

Sadykov Pernekhan Ibadullaevich - Chief Researcher, Doctor of Technical Sciences, LLP TsELSIM, Almaty, Republic of Kazakhstan; pernekhan.sadykov@inbox.ru, https://orcid.org/0000-0001-8384-7028;

Barvinov Andrei Vladimirovich - Head of Production, Candidate of Technical Sciences, LLP TsELSIM, Almaty, Republic of Kazakhstan; barvinov00@inbox.ru, https://orcid.org/0000-0002-2420-6121;

Sarsenbaev Nurali Bakytzhanovich - Senior Researcher, Doctor of PhD, LLP TseLSIM, Almaty, Republic of Kazakhstan; sarsenbayev_n@inbox.ru, https://orcid.org/0000-0001-7054-4247;

Estemesov Marat Zatkalievich - Senior Researcher, Candidate of Technical Sciences, LLP TseLSIM, Almaty, Republic of Kazakhstan; myestemesov@inbox.ru, https://orcid.org/0000-0002-4032-5710;

Uralkhanova Aknur Uralkhanzyzy - Engineer, Master of Engineering, TseLSIM LLP, Almaty, Republic of Kazakhstan; uralkhanova@inbox.ru, https://orcid.org/0000-0002-3344-3145;

Tulaganov Abdukabil Abdunabievich - head of the construction material department of Tashkent Architectural-Constructional Institute, Doctor of Engineering Science, Professor, Tashkent Architectural-Constructional Institute, Tashkent, Uzbekistan; a_tulaganov@inbox.ru, https://orcid.org/0000-0002-5851-7403

REFERENCES

[1] Sadykov P. About storages of technogenic raw materials and their impact on the environment // Journal: Regional Bulletin of the East (UKGU), No. 3, 2002. S.13-16.

[2] Sadykov P.I., Estemesov Z.A. Silicate-forming processes occurring during hardening of an eco-slag binder // In Journal: Complex Use of Mineral Raw Materials, No. 5, 2002. P.78-80.

[3] Sadykov P.I., Estemesov Z.A. Physico-chemical silicate-forming processes occurring in phosphorus slag dumps // Journal: Hydrometeorology and Ecology, No. 3, 2002. P.148-151.

[4] Estemesov Z.A., Barvinov A.V., Sarsenbaev N.B. Hidden problems associated with the use of granular phosphorus slag in cement // Sat .: High technology and innovation, part 6, Belgorod, 2019. P.29.

[5] Kurakbaeva R.Kh.,.Dorfman Y.A, Polimbetova G.S., Shokorova L.A., Kuatbaev K.K., Kozlovsky V.A. Mechanochemical oxidation of bound and free oxygen of trace amounts of calcium phosphide in electrothermophosphorus slag // Journal of Applied Chemistry, vol. 3, 1992. S. 487-497.

[6] Dorfman Ya.A., Kurakbaeva R.Kh., Polimbetova G.S. Catalytic neutralization of electrothermophosphorus slag // Journal of Applied Chemistry, Edition10, 1992. P. 2179-2183.

[7] Kurakbaev R.H., Dorfman Ya.A., Polimbetova, etc. Preparation of binders from electrothermal phosphorus slag // Izvestiya of the Academy of Sciences of KazSSR, chemical series. 1991, No 2. P. 18-23.

[8] Sh. Moldabekov. Purification of phosphorus, fluorine and sulfur-containing gases produced by phosphorus and its compounds: Abstract. Thesis of Dr. of Technical Sciences. Moscow: 1984. 36 p. [Russian].

[9] Turgaeva K.S. Hygienic working conditions in the production of cast slag crushed stone at the Zhambul phosphorus plant / In the book: The use of slag obtained through electrothermal processing of phosphorus ores from the Karatau deposit of the Kazakh SSR for the manufacture of building materials and products. Alma-Ata: NIIStromproekt, 1975. p. 143. 146. [Russian].

[10] Chemical encyclopedic dictionary. Moscow: SE, 1983. p.791.

[11] Sarsenbayev N.B., Sarsenbayev V.K., Aubakirova T.S., Aimenov J.T., Abdiramanova K.S. Phase composition and structure-formation of the low-clinkered floral cements // Eurasian Chemico-Technological Journal. 2014. V. 16. Edition 4. P. 333-338.

[12] Aymenov Zh.T., Sarsenbayev B.K., Sarsenbayev N.B., Aldiyarov Zh.A. Use of solar energy for heliothermal treatment of concretes on the basis of alkali cements // The 15th Asian Regional Conference of Soil Mechanics and Geotechnical Engineering, Japan, 2015.

[13] Aymenov A.Zh., Sarsenbayev N.B., Khudyakova T.M., Sarsenbayev B.K., Kopzhassarov B.T. Influence of addition of polymetallic ores' tailings on properties of composite cements. SCOPUS Scientific Journal. Eurasian Chemico-Technological Journal 2016. p. 153-160.

[14] Poluboyartsev A.G., Patrushev D.A., Yumanova L.V., Bogacheva G.N., Amelin E.S., Torsis E.T. The interaction of molten phosphorus slag with water, water vapor and air / In the book: Slag phosphorus industry. Chelyabinsk, 1970, S. 41-44. [USSR].

[15] Castred Yu.K. Phosphate wastes land reclamation // In the book: Solid waste – generation, collection, processing and disposal. Translated from English by E.G. Teterina and A.S. Syutnikova. Moscow: Stroyizdat, 1979. S. 473-480. [USA].

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.23**
Volume 2, Number 440 (2020), 56 – 61

UDC 541.128: [546.171.5+547.235]
IRSTI 31.15.33

S.A. Dzhumadullaeva[1], A.B. Bayeshov[2], A.V. Kolesnikov[3]

[1]Khoja Akhmet Yassawi Kazakh-Turkish International University, Turkistan, Kazakhstan;
[2]Institute of Fuel, Catalysis and Electrochemistry named after D.V.Sokolsky, Almaty Kazakhstan;
[3]JSC D.Mendeleyev University of Chemical Technology of Russia, Moscow, Russia.
E-mail: sveta.jumadullayeva@ayu.edu.kz

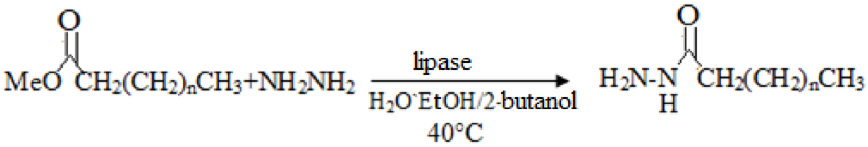
STUDY OF THE CATALYTIC HYDRAZINOLYSIS OF HIGHER FATTY ACIDS

Abstract. In this work, the reaction of hydrazinolysis of higher fatty acid in the presence of an ionite catalyst is considered for the first time. Synthetic commodity anion exchange resin AB-17-8 was used as a catalyst. Before use, the anionite was converted to OH-form and its exchange capacity was determined. The experiments were made in the static conditions in a glass reactor with mixing of the reaction mixture.The reaction of palmitic acid with hydrazine yielded the corresponding hydrazide. The influence of various factors (quantity of hydrazine hydrate, catalyst, butyl alcohol, temperature, reaction duration) on the formation of palmitic acid hydrazide was studied. It is shown that with an increase in the amount of hydrazine hydrate in the initial mixture from 2.0 to 2.52 g per gram of palmitic acid, the yield of hydrazide increases, and further increase in the concentration of this reagent leads to a decrease in the selectivity of the process, due to the occurrence of side condensation reactions. Increasing the amount of catalyst from 2 to 3 g per gram of palmitic acid leads to an increase in the yield of hydrazide. It reveals optimum conditions of synthesis under which the most palmitic hydrazide yield made 90%. The analysis of the initial substances and the reaction product was carried out using the photocolorimetric method. As a result, the IR spectroscopic researches of the mechanism of hydrazinolysis reaction of the palmitic acid with active centers of anion-exchange. It is shown that the reaction proceeds with the formation of transition complexes on the surface of the anion exchange resin. The practical value of this work is to develop an effective method of palmitic acid hydrazide preparation.

Keywords: palmitic acid, hydrazine, hydrazide, catalyst.

Introduction. Higher fatty acid hydrazides and their derivatives are widely used in medical practice, in various sectors of the national economy [1-4]. For example, hydrazides of oleic, linoleic, linolenic and palmitic acids have been used as antibacterial, anti-fungal, and anthelminthic drugs, fungicides, chelating agents, and metal corrosion inhibitors [5,6].

There are various methods of obtaining hydrazides of higher fatty acids [6]. For example, the most promising way to produce hydrazides is the hydrazinolysis of esters, mainly methyl or ethyl esters of the corresponding carboxylic acids, when heated in a solvent medium. Hydrazides of oleic, linoleic, and linolenic acids have been prepared from the corresponding methyl esters under argon within 3–4 h in anhydrous alcohol [6]. Another method of synthesis of these compounds is enzymatic hydrazinolysis of methyl esters with lipase in an aqueous-alcoholic medium at 40°C [5]. The drawbacks of this method are mediocre yield of the hydrazides (70–75%), poor selectivity of the process, sophisticated isolation of the target product from the reaction mixture, and the need to grow microorganisms [5].



In addition, methods are known based on the thermal decomposition of carboxylic acid salts with hydrazine [7]. The disadvantage of these methods is that, along with the main product, are obtained incommensurate amounts of impurities - 1,2-diacylhydrazines and cyclic compounds. The yield of the main product (hydrazide) is increased, in particular, by azeotropic distillation of water. Also known is a method of producing hydrazides by thermal decomposition of salts of carboxylic acids with hydrazine hydrate, including mixing carboxylic acid and hydrazine hydrate in a molar ratio of CA: HH = 1: 1.2, heating under reflux in the presence of butanol, active aluminum oxide and benzene, distilling water as an azeotrope at a temperature of 95 °C for 2-8 hours, filtering the melt of the reaction mixture, crystallization, washing and drying the product in vacuum [8]. The yield of hydrazides is 80-95%.

The disadvantage of this method is that it is suitable for obtaining only hydrazides of lower carboxylic aliphatic acids with the radicals R = CH_3, i-C_3H_7. In addition, this method uses solvents that deteriorate the organoleptic properties of the product, which requires additional purification of the target product.

At present, the synthesis of carboxylic acids and their derivatives using heterogeneous catalysts - ionites is the most promising method [8-10]. In this regard, the synthesis of practically important higher fatty acid hydrazides in the presence of heterogeneous catalysts is an important task.

The purpose of this study is to investigate the hydrazinolysis of palmitic acid in the presence of the anion-exchanger AV-17-8 in the OH-form.

Experimental part. Experiments are carried out in static conditions. In a three-neck round-bottom flask with a capacity of 250 ml, equipped with a mechanical stirrer, a thermometer and a reflux condenser, 1 g (0.0039 mol) of palmitic acid, 2.52 g (0.0504 mol) of hydrazine hydrate, 3 g of anion exchanger AV-17-8 in OH -form, 8 g (0.44 mol) of water are introduced. The reaction mixture is heated on a water bath, stirring for 3 hours at a temperature of 95°C. After this time, the mixture is cooled and the anion-exchanger is filtered off from the liquid part, washed with 30 ml of water. The water is distilled off from the solution, the remaining solid residue is dried at 60°C. The analysis of palmitic acid hydrazide is carried out by the photocolorimetric method. The melting point of hydrazide is 150-152°C. The IR spectra of the starting materials and reaction products are taken on "Impact 410" spectrometer (USA).

Results and discussion. Palmitic acid hydrazinolysis was investigated in the presence of anion exchanger AV-17-8 in the OH-form.

$$C_{15}H_{31}COOH + N_2H_4 \xrightarrow{Kt} C_{15}H_{31}CONHNH_2 + H_2O$$

Under the conditions studied, the main product of the interaction of palmitic acid with hydrazine hydrate is palmitic hydrazide. The influence of various factors (the amount of hydrazine hydrate and anion-exchanger, temperature and duration of the reaction) on the formation of hydrazide are given in the table. During hydrazinolysis of palmitic acid, the optimum process conditions are the mass ratio palmitic acid: hydrazine hydrate : water: anion-exchanger = 1:2.52:8:3, temperature of 95°C, 3 hours of reaction time, while the hydrazide yield amounted to 90%.

Table 1- Palmitic acid hydrazinolysis (palmitic acid mass is 1 g)

hydrazine hydrate, g	anion exchanger, g	water,g	reaction time, hours	temperature, °C	the hydrazide yield, %
3,86	2	8	3	95	47
3,20	2	8	4	95	64
2,52	2	8	3	95	82
2,52	3	8	3	95	90
2,00	3	8	3	95	45
2,52	3	10	3	95	87
2,52	3	12	3	95	86
2,52	3	8	3	80	53

In the infrared spectrum of palmitic hydrazide, absorption bands of valence vibrations are observed in the region of 1641,1706 cm $^{-1}$ (C = O), 2959, 2927, 2849 cm $^{-1}$ (CH_2, CH_3), 1274- 1094 cm $^{-1}$ (C – C), 3433,3220 cm^{-1} (NH) groups, as well as deformation vibrations in the region of 1509 cm^{-1} (NH) groups.

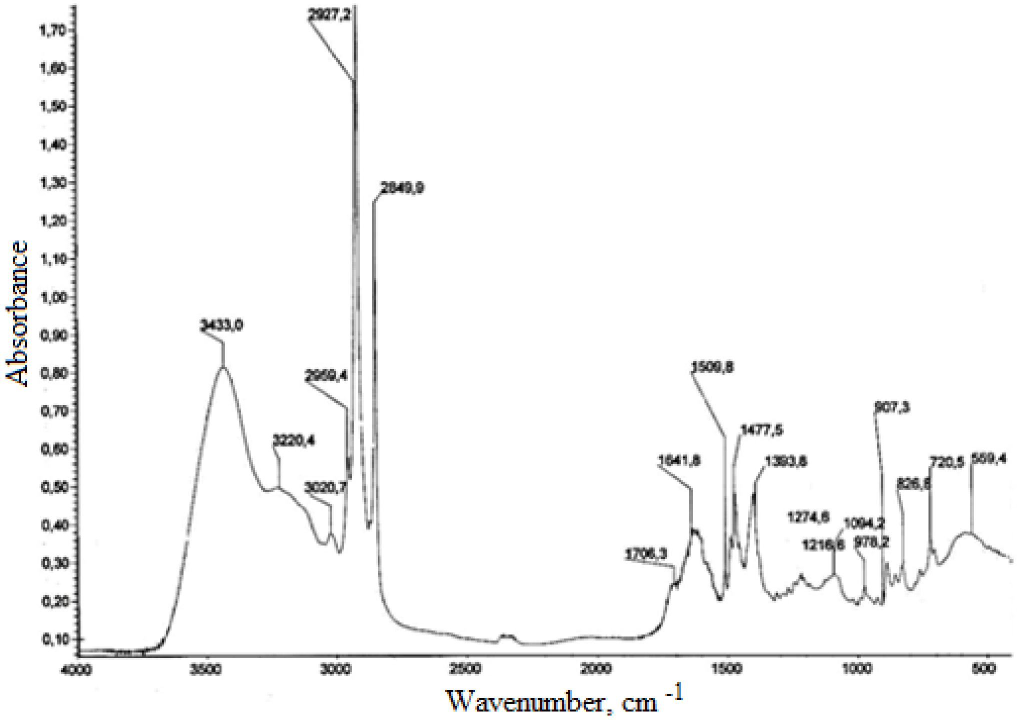
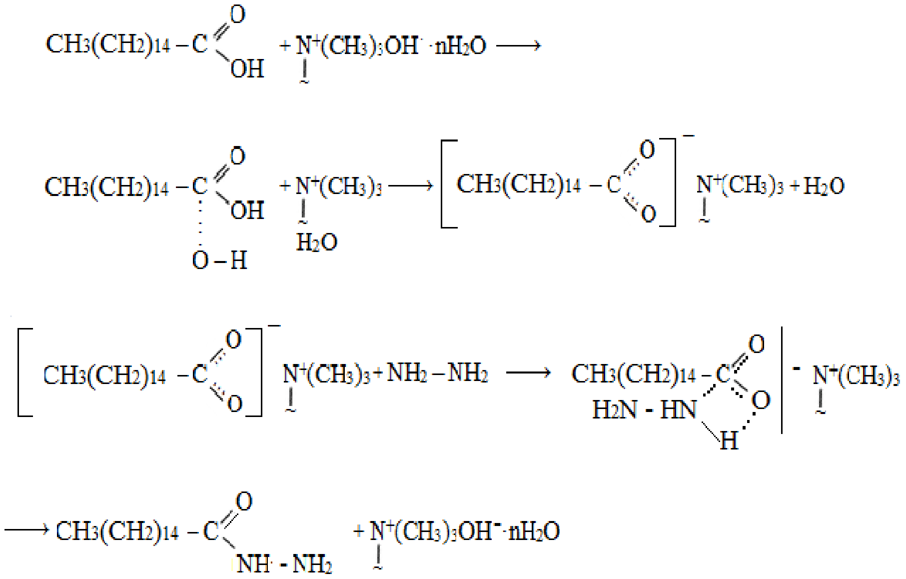


Figure - IR spectrum of palmitic acid hydrazide

The mechanism of hydrazinolysis of higher fatty acids is still not well understood. According to [11-20], it can be assumed that hydrazinolysis of oleic acid in the presence of an ion exchange resin AV-17-8 (OH) is carried out by heterogeneous catalysis and the active centers of the anion exchanger are polymer-bound quaternary ammonium ions and hydroxyl ions . During the adsorption of palmitic acid on the anion-exchange resin , an intermediate complex is formed, which then interacts with hydrazine to form hydrazide and regenerate the active centers of the ion exchanger.



Conclusion. Thus, we first studied the hydrazinolysis of higher fatty acids using the example of palmitic acid in the presence of AV-17-8 (OH) anion exchanger, found the optimal process conditions and made conclusions regarding the reaction mechanism.

С.А. Жұмаділлаева[1], Ә.Б. Баешов[2] , А.В. Колесников[3]

[1]Қожа Ахмет Ясауи атындағы Халықаралық қазақ-түрік университеті, Түркістан, Қазақстан;
[2]Д.В.Сокольский атындағы Жанармай , катализ және электрохимия институты, АҚ, Алматы, Қазақстан;
[3]Д.И. Менделеева атындағы Ресей химия - технологиялық университетінің технопаркі, Москва, Ресей

ЖОҒАРЫ МАЙЛЫ ҚЫШҚЫЛДАРДЫҢ КАТАЛИТТІК ГИДРАЗИНОЛИЗІН ЗЕРТТЕУ

Аннотация. Жоғары майлы қышқылдардың гидразидтері және олардың туындылары медициналық практикада, халық шаруашылығының әртүрлі салаларында кеңінен қолданылады. Айталық, мысалы, олеин, линол,линолен және пальмитин қышқылдарының гидразидтері антибактериалды, вирусқа қарсы , антигельминтті агенттер, фунгицидтер, хелат түзуші агенттер, сонымен қатар полимерлер, тұрақ-тандырғыштар мен бояулар өндірісі үшін қолданылады.

Жоғары майлы қышқылдардың гидразидтерін алудың әртүрлі әдістері белгілі. Мысалы, гидразидтерді алудың анағұрлым қолайлы әдісіне күрделі эфирлердің гидразинолизі, әсіресе жоғары майлы қышқылдардың метилді немесе этилді эфирлерін еріткіште қыздыру әдісі жатады.

Сонымен қатар олеин, линол, линолен және пальмитин қышқылдарының гидразидтерін синтездеуді өздеріне сәйкес метилді эфирлерді қолданып, азот атмосферасында 3-4 сағат бойы абсолюттік спирт ортасында жүзеге асырады. Сондай-ақ, карбон қышқылдарының тұздарын гидразинмен термиялық ыдыратуға негізделген әдістер де белгілі. Бұл әдістердің кемшілігіне негізгі өніммен (гидразидпен) бірге көп мөлшерде 1,2-диацилгидразиндердің және циклды қосылыстардың қоспалары түзілетіндігі жатады. Гидразидтерді алудың келесі әдісі бойынша карбон қышқылдарының тұздарын гидразингидратпен 1:1,2 мольдік қатынасында кері мұздатқышпен бутанол, активті алюминий оксиді және бензол қатысында қыздырып, 95°С температурада 2-8 сағат бойы азеотроп түрінде суды айдап, реакциялық қоспаның қатты бөлігін сүзіп,оны қайта кристалдайды, шаяды және вакуумде кептіреді. Гидразидтер шығымы 80-95%.

Қазіргі кезде карбон қышқылдары және олардың туындыларын гетерогенді катализаторларды-иониттерді қолдану арқылы синтездеу анағұрлым болашағы бар әдіске жатады. Осыған байланысты практикалық жағынан маңызды жоғары карбон қышқылдарының гидразидтерін гетерогенді катализаторлар қатысында синтездеу өзекті мәселе болып табылады.

Бұл жұмыста алғаш рет жоғары майлы қышқылдардың гидразинолиз реакциясы ионитті катализатор қатысында қарастырылды. Катализатор ретінде тауарлы синтетикалық анион алмастырғыш шайыр АВ-17-8 қолданылды. Қолданар алдында анионит ОН-формаға көшірілді және оның алмасу сыйымдылығы анықталды. Тәжірибелер статикалық жағдайда шыны реакторда реакциялық қоспаны араластыру арқылы жүргізілді. Пальмитин қышқылының гидразинмен реакциясы арқылы оған сәйкес гидразид алынды. Пальмитин қышқылы гидразидінің түзілуіне әртүрлі факторлардың (гидразингидраттың, катализатордың, судың мөлшері, температура, реакция ұзақтығы) әсері зерттелді. Бастапқы қоспада 1 г пальмитин қышқылына алынған гидразингидраттың мөлшерін 2-2,52 грамға дейін арттырғанда гидразид шығымы жоғарылады, бұл реагенттің концентрациясын ары қарай арттыру кезінде жанама конденсация реакцияларының жүруіне байланысты процестің селективтілігінің төмендейтіндігі көрсетілді. 1 г пальмитин қышқылына есептелген катализатордың мөлшерін 2-3 грамға дейін арттырғанда гидразид шығымы жоғарылайтындығы анықталды.Синтездің оңтайлы жағдайларында пальмитин қышқылы гидразидінің шығымы 90 % болды. ИҚ-спектроскопиялық зерттеулер нәтижесінде пальмитин қышқылының гидразинолиз реакциясы аниониттің активті орталықтарының қатысуымен жүзеге асатын механизмі ұсынылды. Реакцияның анионит бетінде ауыспалы комплекстердің түзілуімен жүретіндігі көрсетілді. Бұл жұмыстың практикалық маңыздылығы пальмитин қышқылының гидразидін алудың тиімді әдісін ойластыру болып табылады.

Түйін сөздер: пальмитин қышқылы, гидразин, гидразид, катализатор.

С.А. Джумадуллаева[1] , А.Б. Баешов[2], А.В. Колесников[3]

[1]Международный казахско-турецкий университет имени Ходжа Ахмеда Ясави, Туркестан, Казахстан;
[2]Институт топлива, катализа и электрохимии имени Д.В.Сокольского, АО, Алматы, Казахстан;
[3]Технопарк Российского химико-технологического университета имени Д.И.Менделеева, Москва, Россия

ИССЛЕДОВАНИЕ КАТАЛИТИЧЕСКОГО ГИДРАЗИНОЛИЗА ВЫСШИХ ЖИРНЫХ КИСЛОТ

Аннотация. Гидразиды высших жирных кислот и их производные находят широкое применение в медицинской практике, в различных отраслях народного хозяйства. Так, например, гидразиды олеиновой, линолевой, линоленовой, пальмитиновой кислот используются в качестве антибактериальных, противогрибковых, антигельминтных средств, фунгицидов, хелатообразующих агентов, а также применяются для производства полимеров, стабилизаторов и красок.

Существуют различные методы получения гидразидов высших жирных кислот. Например, наиболее удобным способом получения гидразидов является гидразинолиз сложных эфиров, преимущественно метиловых или этиловых эфиров соответствующих высших жирных кислот при нагревании в среде растворителя.

Синтез гидразидов олеиновой, линолевой, линоленовой и пальмитиновой кислот осуществляют также из соответствующих метиловых эфиров в атмосфере азота в течение 3-4 ч в среде абсолютного спирта. Кроме того, известны способы, основанные на термическом разложении солей карбоновых кислот с гидразином . Недостатком этих способов является то, что наряду с основным продуктом (гидразидом), получаются несоразмерные количества примесей - 1,2-диацилгидразинов и циклических соединений . Выход основного продукта повышают, в частности, азеотропной отгонкой воды. Также известен способ получения гидразидов термическим разложением солей карбоновых кислот с гидразингидратом, включающий смешивание карбоновой кислоты и гидразингидрата в мольном соотношении 1:1,2, нагревание с обратным холодильником в присутствии бутанола, активной окиси алюминия и бензола, отгонку воды в виде азеотропа при температуре 95^{o}С в течение 2-8 часов, фильтрацию расплава реакционной смеси, кристаллизацию, промывку и сушку продукта в вакууме. Выход гидразидов составляет 80-95%.

В настоящее время синтез карбоновых кислот и их производных с использованием гетерогенных катализаторов - ионитов является наиболее перспективным способом. В связи с этим синтез практически важных гидразидов высших жирных кислот в присутствии гетерогенных катализаторов является актуальной задачей.

В этой работе впервые рассмотрена реакция гидразинолиза высших жирных кислот в присутствии ионитного катализатора. В качестве катализатора использовали товарную синтетическую анионообменную смолу АВ-17-8. Перед использованием анионит переводили в ОН-форму и определяли его обменную емкость. Опыты проводили в статических условиях в стеклянном реакторе с перемешиванием реакционной смеси. Реакцией пальмитиновой кислоты с гидразином был получен соответствующий гидразид. Изучено влияние различных факторов (количества гидразингидрата, катализатора, воды, температуры, продолжительности реакции) на образование гидразида пальмитиновой кислоты. Показано, что с повышением количества гидразингидрата в исходной смеси от 2,0 до 2,52 г на грамм пальмитиновой кислоты выход гидразида возрастает, дальнейшее увеличение концентрации этого реагента приводит к снижению селективности процесса, за счет протекания побочных реакции конденсации. Повышение количества катализатора от 2 до 3 г на грамм пальмитиновой кислоты приводит к возрастанию выхода гидразида. В оптимальных условиях синтеза выход гидразида пальмитиновой кислоты составил 90 %. Анализ исходных веществ и продукта реакции проводили фотоколориметрическим методом. В результате ИК- спектроскопических исследований предложен механизм реакции гидразинолиза пальмитиновой кислоты с участием активных центров анионита. Показано, что реакция протекает с образованием переходных комплексов на поверхности анионита. Практическая значимость работы состоит в разработке наиболее эффективного способа получения гидразида пальмитиновой кислоты.

Ключевые слова: пальмитиновая кислота, гидразин, гидразид, катализатор.

Information about authors:

Dzhumadullaeva Sveta Absadykovna - candidate of chemical Sciences, Professor of the Khoja Akhmet Yassawi Kazakh-Turkish International University, Turkistan, E-mail: sveta.jumadullayeva@ayu.edu.kz , https://orcid.org/0000-0003-2673-2915;

Bayeshov Abduali Bayeshovich - doctor of chemical Sciences, academic of the National Academy of Sciences of the Republic of Kazakhstan, Institute of Fuel, catalysis and electrochemistry named after D.V.Sokolsky, Almaty, E-mail: bayeshov@mail.ru , https://orcid.org/0000-0003-0745-039X;

Kolesnikov Artem Vladimirovich - candidate of technical Sciences, senior scientific researcher of JSC D.I.Mendeleyev University of Chemical Technology of Russia, Moscow. E-mail: artkoles@list.ru, https://orcid.org/0000-0002-4586-6612

REFERENCES

[1] Ioffe B.V., Kuznetsov M.A., Potekhin A.A. **(1979)** Chemistry of organic derivatives of hydrazine [Khimiya organicheskikh proizvodnykh gidrazina]. L.: Himiya,. 224 p. (in Russ.).

[2] Colla V.E., Berdinsky I.S. **(1976)** Pharmacology and chemistry of derivatives of hydrazine [Farmakologiya i khimiya proizvodnykh gidrazina]. Joshkar-Ola: Mariyskiy book edition, 264 p. (in Russ.).

[3] Toliwal C., Jadav K., Patel K. **(2009)** Synthesis and biological evaluation of fatty hydrazides of By-products of oil processing industry. Indian J. Pharm. Sci. . Vol. 71 (2). P. 144-149. doi: 10.4103/0250-474X.54282 (in Eng.).

[4] Yousef E. A., Zaki M. E., Megahed M. G. **(2003)** Fatty acid hydrazides in organic synthesis. Heterocyclic Comm. N 9. P. 293-298 (in Eng.).

[5] Dzhumadullaeva S.A., Baeshov A.B. **(2019)** Study of kinetics and mechanism of heterogenous catalytic hydrazinolysis of oleic acid. Russ. J. Gen. Chem. Vol. 89, P. 190-193. doi: 10.1134/S1070363219020038 (in Eng.).

[6] Chrissie A. C., James A.K., Neil P. J. P. **(2010)** Preparation of saturated and unsaturated fatty acid hydrazides and long chain *C*-glycoside ketohydrazones. Green Chemistry. . Vol. 12. P. 2012-2018 (in Eng.).

[7] Drozdetsky A.G., Radushev A.V., Turbin A.S., et. al. **(2000)** The method of obtaining hydrazides of aliphatic carboxylic acids and their mixtures [Sposob polucheniya gidrazidov alifaticheskikh karbonovykh kislot i ikh smesey]. Patent № 2147020. Russian Federation [Patent Rossiyskoy Federatsii] (in Russ.).

[8] Dzhumadullayeva S.A., Bayeshov A.B., Altynbekova M.O., Abzhalov B.S. **(2018)** Supramolecular complexes of ionites with organic substrates. News of National Academy of Sciences of the republic of Kazakhstan. Series of chemistry and technology. Volume 2, Number 428 (2018), PP. 26-30. ISSN 2518-1491 (Online), ISSN 2224-5286 (Print). https://doi.org/10.32014/2018.2518-1491

[9] Dzhumadullaeva S.A., Altynbekova M.O. **(2013)** A Mechanism for the Hydrazinolysis of Benzoic Acid in the Presence of Ion-exchange Catalyst. Russian Journal of Physical Chemistry A. Vol. 787, (11), PP. 1943-1945 (in Eng.). https://doi.org/10.1134/S0036024413110083 ISSN 0036-0244 (Print).

[10] Dzhumadullaeva S.A., Baeshov A.B. **(2017)** Ion-Exchange Resin Catalysts in the Liquid-Phase Hydrazinolysis of Cinnamic Acid. Kinetics and Catalysis. Vol. 58 (1). PP. 26-29 (in Eng). (Print). https://doi.org/10.1134/S0023158417010025

[11] Dzhumadullayeva S.A., Baeshov A.B. **(2017)** Reaction of hydrazinolysis of oxalic acid at presence of sulfonic acid cation exchanger. Reports of the News of National Academy of Sciences of the republic of Kazakhstan. Volume. 6, Number 426, PP.87-91. ISSN 2518-1483 (Online), ISSN 2224-5227 (Print). https://doi.org/10.32014/2018.2518-1483

[12] Tsundel G. **(1969)** Hydration and intermolecular interaction. Investigation of polyelectrolytes by infrared spectroscopy [Gidra-tatsiya i mezhmolekulyarnoye vzoimodeystviye. Issledovaniye polielektrolitov metodom infrakrasnoy spektroskopii]. M.: Mir,. 310 p. (in Russ.).

[13] Semushin A.M., Yakovlev V.A., Ivanova E.V. **(1980)** Infrared absorption spectra of ion-exchange materials [Infrakrasnyye spektry pogloshcheniya ionoobmennykh materialov]. L .: Himiya, Leningradskoe otdelenie,. 96 p. (in Russ.).

[14] Gragerov I.P., Pogorelyy V.K., Franchuk I.F. **(1978)** Hydrogen connection and fast proton exchange [Vodorodnaya svyaz' i bystryy protonnyy obmen]. Kiev: Naukova Dumka, 215 p. (in Russ.).

[15] Dzhumadullayeva S.A., Bayeshov A.B. **(2019)** Study of the catalytic reaction of hydrazinolysis of aliphatic carboxylic acids. News of National Academy of Sciences of the republic of Kazakhstan. Series of chemistry and technology.Volume 2, Number 434, P. 61–65. ISSN 2518-1491 (Online), ISSN 2224-5286(Print). https://doi.org/10.32014/2019.2518-1491.20

[16] Kiselev A.V., Lygin V.I. **(1972)** Infrared spectra of surface compounds and adsorbed substances [Infrakrasnyye spektry poverkhnostnykh soyedineniy i adsorbirovannykh veshchestv]. M.: Nauka, 459 p. (in Russ.).

[17] Bellamy L. **(1957)** Infrared spectra of molecules [Infrakrasnyye spektry molekul]. M.: IL,. 444 p. (in Russ.).

[18] Librovich N.B., Mayorov V.D., Saveleva V.A. (**1975)** Ion $H_5O_2^+$ in vibrational spectra of aqueous solutions of strong acids [Ion $H_5O_2^+$ v kolebatel'nykh spektrakh vodnykh rastvorov sil'nykh kislot]. Dokl. AN SSSR**.** Vol. 225 (6). P. 1358-1360. (in Russ.).

[19] Librovich N.B., Sakun V.P., Sokolov N.D. **(1978)**Vibrational spectrum of a hydrated proton [Kolebatel'nyy spektr gidratirovannogo protona]. Teoret. and exper. Chemistry**.** Vol. 14 (4). P. 435-446. (in Russ.).

[20] UglyanskayaV.A., Chikin G.A., Selemenev V.F., Zavyalova T.A. **(1989)** Infrared spectroscopy of ion-exchange materials [Infrakrasnaya spektroskopiya ionoobmennykh materialov]. Voronezh: Ed. VSU,. 205 p. (in Russ.).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.24**
Volume 2, Number 440 (2020), 62 – 68

UDC 547.7/.8:547.796.1

S.D. Fazylov[1,3], O.A. Nurkenov[1,4], A.E. Arinova[3],
T.M. Seilkhanov[2], A.M. Gazaliev[1], M.K. Ibraev[4], A.S. Fazylov[4]

[1]Institute of Organic Synthesis and Coal Chemistry of the RK, Karaganda, Republic of Kazakhstan;
[2]Kokshetau State University named after Sh.Ualichanov, Kokshetau, Republic of Kazakhstan;
[3]Karaganda State University named after E.A. Buketov, Republic of Kazakhstan;
[4]Karaganda State Technical University, Karaganda, Republic of Kazakhstan.
E-mail: iosu8990@mail.ru, nurkenov_oral@mail.ru

SYNTHESIS OF PROPERTIES N-METHYL-2-(PYRID-4-YL)-3,4-FULLEROPYRROLIDINE

Abstract. The article is devoted to the reactions of [2+3] cycloaddition of pyridine-4-aldehyde to fullerene C60, as well as to the preparation of its water-soluble from of the resulting reaction product N-methyl-2-(pyrid-4-yl)-3,4-fulleropyrrolidine. A literature review of organic compounds containing the pyrrolidine cycle was carried out. It is noted that such compounds have a wide spectrum of biological activity and are part of many drugs of both natural and synthetic origin. In this regard, an interesting "pharmacophore" group is the pyridine cycle, which is part of about 5% of all known drugs. The reaction of pyridin-4-aldehyde with fullerene C60 was carried out in the presence of sarcosine under the conditions of the Prato reaction.

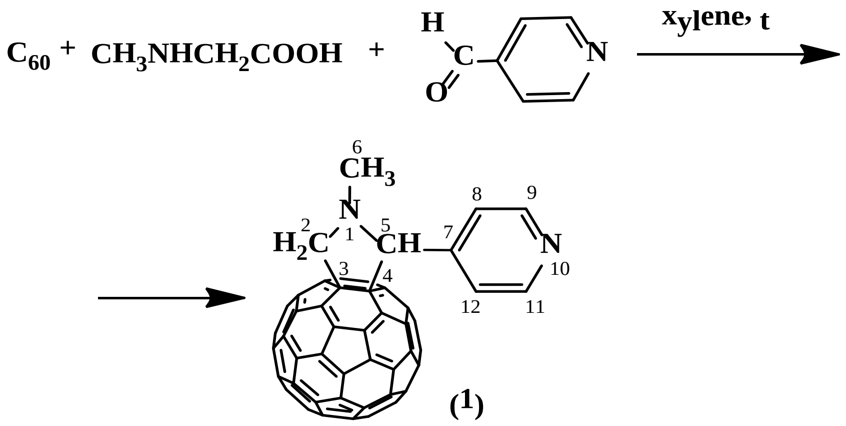
The reaction mechanism of 1,2-dipolar cycloaddition, leading to fulleropyrrolidine, is described. The water-soluble complex fulleropyrrolidinas with poly-N-vinylpyrrolidone was obtained.

The structures of the synthesized compounds were studied by IR, UV, ^{1}H and ^{13}C NMR spectroscopy, as well as by the date of two-dimensional spectra of COSY (1H-1H) and HMQC (^{1}H-^{13}H). The values of chemical shifts, multiplicity and integrated intensity of ^{1}H and ^{13}C NMR signals in one-dimensional NMR spectra were determined. Using spectra in the formats COSY (1H-1H) and HMQC (1H-13C) homo- and heteronuclear interaction were established, confirming the structure of the studied compounds.

Key words: fullerene C60, sarcosine, pyridine-4-aldehyde, fulleropyrrolidines, Prato reaction, NMR spectra.

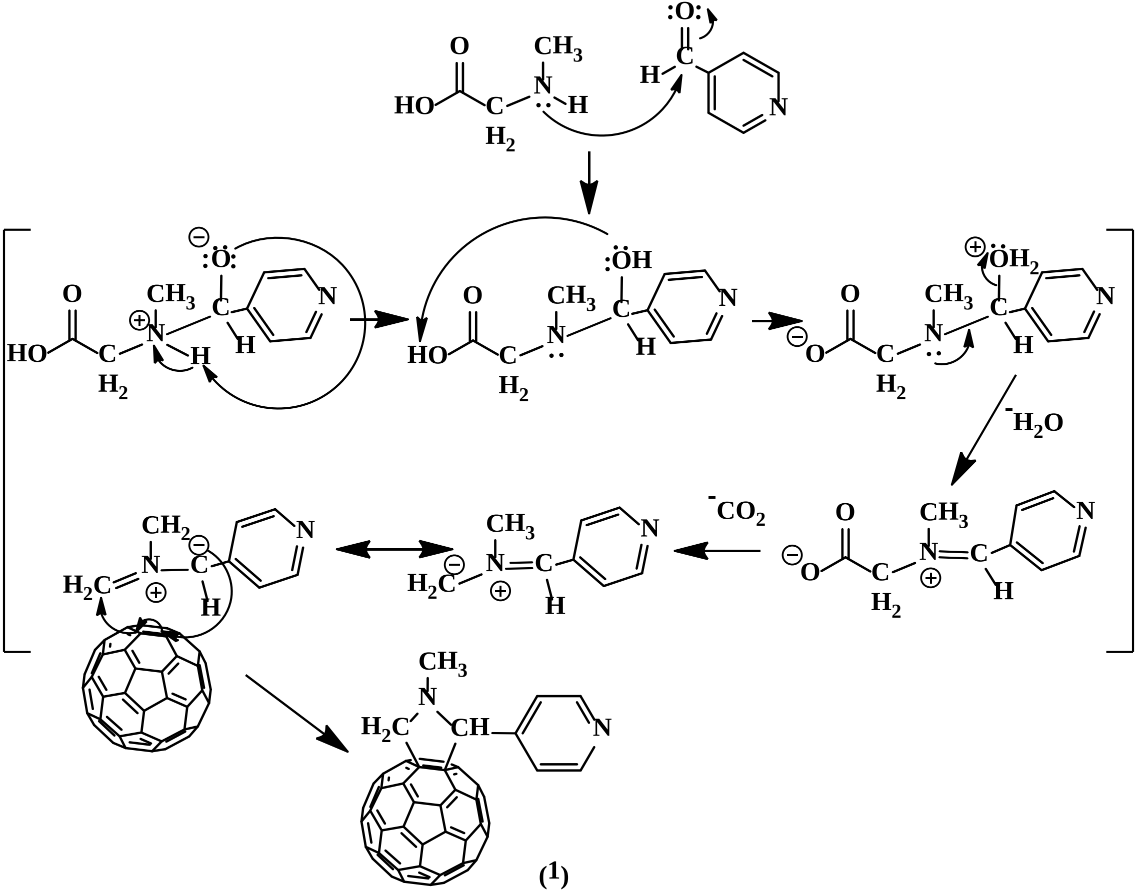
Currently, among a large number of functionalized C60 fullerene compounds, fulleropyrrolidine derivatives are one of the most intensively studied classes [1-3]. The 1,3-dipolar cycloaddition of azomethinilides to fullerene, known as the Prato reaction [4], is one of the most effective ways in obtaining fulleropyrrolidines. Compounds containing the pyrrolidine cycle in common organic compounds have a wide spectrum of biological activity and are part of many drugs of both natural and synthetic origin, for example, proline, atropine. It should be noted that some of the most important aspects of the biological activity of fullerens and its derivatives include the fight against HIV and antibacterial activity, inhibition of enzymes, antitumor therapy, controlled drug delivery, neuroprotective properties, and antioxidant activity. In fullerene synthesis, studies of the synthesis of C60 fullerene derivatives containing new "pharmacophore" groups are of great interest [4-12]. In this regard, an interesting "pharmacophore" group is the pyridine cycle, which is pert of about 5% of all known drugs. However, compounds containing both the pyrrolidine, pyridine rings and the fullerene sphere have so far been little studied.

Taking into account the scientific and applied prospects of the pyridine series and fullerene, we synthesized and conducted an NMR study of the structural features of the new fulleropyrrolidine 1 by the three-component condensation of fullerene C60, N-methylglycine (sarcosine) and pyridine-4-aldehyde under the conditions of the Prato reaction. One of the main factors affecting the yield of the final product in this reaction is the homogeneity of the medium, therefore the synthesis of fulleropyrrolidine 1 was carried out in xylene while the reaction medium was heated for 3 hours. The presence of an amino acid in the reaction medium, which is a zwitterionic compound, probably negatively affects on the reaction rate (heterogeneity factor) [13-19].



(1)

The mechanism of formation of N-methyl-2-(pyrid-4-yl)-3,4-fulleropyrrolidine (**1**) involves the condensation of an α-amino acid (sarcosine) with an aldehyde (pyridin-4-aldehyde), leading to the formation of an ammonium salt, which undergoes decarboxylation process to obtain an *insitu* azomethine ylide. The latter reacts with a 6,6-double bond of fullerene by 1,3-dipolar cycloaddition, forming a pyrrolidine cycle.



(1)

The structure of the obtained new fulleropyrrolidine **1** was established by IR, UV, ^{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).

In the spectrum of IR compound **1**, bands for C–N bonds of the pyridine ring are observed; vibrational frequencies of the fullerene skeleton, C–H, and N–H bonds are present (figure 1).

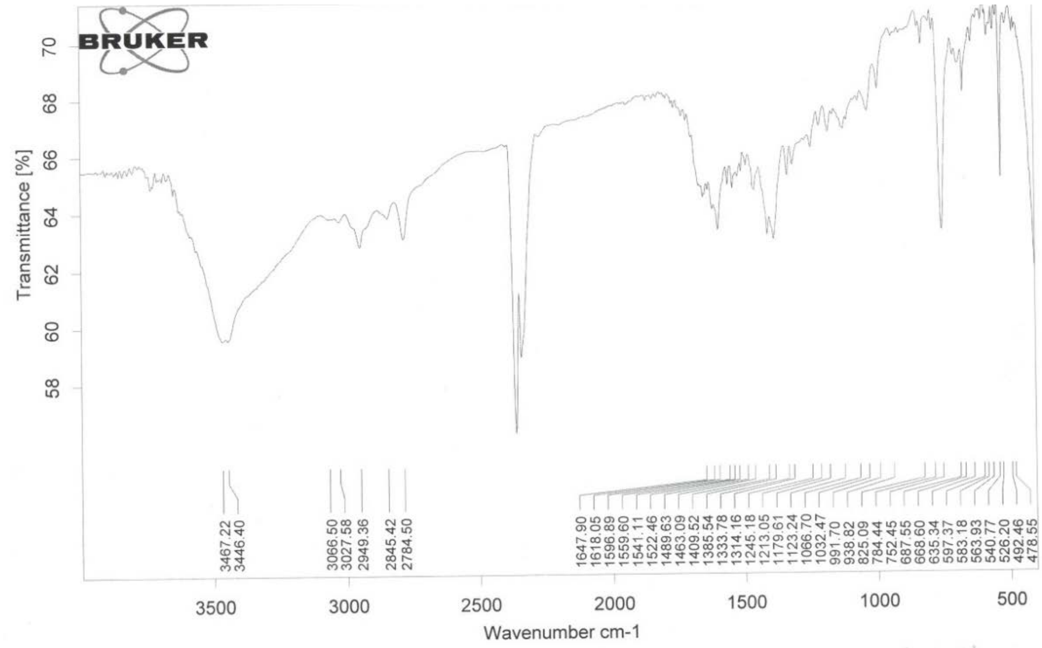


Figure 1 - IR spectrum of compound 1

The UV spectrum of compound **1** has 310, 319, and 430 nm (rigure 2). A peak with a low intensity at 430 nm is characteristic of all [6,6] - closed adducts of fullerene C60.

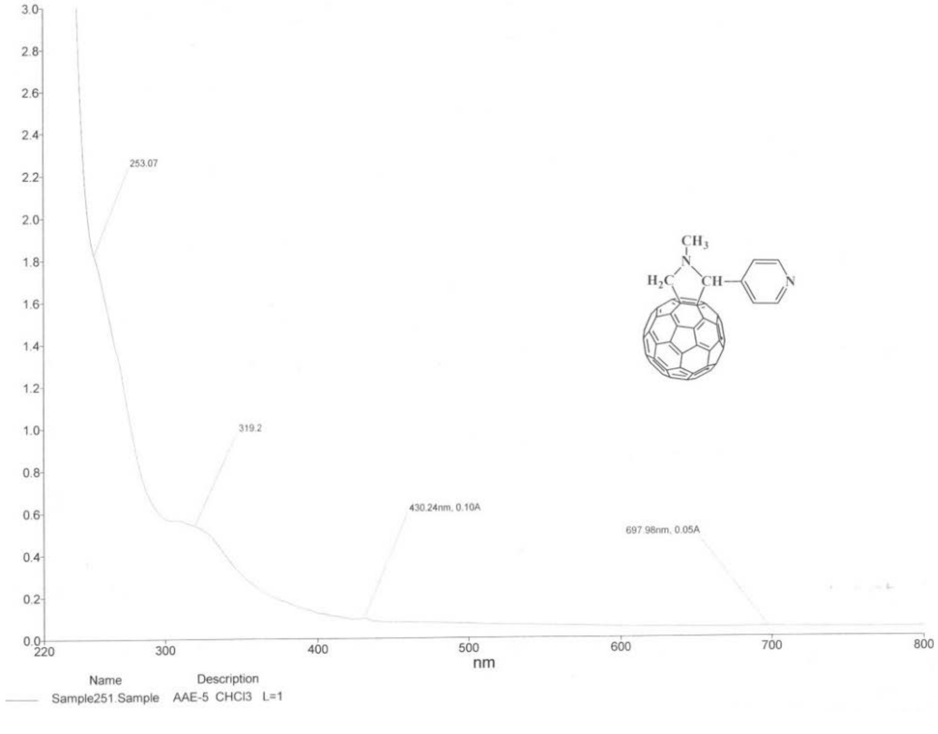


Figure 2 - UV spectrum of compound 1

The ^{1}H NMR spectrum of compound **1** is characterized by the presence of a three-proton singlet signal at 2.86 ppm. protons of the H-6,6,6N-methyl fragment of the pyrrolidine ring. Single-proton singlet signal at 4.97 ppm indicates the presence of the metin proton H-5 in the pyrrolidine cycle. The appearance of two single-proton doublet signals at 4.33 and 5.04 ppm with the same spin-spin coupling constant of ^{2}J 9.4 Hz confirms the presence of two axial and equatorial protons H-2ax and H-2eq of the pyrrolidine ring bonded to the fullerene nucleus. The aromatic pyridine protons H-8, 12 and H-9, 11 were manifested by broadened two-proton siglets at 7.79 and 8.72 ppm respectively.

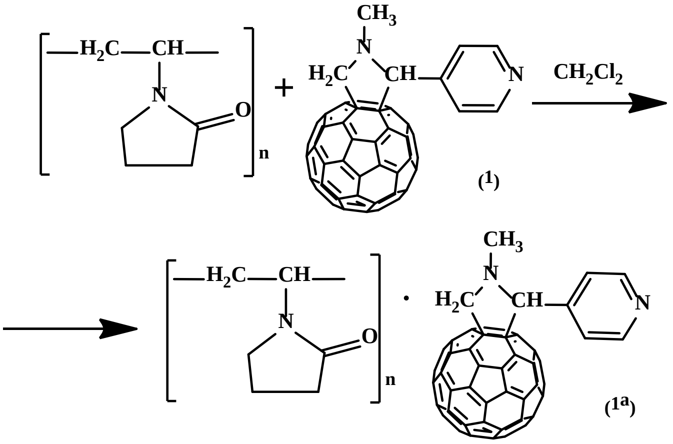
In the ^{13}C NMR spectrum of compound **1**, signals of the pyrrolidine ring with an N-methyl substituent are observed at 40.07 (C-6), 70.12 (C-2) and 82.42 (C-5) ppm. The carbon atoms of the pyridine fragment resonated at 124.24 (C-8.12), 150.13 (C-9.11) and 155.68 (C-7) ppm. Numerous signals in the range of 136-148 ppm belong to sp^2-hybridized carbon atoms of the fullerene nucleus.

The structure of compound **1** was also confirmed by two-dimensional NMR spectroscopy COSY (^1H-^1H) and HSQC (^1H-^{13}C), which allows one to establish spin-spin interactions of a homo- and heteronuclear nature. The observed correlations in the molecule are presented in the diagrams. In the spectra of the ^1H-^1H COSY compound, spin-spin correlations are observed through two bonds of methylene protons H^{2ax}-H^{2eq} (4.33, 5.04 and 5.04, 4.33) ppm and through three proton bonds of the neighboring methine groups $H^{8,12}$ –$H^{9,11}$ (7.79, 8.72 and 8.72, 7.79) ppm pyridine ring. Heteronuclear interactions of protons with carbon atoms through one bond were established using ^1H-^{13}C HSQC spectroscopy for the following pairs present in the compound: H^6-C^6 (2.86, 40.06), H^{2ax}-C^2 (4.33, 70.12), H^{2eq}-C^2 (5.04, 70.12) H^5-C^5 (4.97, 82.42), $H^{8.12-}C^{8.12}$ (7.79, 124.24), $H^{9,11}$-$C^{9,11}$ (8.72, 150.13) ppm (figure 3).

Figure 3 - Correlations in the spectra of COZY (^1H-^1H) (a) and HMQC (^1H-^{13}C) (b) of compounds **1**

The main problem that impedes the biological studies of fullerene derivatives and the creation of therapeutic agents based on them is the insolubility of fullerenes in water. One of the possible ways to overcome this problem is to obtain water-soluble complexes of fullerene derivatives with water-soluble polymers approved for use in medicine, for example, with poly-N-vinylpyrrolidone.

In this regard, a complex of compound **1** with poly-N-vinylpyrrolidone in methylene chloride was obtained:



The formation of complex **1a** occurs as a result of solubilization of fullerenepyrrolidine **1** by PVP chains and the physical interaction of the lactam group with the fullerene sphere. The resulting complex **1a** is soluble in water.

Thus, using the reaction [2+3] cycloaddition, the reaction of addition of pyridin-4-aldehyde to C60-fullerene in the presence of sarcosine under the conditions of Prato reactions was carried out. A new compound N-methyl-2-(pyrid-4-yl)-3,4- fulleropyrrolidine was obtained and its water-soluble derivative. The structure of the obtained substances was proved by ^1H and ^{13}C NMR spectroscopy, as well as by the data of two-dimensional spectra of COSY (^1H-^1H) and HMQC (^1H-^{13}C).

Research funding source. This work was financially supported by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant AR051311054).

Experimental part

The IR spectrum was recorded on a Vertex 70V spectrophotometer (Bruker) in KBr pellets. UV spectra were recorded on a Lambda 750 spectrophotometer (PerkinElmer). The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d$_6$ on a JNM-ECA 400 spectrometer (399.78 and 100.53 MHz ^{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.

N-Methyl-2- (pyrid-4-yl) -3,4-fulleropyrrolidine (1). To a solution of 100 mg (0, 1388 mmol) of C60 in 20 ml of xylene were added 14, 78 mg (0, 138 mmol) of pyridin-4-aldehyde and 123,6 mg (1,388 mmol) of sarcosine (molar ratio of reactants 1: 1, respectively). The reaction mixture was boiled for 3 hours at 110-120^{0}C. After removal of the solvent, the residue was chromatographed on a silica gel column, eluting with toluene unreacted C60 and product1. Yield 28 mg (23%). ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.86 s (3H, H-6.6.6), 4.33 d (1H, H-2ax, ^{2}J 9.4), 4.97 s (1H, H-5), 5.04 d (1H, H- 2eq, ^{2}J 9.4), 7.79 br. s (2H, H-8.12), 8.72 br. s (2H, H-9.11). ^{13}C NMR spectrum, δC, ppm: 40.07 (C-6), 70.12 (C-2), 82.42 (C-5), 124.24 (C-8,12), 150.13 (C-9,11), 155.68 (C-7). IR spectrum, ν, cm-1: 526, 825, 1409, 1596, 2784, 2949, 3446, 3467. UV spectrum (CHCl$_3$), λmax, nm: 310, 319, 430.

The method of obtaining complex (1a). To a solution of 2 mg of fulleropyrrolidine **1** in 2 ml of methylene chloride was added 200 mg of PVP in 3 ml of methylene chloride. The reaction mixture was stirred for 30 minutes at room temperature. After removal of solvent, the residue was dried by vacuum.

С.Д. Фазылов, О.А. Нүркенов, Т.М. Сейлханов, А.Е. Аринова,
А.М. Газалиев, М.К. Ибраев, А.С.Фазылов

[1] ҚР органикалық синтез және көмір химия институты, Қарағанды, Қазақстан;
[2]Ш. Уәлиханов атындағы Көкшетау мемлекеттік университеті, Қазақстан;
[3] Е. А. Бөкетов атындағы Қарағанды мемлекеттік университеті, Қазақстан;
[4]Қараганды мемлекеттік техникалық университеті, Қазақстан

N-МЕТИЛ-2-(ПИРИД-4-ИЛ)-3,4-ФУЛЛЕРОПИРРОЛИДИННІҢ СИНТЕЗІ ЖӘНЕ ҚАСИЕТТЕРІ

Аннотация. Мақала пиридин-4-альдегидтің C$_{60}$ фуллеренге [2+3]-циклоқосылу реакциясын және реакция нәтижесінде алынған өнім N-метил-2-(пирид-4-ил)-3,4-фуллеропирролидиннің суда еритін туындысын алу әдістемелерін зерттеугеарналған. Құрамында пирролидинді циклі бар органикалық заттардың алыну жолдары мен қасиеттері туралы әдебиеттік шолу жасалған. Ол заттардың биологиялық қасиеттерінің кең аумақтылығы және олардың көптеген дәрілік табиғи және синтетикалық заттардың құрамына кіретіні талқыланған. Фуллерендік синтезде фуллерен C$_{60}$ құрамында жаңа «фармакопиялық» топтары бар заттарды синтездеуге арналған ғылыми жұмыстарына көп көңіл бөлінетіні айтылады. Органикалық заттардың құрамына фуллеренді фрагменттердің болуы осы заттардың биологиялық қасиеттерін жақсартуы немесе жаңа, бұрын болмаған механикалық, химиялық, физикалық және биологиялық қасиеттердің пайда болуына әкелетіні көсетіледі. Бұл жаңа ерекше қасиеттер нано масштабтағы факторлардың әсерлерімен байланысты болуы айтылады. Фуллереннің көптеген жаңа туындылары адамның иммунды жетіспеушілік ауруларына және бактерияларға қарсы, сондай-ақ ферменттерді тежеушілік, қатерлі ісікке қарсы, нейропротекторлық терапияда, сонымен бірге антиоксидантты қасиеттерді көптеп көрсететіне назар аударады. Жұмыста пиридин-4-альдегидтің C$_{60}$ фуллеренмен қосылу реакциясы үшінші реагент амин қышқылы глициннің (саркозиннің) қатысуында Прато реакциясы жағдайында жүргізіледі. Реакциялық жағдайдың тиімді жолдарын табу үшін еріткіштердің (толуол, ксилол) табиғатының, реакцияның жүру уақыты ұзақтығының, әрекеттесуші заттардың мөлшерлік қатынасының, сондай-ақ реакциялық ортаның температуралық режимінің әсерлері зерттелген. Осы зерттеулердің нәтижесінде алынатын өнім реакциялық ортадан 28% бөлініп алынады. Алынған ғылыми нәтижелерді талдау мәліметтері бойынша 1,3-диполярлы циклді қосылу реакциясының іске асырылғаны туралы тұжырым жасалады. Аланған жаңа N-метил-2-(пирид-4-ил)-3,4-фуллеропирролидиннің биологиялық қасиеттерін зерттеу үшін оның суда еритін қосылысы поли-N-винилпирролидонмен ковалентті байланыссыз жағдайда алынады. Жұмыста синтезделініп алынған заттардың химиялық-физикалық қасиеттерінқазіргі заманғы ИК-, УФ-, ЯМР ^{1}Н және ^{13}С спектроскопия, сондай-ақ қосөлшемді COSY (^{1}H-^{1}H) и HMQC (^{1}H-^{13}C) спектрлерімен зерттеу нәтижелері келтірілген. Алынған заттардың құрылысындағы ^{1}Н мен ^{13}С атомдарының ЯМР-спектрлеріндегі химиялық жылжулары мен интегралды сызықтары талқыланған. Қосөлшемді COSY (^{1}H-^{1}H) и HMQC (^{1}H-^{13}C) спектрлері бойынша алынған заттардағы гомо- мен гетероядролы әрекеттесушілерді талқылау нәтижесінде алынған жаңа заттардың құрылысы дәлелденеді.

Түйін сөздер: фуллерен C60, саркозин, пиридин-4-альдегид, фуллеропирролидиндер, Прато реакциясы, ЯМР-спектрлер

С.Д. Фазылов, О.А. Нуркенов, А.Е. Аринова, Т.М. Сейлханов,
А.М. Газалиев, М.К. Ибраев, А.С. Фазылов

[1]Институт органического синтеза и угольной химии РК, Караганда, Казахстан;
[2]Государственный университет имени Ш. Уалиханова, Кокшетау, Казахстан;
[3]Карагандский государственный университет им. Е.А. Букетова, Казахстан;
[4]Карагандинский государственный технический университет, Казахстан

СИНТЕЗ И СВОЙСТВА N-МЕТИЛ-2-(ПИРИД-4-ИЛ)-3,4-ФУЛЛЕРОПИРРОЛИДИНА

Аннотация. Статья посвящена изучению реакции [2+3] циклоприсоединения пиридин-4-альдегида к фуллерену C_{60}, а также получению водорастворимой формы полученного продукта реакции N-метил-2-(пирид-4-ил)-3,4-фуллеропирролидина. Проведен литературный обзор по органическим соединениям, содержащим пирролидиновый цикл. Отмечено, что такие соединения обладают широким спектром биологической активности и входят в состав многих лекарственных препаратов как природного, так и синтетического происхождения. В этом плане интересной «фармакофорной» группой является пиридиновый цикл, который входит в состав около 5 % от всех известных лекарственных препаратов. Однако соединения, содержащие одновременно пирролидиновый, пиридиновый циклы и фуллереновую сферу исследованы пока мало. В фуллереновом синтезе большой интерес представляют исследования синтеза производных фуллерена C_{60}, содержащие в своем составе новые «фармакофорные» группы. Показано, что наличие фуллеренового фрагмента в структуре соединения может привести к существенному улучшению или появлению качественно новых механических, химических, физических, биологических и других свойств соединений. Эти свойства связаны с проявлением наномасштабных факторов. Отмечено, что некоторые из наиболее важных аспектов биологической активности фуллеренов и его производных включают борьбу с ВИЧ и антибактериальную активность, ингибирование ферментов, противоопухолевую терапию, контролируемую доставку лекартственных средств, нейропротекторные свойства, а также антиоксидантную активность. Реакция взаимодействия пиридин-4-альдегида и фуллерена C_{60} проводилась в присутствии аминокислоты глицина (саркозина) в условиях реакций Прато. С целью нахождения оптимальных условий реакции проведено изучение влияния природы растворителей, соотношение реагирующих веществ, продолжительность реакции, а также температурный режим реакционной среды. На основании анализа полученных данных описан механизм реакции 1,3-диполярного циклоприсоединения, приводящее к фуллеропирролидину. Для изучения биологических свойств получен водорастворимый комплекс нового фуллеропирролидина с поли-N-винилпирролидоном. Исследованы строения синтезированных соединений методами ИК-, УФ-, ЯМР ^{1}H и ^{13}C 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}H и ^{13}C 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: фуллерен C_{60}, саркозин, пиридин-4-альдегид, фуллеропирролидины, реакция Прато, ЯМР-спектры.

Information about the authors:

Fazylov Serik Drakhmetovich – Corresponding member of NAS RK, Doctor of chemical sciences, Professor, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan. e-mail: iosu8990@mail. ru, https://orcid.org/0000-0002-4240-6450;

Nurkenov Oralgazy Aktayevich – Doctor of chemical sciences, Professor, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, e-mail: nurkenov_oral@mail.ru, https://orcid.org/0000-0002-2771-0411;

Gazaliev Arstan Maulenovich – Academician of the National Academy of Sciences of the Republic of Kazakhstan, Deputy Director for Research, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan. https://orcid.org/0000-0003-2161-0329;

Arinova Anar Erikovna – Doctoral student of Buketov Karaganda State University, e-mail: arinova-anar@mail.ru, https://orcid.org/0000-0002-7780-4555;

Ibraev Marat Kerimbaevich – Doctor of chemical sciences, Professor, Karaganda State Technical University, e-mail: mkibr@mail.ru, https://orcid.org/0000-0003-0798-5562;

Fazylov Arman Serikovich – undergraduate of the Karaganda State Technical University, e-mail: arman1708@yahoo.com, https://orcid.org /0000-0003-2905-9121

REFERENCES

[1] Sidorova L.N., Yurovskoy M.A., Borshensky A.Ya., Trushkova I.V. (2005) Fullerenes. Examination Publishing House, Russia. ISBN: 5-472-00294-X

[2] Khakina E.A., Kraevaya O.A., Popova M.L., Peregudov A.S., Troyanov S.I., Chernyak A.V., Martynenko V.M., Kulikov A.V., Schols D., Troshin P.A. (2017) Synthesis of different types of alkoxy fullerene derivatives from chlorofullerene $C_{60}Cl_6$. Org. Biomol. Chem. . 15: 773-775. https://doi.org/10.1039/C6OB02251K (in Eng.).

[3] Fazylov S.D., Nurkenov O.A., Arinova A.E., Tuktarov A.R., Khuzin A.A., Turdybekov K.M. (2014) Synthesis and structure of N-Methyl-1-phenylfullereno-C60[1,9]pyrrolidines Based on Aminoaldehydes. Russ. J. Gen. Chem. Vol. 84. N 10. P. 2058. https://doi.org/10.1134/S1070363214100375 (in Eng.).

[4] Fazylov S.D., Nurkenov O.A., Arinova A.E., Seilkhanov T.M., Tuktarov A.R., Khuzin A.A., Bakirova R.E., Muravleva L.A. (2015) Synthesis and Structure of N-Methyl-1-[(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)phenyl]fullerene-C60-[1,9c]pyrolidine. Russ. J. Gen. Chem. 85. 5:1049-1051 (in Eng.).

[5] Bosi S. (2003) Fullerene derivatives: an attractive tool for biological applications. European Journal of Medicinal Chemistry, 38:913-923.

[6] Nakajima N., Nishi C., Li F.M., Ikada N.Y. Photo-induced cytotoxicity of water-soluble fullerene. Fuller. Sci. Technol. 4:1-19 (in Eng.).

[7] Mashino T., Nishikawa D., Takanashi, Usui U., Yamori T., Seki M., Endo T., Mochizuki M. (2003) Antibacterial and antiproliferative activity of cationic fullerene derivatives. Bioorg. Med. Chem. Lett. 13: 4395-4397 (in Eng.).

[8] Fazylov S.D., Nurkenov O.A., Zhurinov M.Zh., Arinova A.E., Tuktarov A.R., Issayeva A.Zh., Shaihova B.K. (2018) Catalyzed by palladium complex the cycloadditional of hydrazones to Fullerene C60. *News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology. N5*. P.26-31. https://doi.org/ 10.32014/2018.2518-1491.4 (in Eng.).

[9] Mashino T., Shimotohno K., Ikegami N., Nishikawa D., Okuda K., Takanashi K., Nakamura S., Mochizuki M. (2005) Human immunodeficiency virus-reverse transcriptase inhibition and hepatitis C virus RNA-dependent RNA polymerase inhibition activities of fullerene derivatives. Bioorg. Med. Chem. Lett. 15:1107-1109.

[10] Bosi S., Ros T.D., Spalluto G., Balzarini J., Prato M. (2003) Fullrerene derivatives: an atractive tool for biological applications. Bioorg. Med. Chem. Lett. 13: 4437 (in Eng.).

[11] Friedman SH, Ganapathi PS, RubinY, Kenyon GL (1998) Optimizing the binding of fullerene inhibitors of the HIV-1 protease through predicted increases in hydrophobic desolvation. J. Mend. Chem. Vol. 41:2424-2429 (in Eng.).

[12] Mashino T., Nishikawa D., Takanashi K., Usui U., Yamori T., Seki M., Endo T., Mochizuki M. (2003) Antibacterial and antiproliferative activity of cationic fullerene derivatives. Bioorg. Med. Chem. Lett. 13:4395-4397 (in Eng.).

[13] Bosi S., Da Ros T., Castellano S., Bafni E., Prato M. (2000) Antimycobacterial activity of ionic fullerene derivatives. Bioorg. Med. Chem. Lett. Vol. 10:1043-1045 (in Eng.).

[14] Gareth A. (2005) Hughes Nanostructure-mediated drug delivery. Nanomedicine: Nanotechnology, Biology, and Medicine. 1:22–30 (in Eng.).

[15] Homma, T., Harano, K. Isobe, H., Nakamura E. (2011) Preparation and Properties of Vesicles Made of Nonpolar Polar Nonpolar Fullerene Amphiphiles. JACS. 133:6364-6370 (in Eng.).

[16] Ikeda A., Iizuka T., Maekubo N., Aono R., Kikuchi J., Akiyama M., Konishi T., Ogawa T., Ishida-Kitagawa N., Tatebe H., Shiozaki K. (2013) Cyclodextrin Complexed [60]Fullerene Derivatives with High levelsof Photodynamic ActivitybylongWavelength Excitation. ACS medicinal chemistry letters. 4:752. https://doi.org/10.1021/ml14001535 (in Eng.).

[17] Dumpis M.A., Nikolaev D.N., Litasova, E.V., Iljin, V.V. Brusina, M.A., Piotrovsky, L.B. (2018) Biological activity of fullerenes – Reality and Prospects. *Reviews on Clinical Pharmacology and Drug Therapy. Vol. 16*. P.4. https://doi.org/ 10.17816/RCF1614-20 (in Eng.).

[18] Sun G.X., Yang M.Y., Shi Y.X., Sun Z.H., Liu X.H., Wu H.K., Li B.J., Zhang Y.G. (2014) Isodonrugosus (Wall. ex Benth.) Codd in Vitro Cultures: Establishment, Phytochemical Characterization and In Vitro Antioxidant and Anti-Aging Activites. Int. J. Mol. Sci. 15:8075. https://doi.org/10.3390/ijms20020452 (in Eng.).

[19] Kraevaya O.A., Peregudov A.S., Troyanov S.I. (2019) Diversion of the Arbuzov reaction: alkylation of C–Cl instead of phosphonic ester formation on the fullerene cage. Org. Biomol. Chem. 17: 7155-7160. https://doi.org/10.1039/C9OB00593E (in Eng.).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.25**
Volume 2, Number 440 (2020), 69 – 74

UDC 547.99
IRSTI 31.23.23

Y.S. Ikhsanov, G.E. Tasmagambetova, Y.A. Litvinenko, G.Sh. Burasheva, G.A.Seitimova

Al-Farabi Kazakh National University
Center of Physico-chemical Methods of Research and Analysis
Republic of Kazakhstan, Almaty, Kazakhstan
E-mail: erbol.ih@gmail.com, rumex1978@gmail.com, sitigulnaz@mail.ru,
gauharbur@mail.ru, guljaina_98.14@mail.ru

PHYTOCHEMICAL COMPOSITION OF LIPOPHILIC FRACTION OF PLANTS OF THE PLANT ROSA CANINA L. GENUS ROSA

Abstract. The genus of wild rose, or *Rosa L.*, belongs to the family Rosaceae. It has many cultural forms, bred under the general name *Rosa*. At the moment, more than 400 species of rose hips are known. Usually these are upright shrubs, less often creepers, sometimes low tree-like forms or almost herbaceous plants. Rosehip is common in the temperate and subtropical zones of the Northern Hemisphere, it can often be found in the mountainous regions of the tropical zone. Some species of rose hips are common from the Arctic Circle in the north to Ethiopia in the south. On the American continent - from Canada to Mexico, Favorable conditions for Rosehip are in the Mediterranean region. Several species of the Rosehip genus have an extensive distribution area.

Kazakhstan has significant resources of medicinal raw materials of plant origin. Among the most priority representatives of the wild flora are species of the rosehip genus - Rosa L. as a most valuable medicinal plant. In total, 21 species of wild rose grow in the republic, including 5 in the central Kazakhstan: *R. glabrifolia* - sh. naked, *R. laxa* Retz. - w. loose, *R. acicularis Lindl.* - (*W. needlefish*), *R. majalis Herrm. (R. cinnamomea L.) - sh. May (W. cinnamon) and R. pimpinellifolia L. (R. spinosissima L.)* - W. femoral cell. Kazakhstan species of the genus *Rosa L.*

Rose hips are characterized by a high content of biologically active substances and are widely used both in medicine and in cooking.

In this paper, a comparative analysis of rose hips, *Rosa canina L.*, harvested in the fall of 2018 is carried out.

Plant raw materials are collected in the southern region of the Republic of Kazakhstan (Almaty region). The crushed air-dry raw materials were extracted with hexane and chloroform in the ratio of raw materials-reagent (1:10) in a Soxhlet apparatus. The resulting extract was concentrated under mild conditions to a thick concentrate, which was analyzed on a gas chromatograph with a mass selective detector.

The analyzes were carried out on a gas chromatograph with a mass spectrometric detector 6890N / 5973C (Agilent, USA). The peaks detected in the chromatograms were identified using the NIST'11 and Wiley 10 mass spectral libraries.

The article first studied and conducted a comparative analysis of lipophilic substances contained in the fruits of the plant *Rosa canina L*, harvested in the Almaty region.

The extracts mainly include hydrocarbons, derivatives of higher carboxylic acids, higher alcohols and some other substances, in particular butyl tetradecyl ether of hydrochloric acid, [4- (2-methylpentanoylsulfamoyl) phenyl] amide of 2-methylpentanoic acid in hexane extract and, butyl undecyl ether sulfuric acid, eicosyl trifluoroacetate and ethoxycarbonyl-3-methyl-4-azafluorenone, 2-fluorenilim in the chloroform extract.

Further work will be continued in order to determine the potential biological activity of the obtained extracts.

Keywords: *Rosa canina L.*, СКФ-экстракция, никотин, GC-MS, химический состав.

Introduction

The rosehip genus, Rosa L., belongs to the family *Rosaceae*. It has many cultural forms, bred under the general name Rosa. At the moment, more than 400 species of rose hips are known. Usually these are upright shrubs, less often creepers, sometimes low tree-like forms or almost herbaceous plants. Rosehip is common in the temperate and subtropical zones of the Northern Hemisphere, it can often be found in the mountainous regions of the tropical zone. Some species of rose hips are common from the Arctic Circle in the north to Ethiopia in the south. On the American continent - from Canada to Mexico. Favorable conditions for Rosehip are in the Mediterranean region. Several species of the Rosehip genus have an extensive distribution area [1-3].

Kazakhstan has significant resources of medicinal raw materials of plant origin. Among the most priority representatives of the wild flora are species of the rosehip genus - *Rosa L.* as a most valuable medicinal plant. In total, 21 species of wild rose grow in the republic, including 5 in the central Kazakhstan: *R. glabrifolia - sh. naked, R. laxa Retz. - w. loose, R. acicularis Lindl. - (W. needlefish), R. majalis Herrm. (R. cinnamomea L.) - sh. May (W. cinnamon) and R. pimpinellifolia L. (R. spinosissima L.) - W. femoral cell.* Kazakhstan species of the genus *Rosa L* [4-5].

Rosehip (canine) (*R. canina*). Branched tall shrub with curved, sparse spikes with single flowers of pale pink or white color. Fruits are smooth, fleshy, light or bright red, spherical or oval-spherical elongated-oval; the flesh is sweet, edible, thick. Sepals fall off before ripening. The pulp content in relation to the weight of the dry fruit is 54.9-65%; seed content 35.0–45.1%. The fruits of this type of rosehip are a weak source of vitamin C. The content of ascorbic acid in the pulp of fruits is usually extremely limited - from 0 to 0.95% and carotene 3.8-12.9 mg% [6].

In this article, we consider lipophilic substances in the composition of *R. canina* fruits identified in hexane and chloroform extracts.

Materials and Methods

Plant raw materials are collected in the southern region of the Republic of Kazakhstan (Almaty region). The crushed air-dry raw materials (500 g) were extracted with hexane in the ratio of raw materials-reagent (1:10) in a Soxhlet apparatus. The extract obtained was concentrated under mild conditions (water bath temperature 40-45 ° C) using a vacuum water-jet pump, to a thick concentrate, which was analyzed on a gas chromatograph with a mass-selective detector. The analyzes were performed on a gas chromatograph with a 6890N / 5973C mass spectrometric detector (Agilent, USA) equipped with a Combi-PAL autosampler (CTC Analytics, Switzerland). For GC-MS analysis, 1.00 μl of the sample was injected into the injector of a gas chromatograph using an autosampler at an injector temperature of 250°C. Chromatography was performed using an HP-5ms capillary column (Agilent, USA) with a length of 30 m, an inner diameter of 0.25 mm, and a film thickness of 0.25 μm at a constant carrier gas velocity (helium,> 99.995%, Orenburg-Tekhgaz, Russia) equal to 1.0 ml / min. The program for heating the chromatographic column: holding for 5 min at 40 ° C, heating at a speed of 10 ° C / min to 280 °C, holding for 5 min. The total chromatographic time was 34 minutes. The temperatures of the quadrupole and the MSD ion source were 150 and 230 ° C, respectively [7–16].

Mass spectrometric detection was carried out in the ion scanning mode in the m / z range from 40 to 550 with a solvent delay of 5 min. The peaks detected in the chromatograms were identified using the NIST’11 and Wiley 10 mass spectral libraries [17–25]. Data are presented in tables 1 and 2.

Results and discussion

Table 1 - The data of chromatography-mass spectrometry
of a hexane extract obtained from rose hips *Rosa canina L.*

№	Retention time	Name of compound	Gross formula	Quantity,%
1	26,89	Gentriacontan	$C_{31}H_{64}$	3,00
2	28,46	Heptocazane	$C_{27}H_{56}$	9,63
3	28,76	Bis 2 (ethyl hexyl) phthalate	$C_{24}H_{38}O_4$	3,89
4	29,21	butyl tetradecyl ether hydrochloric acid	$C_{18}H_{38}O_3S$	3,75
5	29,93	Pentacosin	$C_{25}H_{52}$	21,87
6	30,04	1-heptacosanol	$C_{27}H_{56}O$	14,69
7	30,63	Nonhexacontanoic acid	$C_{38}H_{13}O_2$	1,99
8	31,32	Octadecan	$C_{18}H_{38}$	19,16
9	31,48	Methyl 2-oxo octadecanoate	$C_{39}H_{36}O_3$	3,10
10	31,64	Methyl -5.9.21-octa-cosatrienoate	$C_{29}H_{52}O_2$	3,82
11	31,82	[4- (2-Methylpentanoylsulfamoyl) phenyl] amide 2-methylpentanoic acid	$C_{18}H_2O_4S$	3,00
12	32,97	Octadecanoic acid 2-oxo-methyl ester	$C_{39}H_{36}O_3$	9,63

12 substances were identified in the hexane extract of the rosehip *Rosa canina L.*, of which Heptocazane, Pentacosin, Octadecane, belonging to the hydrocarbon class, have a high percentage, higher alcohols 1-Heptacosanol, derivatives of higher carboxylic acids (Methyl 2-oxo octadecanoate) , Methyl-5,9,21-octa-cosatrienoate, 2-oxo-methyl ether of octadecanoic acid) and higher carboxylic acids Neagexacontanoic acid. In addition, Bis 2 (ethyl hexyl) phthalate (a phthalic acid derivative) and butyl tetradecyl ether of hydrochloric acid were identified in the extract.

Table 2 - Chromatography-mass spectrometry data of a chloroform extract obtained from rose hips of *Rosa canina L.*

№	Retention time	Name of compound	Gross formula	Quantity,%
1	28,47	2-methyl okatacosan	$C_{29}H_{60}$	8,14
2	29,22	Butyl undecyl sulfuric acid ester	$C_{15}H_{32}O_3S$	3,23
3	29,93	Octadecan	$C_{18}H_{38}$	21,23
4	30,04	Eicosyl trifluoroacetate	$C_{24}H_{41}F_3O_2$	14,27
5	31,24	Naphthalene, decahydro-1,4a-dimethyl-7- (1-methylethyl) -, [1S- (1α, 4aα, 7α, 8aβ)] glucopyranosyloxy) -1-butenyl] -4	$C_{15}H_{28}$	1,36
6	31,31	Octacosan	$C_{18}H_{58}$	25,51
7	31,37	4- [3 - (β-d-hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one,	$C_{27}H_{38}O_{12}$	1,54
8	31,82	3-benzyl-2,4-pentanedione	$C_{12}H_{14}O_{12}$	4,46
9	32,97	1 eicosen	$C_{20}H_{40}$	5,51
10	33,62	ethoxycarbonyl-3-methyl-4-azafluorenone, 2-fluorenilimim	$C_{29}H_{22}N_2O_2$	6,34

10 compounds were identified in the chloroform extract of rosehip *Rosa canina L.*

The dominant hydrocarbons are 2 methyl okatacosan, octadecane, octacosan and naphthalene, decahydro-1,4a-dimethyl-7- (1-methylethyl) -, [1S- (1α, 4aα, 7α, 8aβ)] glucopyranosyloxy) -1-butenyl] -4.

Separately, it should be noted that eicosyl trifluoroacetate belongs to the class of organohalogen compounds, which are relatively rare in plant objects. In addition, a homolog of butyl tetradecyl ether of hydrochloric acid was identified. Butyl undecyl ether of sulfuric acid was also detected in the hexane extract. Ethoxycarbonyl-3-methyl-4-azafluorenone, 2-fluorenylimime, which is a natural dye, was also identified in the chloroform extract.

Conclusion

For the first time, a comparative analysis of lipophilic substances contained in the fruits of the plant *Rosa canina L*, harvested in the Almaty region, was studied and carried out.

The extracts mainly include hydrocarbons, derivatives of higher carboxylic acids, higher alcohols and some other substances, in particular butyl tetradecyl ether of hydrochloric acid, [4- (2-methyl-pentanoylsulfamoyl) phenyl] amide of 2-methylpentanoic acid in hexane extract and, butyl undecyl ether sulfuric acid, eicosyl trifluoroacetate and ethoxycarbonyl-3-methyl-4-azafluorenone, 2-fluorenilim in the chloroform extract.

Further work will be continued in order to determine the potential biological activity of the obtained extracts.

Е.С. Ихсанов, Г.Е. Тасмагамбетова, Ю.А. Литвиненко, Г.А. Сейтимова, Г.Ш. Бурашева

Әл-Фараби атындағы Қазақ ұлттық университеті,
Физикалық-химиялық зерттеулер және талдау әдістері орталығы
Қазақстан Республикасы, Алматы, Қазақстан

ROSA CANINA L. ӨСІМДІК ЖЕМІСТЕРІНІҢ ЛИПОФИЛЬДІ ФРАКЦИЯСЫНЫН ФИТОХИМИЯЛЫҚ ҚҰРАМЫ

Аннотация. Итмұрын немесе раушан (*Rosa* L.), Қызғылт түсті (*Rosaceae*) отбасына жатады. Жалпы Роза деп аталатын көптеген мәдени нысандары бар. Қазіргі уақытта итмұрынның 400-ден астам түрі белгілі. Әдетте бұл тік бұталар, сирек Лиана, кейде биік емес ағаш тәріздес немесе шөпті өсімдіктер. Итмұрын

Солтүстік жарты шарның қалыпты және субтропикалық аймақтарында таралған, оны тропикалық белдеудің таулы аудандарында кездестіруге болады. Итмұрынның кейбір түрлері солтүстіктегі полярлық шеңберден оңтүстіктегі Эфиопияға дейін жетеді. Ал Америка құрлығында-Канададан Мексикаға дейін барады. Итмұрын үшін қолайлы жағдай Жерорта теңізі аймағы. Итмұрын түрінің бірнеше кең таралу аймағы бар.

Қазақстанда өсімдік тектес дәрілік шикізаттың елеулі ресурстары бар. Жабайы өсетін флораның ең басым өкілдерінің қатарына итмұрын – *Rosa* L. тегінің түрлері жатады. Республикада итмұрынның 21 түрі өседі, оның ішінде Орталық Қазақстанда-5: *R. glabrifolia* – бас сүйекті итмұрын, *R. laxa Retz.* – борпылдақ итмұрын, *R. acicularis Lindl.* – (ине итмұрын), *R. majalis Herrm.* (*R. cinnamomea* L.*)* – май итмұрын (сиыр итмұрын) и *R. pimpinellifolia* L. (*R. spinosissima* L.) – бедренцелистік итмұрын.

Итмұрын жемістері биологиялық белсенді заттардың жоғары болуымен ерекшеленеді және медицинада да, кулинарияда да кеңінен қолданылады.

Бұл жұмыста 2018 жылдың күзінде дайындалған итмұрын, *Rosa canina* L. жемістеріне салыстырмалы талдау жүргізіледі.

Өсімдік шикізаты Қазақстан Республикасының оңтүстік өңірінде (Алматы облысында) жиналған. Ұсақталған ауа-құрғақ шикізат Сокслет аппаратындағы шикізат-реагент (1:10) қатынасында гексан және хлороформмен экстрагерленді. Алынған сығынды масс-селективті детекторы бар газды хроматографта талдаған қалың концентратқа дейін жұмсақ жағдайларда шоғырландырды.

Талдаулар 6890N/5973C (Agilent, АҚШ) масс-спектрометриялық детекторы бар газды хроматографта жүргізілді. Хроматограммаларда табылған шыңдарды сәйкестендіруді NIST'11 және Wiley 10 масс-спектрлері кітапханаларының көмегімен жүргізді.

Мақалада алғаш рет Алматы облысында дайындалған *Rosa canina* L. өсімдігінің жемістеріндегі липофильді заттарға салыстырмалы талдау жүргізілді және зерттелді.

Сығындылардың құрамына негізінен көмірсутектер, жоғары карбон қышқылдарының туындылары, жоғары спирттер және басқа да заттар табылды , оның ішінде тұз қышқылының тетрадецил эфирі бутилі, [4- (2-метилпентаноилсульфамоил) фенил] гексан сығындысындағы 2-метилпентан қышқылы амиді және күкірт қышқылының бутил ундецил эфирі, Эйкозил трифторацетат және этоксикарбонил-3-метил-4 – азафлуоренон.

Одан кейінгі жұмыстар алынған сығындылардың әлеуетті биологиялық белсенділігін анықтау мақсатында жалғасатын болады.

Түйін сөздер:. *Rosa canina* L., ЖКФ-экстракция, никотин, GC-MS, химиялық құрамы.

Е.С. Ихсанов, Г.Е. Тасмагамбетова, Ю.А. Литвиненко, Г.А. Сейтимова, Г.Ш. Бурашева

Казахский национальный университет имени аль-Фараби,
Центр физико-химических методов исследования и анализа
Республика Казахстан, Алматы, Казахстан

ФИТОХИМИЧЕСКИЙ СОСТАВ ЛИПОФИЛЬНОЙ ФРАКЦИИ ПЛОДОВ РАСТЕНИЯ *ROSA CANINA L.* РОДА ШИПОВНИК (*ROSA*)

Аннотация. Род шиповник или роза (*Rosa L.*) относится к семейству розоцветных (Rosaceae). Имеет множество культурных форм, разводимых под общим названием Роза. На данный момент известны более 400 видов шиповника. Обычно это прямостоящие кустарники, реже лианы, иногда невысокие древовидной формы или почти травянистые растения. Шиповник распространён в умеренных и субтропических зонах Северного полушария, нередко его можно встретить в горных районах тропического пояса. Некоторые виды шиповника распространены от полярного круга на севере до Эфиопии на юге. На американском континенте - от Канады до Мексики. Благоприятнейшие условия для шиповника находятся в области Средиземноморья. Несколько видов рода шиповник имеют обширный ареал распространения .

Казахстан обладает значительными ресурсами лекарственного сырья растительного происхождения. К числу наиболее приоритетных представителей дикорастущей флоры относятся виды рода шиповник – Rosa L. как ценнейшего лекарственного растения. Всего в республике произрастает 21 вид шиповника, в том числе в Центральном Казахстане – 5: *R. glabrifolia* – ш. гололистый, *R. laxa Retz.* – ш. рыхлый, *R. acicularis Lindl.* – (ш. иглистый), R. majalis Herrm. (R. cinnamomea L.) – ш. майский (ш. коричный) и *R. pimpinellifolia* L. (*R. spinosissima L.*) – ш. бедренцелистый. Казахстанские виды рода Rosa L.

Плоды шиповника отличаются высоким содержанием биологически активных веществ и широко применяются как медицине, так и кулинарии.

В данной работе проводится сравнительный анализ плодов шиповника *Rosa canina L.,* заготовленного осенью 2018 года.

Растительное сырье собрано в южном регионе Республики Казахстан (Алматинская область). Измельченное воздушно-сухое сырье экстрагировали гексаном и хлороформом в соотношение сырье-реагент (1:10) в аппарате Сокслета. Полученный экстракт концентрировали в мягких условиях до густого концентрата, который анализировали на газовом хроматографе с масс-селективным детектором.

Анализы проводили на газовом хроматографе с масс-спектрометрическим детектором 6890N/5973C (Agilent, США). Идентификацию пиков, обнаруженных на хроматограммах, проводили при помощи библиотек масс-спектров NIST'11 и Wiley 10.

В статье впервые изучен и проведён сравнительный анализ липофильных веществ, содержащихся в плодах растения *Rosa canina L*, заготовленного в Алматинской области.

В состав экстрактов входят преимущественно углеводороды, производные высших карбоновых кислот, высшие спирты и некоторые другие вещества, в частности, бутил тетрадециловый эфир соляной кислоты, [4- (2-метилпентаноилсульфамоил) фенил] амид 2-метилпентановой кислоты в гексановом экстракте и бутил ундециловый эфир серной кислоты, Эйкозил трифторацетат и этоксикарбонил-3-метил-4- азафлуоренон, 2-флуоренилимим в хлороформенном экстракте.

Дальнейшие работы будут продолжены с целью определения потенциальной биологической активности полученных экстрактов.

Ключевые слова: *Rosa canina L.*, СКФ-экстракция, никотин, GC-MS, химический состав.

Information about authors:

Ikhsanov Yerbol Saginovich - PhD, Senior lecturer Department of Chemistry and Chemical Technology of the Al-Farabi Kazakh National University, Kazakh National University, e-mail: erbol.ih@gmail.com, https://orcid.org/0000-0003-4640-9584;

Litvinenko Yuliya Alekseevna - candidate of chemical sciences,Senior lecturer, Department of Chemistry and Chemical, Technology of the Al-Farabi Kazakh National University, e-mail: yuliya_litvinenk@mail.ru, https://orcid.org/0000-0002-6387-187X;

Seitimova Gulnaz Absattarovna - Ph.D. Senior lecturer at the Faculty Department of Chemistry and Chemical Technology of the Al-Farabi Kazakh National University, e-mail: sitigulnaz@mail.ru, https://orcid.org/0000-0002-5157-1255;

Burasheva Gauhar Shahmanovna - Doctor of Science, professor, Department of Chemistry and Chemical Technology of the Al-Farabi Kazakh National University, e-mail: gauharbur@mail.ru, https://orcid.org/0000-0003-2935-3531;

Tasmagambetova Gulzhaina Erzhanovna - Graduate student of the Faculty of Chemistry and Chemical Technology, e-mail: guljaina_98.14@mail.ru, https://orcid.org/0000-0003-1892-2268

REFERENCES

[1] Nađpal J. D., Lesjak M. M., Šibul F. S., Anačkov G. T., Četojević-Simin D. D., Mimica-Dukić N. M., Beara I. N. (2016). *Comparative study of biological activities and phytochemical composition of two rose hips and their preserves: Rosa canina L. and Rosa arvensis Huds. Food Chemistry, 192, 907–914.* doi:10.1016/j.foodchem.2015.07.089

[2] Ouerghemmi S., Sebei H., Siracusa L., Ruberto G., Saija A., Cimino F., & Cristani M. (2016). *Comparative study of phenolic composition and antioxidant activity of leaf extracts from three wild Rosa species grown in different Tunisia regions: Rosa canina L., Rosa moschata Herrm. and Rosa sempervirens L. Industrial Crops and Products, 94, 167–177.* doi:10.1016/j.indcrop.2016.08.019

[3] Ognyanov M., Remoroza C., Schols H. A., Georgiev Y., Kratchanova M., & Kratchanov C. (2016). *Isolation and structure elucidation of pectic polysaccharide from rose hip fruits (Rosa canina L.). Carbohydrate Polymers, 151, 803–811.* doi:10.1016/j.carbpol.2016.06.031

[4] Winther K., Warholm L., Campbell-Tofte J., Marstrand K. (2018). *Effect of Rosa canina L (Rose-hip) on cold during winter season in a middle-class population: A randomized, double-blinded, placebo-controlled trial. Journal of Herbal Medicine.* doi:10.1016/j.hermed.2018.04.003

[5] Jakovljevic M., Moslavac T., Bilic M., Aladic K., Bakula F. (2018). *Supercritical CO2 extraction of oil from rose hips (Rosa canina L.) and cornelian cherry (Cornus mas L.) seeds. Croatian Journal of Food Science and Technology, 10(2), 197–205.* doi:10.17508/cjfst.2018.10.2.08

[6] Saricaoglu F. T., Atalar I., Yilmaz V. A., Odabas H. I., & Gul O. (2019). *Application of multi pass high pressure homogenization to improve stability, physical and bioactive properties of rosehip (Rosa canina L.) nectar. Food Chemistry.* doi:10.1016/j.foodchem.2019.01.002

[7] Azmir J., Zaidul I.S.M., Rahman M.M., Sharif K.M., Mohamed A., Sahena F., Jahurul M.H.A., Ghafoor K., Norulaini N.A.N., Omar A.K.M. (2013). Techniques for extraction of bioactive compounds from plant materials: a review. J. Food Eng, vol. 117, no. 4, 426–436, sci-hub.tw/10.1016/j.jfoodeng.2013.01.014

[8] Kou Y., Yuan C., Zhao Q., Liu G., Nie J., Ma Z., Zhao L. (2016). *Thidiazuron Triggers Morphogenesis in Rosa canina L. Protocorm-Like Bodies by Changing Incipient Cell Fate. Frontiers in Plant Science, 7.* doi:10.3389/fpls.2016.00557

[9] Ikhsanov Y.S., Sultanova N.A., Abilov Z.A., Choudhary M.I. (2018). Investigation of components of hexane extract from Tamarix hispida by method of gas chromatography. Izvestiya vysshikh uchebnykh zavedenii khimiya khimicheskaya tekhnologiya,vol.61, no6, 83-87, doi: https://doi.org/10.6060/tcct.20186106.5706

[10] Gruenwald J., Uebelhack R., Moré M. I. (2019). *Rosa canina - Rose Hip Pharmacological Ingredients and Molecular Mechanics Counteracting Osteoarthritis – a Systematic Review. Phytomedicine, 152958.* doi:10.1016/j.phymed.2019.152958

[11] Jafarirad S., Mehrabi M., Divband B., Kosari-Nasab M. (2016). *Biofabrication of zinc oxide nanoparticles using fruit extract of Rosa canina and their toxic potential against bacteria: A mechanistic approach. Materials Science and Engineering: C, 59, 296–302.* doi:10.1016/j.msec.2015.09.089

[12] Jiménez S., Gascón S., Luquin A., Laguna M., Ancin-Azpilicueta C., Rodríguez-Yoldi M. J. (2016). *Rosa canina Extracts Have Antiproliferative and Antioxidant Effects on Caco-2 Human Colon Cancer. PLOS ONE, 11(7), e0159136.* doi:10.1371/journal.pone.0159136

[13] Ikhsanov Y.S., Nauryzbaev M,, Musabekova A., Alimzhanova M., Burashev E.(2019). Study of nicotiana tabacum l extraction, by methods of liquid and supercritical fluid extraction, journal-Journal of Applied Engineering Science,Vol.17, no. 3 doi:10.5937/jaes17-21189

[14] Taghizadeh M., Rashidi A. A., Taherian A. A., Vakili Z., Sajad Sajadian M., Ghardashi M. (2016). Antidiabetic and Antihyperlipidemic Effects of Ethanol Extract of Rosa canina L. fruit on Diabetic Rats. Journal of Evidence-Based Complementary & Alternative Medicine, 21(4), NP25–NP30. doi:10.1177/2156587215612626

[15] Erfani M., Tabatabaei Z. G., Sadigh-Eteghad S., Farokhi-Sisakht F., Farajdokht F., Mahmoudi J., Nasrolahi A. (2019). *Rosa canina L. methanolic extract prevents heat stress-induced memory dysfunction in rat. Experimental Physiology*. doi:10.1113/ep087535

[16] Kiralan M., Yildirim G. (2019). *Rosehip (Rosa canina L.) Oil. Fruit Oils: Chemistry and Functionality, 803–814.* doi:10.1007/978-3-030-12473-1_43

[17] Kilinc K., Demir S., Turan I., Mentese A., Orem A., Sonmez M., Aliyazicioglu Y. (2019). *Rosa canina Extract has Antiproliferative and Proapoptotic Effects on Human Lung and Prostate Cancer Cells. Nutrition and Cancer, 1–10.* doi:10.1080/01635581.2019.1625936

[18] Valcheva-Kuzmanova, S., Denev, P., Eftimov, M., Georgieva, A., Kuzmanova, V., Kuzmanov, A., … Tzaneva, M. (2019). *Protective effects of Aronia melanocarpa juices either alone or combined with extracts from Rosa canina or Alchemilla vulgaris in a rat model of indomethacin-induced gastric ulcers. Food and Chemical Toxicology, 132, 110739.* doi:10.1016/j.fct.2019.110739

[19] Hu, X.-Y., Corp, N., Quicke, J., Lai, L., Blondel, C., Stuart, B., … Moore, M. (2018). *Rosa canina fruit (rosehip) for osteoarthritis: a cochrane review. Osteoarthritis and Cartilage, 26, S344.* doi:10.1016/j.joca.2018.02.685

[20] Chemat, F., Vian, M. A., & Cravotto, G. (2012). Green Extraction of Natural Products: Concept and Principles. International Journal of Molecular Sciences, vol.13, no.7, 8615–8627. doi:10.3390/ijms13078615

[21] Farajpour, R., Sadigh-Eteghad, S., Ahmadian, N., Farzipour, M., Mahmoudi, J., & Majdi, A. (2017). *Chronic Administration of Rosa canina Hydro-Alcoholic Extract Attenuates Depressive-Like Behavior and Recognition Memory Impairment in Diabetic Mice: A Possible Role of Oxidative Stress. Medical Principles and Practice, 26(3), 245–250.* doi:10.1159/000464364

[22] Al-Yafeai A., Malarski A., Böhm V. (2018). *Characterization of carotenoids and vitamin E in R. rugosa and R. canina : Comparative analysis. Food Chemistry, 242, 435–442.* doi:10.1016/j.foodchem.2017.09.070

[23] Nowrouzi F., Azadbakht M., Kalehoei E., Modarresi M. (2019). *Protective Effect of Rosa Canina Extract Against Doxorubicin-induced Testicular Toxicity in Mice. Brazilian Archives of Biology and Technology, 62.* doi:10.1590/1678-4324-2019180017

[24] Fattahi A., Niyazi F., Shahbazi B., Farzaei M. H., Bahrami, G. (2016). *Antidiabetic Mechanisms of Rosa canina Fruits. Journal of Evidence-Based Complementary & Alternative Medicine, 22(1), 127–133.* doi:10.1177/2156587216655263

[25] Myrzakhanova M. N., Kaa S. A. New trends of medical media in training and practice // NEWS of the National academy of sciences of the Republic of Kazakhstan. Series of biological and medical. 2018. Vol. 5, N 329. P. 67-70. (in Eng). https://doi.org/10.32014/2018.2518-1629.9

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.26**
Volume 2, Number 440 (2020), 75 – 82

UDC 664.66
IRSTI 65.09.03

M.K. Kassymova[1], Z.I. Kobzhasarova[1], G.E. Orymbetova[1], G. Nurynbetova[1], Anita Blija[2]

[1]M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;
[2]Latvian University of Agriculture, Jelgava, Latvia
e-mail: mahabbat 67@mail.ru;

USE SUNFLOWER OIL PRODUCED BY JSC «SHYMKENTMAY» AT THE DEVELOPMENT OF TECHNOLOGY OF EMULSION PRODUCT

Abstract. On the basis of the conducted researches on factors of formation of consumer properties of emulsion products, recipes and technology of low-calorie emulsion sauces have been developed.

On the basis carried out of the studies the factors of the formation of consumer properties of emulsion products of special purpose, recipes and technology for obtaining low-calorie emulsion sauces were developed.

The expediency and effectiveness of the use of deodorized refined vegetable oils of JSC "Shymkentmai" were substantiated.

An organoleptic evaluation of the experimental emulsion products were carried out in comparison with the traditional ones, which were evaluated according to the following parameters: appearance, consistency, odor and taste. It has been established that a of fat content 35% emulsion product on the basis of sunflower oil produced by JSC «Shymkentmai» with a plant additive were characterized by a higher value of the total quality index due to the delicate taste and absence of foreign flavors.

It is revealed that the calorie content of the new emulsion product is significantly reduced by reducing the prescription amount of vegetable oil, while maintaining high organoleptic parameters. Low amounts of protein in the formulations of the new emulsion product should be considered as a positive moment, as emulsion product is a sauce that is served to the main dish, including meat, fish and poultry.

Key words: emulsion product, functionality, sunflower oil, consumer value.

Introduction. The market for fat products is constantly expanding due to new products developed in accordance with the latest achievements and recommendations of the science of nutrition. Great opportunities for the development of the range of mayonnaise and mayonnaise sauces are associated with an increase in their food value and a decrease in energy value due to a directed change in the formulation composition, with the perfection of the fat phase, the introduction of vitamins, minerals, dietary fiber and other physiologically functional food ingredients [1-4].

The production of fatty products, including emulsion, for the nutrition of various population groups with a balanced complex of biologically active substances: lipids, fatty acids, proteins, vitamins and minerals, is possible on the basis of the development of effective methods for processing vegetable oils produced by JSC "Shymkentmai".

However presently presented at the home market the assortment of mayonnaises and mayonnaise sauces on the basis of vegetable oils produced by JSC "Shymkentmai" for the healthy eating very were limited.

The necessary conditions for the production of emulsion products of a functional purpose are [5-7]:

- the use of high-quality vegetable oils, which allow obtaining high-quality products;
- use of non-traditional types of emulsifiers (wheat germ);
- the use of vegetable additives (powder from jid).

In this regard, the development of new formulas for emulsion sauces with low calorie content is topical, since their emulsion nature allows not only to enrich the product with a large number of biologically active additives intended for replenishment of essential substances (essential nutritional factors) in the body, but also to reduce caloric content by replacing sugar sweeteners of plant origin, as well as get a tasty product, useful for the health of all population groups [8-11].

The aim of the work is to study the use of sunflower refined oil produced by JSC "Shymkentmai" in the development of an emulsion product for functional purposes.

Objects and methods. **As research object, the refined and unrefined deodorized oils** (**produced by JSC "Shymkentmai"**)**, emulsive sauce, were chosen.**

At the carrying out of researches applied the generally accepted, standard methods of determination of physical and chemical properties of raw material and ready products. The colored was determined by the method of determination of the colored number with the use of Lovibond colorimeter according to QOST 5477-93 [12]. Determination of viscidity of the food emulsive systems were carried out on the rotary viscometer-stirrer of " Rheotest -2".

Rheotest is a rotary viscometer-stirrer, suitable for realization of more exact rheological researches of non-newtonian liquids. The test temperature can be regulated a wide range by temperature control. Rheotest is characterized the scientifically-reasonable principle of measuring, and also wide range of measuring of moving tension, speed of change and viscidity [13,14].

The use of water-fat emulsions is most preferable, since it helps stabilize the physiological functions of the human gastrointestinal tract and is easily digestible. In addition, this is one of the possible ways to optimize the fat diet and nutrition structure of the population of Kazakhstan at the expense of developing new types of sauces [15,16].

Results and discussions. When developing the formulations of the emulsion fat product, as a fat basis, were used the refined deodorized and unrefined sunflower oils, produced by JSC "Shymkentmai".

Organoleptic and physicochemical parameters of refined deodorized and unrefined sunflower oils are given in tables 1 and 2.

Table 1 - Organoleptic characteristics of refined deodorized and unrefined sunflower oils

Indicator name	Characteristics of sunflower oil	
	unrefined sunflower oils	Sunflower refined deodorized oil "High grade"
Transparency	Sediment and light turbidity or «grid» over sediment allowed	Transparent without sediment
Smell and taste	Characteristic of sunflower oil, without foreign smell, smack and bitterness	Without smell, impersonal taste

Table 2 - Physicochemical parameters of refined deodorized and unrefined sunflower oils

Indicator name	unrefined sunflower oils	Sunflower refined deodorized oil "High grade"
Color number, Mg of iodine, no more	15	6
Acid number, mg KOH/g, no more	1,5	0,30
Mass fraction of non-fatty impurities , %, no more	0,05	Absence
Mass fraction of phosphorus-containing substances,%, not more than:		Absence
in terms of stearoololeucitin	0,20	
in terms of P_2O_5	0,018	
foam (qualitative test)	0,15	Absence
Mass fraction of moisture and volatile substances , %, no more	Not standardized	0,10
Flash point of extraction oil, ^{0}C, not less	Not standardized	Not standardized
Peroxide number, mole of active oxygen / kg, no more	Not standardized	4,0
An anisidine number, no more	7,0	3,0

The acidic and peroxidic numbers of the oil under investigation meet the requirements for the permissible levels of oxidative damage for unrefined oils in accordance with TR 1556-1958-AO-016-2017 [17].

Due to the complete conformity of organoleptic and physicochemical parameters of vegetable oils to the characteristics and values recorded in the normative and technical documentation for this type of product, the above oils were used for the preparation of experimental and control samples of mayonnaise sauce. It should also be noted that the peroxide number of oils in both cases does not exceed 1.0 mmol (½ O) / kg, which indicates a high quality of raw materials and its suitability for the preparation of emulsion products.

Proceeding from the foregoing, the refined deodorized sunflower oil produced by JSC "Shymkentmai" is the most preferred raw material for the production of mayonnaise sauce with improved consumer characteristics.

In laboratory conditions samples of a emulsion product of fat content of 35% with used of the refined sunflower oil produced by JSC "Shymkentmai" were developed.

An organoleptic evaluation of the experimental emulsion products were carried out in comparison with the traditional ones, which were evaluated according to the following parameters: appearance, consistency, odor and taste (table 3).

To assess the organoleptic characteristics of model compositions of emulsion product, a 5-point scale was used.

Table 3 - Organoleptic quality indices of emulsion product

Indicators	An experience	Control	Average Score	
			An experience	Control
Appearance, consistency	Homogeneous creamy, with single air bubbles	Homogeneous creamy, slightly stretched with single air bubbles	4,99	4
Taste and smell	Delicate taste, sour, without bitterness, with the smell and smack of jid and citric acid	Pleasant, slightly pungent and sour taste, with a slight smell and taste of unrefined sunflower oil, mustard and citric acid	4,98	3,8
Color	Bright yellow, homogeneous throughout the mass	White, homogeneous throughout the mass	5	4,5

Based on the results obtained, emulsion product with a fat content of 35% based on sunflower oil produced by JSC “Shymkentmai” with a vegetable additive is characterized by a higher value of the total quality index due to a delicate taste and the absence of foreign flavors. The control sample of mayonnaise is perceived more acidic, and notes of the original oil are felt in the taste.

Physicochemical parameters of a mayonnaise sauce fat content of 35% on the basis of sunflower oil produced by JSC “Shymkentmai” with a plant additive (table 4) were studied.

Table 4 - Physical and chemical parameters of the emulsion product of fat content of 35%
on the basis of sunflower oil produced by JSC "Shymkentmai" with vegetable additive

Indicator name	An experience	Control
Moisture content, %:	52,5	50,5
Acidity in terms of acetic acid, %	0,35	0,6
Emulsion stability, % undamaged emulsion	100,0	98,0
Effective viscosity at 20°C, Pa*c	13,6	11,8

The data obtained, summarized in tables 3 and 4, indicate that the samples of products comply with GOST R 53590-2009 and GOST 31761-2012 in all respects. It was found that the experimental samples of the emulsion product were better in all respects than the control samples.

We analyzed food and energy value of emulsion product (table 5).

Table 5 - Food and energy value of emulsion product (per 100 g of product)

Indicator name	Indicator value
Proteins, g	1,0
Fat, g	35,0
Carbohydrate, g	1,8
Energy value, kkal/100 g	326,2

Caloric content of the new emulsion product is significantly reduced by reducing the prescription amount of vegetable oil, while maintaining high organoleptic parameters. Low amounts of protein in the formulations of the new emulsion product should be considered as a positive moment, as the emulsion product is a sauce that is served to the main dish, including meat, fish and poultry [18-20].

The mineral and vitamin composition of the emulsion product were also determined, which is presented in table 6.

Table 6 - Mineral and vitamin composition of the emulsion product

Product name	Vitamins, mg/100 g			Mineral substance, mg/100 g				
	A	E	β-carotin	K	Na	Ca	Mg	Fe
Emulsion product	7,0	0,48	4,0	63	513	57	11	0,4

According to the data presented in table 6, it can be concluded that the emulsion product has a balanced chemical composition: a reduced amount of fats; have a positive effect on the physiological processes of the body.

One of the important consumer properties of food is the safety property.

In accordance with GOST R 53590-2009, mayonnaise and emulsion products should be stored at the manufacturer and the consumer in warehouse, commercial refrigerated rooms or refrigerators with air circulation, at a temperature not lower than 0 ° C and not higher than 10 ° C. It is not allowed to storage mayonnaises and emulsion products in direct sunlight [21].

Decrease in consumer properties of emulsion product was studied, analyzing the dynamics of changes stability and, organoleptic indices.

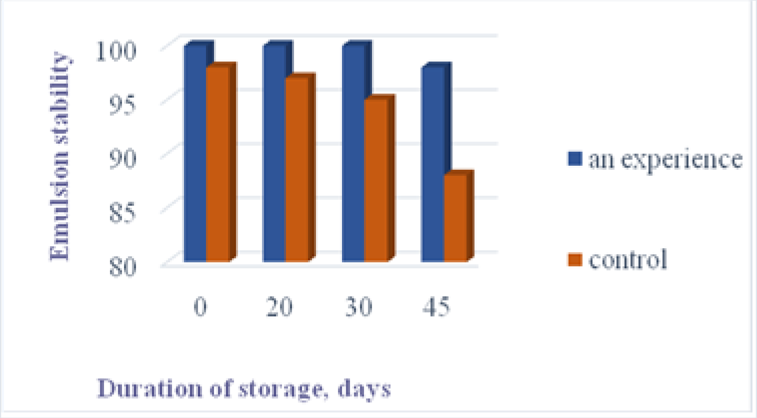
To reveal the dynamics of changes in the quality characteristics of the developed products, they were packaged in polymer cups weighing 250 g and stored at a temperature of 10 ° C and relative humidity of not more than 75% for 45 days. Storage modes were chosen in accordance with the requirements of GOST R 53590-2009, taking into account that 10 ^{0}C is the maximum permissible. The dynamics of change in the quantity of emulsions of control samples and the developed products is presented in the table 7 and in figure.

Table 7 - Physicochemical parameters of experimental and control batches
of low-calorie products and their change during storage.

Indicator name	Indicator value	
	Control	An experience
freshly worked		
Emulsion stability, %, undamaged emulsion	98	100
After 20 days storage at temperature of 10 ^{0}C		
Emulsion stability, %, undamaged emulsion	97	100
After 30 days storage		
Emulsion stability, %, undamaged emulsion	95	100
After 45 days storage at a temperature of		
Emulsion stability, %, undamaged emulsion	88	98

Analyzing the dynamics presented in figure 1, we can conclude that the emulsion product with jid powder and wheat germ flour are more resistant to storage than the comparison samples. Based on the fact that according to the norms the emulsion stability is not less than 97%, the shelf life of the mayonnaise with a mass fraction of fat of 35% at a temperature of 10 ° C. Thus, the shelf life of the emulsion product is up to 45 days.

The conducted researches showed that low-calorie sauces, both freshly prepared and stored, obtained according to the developed recipes, have high organoleptic and physicochemical parameters.



Effect of the storage time on the emulsion stoichiometry of samples of emulsion products

Conclusion. Based on the studies of the factors of formation of consumer properties of emulsion products, recipes and technology for obtaining low-calorie emulsion sauces have been developed.

The expediency and effectiveness of the use of deodized refined vegetable oils of JSC "Shymkentmai" is substantiated.

It has been established that emulsion product of fat content of 35% on the basis of sunflower oil produced by JSC “Shymkentmai” with a plant additive is characterized by a higher value of the total quality index due to the delicate taste and absence of foreign flavors. The control sample of mayonnaise is perceived more acidic, and notes of the original oil are felt in the taste.

It is revealed that the calorie content of the new emulsion product is significantly reduced by reducing the prescription amount of vegetable oil, while maintaining high organoleptic parameters. Low amounts of protein in the formulations of the new emulsion product should be considered as a positive moment, as emulsion product is a sauce that is served to the main dish, including meat, fish and poultry.

М.К. Касымова[1], З.И. Кобжасарова[1],
Г.Э. Орымбетова[1], Г. Нурынбетова[1], Анита Блиджа[2]

[1] М.Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент, Қазақстан;
[2]Латвия ауылшаруашылық университеті, Елгава, Латвия

«ШЫМКЕНТМАЙ» АҚ ШЫҒАРАТЫН КҮНБАҒЫС МАЙЫН ПАЙДАЛАНЫП ЭМУЛЬСИЯЛЫҚ ТҰЗДЫҚ ТЕХНОЛОГИЯСЫН ӨҢДЕУ

Аннотация. Зерттеу нәтижелеріне сәйкес, майонез өнімдерінің нарығы қарқынды дамып келеді деген қорытындыға келуге болады, алайда бөлшек сауда желілерінде ұсынылған майонез тұздықтарының ассортименті нашар және біркелкі емес, өнімнің осы түріне физиологиялық белсенді ингредиенттердің болуына байланысты тұтынушылардың денсаулығын сақтауға бағытталған өнімдер жоқ. Тұтынушылардың талғамы мен уәждерін зерттеу қазіргі тұтынушы табиғи ингредиенттер мен диеталық қоспалардың артықшылықтарын жақсы білетіндігін, құрамы бойынша теңгерімді және пайдалы қоспалардан тұратын өнімге қызығушылық танытатынын және майонездің құнынан гөрі мұндай өнім үшін көбірек төлеуге дайын екендігін көрсетті.

Эмульсиялық өнімдердің тұтынушылық қасиеттерін қалыптастыру факторлары бойынша жүргізілген зерттеу негізінде төмен калориялы эмульсиялық тұздық рецептісі және технологиясы өңделді.

«Шымкентмай» АҚның дезодоризацияланған тазартылған өсімдік майларын қолданудың орындылығы мен тиімділігі негізделген.

Сыртқы түрі, консистенция, иіс және дәм тәрізді органолептикалық көрсеткіштері бойынша тәжірибелі үлгіге бағалау жүргізілді. Шымкентмай» АҚ шығаратын күнбағыс майы негізінде өсімдік текті қоспалар (жиде ұнтағы мен бидай өскіні) қосылған майлылығы 35% болатын эмульсиялық тұздық бөгде дәмнің болмауы және нәзік дәмнің арқасында сапаның жиынтық көрсеткішінің жоғары мәнімен сипатталатындығы белгіленді. Органолептикалық көрсеткіштердің ұзақ сақталуы кезінде күнбағыс майының рецептурадағы мөлшерінің азаюының арқасында эмульсиялық тұздықтың калориясы едәуір азаятындығы айқындалды.

Жаңа эмульсиялық тұздық рецептурасындағы ақуыз мөлшерінің төмен болуы эмульсиялық тұздықты негізгі ас - ет, балық пен құс мәзірінде қолданылатын салмақты кез деп есептеуге болады.

Динамиканы талдай отырып, жиде ұнтағы мен бидай өскіні ұны қосылған эмульсия өнімі сақтауға анағұрлым төзімді деген қорытынды жасауға болады. Нормаларға сәйкес, эмульсияның тұрақтылығы кем дегенде 97%, 10 ° C температурада майонездегі майдың массасы 35%. Осылайша, майонез тұздығының жарамдылық мерзімі - 45 күнге дейін. 45 күн ішінде майонез тұздығының органолептикалық сипаттамалары шамалы өзгереді, бұл олардың жоғары көрсеткіштерімен расталады.

Жиде ұнтақтардың химиялық құрамы зерттелген. Жиде ұнтағы құрамында жеткілікті мөлшерде суда және майда еритін витаминдер, сонымен қатар минералды элементтер бар.

Тазартылған «Донья» күнбағыс майы негізінде майонез соусын жиде ұнтағы мен бидай өскіні ұнды қолдану жағдайында мыналарға мүмкіндік береді:

- Оңтүстік Қазақстанда май және май өнімдеріне сұранысты арттыру;
- отандық шикізат негізінде пайдалы тамақтану үшін майонез тұздықтарының түрлерін кеңейту;
- бидай өмкіні ұнын эмульгатор ретінде, ал жиде ұнтағын тәттілендіргіш және функционалды ингредиент ретінде пайдалану арқылы функционалды, төмен калориялы жаппай тұтыну өнімін алу.
- халықтың тамақтануындағы дәрумендер мен минералдардағы тапшылықты азайту;
- осы өнімдердің тұтынушылық сипаттамаларының жақсаруына байланысты майонез соусына сұранысты арттыру.

Түйін сөздер: эмульсиялық өнім, функциялық, күнбағыс майы, тұтынушылық құндылығы.

М.К. Касымова[1], З.И. Кобжасарова[1],
Г.Э. Орымбетова[1], Г. Нурынбетова[1], Анита Блиджа[2]

[1]Южно-Казахстанский государственный университет им. М. Ауэзова, Шымкент, Казахстан;
[2]Латвийский сельскохозяйственный университет, Елгава, Латвия

ИСПОЛЬЗОВАНИЕ ПОДСОЛНЕЧНОГО МАСЛА, ВЫПУСКАЕМОЙ АО «ШЫМКЕНТМАЙ» ПРИ РАЗРАБОТКЕ ТЕХНОЛОГИИ ЭМУЛЬСИОННОГО ПРОДУКТА

Аннотация. По результатам проведенного исследования можно сделать вывод о том, рынок майонезной продукции быстро развивается, однако ассортимент майонезных соусов, представленный в торговых сетях, беден и однообразен, отсутствуют продукты, направленные на поддержание здоровья покупателей за счет наличия в составе данного вида продуктов физиологически активных ингредиентов. Изучение потребительских предпочтений и мотиваций выявило, что современный потребитель хорошо осведомлен о пользе натуральных ингредиентов и биологически активных добавок, и заинтересован в продукте, сбалансированном по составу и содержащем полезные для здоровья добавки, при этом готов платить за такой продукт больше, чем стоимость майонезов, представленных в розничной сети.

На основании проведенных исследований по факторам формирования потребительских свойств эмульсионных продуктов разработаны рецептуры и технология низкокалорийных эмульсионных соусов.

Обоснована целесообразность и эффективность применения дезодированных рафинированных растительных масел АО «Шымкентмай».

Проведена органолептическая оценка опытных образцов продукта по следующим показателям: внешний вид, консистенция, запах и вкус. Установлено что, эмульсионный продукт жирности 35% на основе подсолнечного масла, выпускаемой АО «Шымкентмай», с растительной добавкой (порошок джида и мука из зародышей пшеницы) характеризуется более высоким значением совокупного показателя качества за счет нежного вкуса и отсутствия посторонних привкусов.

Выявлено, что калорийность данного эмульсионного продукта существенно снижена за счет уменьшения рецептурного количества растительного масла, при сохранении высоких органолептических показателей. Низкое количество белка в рецептурах нового эмульсионного продукта следует рассматривать как положительный момент, поскольку эмульсионный продукт – это соус, который подается к основному блюду, в том числе из мяса, рыбы и птицы.

Анализируя динамику, можно сделать вывод, что эмульсионный продукт с порошком джида и пшеничной зародышевой мукой более устойчив к хранению. Основываясь на том, что в соответствии с нормами стойкость эмульсии не менее 97%, продолжительность хранения майонеза с массовой долей жира 35% при температуре 10°С. Таким образом, срок годности майонезного соуса – до 45 суток. В течение 45 суток хранения незначительно изменяют свои органолептические показатели, что подтверждает их высокая балльная оценка.

Изучены химический состав порошка джида. Порошок джида в достаточном количестве в своем составе содержат водо- и жирорастворимые витамины, а также минеральный элементы.

Использование майонезного соуса на основе рафинированного подсолнечного масла «Доня» с добавлением порошка джида и муки зародышей пшеницы позволит:

- повысить спрос на масложировую продукцию ЮКО;
- расширить ассортимент майонезных соусов для здорового питания на основе отчественного сырья;
- получить функционального-низкокалорийнного продукта массового потребления за счет применение муки зародышей пшеницы в качестве эмульгатора, а порошка джида в качество сахарозаменителя и функционального ингредиента.
- уменьшить дефицит в питании населения в витаминах и минеральных веществ;
- повысить спрос на майонезного соуса в связи с улучшенными потребительскими характеристиками указанных продуктов.

Ключевые слова: эмульсионный продукт, функциональность, подсолнечное масло, потребительская ценность.

Information about authors:

Kassymova M. K. – candidate of chemical science, associate professor, M. Auezov South Kazakhstan state university, Textile and Food Engineering higher school, Shymkent, Kazakhstan; mahabbat_67@mail.ru; https://orcid.org/0000-0002-7150-3014;

Kobjasarova Zibo Isakovna – candidate of technical science, associate professor, M. Auezov South Kazakhstan state university, Textile and Food Engineering higher school, Shymkent, Kazakhstan; ; https://orcid.org/0000-0001-5419-7484;

Orymbetova Gulbagi Emitovna – candidate of technical science, associate professor, M. Auezov South Kazakhstan state university, Textile and Food Engineering higher school, Shymkent, Kazakhstan; orim_77@mail.ru https://orcid.org/0000-0001-8987-3366;

Nurynbetova Gulaina – master, teacher, M. Auezov South Kazakhstan state university, Textile and Food Engineering higher school, Shymkent, Kazakhstan; stone_lady.99@mail.ru, https://orcid.org/0000-0002-2391-3633;

Anita Blija – Dr. ing.,professor, Department of Nutrition, Latvia University of Agriculture, Jelgava, Latvia, Blijaa@llu.lv, https://orcid.org/0000-0001-5429-8218

REFERENCES

[1] Yeliseyeva LG. (2006). Commodity research and Expertise of production Goods. [Tovorovedenıe ı ekspertıza proızvodstvennyh tovarov]. –Moscow. ISBN: 5-7709-0380-5. 175 p. (in Russian).

[2] Donchenko L.V., Firsov G.G. (2007). Pectin: basic properties, production and application. [Pektın: osnovnye svoıstva, proızvodstvo ı prımenenıe].- Moscow. ISBN 5-93913-032-1. 276 p. (in Russion).

[3] Vorobyova A.V., Volkova N.N. (2008). Modern trends in the creation of emulsion products for healthy eating. [Sovremennye tendentsıı sozdanııa emulsıonnyh produktov dlıa zdorovogo pıtanııa]. Food industry. N11. P.72-73 (in Russian).

[4] Volkova N.N. (2008). Development of technologies for low-calorie emulsion sauces based on natural ingredients. [Razrabotka sposoba poluchenııa nızkokalorıınyh emulsıonnyh sousov na osnove naturalnyh ıngredıentov]. The dissertation author's abstract on competition of a scientific degree of the candidate of technical sciences. Moscow.2008 (in Russian).

[5] Eliseeva N.E., Nechaev A.P. (2007). Functional mayonnaise and sauces are sources of soluble dietary fiber. [Funktsıonalnye maıonezy ı sousy – ıstochnıkı rastvorımyh pıevyh volokon]. Fat and oil industry. N.3. P.26 (in Russian).

[6] Ershova TA, Bozhko S.D. (2011). Investigation of structural and mechanical properties of mayonnaise. [Issledovanıe strukturno-mehanıcheskıh svoıstv maıonezov]. Fat and oil industry. N.1.P.30-32 (in Russian).

[7] Zhitnikova V.C. (2008). Emulsive products of a functional purpose on a fruit and vegetable basis. [Zhitnikova B.C. Emulsionnyye produkty funktsionalnogo naznacheniya na plodoovoshchnoy osnove]. Food industry. N.2. P.46-47 (in Russian).

[8] McKenna Brian M. (2008). Structure and texture of food. Products of emulsion nature. [Struktura i tekstura pishchevykh produktov. Produkty emulsionnoy prirody]. St. Petersburg. Publishing house Profession. ISBN: 978-5-93913-158-2. 480 p. (in Russian).

[9] Kinshakov K.D. (2011). Development of formulas for an emulsion product with functional properties. [Razrabotka retseptur emulsionnogo produkta s funktsionalnymi svoystvami]. Storage and processing of agricultural raw materials. N.12.P.46-48 (in Russian).

[10] Tereshuk L.V, Savelyev I.D, Starovoitova K.V. (2010). Emulsifying systems in the production of milk-fat emulsion products. [Emulgiruyushchiye sistemy v proizvodstve molochno-zhirovykh emulsionnykh produktov]. Technique and technology of food production. N.4.P.59-64 (in Russian).

[11] Volkova N.N. (2008). Ingredient composition - the basis for obtaining high-quality food. [Ingrediyentnyy sostav – osnova polucheniya vysokokachestvennykh pishchevykh produktov]. Storage and processing of agricultural raw materials. N.11.P.30. (in Russian).

[12] GOST 5477-93 Vegetable oils. Methods for determining chroma. [Masla rastitelnyye. Metody opredeleniya tsvetnosti]. 1993 (in Russian).

[13] Zabodalova L.A., Belozerova M.S. (2016). Engineering rheology. [Inzhenernaya reologiya]. Study guide. - St. Petersburg: ITMO University. 41p. (in Russian).

[14] Aret V.A., Nikolaev B.L., Nikolaev L.K. (2009). Physical and mechanical properties of raw materials and finished products. [Fiziko-mekhanicheskiye svoystva syrya i gotovoy produktsii]. Study guide. - SPb .: GIORD. ISBN 978-5-9506-0633-5. 448 p. (in Russian).

[15] Voskanyan O.S. (2004). Research and development of technology for the production of emulsion products for functional purposes. [Issledovaniye i razrabotka tekhnologii proizvodstva emulsionnykh produktov funktsional'nogo naznacheniya]. The dissertation author's abstract of the thesis for the degree of Doctor of Technical Sciences. Moscow. 2004 (in Russian).

[16] Morina, I.V. (2011). Development of technology for a functional low-fat emulsion product with a synbiotic complex. [Razrabotka tekhnologii funktsionalnogo nizkozhirnogo emulsionnogo produkta s sinbioticheskim kompleksom]. Moscow. ISBN 5-901065-17-4. 188 p. (in Russion).

[17] TP 1556 – 1958 – AO – 016 – 2017 (in Russian).

[18] Asilbekov N., Kassymova M.K., Nurymbetova G. (2017). Prospects for the development of production of fat-and-oil emulsions for functional purposes. [Perspektivy razvitiya proizvodstva maslozhirovykh emulsiy funktsionalnogo naznacheniya]. Int. scientific and practical conf. "Food security in the context of new ideas and solutions". Semey. T. 1. P.350-354 (in Russian).

[19] Ivashina O.A. (2016). Development and research of technology of spreads of functional purpose with a reduced content of trans-isomers of fatty acids. [Razrabotka i issledovaniye tekhnologii spredov funktsionalnogo naznacheniya so snizhennym soderzhaniyem transizomerov zhirnykh kislot]. The dissertation author's abstract on competition of a scientific degree of the candidate of technical sciences. Kemerova. 2016. P.4 (in Russian).

[20] Orymbetova G.E., Conficoni D., Kassymova M.K., Kobzhasarova Z.I., Orymbetov E.M., Shambulova G.D. (2018) Risk assessment of lead in milk and dairy products//NEWS of The Academy Of Sciences Of The Republic Of Kazakhstan. Series chemistry and technology -volume 6,-Number 432.-2018.-P.23-27 (in Eng.) ISSN 2224-5286 (Print). https://doi.org/10.32014/2018.2518-1491.22

[21] GOST P 53590-2009 Mayonnaises and mayonnaise sauces. General specifications. [Mayonezy i sousy mayoneznyye. Obshchiye tekhnicheskiye usloviya]. 2009 (in Russian).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.27**
Volume 2, Number 440 (2020), 83 – 91

UDC 666.965.2:691.33

T.K. Kuatbayeva[1], Zh. T. Nashiraliyev[1],
Z. M. Zhambakina[1], M. G. Bruyako[2], A. T. Orynova[3]

[1]Satbayev University, Almaty, Kazakhstan;
[2] Federal state budget educational institution of higher education
“Moscow State University of Civil Engineering”, Moscow, Russian;
[3] NIISTROMPROJECT LLC, Almaty, Kazakhstan.
E-mail: aitzhanova.tokzhan@mail.ru, nash_zhan@mail.ru, zhambakina@bk.ru, mbruyako@yandex.ru,
orynova_ainur@mail.ru

USE OF OIL AND BITUMINOUS ROCKS AND WASTE FROM THEIR PROCESSING IN CREATION OF COMPOSITE SILICATE MATERIALS

Abstract. The article considers the issues of technology of silicate materials of dense and cellular structure with usage of oil bituminous rocks and waste from their processing, in particular: the optimization of the ratios of the raw components of a silicate materials mixture, the development of optimal technological parameters for the production of silicate materials, and the technological aspects of the production of the above materials.

The optimal compositions of binders with use of waste products from OBR are studied in this work as an activating component of lime or cement. The stability of the samples was studied in various media with a low and high content of basic calcium hydrosilicate. If they contain insoluble silicates and aluminosilicates containing silica, they are acid resistant. Alkali-resistant rocks containing oxides corresponding to strong bases are combined with oxides corresponding to weak acids, for example, calcium and magnesium carbonates.

As a result of the experimental work, technological processes for the manufacture of silicate materials (of dense and cellular structure) based on the OBR and waste from their processing are substantiated and developed. The paper reveals the chemical-mineralogical and the structural features of oil bituminous rocks and waste from their processing. The optimal ratio of the waste mixture of oil and bituminous rocks with lime and the technological parameters that ensure the grade of lime-sand binder from 400 to 500 are established. Silicate materials based on this mixture have high physical and mechanical properties and comply with the requirements of the ST standards of the Republic of Kazakhstan for silicate brick and GOST state standard for aerated concrete.

Thus, the compositions and conditions for the preparation of these binders with high resistance in large temperature, pressure and aggressive environments are proposed in this work.

Key words: oil bituminous rocks and waste from their processing, structure, mechanochemical activation, silicate materials, binder, cellular concrete, durability.

Introduction. One of the problems of the global scale of the twenty-first century is the human impact on the environment. In this regard, the utilization of oil bituminous rocks (hereinafter - OBR) and waste from their processing is given special attention [1].

The solution to the above problem is the creation and development of non-waste environmentally friendly and mobile technology in creating systems of silicate composite materials and technology for the synthesis of artificial stone, energy-saving and low-energy-consuming man-made products.

The presence of a large number of deposits of the OBR and bitumen-containing sands (hereinafter referred to as the Kir) in Kazakhstan, and as a result, replenishment of scarce oil products, determines the organization of the processing of the OBR with the receipt of 15-30% of bitumen and 70-85% of the mineral part of the sandy type feldspar-quartz, clay and carbonate composition. Currently, more than 50 deposits have been examined and developed only in the western regions of Kazakhstan and reserves of more than 20 million m3 have been determined [2].

The mineral part of the OBR under the microscope is represented by isometric grains of a darkish color, angular and low-rounded, 0.10-0.15 mm in size, which indicates fine grain size. The specified type of raw material contains up to 70% quartz, 24% feldspars, 3% calcite, single grains of sulfides, apatites, and barite. Voidness - 42%, average density - 1290 kg / m3. The chemical composition is presented in table 1.

Table 1 - chemical composition (%) of the mineral part of the OBR processing

Product name	SiO_2	Al_2O_3	Fe_2	Ca	M	K_2	Na	SO	C	П
Mineral part of the OBR processing	82,6	9,3	2,0	1,3	0,3	1,8	1,2	0,8	-	1,4

The OBR processing waste is a group of calcareous-siliceous materials that are dispersed systems of insoluble particulate matter of an amorphous or submicrocrystalline structure with a significant amount of free kinetic energy sufficient for the mutual attraction of the macroparticles with the formation of water-resistant structural bonds. This makes it possible to minimize fuel and energy processing costs, to carry out directional regulation of structure formation in materials hardening without heat treatment, thereby intensifying the technological process for the production of silicate materials and products based on them [3].

The physicochemical, mineralogical, and structural features of the OBR and mineral waste from their processing are represented by two main groups - siliceous materials containing more than 50% SiO_2 and limestone-siliceous materials containing 20-50% CaO and 20-50% SiO_2.

Materials and methods. In this work, we studied the optimal composition of binders using waste from the OBR processing as an activating component of lime or cement. To obtain comparative data, natural sand was used, the composition of which is identical to the waste of the OBR processing, i.e. quartz-feldspar mineralogical composition.

Mechanochemical activation was applied by co-grinding the components of the mixture [4]. Shredding of waste from the OBR processing occurs more quickly than its natural counterpart. This is facilitated by the presence of defects on the surface of the grains of the waste of the OBR processing; surface melting and deeper cracks along the cleavage of feldspar crystals and others in the process of heat treatment of the rock while removing bitumen.

Lime and sand binder. Obtained by co-grinding the waste from the processing of OBR with lime, to a specific surface of 300 m^2/kg. The optimal ratio of lime and waste from the OBR processing are in the range from 0.5:1 to 1:1, at which the activity of lime-sand binder has the highest rates, i.e. strength of 42-50 MPa.

The properties of samples of calcareous-sand binders, depending on the composition and conditions of hardening, vary significantly - samples subjected to autoclaving have a higher strength than samples steamed and hardening under ordinary conditions. It is possible to note the linear nature of the dependence of strength values in the direction of increase, with a corresponding increase in the content of lime in the composition of binders [5].

We studied the possibility of using OBR processing waste as an additive to cement. An evaluation criterion for mechanical activation was the heat of hydration of the activated mixture from the waste of the OBR and the strength of the composite materials based on it - binders with the addition of waste from the OBR are at the same level as with the addition of blast furnace clinker [6].

Results of research. Studies of the impact of additives from OBR processing waste showed that the compressive strength of samples depends on the hardening conditions - for samples with composition: 70% cement clinker and 30% of OBR processing waste hardening under ordinary conditions, compressive strength in 28 days is 46, 0 MPa. After autoclaving, the samples show composition: 50% cement clinker and 50% OBR processing waste, compressive strength is 50.0-53.8 MPa. This composition is optimal and the obtained results on compressive strength are objectively approximated with a normal density value of 27.3%, which is one of the smallest. Hence, it can be considered that the waste of the OBR processing is an active additive and increases the grade of cement.

Considering the fact that most of the known deposits of OBR are located near oil producing regions where cement with special properties (grouting) is used, the one in contact with various mineralized waters, accompanied by high temperature conditions and pressure, the possibility of OBR processing products as active additives to obtain special cements was reviewed.

Studies of the stability of binders in solutions of magnesium sulfate, sodium sulfate, magnesium chloride and sodium, in natural mineralized waters typical of Kazakhstan (sulfate-chloride and chloride-sulfate), resistance to atmospheric conditions and alternate freezing and thawing [7]. The mineralogical composition, structure and dispersion of the siliceous component have a great influence on the resistance of autoclaved materials to the aggressive action of sodium and magnesium sulfate solutions [8].

Lime-sand samples made from mineral wastes from OBR processing turned out to be more resistant than cement-sand samples made from traditional raw materials. But in sodium sulfate solutions, the above calcareous samples turned out to be less stable. Therefore, impurities of feldspar rocks in sands are not only acceptable, but also desirable, especially if the products are used under conditions of further exposure to magnesium-sulfate corrosion. The durability of lime-sand products can be increased by increasing the dosage of lime in lime-sand mixtures. The resistance of lime-sand products containing sodium salts can be increased by introducing a certain amount of ground sand [9]. The stability of the samples was studied in various media with a low and high content of basic calcium hydrosilicate. If they contain insoluble silicates and aluminosilicates containing silica, they are acid resistant. Alkali-resistant rocks containing oxides corresponding to strong bases are combined with oxides corresponding to weak acids, for example, calcium and magnesium carbonates.

We performed a series of experiments in which the test samples of cement containing up to 50% of the waste of the OBR processing were closed with a 5% solution of Na_2SO_4 in one case, and in the other with a 3% solution of $MgSO_4$. The experimental results are shown in table 2.

Table 2 - Influence of aggressive environments on the change in bending strength (MPa)
of cements with the addition of OBR processing waste

Materials and conditions of preparation	Hardening conditions	Storage in 5% Na_2SO_4 for			Storage in 3% $MgSO_4$ for		
		1 day	6 day	12day	1 day	6 day	12day
cement with 50% of waste from OBR processing and sealed with water	under normal conditions	3,6	2,7	1,6	3,6	2,9	1,1
	steaming at 75^{0}C	4,4	4,1	3,3	4,4	4,0	3,0
	autoclaving at 175^{0}C	5,2	4,6	4,2	5,2	4,8	5,0
cement with 50% waste from the processing of OBR and sealed with 5% solution of Na2SO4	under normal conditions	4,0	3,6	3,8	4,6	4,4	4,4
	steaming at 75^{0}C	6,3	6,4	7,0	6,3	6,0	6,6
	autoclaving at 175^{0}C	7,4	7,6	7,8	7,4	7,6	7,8
cement with 50% waste from OBR processing and cured with 2% MgSO4 solution	under normal conditions	4,2	4,8	4,4	4,2	4,9	4,6
	steaming at 75^{0}C	5,8	5,5	5,8	5,8	5,9	6,0
	autoclaving at 175^{0}C	6,2	6,4	6,6	6,2	6,5	6,8

After molding, part of the samples hardened under ordinary conditions, the other was steamed at 75 ^{0}C, and the third part was autoclaved at 175 ^{0}C. Hardened samples were placed in solutions of sodium sulfate and magnesium. After the expiration of the storage period, they were subjected to a strength test.

Mixing with sulfate solutions, increasing the temperature of the hardening conditions, storage in aggressive solutions - all these improves the strength of the samples. In particular, samples made from a mixture inoculated with a 5% sodium sulfate solution and hardened under conditions of steaming at 75 °C, after 12 months of storage in solutions of 5% Na2SO4, and 3% MgSO4, reduced the strength by 5% (table 3.2.1) and the samples made from the mixture, sealed with a 3% MgSO4 solution and solidified under the same conditions, after storage in a 5% sodium sulfate solution and after the same test periods, not only did not reduce the strength, but, on the contrary, increased it by 5%, and when stored in 3% MgSO4, these same samples reduced strength by 4% [10] .

It should be noted that samples hardened in hydrothermal conditions at 175 °C have absolute resistance, which not only does not decrease, but, on the contrary, increases in aggressive sulfate solutions.

From this it follows that when using cements with the addition of waste products of the OBR processing used for laying boreholes, sulfate resistance can be improved by introducing sulfate salts into their composition. This mechanism of action, conventionally called the “affinity” of the composition of cement with the test medium, can be common for other types of binders and aggressive environments [11].

Silicate materials with a cellular structure. We studied silicate materials of a cellular structure based on OBR and waste from their processing. The ratio of cement to lime was established on experimental basis: the ratio of the waste of the processing of OBR and binder (50% lime and 50% cement) is accepted - 1.5: 5 and 1.75: 1 and they correspond to a water-hard ratio - 0.45 and 0.44. Under these conditions, the compressive strength of the samples is 5.1 and 5.2 MPa, with a density of 730-742 kg/m3. When the ratio of the waste of processing OBR and binder (60% lime and 40% cement) is 1.5: 1 and 1.75: 1, the density of the samples is 738-742 kg / m3, and the compressive strength is 5.2 and 5, 1 MPa. Data strength characteristics of these compositions are presented in table 3.

Table 3 - The effect of the ratio of the mixture components
on the density and strength of samples with a cellular structure

The ratio (products of processing OBR: astringent)	The composition of the binder (50% lime and 50% cement)			The composition of the binder (60% lime and 40% cement)		
	W/H	Density, kg/m^3	Compressive strength, MPa	W/H	Density, kg/m^3	Compressive strength, MPa
1:1	0,48	720	4,01	0,46	730	3,8
1,25:1	0,47	723	4,6	0,47	733	4,3
1,5:1	0,45	730	5,1	0,45	738	5,2
1,75:1	0,44	736	5,2	0,44	742	5,1
2:1	0,43	740	3,38	0,44	750	3,6

The structural properties of cellular concrete indicators and a number of its properties are influenced by the amount of blowing agent [13]. The compressive strength of the samples increases with the consumption of aluminum powder of 0.058 by weight of the dry components for the mixture, where the ratio of the components of the waste of the processing of OBR and binder is 1.5: 1, and with a ratio of 1.75: 1, the optimal consumption of aluminum powder is 0.060%.

Thus, the waste of OBR processing both in milled and not in milled form is suitable as a siliceous component for the production of silicate materials with a cellular structure that meet the requirements of the standards with respect to its properties [14].

In order to reduce water absorption and increase the hydrophobic properties of cellular concrete, natural OBR is introduced into the mixture in an optimal dosage of 10%. Natural OBR contained in the mixture up to 10% ensures the hydrophobicity of products: reduces water absorption by 25%, vapor permeability by 45%, shrinkage by 20%, adsorption moisture by 2.2 times. In addition, it contributes to the modification of the capillary-porous structure in the intergranular space of the material and the creation of fine crystallinity and fine porosity, which leads to a decrease in deformation stresses by 4.3 times compared to materials without additives. Samples made from a mixture with the addition of 10% OBR are more frost-resistant than those without the additive — they withstood up to 100 cycles without destruction [15].

Silicate materials of dense structure. Dense silicate materials based on OBR and their waste were studied. To increase the activity of the interaction of the components, the raw material was partially milled (to activate it) and introduced into the mixture from 10 to 20%. A positive effect of the addition of the ground part of the OBR processing waste on the strength of pressed silicate samples was observed. Combined grinding of waste products from OBR and lime significantly contributes to an increase in the strength of the samples - up to 30 MPa, with a binder content of 22-25%.

With a constant ratio of binder and waste processing OBR, equal to 1: 3, with an increase in press pressure increases the density of the samples and at the same time decreases water absorption [16].

With a constant composition of a mixture of a binder -25% and non-ground product of processing OBR - 75% and a pressure of 20.0 MPa, with increasing humidity of the mixture, the density of the samples increases, and the compressive strength increases to a certain value of the moisture of the mixture - 7-9%, in which the density and strength are respectively 1810 and 1826 kg / m; 24.84 and 25.1 MPa. With increasing temperature of the processed medium, the strength of the samples increases. Strength and density indicators of the tested samples are shown in table 4.

Table 4 - the Effect of hardening conditions on the properties
of silicate material based on waste processing OBR

Mixture composition, %		Hardening conditions	Density, kg/m^3	Compressive strength, MPa
Binding	OBR processing waste			
25	75	steaming at 80^{0}C	1830	10,8
25	75	steaming at 120^{0}C	1840	16,4
25	75	autoclaving 175^{0}C	1858	25,0

Frost resistance of pressed samples after 25 cycles of alternate freezing and thawing, in general, meets the requirements of GOST 379-2015 [17] on silicate stones and bricks: compressive strength - 29.7 MPa; density - 1870 kg / m; water absorption - 9.2%; frost resistance - 25 cycles; brand - 250.

Thus, as a result of the tests we were able to establish the technological aspects of obtaining silicate materials based on OBR and waste from their processing.

The quality of silicate products is closely related to the composition and structure of the neoplasms represented by CSH (1) and tobermorite, the structure of which varies from gel to fine crystalline.

The parameters of the microporous structure of phase-forming calcium hydrosilicates vary from the hardening conditions and determine the operational properties of the material. The less porous and more homogeneous structure that takes place during hardening of samples under wet conditions or by steaming corresponds to the highest strength and frost resistance of materials [18].

The strength of the samples both after molding and after hardening increases with increasing pressure. The strength of samples after molding intensively increases by more than three times with an increase in pressing pressure from 5.0 to 20.0 MPa, then with a further increase in pressure from 30.0 to 40.0 MPa, the strength of samples after molding increases by 19%.

The increase in the strength of the samples with increasing pressure is due to the fact that during compaction by pressing, “constrained” conditions are created under which the interacting particles are significantly closer to each other, the solvated solid phase is densely packed, and the polarization interactions of the particles of the components are greatly enhanced. With less pressure, the distance between the particles is greater meaning that the concentration of the solid phase decreases and the solvated particles of the components are disconnected, and the water contained between them has thick interlayers, which leads to a weakening of the polarization interaction and reduces the rate of formation of cement substances [19].

On the basis of non-ground waste from the processing of OBR, it is possible to manufacture cellular concrete products with a density of 700-728 kg / m3 and compressive strength of 5.4 - 5.9 MPa. In the manufacture of cellular concrete with the addition of 10% natural OBR, the hydrophobicity of products is achieved up to 85%.

According to their physical and mechanical properties, pressed silicate materials and products meet the requirements of standards: stamp 75 to 250, density 1810-1920 kg / m, water absorption 7-10%, frost resistance 15-50 cycles. Silicate brick based on the non-ground product of processing OBR and lime-sand binder during autoclaving has the brand name “200”, and with the addition of an additional 5% cement, the autoclave treatment can be replaced by steaming.

Conclusion. Based on the results of the work, technological processes for the manufacture of silicate materials (dense and cellular structure) based on OBR and the waste from their processing are substantiated and developed. The chemical-mineralogical and structural OBR and waste from their processing have been identified [20], namely:

- OBR of semi-dark color contains up to 15% of the organic part and up to 85% of the mineral part, including 70% of quartz and 30% feldspar minerals. The structure of grains along cracks, cleavages and surface grooves is saturated by the organic components (bitumen);
- waste from OBR processing consists of a fine-grained sandy substance of feldspar-quartz composition.

The surface of the grains of quartz and feldspar is darkly colored, slightly melted, has numerous defects and cracks along the cleavages. In terms of chemical composition, in addition to silicon dioxide, aluminum oxides and alkali metals are present [21].

It was determined that the optimal ratio of the mixture of waste from OBR processing with lime and the technological parameters ensure that the lime-sand binder is 400 to 500 grit. Silicate materials based on it have high physical and mechanical properties and meet the requirements of ST for silicate brick and GOST for cellular concrete.

In addition, the presence in OBR system of up to 15% bitumen does not significantly affect the phase composition of hydrated components having less crystallinity, a more gel-like structure; promotes the formation of a thin film on the surface of the interacting particles, reducing the speed of their interaction. Hydrated neoplasms in the studied materials have a microporous structure. These factors have a positive effect on the strength characteristics of the material.

Silicate materials of a cellular structure made on the basis of OBR in an amount of 10% in a mixture of waste from OBR, lime or cement achieve significant hydrophobicity, which positively affects the reduction of water absorption by 25%, sorption moisture by 2.2 times, shrinkage by 20%, vapor permeability up to 2 times, which significantly improves the performance of products.

Cementing materials based on wastes from processing of OBR in a mixture with lime or cement, have low heat and in heat-moisture conditions they intensively gain the required grade, have high sulfate resistance, in conditions of elevated temperature and hostile environment, which simulates working conditions when drilling boreholes. The compositions and conditions for the preparation of these binders, which are highly resistant under conditions of high temperature, pressure and aggressive environment, are proposed.

Т.К. Куатбаева[1], Ж. Т. Наширалиев[1],
З. М. Жамбакина[1], М. Г. Бруяко[2], А. Т. Орынова[3]

[1]Satbayev University, Алматы, Қазақстан;
[2]ФГБОУВО «Ұлттық зерттеу Мәскеу мемлекеті Құрылыс университеті», Мәскеу, Ресей;
[3] «НИИСТРОМПРОЕКТ» ЖШС, Алматы, Қазақстан

МҰНАЙ БИТУМИНОЗДЫ ЖЫНЫСТАР МЕН ОЛАРДЫ ӨҢДЕУДІҢ ҚАЛДЫҚТАРЫПАЙДАЛАНЫП ЖӘНЕ ӨҢДЕП СИЛИКАТТЫ МАТЕРИАЛДАРДЫН ЖАСАУ

Аннотация. Мақалада мұнай битуминозды жыныстарды және оларды қайта өңдеу қалдықтарын қолдана отырып, тығыз және ұяшықты құрылымдағы силикатты материалдар технологиясы, атап айтқанда: силикатты материалдар қоспасының шикізат құрамдастарының арақатынасын оңтайландыру, силикатты материалдарды дайындаудың оңтайлы технологиялық параметрлерін әзірлеу, жоғарыда аталған материалдар өндірісінің технологиялық аспектілері мәселелері қарастырылған.

Мұнай битуминозды жыныстар мен оларды қайта өңдеу қалдықтарының химиялық-минералогиялық және құрылымдық ерекшеліктері анықталды. Шикізаттың химиялық-минералогиялық құрамын, оның контактілі-конденсациялық қасиеттерін назарға ала отырып, жұмыста әктің немесе цементтің активтендіруші компоненті ретінде МБЖ қайта өңдеу қалдықтарын пайдалана отырып тұтқыр заттардың оңтайлы құрамы зерттелді. Тұтқыр қасиеттерді айқындау және күшейту үшін қоспа компоненттерін бірге ұсақтау жолымен механикалық-химиялық активациялау қолданылды. Дисперсиялықтың жоғарылауы және сонымен бірге шикізаттың белсенділігі көп дәрежеде жоғары қаттылықпен сипатталатын материалдарды бірге ұнтақтау кезінде байқалады.

Мұнайбитуминозды жыныстар минералдарының жоғары ерігіштігі олардың әкпен өзара әрекеттесуін белсендіреді. Әктасты-құмды тұтқыр материалдар үлгілерінің қасиеттері, құрамы мен қатаю жағдайларына байланысты айтарлықтай өзгереді - автоклавты өңдеуден өткен үлгілер буландырылған және әдеттегі жағдайларда қататын үлгілерге қарағанда беріктігі жоғары болады. Байланыстырғыш құрамындағы әктас мөлшерінің тиісті ұлғаюымен беріктілік мәндерінің ұлғаю жағына тәуелділігінің сызықтық сипаты белгіленеді. Мұнай битуминозды жыныстарды қайта өңдеу қалдықтар қоспасының әктаспен оңтайлы арақатынасы және технологиялық параметрлер анықталды, олар әктас-құмды тұтқырғыштың маркасын 400-ден 500-ге дейін қамтамасыз етуге мүмкіндік береді.

МБЖ қайта өңдеу қалдықтарын цементке қоспа ретінде пайдалану мүмкіндігі зерттелді. Механикалық активтендірудің бағалау критерийі МБЖ қайта өңдеу қалдықтарынан белсендірілген қоспаныың гидратациялау жылылығы және оның негізіндегі композициялық материалдардың беріктігі болып табылады - МБЖ қайта өңдеу қалдықтары қосылған байланыстырғыш домна қожын қосқандағыдай деңгейде болады.

Сығылуға беріктігі бойынша алынған нәтижелер ең аздарының бірі болып табылатын қалыпты қоюлықтың мәнімен объективті түрде апроксимацияланады. Меншікті беті аз мұнай битуминозды жыныстарды қайта өңдеудің құмды өнімдерін қосқан кезде цемент үлгілерінің жұқа ұсақтауға қарағанда беріктігі жоғары болуы тиіс. Мұнай битуминозды жыныстардың қайта өңделген меншікті беті аз құмды өнімдерін қосқан кезде цемент үлгілері ұсақ майдаланғандарға қарағанда беріктігі жоғары болды. Мұны суспензиядағы материалдың ірі фракциялары pH-ортаның мәнін төмендететіні түсіндіреді, бұл цемент сияқты сілтілі реакциясы бар аралас байланыстырғыштың гидратациясы мен гидролизін жеделдетуге ықпал етеді. Мұндай механизм цементтің мұнайбитуминозды жыныстарды қайта өңдеудің құмды өнімдерімен қышқылдық-негіздігімен өзара әрекеттесуіне негізделген. МБЖ қайта өңдеу қалдықтары белсенді қоспа болып табылады және цементтің маркалығын арттырады, сондай-ақ жылу өңделген алюминосиликат құрамы сазы, күл-шығару, шлактар және басқа да техногендік заттар түріндегі пирогенді өнімдермен салыстырылатын белсенді қоспа болып табылады, бұл олардан мұнай өнімдерін алу процесіндегі термиялық әсермен түсіндіріледі. Мұнайбитуминозды жыныстардың белгілі кен орындарының басым бөлігі арнайы қасиеттері бар (ауырлатылған, тұзға төзімді, ыстық пен тұзға төзімді, тампонаждық) цементтер көп мөлшерде тұтынылатын мұнай өндіруші аудандарға жақын орналасқанын ескере отырып, мұнайбитуминозды жыныстарды қайта өңдеу өнімдерін арнайы цементтер алу үшін белсенді қоспалар ретінде пайдалану мүмкіндігі қарастырылды. Кальцийдің төмен және жоғары негіздегі гидросиликаттарының үлгілері түрлі орталарда төзімділігі зерттелді.

Атап айтқанда, құрамында мұнай битуминозды жыныстарды қайта өңдеудің құмды қалдықтары бар сыналатын цементтер магний мен натрийдің сульфатты ерітінділеріне салынып, автоклав жағдайында қатайтылғаннан кейін сульфатты ерітінділерде сақталды. Жасалған үлгілер осы агрессивті ерітінділерде абсолютті төзімділікті көрсетті. Бұл әрекет механизмі цемент құрамының пайдалану ортасымен "туыстық" деп шартты түрде атадық. Көрсетілген қағида тұтқыр материалдар мен агрессивті орталардың басқа түрлеріне қолданылуы мүмкін. Құрамында кремнезем бар ерімейтін силикаттар мен алюмосиликаттар болған жағдайда олар қышқылға төзімді болып табылады. Жүргізілген эксперименталдық жұмыстар нәтижесінде МБЖ және оларды қайта өңдеу қалдықтары негізінде силикатты материалдарды (тығыз және ұяшықты құрылымды) дайындаудың технологиялық процестері негізделді және әзірленді. Мұнай битуминозды жыныстардың қайта өңделген техногенді минералдық өнімдері ұнтақталған, сондай-ақ ұнтақталмаған түрінде қасиеттері бойынша стандарт талаптарына сай ұяшықты құрылымдағы силикатты материалдарды өндіру үшін кремнеземдік компонент ретінде жарамды болып табылады. Силикатты қоспаға табиғи мұнай битуминозды жыныстың 5% - ға дейінгі қоспасы бұйымдардың гидрофобиялығын қамтамасыз етеді: су сіңірілуін 25% - ға, бу өткізгіштігін 45% - ға, адсорбциялық ылғалдылықты 2,2 есе, капиллярлы сору 7 есе, аязға төзімділікті 100 циклге дейін азайтады. Силикат қоспасына мұнайбитуминозды жынысты қосу капиллярлы-кеуекті құрылымды модификациялауға және ұсақ кристалдылықты және ұсақ кеуекті құруға ықпал етеді.

Әк бар мұнай битуминозды жыныстарды қайта өңдеу қалдықтарынан алынған әк-құмды байланыстырғыш негізіндегі силикатты материалдардың жоғары физикалық-механикалық және пайдалану қасиеттері бар және олар силикатты кірпіш пен ұяшықты бетонға қойылатын нормативтік талаптарға сәйкес келеді.

Түйін сөздер: мұнай битуминозды жыныстар мен оларды өңдеудің қалдықтары, құрылым, механохимиялық активтендіру, силикатты материалдар, тұтқыр, ұялы бетон, беріктік.

Т.К. Куатбаева[1], Ж. Т. Наширалиев[1],
З. М. Жамбакина[1], М. Г. Бруяко[2], А. Т. Орынова[3]

[1]Satbayev University, Алматы, Казахстан;
[2]ФГБОУВО «Национальный исследовательский Московский государственный
строительный университет», Москва, Россия;
[3]ТОО «НИИСТРОМПРОЕКТ», Алматы, Казахстан

ИСПОЛЬЗОВАНИЕ НЕФТЕБИТУМИНОЗНЫХ ПОРОД И ОТХОДОВ ИХ ПЕРЕРАБОТКИ В СОЗДАНИИ КОМПОЗИЦИОННЫХ СИЛИКАТНЫХ МАТЕРИАЛОВ

Аннотация. В статье рассмотрены вопросы технологии силикатных материалов плотной и ячеистой структуры с применением нефтебитуминозных пород и отходов их переработки, в частности: оптимизация соотношений сырьевых составляющих смеси силикатных материалов, разработка оптимальных технологических параметров изготовления силикатных материалов, технологические аспекты производства вышеуказанных материалов.

Выявлены химико-минералогические и структурные особенности нефтебитуминозных пород и отходов их переработки. Принимая во внимание химико-минералогический состав сырья, его контактно-конденсационные свойства, в работе исследовались оптимальные составы вяжущих веществ с использованием отходов переработки НБП, как активизирующего компонента извести или цемента. Для проявления и усиления вяжущих свойств была применена механохимическая активация путем совместного измельчения компонентов смеси. Повышение дисперсности и вместе с тем активности сырья в большей степени отмечается при совместном помоле материалов, характеризующихся повышенной твердостью.

Повышенная растворимость минералов нефтебитуминозных пород активизирует их взаимодействие с известью. Свойства образцов известково-песчаных вяжущих материалов, в зависимости от состава и условий твердения, изменяются в значительных пределах - образцы, прошедшие автоклавную обработку, имеют более высокую прочность, чем образцы, пропаренные и твердеющие в обычных условиях. Отмечается линейный характер зависимости значений прочности в сторону увеличения, с соответствующим увеличением содержания извести в составе вяжущих. Установлено оптимальное соотношение смеси отходов переработки нефтебитуминозных пород с известью и технологические параметры, которые позволяют обеспечить марочность известково-песчанного вяжущего от 400 до 500.

Изучалась возможность использования отходов переработки НБП как добавки к цементу. Оценочным критерием механической активации явилась теплота гидратации активизированной смеси из отходов переработки НБП и прочность композиционных материалов на ее основе - вяжущие с добавкой отходов переработки НБП, находятся на том же уровне, что и при добавке доменного шлака. Полученные результаты по прочности на сжатие, объективно апроксимируются со значением нормальной густоты, являющийся одной из наименьших. При добавке песчаных продуктов переработки нефтебитуминозных пород с меньшей удельной поверхностью цементные образцы имели более высокую прочность, чем при более тонком измельчении. Это объясняется тем, что более крупные фракции материала в суспензии снижают значение pH среды, что способствует ускорению гидратации и гидролиза смешанного вяжущего, имеющего щелочную реакцию, как и цемент. Такой механизм основан на кислотно-основном взаимодействии цемента с песчаными продуктами переработки нефтебитуминозных пород. Отсюда можно считать, что отходы переработки НБП являются активной добавкой и повышают марочность цемента, а также являются активной добавкой, сравнимой с пирогенными продуктами типа термообработанных глин алюмосиликатного состава, золы-уноса, шлаков и других техногенных веществ, что объясняется результатом термического воздействия в процессе извлечения из них нефтепродуктов.

Учитывая то, что большинство известных месторождений нефтебитуминозных пород находятся вблизи нефтедобывающих районов, где потребляются в больших количествах цементы со специальными свойствами (утяжеленные, солестойкие, термосолестойкие, тампонажные), рассматривалась возможность использования продуктов переработки нефтебитуминозных пород в качестве активных добавок для получения специальных цементов. Изучалась стойкость образцов в различных средах низко-и высокоосновных гидросиликатов кальция. В частности, испытываемые цементы, содержащие песчаные отходы переработки нефтебитуминозных пород, затворяли сульфатными растворами магния и натрия, с последующим твердением в автоклавных условиях и последующим хранением в сульфатных растворах. Полученные образцы имели абсолютную стойкость в этих агрессивных растворах. Этот механизм действия нами назван условно «родственностью» состава цемента с средой эксплуатации. Указанный принцип может быть распространен на другие виды вяжущих материалов и агрессивных сред. При наличии в них нерастворимых силикатов и алюмосиликатов, содержащих кремнезем, они являются кислотостойкими.

В результате проведенных экспериментальных работ обоснованы и разработаны технологические процессы изготовления силикатных материалов (плотной и ячеистой структуры) на основе НБП и отходов их переработки. Техногенные минеральные продукты переработки нефтебитуминозных пород как в молотом, так и в немолотом виде являются пригодными в качестве кремнеземистого компонента для производства силикатных материалов ячеистой структуры, по свойствам отвечающим требованиям стандарта. Добавка в силикатную смесь до 5 % природной нефтебитуминозной породы обеспечивает гидрофобность изделий: уменьшает водопоглощение на 25 %, паропроницаемость на 45 %, адсорбционную влажность в 2,2 раза, капиллярный подсос в 7 раз, морозостойкость до 100 циклов. Добавка нефтебитуминозной породы в силикатную смесь способствует модифицированию капиллярно-пористой структуры и созданию мелкокристалличности и мелкопористости.

Силикатные материалы на основе известково-песчаного вяжущего, полученного из отходов переработки нефтебитуминозных пород с известью, имеют высокие физико-механические и эксплуатационные свойства и соответствуют нормативным требованиям к силикатному кирпичу и ячеистому бетону.

Ключевые слова: нефтебитуминозные пород и отходы их переработки, структура, механохимическая активация, силикатные материалы, вяжущее, ячеистый бетон, долговечность.

Information about authors:

Kuatbayeva Togzhan Kuangaliyevna, Doctor of Technical sciences, Professor at Construction and construction materials department, Satbayev University, Almaty, Republic of Kazakhstan; aitzhanova.tokzhan@mail.ru; https://orcid.org/0000-0002-5314-3561

Nashiraliyev Zhankeldi Turtemirovich, Candidate of Technical sciences, Associated professor at Construction and construction materials department, Satbayev University, Almaty, Republic of Kazakhstan;; nash_zhan@mail.ru; https://orcid.org/0000-0002-6770-397X

Zhambakina Zauresh Mazhitovna, Candidate of Technical sciences, Professor assistant at Construction and construction materials department, Satbayev University, Almaty, Republic of Kazakhstan; zhambakina@bk.ru; https://orcid.org/0000-0002-3089-563X

Bruyako Mikhail Gerasimovich, Candidate of Technical sciences, Federal state budget educational institution of higher education The Moscow State University of Civil Engineering, Moscow, Russian Federation; mbruyako@yandex.ru; https://orcid.org/0000-0003-1284-6209

Orynova Ainur Torakhmetkyzy, Master of Technics and technologies, Supervisor at KNILSM, NIISTROMPROJECT LLC, Almaty, Republic of Kazakhstan; orynova_ainur@mail.ru; https://orcid.org/0000-0002-9224-1279

REFERENCES

[1] Giel R., Młyńczak M., Plewa M. Evaluation method of the waste processing system operation. Risk, Reliability and Safety: Innovating Theory and Practice – Proceedings of the 26th European Safety and Reliability Conference, ESREL, 2016.

[2] Nadirov, N. K. High-viscosity oils and natural bitumen (History. Pools. Properties) / N. K. Nadirov. A.: “Gylym” 2001. T. 1. 256 s.

[3] G. Zh. Moldabayeva, G. P. Metaxa, Zh. N. Alisheva. Theoretical bases for the implementation of the processes to reduce viscosity in the conditions of natural reservation. News of the national academy of sciences of the Republic of Kazakhstan series of geology and technical sciences, Volume 5, Number 437 (2019), 138–143. https://doi.org/10.32014/2019.2518-170X.135

[4] Kuatbaev A, K., Idrisov D.S., Aitzhanova T.K. Mechanochemistry in improving the quality of composite materials. // Scientific works of the International Symposium on Mechanochemistry. Tashkent. 1995. P.66-67.

[5] Soloviev V.I. Concrete with water-repellent additives. Alma-Ata. Science. 1990. 112 s.

[6] Yartiev A. F. Natural bitumen - a unique energy raw material // Bulletin of Kazan Technological University. 2012. No. 12. T. 15. S. 293-297.

[7] Composition of oil and bituminous rock of the Beke deposit (Kazakhstan) / E. I. Imanbaev, E. K. Ongarbaev, S. V. Simakov, E. Tileuberdi, B. K. Tuleutaev, Z. A. Mansurov // Scientific sheets. 2013. No. 24 (167), issue. 25.S. 139-142.

[8] Ishmukhamedova N.K. Study of the organic fraction of oil bituminous rock of the Satypaldy deposit // Oil refining and petrochemicals. 2016. No. 11. S. 22-24.

[9] Ishmukhamedova N. K. Road bitumens with the modifield additives // Science and technology. 2011, V. 6, P. 76-78.

[10] A. D. Farmer, A. F. Collings, G. J. Jameson, Effect of ultrasound on surface cleaning of silica particles // Int. J. Miner. Process. 2000. Vol. 60. P.101-113.

[11] Sviridenko N. N. Cand. Diss. Regularities of thermal transformations of components of natural bitumen. - Tomsk, Russian Federation, 2016. 134 p.

[12] Moore R. G., Laureshen C. J., Mehta S. A., Ursenbach M, G., Belgrave J. D. M., Weissman J. G., Ktssler R. V. A downhole catalytic upgrading process for heavy oil using in suti combustion // J. Can. Petrol. Technol. 1999. Vol. 38. No. 13. P. 72-96.

[13] Serova R.F., Rakhimova G.M., Tkach S.A., Stasilovich E.A., Rusanov A.A. Obtaining effective modified aerated concrete using industrial wastes and secondary raw materials // International Journal of Experimental Education. 2015. No. 8-1. S. 41-46.

[14] Yu.V. Khomchenko. Improving the efficiency of autoclave materials based on binder modification: Diss. Cand. tech. sciences, BSTU them. V.G. Shukhov, Belgorod, 2008.167 s.

[15] Waldemar Wojcik, Zh. M. Alimzhanova, T. T. Velyanov, A. M. Akhmetova. About one model of pumping oil mixture of different viscosities through single pipeline in an unsteady thermal field. News of the national academy of sciences of the Republic of Kazakhstan series of geology and technical sciences, Volume 5, Number 437 (2019), 207-214 https://doi.org/10.32014/2019.2518-170x.144

[16] M. Zh. Zhurinov, B. B. Teltayev, A. A. Kalybai. Characteristics of road bitumen modified with carbon nanopowder. News of the national academy of sciences of the Republic of Kazakhstan series of geology and technical sciences, Volume 5, Number 437 (2019), 223 - 228 https://doi.org/10.32014/2019.2518-170x146.

[17] GOST 379-2015 “Silicate bricks, stones, blocks and plates. General technical conditions ”, Moscow: Standartinform, 2015

[18] Averin I.A., Pecherskaja R.M., Karmanov A.A., Pronin I.A. (2011). The influence of the conditions of obtaining on the porosity of thin-film nanostructured polymeric materials // Collection of materials of the scientific and technical conference "Testing 2011". Penza. P. 126-128 (in Rusian).

[19] Kenzhaliyev B.K., et al. To the question of recovery of uranium from raw materials // News of the National academy of sciences of the Republic of Kazakhstan. Series of geology and technical sciences. 2019. Vol. 1. P. 112-119. https://doi.org/10.32014/2019.2518-170X.14

[20] Zholtaev G.Zh., Iskaziev K.O., Abayıldanov B.K. Paleosoic deposits as option for reserves replacement and expansion of raw material base for petroleum industryin Mangyshlak // News of the National academy of sciences of the Republic of Kazakhstan. Series of geology and technical sciences. 2018.P. 163-171. ISSN 2518-170X. https://doi.org/10.32014/2018.2518-170X

[21] Rakishev B.R. Technological resources for improving the quality and completeness of use of the mineral raw materials // News of the National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technical sciences. 2017. Vol. 2, N 422. P. 116-124 (in Eng.), doi.org/10.32014/2018.2518-170X

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.28**
Volume 2, Number 440 (2020), 92 – 98

UDC 622.775; 544.47;

A.Z. Abilmagzhanov[1], N.S. Ivanov[1], M.S. Malimbaev[2],
I.Y. Adelbayev[1], A.E. Nurtazina[1], A.D. Altynbek[3], N.M. Shokobayev[1]

[1]JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan;
[2]«KazDesign» LLP, Almaty, Kazakhstan;
[3] «Semyzbay-U» LLP, Stepnyak, Kazakhstan.
E-mail: a.abilmagzhanov@ifce.kz, xumuk777@mail.ru, mambet.malimbayev@caravanresources.com,
clerikc88@mail.ru, nurtazina.aizhan@bk.ru, akmurat.a@mail.ru, nurlan.shokobayev@flsmidth.com

CATALYTIC OXIDATION OF FERROUS IRON TO INCREASE THE EFFICIENCY OF URANIUM LEACHING

Abstract. Currently, enterprises of the metallurgical complex in Kazakhstan are faced with the problem of raw materials quality and the impossibility of productive processing of a number of ores. In recent years, not a single significant mineral deposit has been discovered, and previously discovered deposits are not of industrial interest, due to the low content of mineral components. «Kazatomprom» enterprises producing uranium by in-situ leaching method (ISL) were no exception. Today, the metal content in productive solutions is steadily decreasing; to increase the concentration of uranium production, it is necessary to increase the amount of reagent consumption, which leads to significant costs. The cost of uranium in the world market has decreased, significant production costs lead to a decrease in the profitability of production. The mechanism of uranium oxidation by iron ions is catalytic in nature. To regenerate iron, air oxygen was supplied to the leaching solution along with the oxidizing agent. The paper presents the results of studies on the possibility of intensifying ISL of uranium by introducing sodium nitrite into the leaching solution with additional supply of compressed air or oxygen to the leaching solution to ensure the catalytic oxidation of iron (II) ions by dissolved oxygen. The positive effect of stirring is proven. Research works at the testing ground with simultaneous supply of sodium nitrite and pure oxygen to LS allowed reaching 1.0 and 1.2 g/l Fe (III) concentrations.

Key words: uranium, in-situ leaching, leaching solution, sodium nitrite, oxidation.

Introduction. To increase the extraction of uranium from ores containing uranium (IV) minerals, it is necessary to use oxidizing agents to convert the insoluble tetravalent form of uranium to hexavalent. Since in-situ leaching of uranium-containing ores the solution always contains iron, then interaction reactions of U (IV) with Fe (III) ions are of both theoretical and practical interest [1, 2]. Interaction process of U (IV) with Fe (III) ions can follow two mechanisms:

$$\begin{array}{ll} \text{I} & UO_2 + Fe^{3+} = UO_2^{+} + Fe^{2+} \\ & UO_2^{+} + Fe^{3+} = UO_2^{2+} + Fe^{2+} \\ \text{II} & UO_2 + 4H^{+} = U^{4+} + 2H_2O \\ & U^{4+} + 2Fe^{3+} + 2H_2O = UO_2^{2+} + 2Fe^{2+} + 4H^{+} \end{array} \tag{1}$$

According to the first mechanism, uranium oxidation occurs on the surface of UO_2 without hydrogen ions participation. Since uranium usually dissolves in an acidic medium, the second mechanism, in which the first stage is the dissolution of UO_2 in acid followed by the oxidation of U (IV) in solution, may be equally probable [3].

According to a number of studies, uranium dioxide is poorly soluble in acids. Even at a temperature of 70^0C for 6 hours, 1.76% of uranium is dissolved in sulfuric acid with concentration of 12.5 g/l, at a concentration of 100 g/l - 2.5%. The same amount of uranium dissolves in perchloric acid, and 1.51-

1.28% in hydrochloric acid. In this regard, it can be assumed that the second mechanism does not play a major role in the process, and the oxidation of UO_2 by Fe (III) ions proceeds according to the first mechanism.

However, many's the time, due to the regenerative nature of the reservoir, almost all of the iron will be in divalent form and it must also be oxidized to involve it in the oxidation process [4, 5].

With sodium nitrite appending in leach solutions perhaps two mechanisms of its affecting: direct oxidation of Fe (II) catalytic effect. Direct oxidation of iron occurs by the reaction:

$$Fe^{2+} + NO_2^- + 2H^+ = Fe^{3+} + NO + H_2O \quad (2)$$

Accordingly, the amount of oxidized iron is directly proportional to amount of added sodium nitrite. However, using this method, the generated NO will be bound by divalent iron until it ends in the solution, then when the solution leaves the chink and the pressure drops, intense NO release into the atmosphere will occur, which will negatively impact the environmental situation.

$$Fe^{2+} + NO = [Fe(NO)]^{2+} \quad (3)$$

The second mechanism is based on the catalytic effect of sodium nitrite, in which the divalent nitrite ferrous complex undergoes oxidation. Supply oxygen to the system is necessary and the amount of oxidized ferrum will depend on the concentration of dissolved oxygen [6, 7].

$$4[Fe(NO)]^{2+} + O_2 + 2H_2O = 4Fe^{3+} + 4NO \quad (4)$$

Experimental part. In order to find a satisfactory solution for Fe (II) oxidation, it was decided to establish how the process proceeds at atmospheric pressure with aeration and without aeration in a confined space at overpressure [8, 9].

The oxidation process at atmospheric pressure was carried out in glass tumbler with a volume of 300 ml, a solution volume of 200 ml. The process was conducted while stirring, aeration and in a static position without external actions. Solution composition and the conditions are as follows: Fe^{2+} stock solution 2.5 g/l, sulfuric acid 1.54 g/l, sodium nitrite 50 mg/l. Content of Fe^{3+} after the addition of nitrite was 55.85 mg/l. Air supply for aeration was 12 l/hour. Obtained results are presented in table 1.

Table 1 – Fe^{3+} content under various oxidation conditions

	Time, h					
	0.5	1	2	3	4	5
Aeration of Fe^{3+}, mg/l	111	125	139	139	139	139
Stirring of Fe^{3+}, mg/l	125	167	223	223	258	279
Statics of Fe^{3+}, mg/l	110	13	139	160	167	181

The concentration of ferric iron in the samples was determined using the volumetric method. The method is based on the formation of Fe (III) with sulfosalicylic acid, a fulvous color complex at pH 2-3 and the destruction of this complex upon titration with Trilon B to form a stronger complex Fe (III) with Trilon B, colored in yellow color. Thus, titration is carried out until fulvous color of the solution turns to yellow [10].

Result and discussion. Received data show that the process proceeds most rapidly with solution stirring, and upon aeration after 2 hours, the content of Fe (III) does not change, which indicates that the oxidation process is stopped, it is obvious that nitric oxide is completely blown out of the system. Along with that, stirring has the most favorable effect, due to the elimination of diffusion restrictions, namely, the transfer of dissolved oxygen through the surface of the water mirror into the depth of the solution due to convection. This was mentioned by the authors [11, 12].

Further, the tests were carried out in a pressuretight stainless steel reactor at an air pressure of 8 bar and with different contents of sodium nitrite, solution volume was 6 liters. The composition of the initial solution was the same. Table 2 presents the obtained results [13].

Table 2 – Solution composition in the oxidation of iron at overpressure

Sodium nitrite 50 mg/l								
t, min	2	4	10	20	30	40	50	60
Fe^{3+} mg/l	153	167	223	272	307	349	376	397
Sodium nitrite 150 mg/l								
t, min	10	20	30	40	50	60	70	17 hours
Fe^{3+}, mg/l	321	390	418	446	481	X	726	1075

Dissolved oxygen was 7.8 mg/l, after adding nitrite (50 mg/l) was 6.4 mg/l, which confirms that dissolved oxygen is not disposed of immediately. After two minutes under a dissolved oxygen pressure of 11.3 mg/l. When sampling, there was instant degassing of the solution due to pressure drop. The air bubbles are very small, the solution looks turbid, and after about a minute the solution becomes limpid. The experiment with a sodium nitrite content of 150 mg/l was carried out under similar conditions, after 60 minutes, stirring was carried out for 10 minutes by releasing air from the top point while supplying, which gave a constant movement of the solution. As can be seen from the table, the dynamics of oxidation slows down before stirring, and then there is a sharp jump in the content of Fe (III).

Further, oxidation under pressure was carried out with the participation of pure oxygen, the solution composition is the same, figure 1 shows the reactor in which the process was carried out at an oxygen pressure of 2.5 and 5 bar and a sodium nitrite content of 50 and 150 mg/l. Figure 2 shows the results. Detailed description of the participation of oxidizing agents in the leaching process is described by the following authors [14, 15, 16].

Figure 1 – Oxidation reactor under the oxygen pressure:
1 – reactor; 2 – oxygen supply from the cylinder; 3 – agitator drive; 4 – manometer; 5 – control module

After the first 10 minutes, the solution discolored, the smell of nitric oxide disappeared. After the appearance of 1 g/l Fe^{3+}, the solution acquires a characteristic rusty color. As can be seen from the figure, at a concentration of 50 mg/l sodium nitrite, the iron content weakly depends on the generated oxygen pressure, which may be due to the limitation of the oxidation process by the lack of catalyst. At a concentration of 150 mg/l, the effect of pressure is more pronounced and at 5 bars complete oxidation of iron occurs in 20 minutes.

An analysis of obtained data made it possible to compile a summary table on Fe (III) oxidation rate under various conditions. The results are shown in table 3.

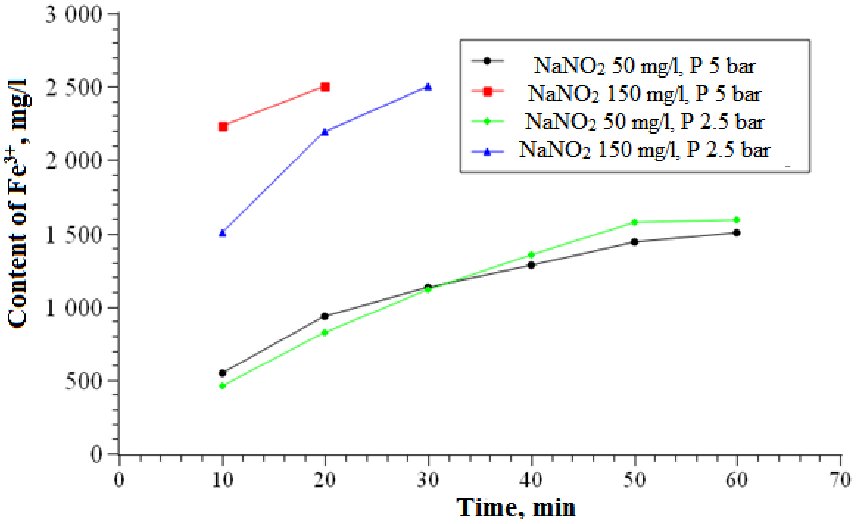


Figure 2 – The dependence of Fe^{3+} content on sodium nitrite concentration and oxygen pressure

Table 3 – Rate of Fe (III) oxidation under various conditions

Average oxidation rate, mg/l*hour							
Static stirring 50 mg/l of $NaNO_2$	P=8 atm, air, 50 mg/l $NaNO_2$	P=8 atm, air, 150 mg/l $NaNO_2$	P=5 atm, oxygen, 50 mg/l $NaNO_2$	P=2.5 atm, oxygen, 50 mg/l $NaNO_2$	P=5 atm, oxygen, 150 mg/l $NaNO_2$	P=2.5 atm, oxygen, 150 mg/l $NaNO_2$	P=5 atm, oxygen, without $NaNO_2$
36	397	520	1500	1500	7500	5000	0

Based on the obtained data, pilot tests were conducted directly on a single block of one of the fields [17]. Oxygen and sodium nitrite were fed directly into the main pipeline with leaching solution in technological acidification construction unit (TAC), sampling was carried out in the node receiving and distribution of solutions, which was located 300 meters from the TAC. The volume of the leach solution was 55 m^3/h, sodium nitrite was supplied with a concentration of 100 and 150 mg/l, the oxygen flow rate was 2 m^3/h. The main provisions for conducting pilot tests are described by the author [18].

Similar works on iron oxidation in the ISL of uranium was carried out by the all-russian scientific research institute of chemical tecnology [19]. Principle of method is the addition of ammonium lignosulfonate, alkali or alkaline earth metals (lignin) for oxidation. Also, a similar technology was used in [20].

First, oxygen was supplied without sodium nitrite for 30 minutes, analysis of the solution showed that iron oxidation did not occur, and then sodium nitrite was turned on. From table 4 it can be seen that the Fe^{3+} content continuously increases over time and with a higher concentration of sodium nitrite, this process is noticeably faster.

Table 4 – Indicators of leaching solution with simultaneous leading of sodium nitrite and oxygen

Indicators of LS		100 $NaNO_2$ mg/l + O_2 15.30	100 $NaNO_2$ mg/l + O_2 16.30	100 $NaNO_2$ mg/l + O_2 18.30	150 $NaNO_2$ mg/l + O_2 10.20	150 $NaNO_2$ mg/l + O_2 10.40	150 $NaNO_2$ mg/l + O_2 11.10	150 $NaNO_2$ mg/l + O_2 11.40
Before leading	pH	1.48	-	1.48	-	-	-	-
	ORP, mV	373	-	372	-	-	-	-
	Fe^{2+}, g/l	2.40	-	2.40	-	-	-	-
	Fe^{3+}, g/l	0.11	-	0.11	-	-	-	-
After leading	pH	1.48	1.51	1.53	1.45	1.45	1.44	1.47
	ORP, mV	390	419	432	400	403	403	412
	Fe^{2+}, g/l	2.48	1.73	1.34	2.01	1.67	1.84	1.28
	Fe^{3+}, g/l	0.2	0.73	1.00	0.42	0.81	0.67	1.17

Conclusion. The process under consideration proceeds rather slowly at atmospheric pressure, while aeration contributes to the complete removal of the catalyst from the system, as a result of which the process ceases. Stirring has a significant effect. Significant intensification of the process is observed during testing at excessive pressure of air or oxygen. The beneficial effect of stirring is also confirmed. Maximum efficiency was recorded when using pure oxygen as an oxidizing agent with its excess pressure and mixing in a confined space. Moreover, the effect of pressure is negligible at low concentrations of oxidizing agent. The oxidation reaction of Fe (III) when using pure oxygen as an oxidizing agent, but without the addition of nitrite does not proceed. Research works at the testing ground with simultaneous supply of sodium nitrite and pure oxygen to LS allowed reaching 1.0 and 1.2 g/l Fe (III) concentrations at nitrite concentrations of 100 and 150 mg/l, but the peak was not reached by iron content in view of the limited duration of the experiments. Thus, the efficiency and feasibility of using sodium nitrite simultaneously with oxygen supply under pressure to leaching solution magistral during Fe^{2+} oxidation in the process of uranium in-situ leaching.

А.З. Абильмагжанов[1], Н.С. Иванов[1], М.С. Малимбаев[2],
И.Е. Адельбаев[1], А.Е. Нуртазина[1], А.Д. Алтынбек[3], Н.М. Шокобаев[1]

[1]АҚ "Д.В. Сокольский атындағы жанармай, катализ және электрохимия институты",
Алматы, Қазақстан;
[2]«КазДизайн» ЖШС, Алматы, Қазақстан;
[3]«Семизбай-U» ЖШС, Степняк, Қазақстан

УРАНДЫ ШАЙМАЛАУ ТИІМДІЛІГІН АРТТЫРУ ҮШІН БИВАЛЕНТТІ ТЕМІРДІ КАТАЛИТИКАЛЫҚ ТОТЫҒУЫ

Аннотация. Қазіргі уақытта Қазақстандағы металлургия кешенінің кәсіпорындары шикізат сапасы және бірқатар кендерді өнімді қайта өңдеу мүмкін еместігі мәселелерімен бетпе-бет келуде. Бұл проблема табиғи, өйткені соңғы онжылдықтарда көптеген ірі кен орындар өздерінің өндірістік мүмкіндіктерін сарқып алды. Сонымен қатар, соңғы жылдары бірде-бір маңызды пайдалы қазба кен орны табылған жоқ. Пайдалы компоненттердің төмен құрамына байланысты ашылған кен орындары өнеркәсіптік қызығушылық тудырмайды.

Уранды жерастылық ұңғыма арқылы шаймалау әдісімен шығаратын "Қазатомөнеркәсіп" да ерекшелік емес. Бүгінгі күні өнімді ерітінділердегі металдың құрамы үнемі төмендейді, уран өндірісінің концентрациясын арттыру үшін реагенттерді тұтыну көлемін арттыру қажет, бұл айтарлықтай шығындарға әкеледі. Сілтісіздендіру ерітіндісіндегі қышқыл концентрациясының жоғарылауымен байланысты элементтердің мөлшері артады, бұл әрі қарай өңдеуге теріс әсер етеді. Күн сайын уран кәсіпорнына жүздеген текше реагенттер қажет. Соңғы жылдары уранның әлемдік нарықтағы бағасы төмендегендіктен, өндірістің айтарлықтай шығындары өндіріс рентабельділігінің төмендеуіне алып келеді. Өнімнің ерітінділеріндегі уранның концентрациясын арттыру үшін ерітіндінің шаймалау потенциалын арттыру қажет. Әдебиеттер бойынша, қабаттағы уран тетравалентті және алтывалентті күйде болады. Жерастылық ұңғыма арқылы шаймалау кезінде ерітіндіге тек алтывалентті уран кіреді, тетравалентті уран қабаттықта қалады. Ерітіндіге тетравалентті уран алу үшін оны алтывалентті күйге дейін тотықтыру керек, ол үшін тотығу агентін енгізу арқылы сілтісіздендіру ерітіндісінің тотығу-тотықсыздану потенциалын арттыру қажет, оның мөлшері өте шектеулі. Бұл тотықтырғыш заттың қоршаған ортаға әсері мен тотықтырғыш заттың өзіндік құнына байланысты. Тотықтырғыштардың келесі түрлері қолданылады: сутек пероксиді, оттегі, үшвалентті темір, натрий нитриті және т.б. Сутек пероксиді тотығы жоғары тотықтырғыш қасиетке ие және "Қазатомөнеркәсіп" кәсіпорындарында кен орнының технологиялық қондырғысын қышқылдандыруда қолданылады. Бірақ қымбатшылық пероксидті үнемі қолдануға мүмкіндік бермейді. Оттегі ең арзан тотықтырғыш болып табылады, алайда оның тиімділігі ауадағы құрамының аздығымен (≈ 21%) және сұйық фазадағы төмен ерігіштігімен шектеледі, оның құрамында тұз көп мөлшерде болуына жол бермейді.

Жерастылық ұңғыма арқылы шаймалау кезінде Шу-Сарысу уран мега-провинциясының кен орындарындағы негізгі тотықтырғыш - үшвалентті темір иондары болып табылады, олар әрдайым қабаттарда болады. Уранның темір иондарымен тотығу механизмі табиғатта каталитикалық болып табылады. Тотығу кезінде темір бивалентті күйге тотықсыздандырылады да процестің жылдамдығы төмендейді, сілтісіздендіру ерітіндісін қайта белсендіруді қажет етеді, яғни ерітіндіге қосымша тотықтырғыш заттарды енгізу арқылы үшвалентті темір иондардың регенерациясы. Сонымен темірді регенерациялау үшін қосымша тотықтырғышты енгізу мүмкіндігі бар. Бұл тотықтырғыш келесі өлшемдерге сәйкес оңтайлы болуы керек: құны - бірінші кезекте қазіргі тау-кен өндірісі кәсіпорындардың қызықты, келесі – тиімділік, соңғысы - пайдаланылған реагенттің зиянсыздығы, өйткені қоршаған ортаға келтіретін залалды азайту өндіріс тіректерінің бірі болып табылады. Әдебиеттер бойынша сілтісіздендіру ерітінділердің тотығу белсенділігін

арттыру үшін атмосфералық оттегін қосымша пайдалануға болады. Сілтісіздендіру ерітіндісіне тотықтырғыш затпен бірге ауа оттегін қамтамасыз етеді. Таза оттегі сияқты ауа оттегінің өзі тиімді еместігі белгілі. Осыған байланысты жұмыстың мақсаты темірдің (II) иондарының ерітілген оттегімен каталитикалық тотығуын қамтамасыз ету үшін сығылған ауаны немесе оттегін сілтісіздендіру ерітіндісіне қосымша қамтамасыз етумен сілтілі ерітіндіге натрий нитритінің тотықтырғышын енгізу арқылы уранды жерастылық ұңғыма арқылы шаймалауды күшейту мүмкіндігін зерттеу болды.

Түйін сөздер: уран, жерастылық ұңғыма арқылы шаймалау, сілтісіздендіру ерітіндісі, натрий нитриті, тотығу.

А.З. Абильмагжанов[1], Н.С. Иванов[1], М.С. Малимбаев[2], И.Е. Адельбаев[1],
А.Е. Нуртазина[1], А.Д. Алтынбек[3], Н.М. Шокобаев[1]

[1]АО "Институт топлива, катализа и электрохимии им. Д.В. Сокольского", Алматы, Казахстан;
[2]ТОО «КазДизайн», Алматы, Казахстан;
[3]ТОО «Семизбай-U», Степняк, Казахстан

КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ ДВУХВАЛЕНТОГО ЖЕЛЕЗА ДЛЯ ПОВЫШЕНИЯ ЭФФЕКТИВНОСТИ ВЫЩЕЛАЧИВАНИЯ УРАНА

Аннотация. В настоящее время предприятия металлургического комплекса в Казахстане, столкнулись с проблемой, качества сырья и с невозможностью продуктивной переработки ряда руд. Данная проблема закономерна, потому как за последние десятилетия многие крупные месторождения исчерпали свои промышленные возможности. Так же за последние годы не было открыто ни одного значительного месторождения полезных ископаемых. Открытые месторождения не представляют промышленного интереса, в связи с незначительными содержаниями полезных компонентов.

Предприятия «Казатомпрома», добывающие уран методом подземного скважинного выщелачивания (ПСВ) не стали исключением. На сегодняшний день содержание металла в продуктивных растворах неуклонно снижается, для увеличения концентрации урановым производствам необходимо увеличивать количество потребления реагентов, что приводит к значительным затратам. С повышением концентрации кислоты в выщелачивающем растворе увеличивается содержание попутных элементов, что негативно скажется на дальнейшей переработке (в особенности большое влияние оказывает оксид кремния). Ежесуточно урановому предприятию необходимы сотни кубов реагентов. Так как в последние годы стоимость урана на мировом рынке снизилась, значительные затраты производства приводят к снижению рентабельности добычи. Для повышения концентрации урана в продуктивных растворах, необходимо увеличить выщелачивающий потенциал раствора. Согласно литературным данным, уран в пласте залегания находится в четырехвалентном и шестивалентном состоянии. При ПСВ в раствор переходит только шестивалентный уран (с сопутствующими элементами), четырехвалентный уран остается в пласте залегания. Для извлечения четырёхвалентного урана в раствор, необходимо окислить его до шестивалентного состояния, для чего необходимо повысить окислительно-восстановительный потенциал выщелачивающего раствора с помощью введения окислителя, количество которых весьма ограничено. Это связано с влиянием окислителя на окружающую среду и стоимостью окислителя. Используются следующие виды окислителей: пероксид водорода, кислород, трехвалентное железо, нитрит натрия и др. Пероксид водорода обладает высокими окислительными свойствами и его используют при закислении технологического блока месторождения на предприятиях «Казатомпрома». Но дороговизна не позволяет использовать пероксид на постоянной основе. Кислород воздуха является самым дешевым окислителем, однако его эффективность ограничена малым содержанием в воздухе (≈ 21% об.) и малой растворимостью в жидкой фазе, чему препятствует значительное солесодержание в том числе.

При ПСВ урана на месторождениях Шу-Сарысуйской урановой мега-провинции основным (природным) окислителем являются ионы трехвалентного железа, которые всегда присутствует в пласте. Механизм окисления урана ионами железа носит каталитический характер. В ходе окисления железо восстанавливается до двухвалентного состояния и скорость процесса падает, что требует повторной активации раствора выщелачивания, т.е. регенерации ионов трехвалентного железа за счет введения в раствор дополнительных окислителей. Так для регенерации железа возможен ввод дополнительного окислителя. Данный окислитель должен быть оптимальным по следующим критериям: стоимость для современных добычных предприятий находится на первом месте, далее является эффективность и последнее это безвредность используемого реагента, т.к. минимизация вреда экологии является одним из столпов производства. Согласно литературным данным, для повышения окислительной активности растворов выщелачивания можно использовать дополнительно кислород воздуха. В выщелачивающий раствор вместе с окислителем подать кислород воздуха. Известно, что кислород воздуха сам по себе не эффективен, также, как и чистый кислород. В связи с этим целью работы стало исследование возможности интенсификации подземного скважинного выщелачивания урана за счет введения в выщелачивающий раствор окислителя нитрита натрия при дополнительной подаче сжатого воздуха или кислорода в выщелачивающий раствор для обеспечения каталитического окисления ионов железа (II) растворенным кислородом.

Ключевые слова: уран, подземное скважинное выщелачивание, выщелачивающий раствор, нитрит натрия, окисление.

Information about authors:

Abilmagzhanov Arlan Zainutallaevich – Candidate of Chemical Sciences, head of Applied Research laboratory of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry”, a.abilmagzhanov@ifce.kz, https://orcid.org/0000-0001-8355-8031

Ivanov Nikolai Sergeevich – Candidate of Chemical Sciences, Leading Researcher in Laboratory of Applied Research, JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry”, n.ivanov@ifce.kz, https://orcid.org/0000-0002-2153-2802

Malimbaev Mambet Sultanovich – Engineer in chief, «KazDesign» LLP, mambet.malimbayev@caravanresources.com, https://orcid.org/0000-0002-5308-3095

Adelbayev Iskander Yersayanovich – master’s degree, senior engineer in Laboratory of Applied Research of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry”, clerikc88@mail.ru, https://orcid.org/0000-0003-1435-8583

Nurtazina Aizhan Erkinbekkyzy – PhD student, master’s degree, senior engineer of Applied Research laboratory of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry”, nurtazina.aizhan@bk.ru, https://orcid.org/0000-0001-7202-5344

Altynbek Akmurat Duisenbayevich – Development deputy director general, «Semyzbay-U» LLP, akmurat.a@mail.ru, https://orcid.org/0000-0002-4075-9703

Shokobayev Nurlan Maratovich – PhD, Junior Researcher in Laboratory of Applied Research, JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry”, nurlanshokobayev@gmail.com, https://orcid.org/0000-0003-1697-4638

REFERENCES

[1] Bugenov ES, Vasilevskij OV (2006) Physicochemical fundamentals and technology for the production of chemical concentrates of natural uranium, Almaty, Republic of Kazakhstan. ISBN:9965-673-97-7

[2] Gromov BV (1978) Introduction to Uranium Chemical Technology, Moscow, Russian Federation. ISBN: 9965-639-49-3

[3] Kenzhaliev K, Surkova TYu, Berkinbayeva A.N, Dosymbayeva ZD, Chukmanova1 MT (2019) To the question of recovery of uranium from raw materials, News of NAS RK, Series of geology and technical sciences, 1:112-119. (in Eng.) https://doi.org/10.32014/2019.2518-170X.14

[4] Turaev NS, Zherin II (2006) Chemistry and technology of uranium, Moscow, Russian Federation. ISBN: 5-98191-019-4

[5] Zelikman AN, Vol'dman GM, Beljaevskaja LV (2003) Theory of hydrometallurgical processes, fourth edition. Moscow, Russian Federation. ISBN 5-89594-088-9

[6] Polinovskij KD (2012) An integrated approach to solving the problem of intensifying the process of underground downhole leaching of uranium [Kompleksnyj podhod k resheniju problemy intensifikacii processa podzemnogo skvazhinnogo vyshhelachivanija urana] P. 64-73 https://cyberleninka.ru/article/n/kompleksnyy-podhod-k-resheniyu-problemy-intensifikatsii-protsessa-podzemnogo-skvazhinnogo-vyschelachivaniya-urana/viewer

[7] Kac D, Rabinovich E (1954) Chemistry of uranium, Moscow, USSR. P.494

[8] Kazanbaev LA, Kozlov PA, Kolesnikov AV (2004) The method of iron ions oxidation in zinc sulfate solutions [Sposob okislenija ionov zheleza v sul'fatnyh cinkovyh rastvorah] Patent of Russian Federation [Patent Rossijskoj Federacii]. (in Russian).

[9] The technique for measuring the iron content by the volumetric method. Instructions: Testing of anion exchange resins and technical requirements for anion exchange resins. Joint Stock Company “National Atomic Company“ Kazatomprom ”” (in Russ.).

[10] Sadykov RH (1986) Underground leaching of uranium abroad. "Solvents and oxidizing agents in PV of uranium and means for supplying gaseous oxidizing agents to the formation [Podzemnoe vyshhelachivanie urana za rubezhom. Rastvoriteli i okisliteli pri PV urana i sredstva podachi gazoobraznyh okislitelej v plast] Inf. Vol. No. 79, Moscow, USSR. (in Russ.).

[11] Sychev AJ (1988) Homogeneous Catalysis by Iron Compounds, Kishinev, USSR. ISBN: 5376004600

[12] Mamilova VA (1980) Uranium mining using underground leaching, Moscow, USSR. FB B 80-48/19

[13] Shilov VP et al. (2007) Oxidation of uranium (IV) with oxygen in slightly acidic and close to neutral solutions [Okislenie urana (IV) kislorodom v slabokislyh i blizkih k nejtral'nym rastvorah] 49:412-416 (in Russ.).

[14] Evseeva LS (1965) Redox properties of sedimentary rocks, Moscow, Russian Federation. Inv. № 1210107-КХ

[15] Polinovskij KD (2017) Patterns of the influence of plant detritus on the dynamics of the ISL process of uranium, Astana, Republic of Kazakhstan. ISBN978-601-06-4434-2

[16] Pirmatov JA, Djusambaev SA, Dujsebaev BO, Zhatkanbaev EE, Vjatchennikova LS, Sadyrbaeva GA (2006) Prospects for underground leaching of uranium at the «Semyzbay» deposit [Perspektivy podzemnogo vyshhelachivanija urana na mestorozhdenii «Semyzbaj»] 18:246-254 (in Russ.).

[17] Rychkov VN (2004) Conducting pilot tests to increase the redox potential of underground uranium leach solutionsю Yekaterinburg: funds of USTU-UPI, Russian Federation. P.30.

[18] Filippov AP, Nesterov JuV, Shatalov VV, Krotkov VV, Mimonov AV (2001) The method of uranium extraction from ore materials [Sposob izvlechenija urana iz rudnyh materialov] Patent of Russian Federation [Patent Rossijskoj Federacii]. (in Russian).

[19] Dement'ev AA, Filippov AP, Rychkov VN, Gontar' EI, Poponin NA, Smirnov AL, Babkin AS, Smyshljaev VJu, Solodov IN (2016) The method of uranium leaching from ores [Sposob vyshhelachivanija urana iz rud]. Patent of Russian Federation [Patent Rossijskoj Federacii]. (in Russian).

[20] Nesterov JuV, Krotkov VV, Filippov AP (2004) The method of uranium extraction from ores [Sposob izvlechenija urana iz rud]. Patent of Russian Federation [Patent Rossijskoj Federacii]. (in Russian).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.29**
Volume 2, Number 440 (2020), 99 – 106

UDC 541.13; 541.64; 544.6;

D.S. Puzikova[1,2], M.B. Dergacheva[1], G.M. Khussurova[1]

[1]"D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry" JSC, Almaty, Kazakhstan;
[2] Al-Farabi Kazakh National University, Faculty of Physics and Technology, Almaty, Kazakhstan
E-mail: d.puzikova@ifce.kz, m_dergacheva@mail.ru, gulinur_k@bk.ru

METHOD FOR MANUFACTURING THIN FILMS OF CUBI$_2$O$_4$ FOR PHOTOELECTROCHEMICAL APPLICATIONS

Abstract. A method has been developed for producing thin semiconductor films of a complex copper-bismuth system ($CuBi_2O_4$) with reduced roughness and increased photoactivity.

The application process is carried out under standard laboratory conditions from aqueous solutions of salts, takes advantage of centrifugation to evenly distribute the coating over the surface, is characterized by low material consumption, and allows the thin nanocrystalline layers formation with a given thickness. Polyethylene glycol (PEG) is used to improve the spraying of solution droplets over the entire surface of the $CuBi_2O_4$ film, which allows the dense uniform films deposition.

Scanning electron and atomic force microscopy data demonstrate the ordering of the growth of $CuBi_2O_4$ particles (size ≈200 nm) and a 1.5-fold decrease in the roughness of the relief when polyethylene glycol is added to the solution. Micrographs show the growth of uniformly sized rounded crystallites.

In a comparative analysis of the XRD diagram of the samples, an increase in the number and intensity of peaks corresponding to the crystalline phase of Kusachiite ($CuBi_2O_4$) with the introduction of PEG into the initial solution is observed.

Based on the photoelectrochemical measurements results, it was found that the addition of polyethylene glycol to the electrolyte helps to increase the photoactivity of the samples by 2 times.

The obtained thin polycrystalline $CuBi_2O_4$ films are promising for use in photoelectrochemical converters.

Keywords*:* Solar energy material, spin coating, $CuBi_2O_4$, polyethylene glycol.

Introduction. A fundamental condition for a hydrogen economy is the ability to renew, purify, and efficiently produce hydrogen.

Currently, non-renewable methods for producing hydrogen, such as steam methane conversion, are cheaper than photoelectrolysis. However, the methane process leads to CO_2 emissions and is ultimately limited to natural gas reserves. On the contrary, photoelectrolysis of water does not lead to environmental pollution, sunlight and water can be considered inexhaustible resources, and with an increase in the efficiency of use of solar energy, it can be expected that internal costs will continue to decrease [1].

A significant advantage of the hydrogen obtained by photoelectrolysis is the relative ease of storage. If necessary, hydrogen can be stored and then converted into electricity in a fuel cell, which makes it particularly advantageous as a fuel for transport or in remote locations without electricity. In addition, it can simply be burned as fuel for heating or cooking, making it a promising alternative to natural gas.

However, despite significant research efforts over the past decades, fundamental problems still impede the commercial use of photovoltaics. Such problems include the low efficiency of sunlight, the corrosive instability of most semiconductors in aqueous solutions, the complex and expensive designs of PEC elements, etc. Obviously, to achieve progress, innovation is needed in both device design and material development.

One of the materials that can provide a high photocurrent density and a large overvoltage of the process of water photolysis is $CuBi_2O_4$, which was first proposed as a possible photocathode material in

2007 [2]. However, relatively little is known about this compound, especially in comparison with such more studied metal oxides as TiO_2, Fe_2O_3, $BiVO_4$, Cu_2O [3] and complex copper chalcogenides (($Cu_2ZnSnS(Se)_4$) [4].

$CuBi_2O_4$ is a p-semiconductor and has many promising physico-chemical properties including magnetic susceptibility, dielectric constant, high-temperature heat capacity, electrochemical capacitance, photoelectrochemical ability and catalytic properties [5-7]. $CuBi_2O_4$ has a small energy of the band gap of 1.5-1.9 eV, and, therefore, can largely absorb the visible parts of the solar spectrum [8-11]. The potential of the conduction band of $CuBi_2O_4$ is more negative than the redox potential of H^+/H_2. Due to this, $CuBi_2O_4$ is widely studied for use as a photocathode for solar energy and decomposition of water with evolution of hydrogen [12-17]. $CuBi_2O_4$ can be used as a promising photocatalyst for the decomposition of organic pollutants and dyes [17].

In recent years, many methods of obtaining $CuBi_2O_4$ have been used. Crystalline $CuBi_2O_4$ nanoparticles were synthesized using various methods, including solid-phase reactions [8,9,18], mechanochemical treatment [19-20], hydrothermal crystallization [21-23], thermal decomposition and complexation [24,25], microwave synthesis [6], ultrasonic method [16], electrochemical synthesis [13,26], magnetron sputtering [28], floating zone method [29], and sol-gel method [30]. Most of these methods are not widely used due to complexity, the use of high temperatures and low reproducibility.

In this work the spin coating method was used, which is carried out under standard laboratory conditions from aqueous salt solutions, uses the advantages of centrifugation to uniformly distribute the coating on the surface, is characterized by low material consumption, allows the formation of thin nanocrystalline layers with a given thickness. It is known that the addition of polymers is often used to the uniform distribution of solution droplets over the entire surface of the deposited films when using the spin-coating method. In this work polyethylene glycol (PEG) is used for this purpose. The investigations of photoelectrochemical properties of $CuBi_2O_4$ thin films are important for the creation of effective photocathodes.

Experimental procedure. A solution for depositing $CuBi_2O_4$ films was prepared by mixing copper nitrate trihydrate and bismuth nitrate pentahydrate (at 0.05M and 0.1M, respectively) with acidification with concentrated (65%) nitric acid. Subsequently, the resulting mixture was evaporated without boiling to an amount of 1/5 of the original volume and cooled to room temperature. The preparation of solutions containing polyethylene glycol - 2000 (PEG) additives was performed after cooling the initial solution, adding PEG in the amount of 0.25 grams to each 5 ml of the solution. After that, the solution was subjected to treatment in an ultrasonic bath. The resulting mixture was used for at least an hour, but not later than a day after preparation.

Films of the complex system copper-bismuth were obtained by the spin coating method. The films were applied to pre-cleaned optically transparent electrodes, which are a fluorinated tin oxide glass (FTO), measuring 10*25 mm. During rotation of the FTO, the electrodes were fixed in the horizontal plane by a special holder, which avoided the displacement of the substrate and eliminated the influence of the position on the uniformity of film deposition. Rotation lasted 90 seconds at a frequency of 500 rpm.

After application, the films were annealed in a muffle furnace for 2 hours at a temperature of 600°C.

In the future, physico-chemical characterization of all samples was carried out.

With the help of an electronic scanning microscope from JEOL (Japan) with the capabilities of the micro analysis "JSM 6610 LV", surface micrographs were obtained. Analysis of the elemental composition excluded the presence of impurities.

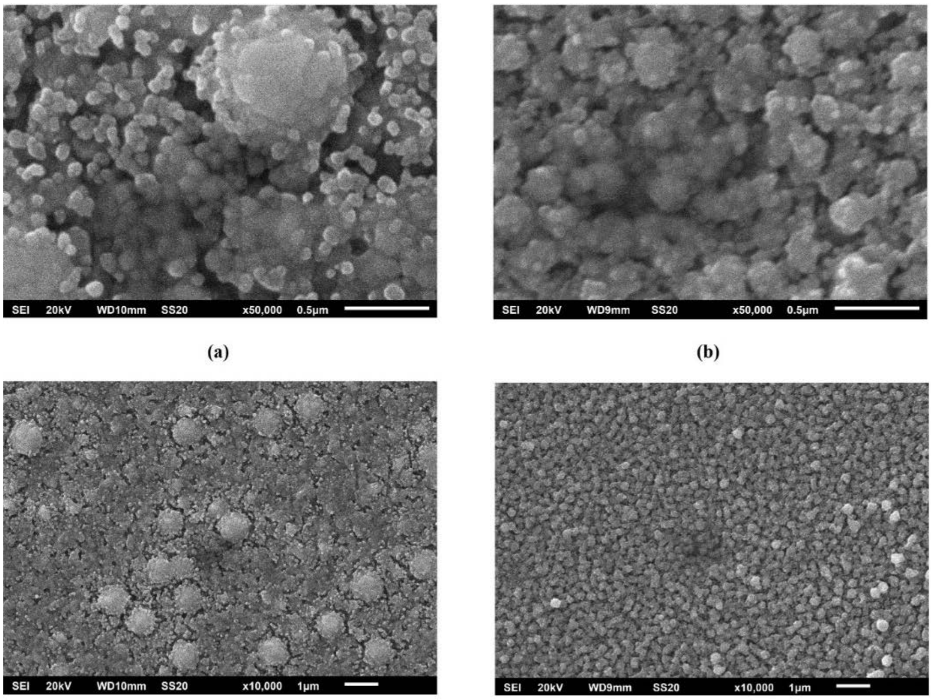
The structure and morphology of the surface were studied by atomic force microscopy (JSPM-5200 (JEOL)). During the measurements, images of topography and contrast images for the phase regions were recorded. During scanning, a region measuring 500x500 nm was examined.

The crystal structure was confirmed by X-ray diffraction on the X-ray diffractometer DRON-4-07.

Photoelectrochemical studies were performed in real time in a solution of 0.2 M Na_2SO_4 + 0.1 M phosphate buffer + 10 mM H_2O_2 under modulated illumination with a wavelength of 465 nm in a GillAC (ACM Instruments) apparatus using a quartz cuvette and a silver chloride reference electrode.

Results and Discussion. Figure 1 compares the results of electron microscopy for $CuBi_2O_4$ films deposited on FTO/glass from solutions without organic constituents (Fig. 1a, c) and from solutions containing PEG (Fig. 1b, d). Microphotographs of the samples surface show that the addition of polyethylene glycol to the solution contributes to the ordered growth of identical in size and shape grains

(190-210 nm), while precipitation from the primary solution observed the development of chaotic formations ranging in size from 85 nm to 820 nm and the presence of significant relief changes.



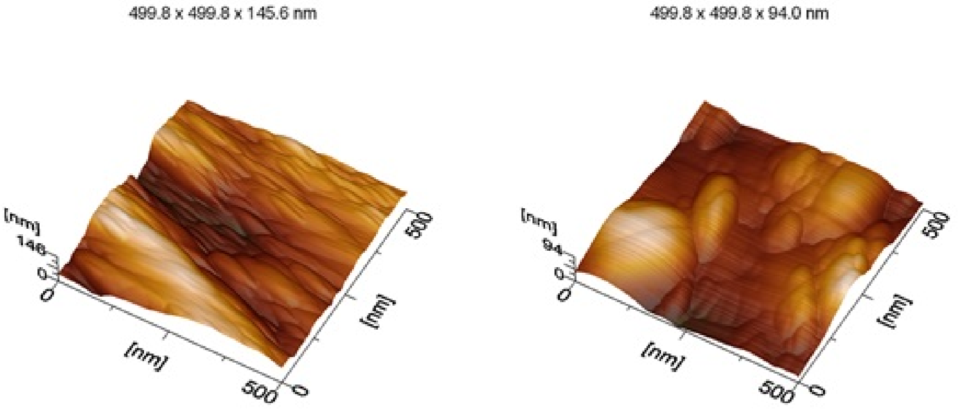
(a) (b)

(c) (d)

Figure 1 - SEM micrographs of the surface of deposited $CuBi_2O_4$ films a, c) without using PEG; b, d) in the presence of PEG

The results of elemental analysis show that the elemental composition of the films corresponds to the composition of the $CuBi_2O_4$ precipitate with an accuracy of ± 2 at %. The introduction of polyethylene glycol into the solution does not affect the composition change and does not contribute to the appearance of impurities in the composition of the precipitate.

Figure 2 shows the results of films investigation on an atomic force microscope. On scans in 3D format, growth figures up to 146 nm (figure 2a) are formed from the initial solution, whereas for films deposited from solutions with polyethylene glycol content only growth up to 94 nm is observed (figure 2b). Experiments showed that when using a solution with PEG, the roughness of the surface decreases by a factor of 1.5, and the crystallites have a rounded shape characteristic of the $CuBi_2O_4$ compound.



(a) (b)

Figure 2 - Micrograph of surface obtained on AFM
for deposited $CuBi_2O_4$ films a) without using PEG; b) in the presence of PEG

Figure 3 shows the X-ray diffraction patterns of $CuBi_2O_4$ films deposited on glass / FTO from the initial solution (figure 3a) and solutions containing PEG (figure 3b). Crystallographic analysis of X-ray data and EDAX measurements confirm the presence of the Kusachiite phase ($CuBi_2O_4$). The peaks of SnO_2 from the substrate on the diffraction diagrams are due to the small thickness of deposited $CuBi_2O_4$ films (less than 500 nm).

From the results of XRD it is obvious that the introduction of polyethylene glycol into the solution positively affects the film structure. There is an increase in the diffraction peaks and their intensities.

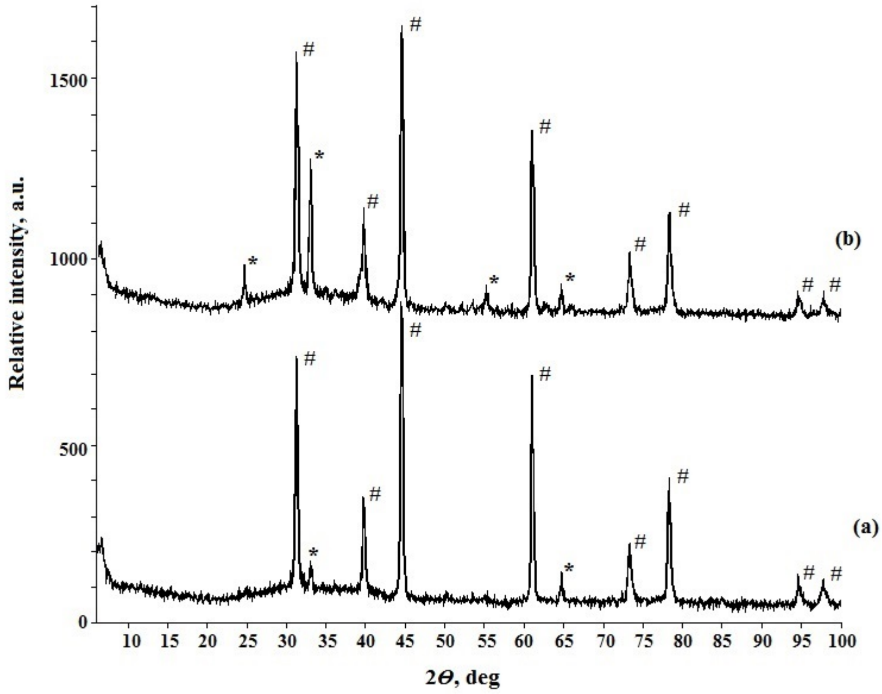


Figure 3 - XRD diagram of deposited $CuBi_2O_4$ films a) without using PEG;
b) in the presence of PEG: # FTO; * $CuBi_2O_4$

The photosensitivity of the deposited $CuBi_2O_4$ films was studied by photoelectrochemistry with modulated illumination with a wavelength of 465 nm (a solution of 0.2 M Na_2SO_4 + 0.1 M phosphate buffer + 10 mM H_2O_2). Figure 4 shows the photocurrent curves for samples of $CuBi_2O_4$ thin films.

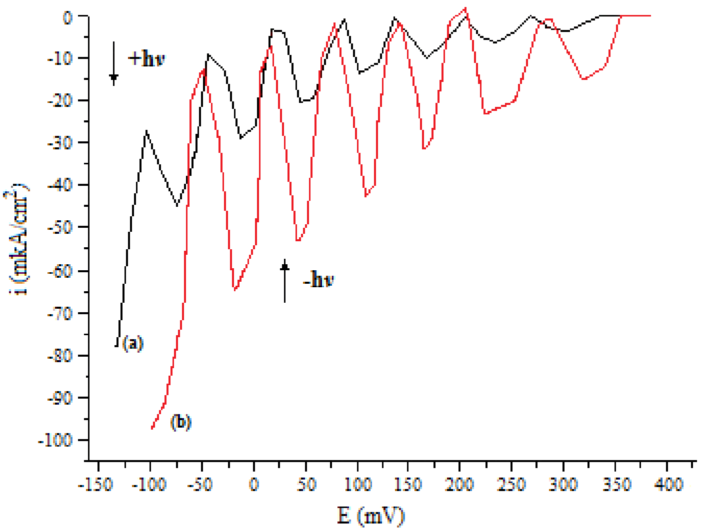


Figure 4 - Photopolarization curve under modulated illumination with a wavelength of 465 nm
in the "light off /light on" mode for the $CuBi_2O_4$ electrode without using PEG (a) and in the presence of PEG (b)

Photoelectrochemical study of deposited films showed that the photocurrents are negative, and the resulting semiconductor is characterized by a p-type conductivity. A comparison of the photocurrent values indicates that the photoelectrochemical activity of films deposited from solutions containing polyethylene glycol was found to be 2 times higher when switching from the light off mode to the light on mode (figure 4b) than the precipitated ones without the addition of PEG (figure 4a).

The developed method of deposition of a complex copper-bismuth $CuBi_2O_4$ system allows obtaining photocathodes with high photosensitivity.

Conclusion. A new composition of a solution for the thin films deposition of the copper-bismuth ($CuBi_2O_4$) complex system on FTO/glass by the spin coating method has been developed.

The physicochemical characterization of samples precipitated from solutions containing and without polyethylene glycol was carried out. The positive effect of the use of PEG is shown.

Surface micrographs showing the ordering of the growth of $CuBi_2O_4$ particles (size ≈200 nm) with the addition of polyethylene glycol to the solution were obtained by SEM.

The results of AFM indicate a 1.5 times decrease in the roughness of the relief and the formation of equidimensional rounded crystallites.

For all films, the XRD method confirmed the presence of the crystalline Kusachiite phase corresponding to the $CuBi_2O_4$ compound. Comparative analysis of the XRD diagram of samples obtained from solutions containing PEG and "pure" (without PEG) shows an increase in the number of peaks and their intensity in the first case.

Based on photoelectric measurements, it is established that $CuBi_2O_4$ films precipitated from solutions containing polyethylene glycol show a photoactivity of 2 times higher.

Thus, the developed method of deposition of a complex copper-bismuth $CuBi_2O_4$ system makes it possible to obtain polycrystalline films with high photosensitivity, p-type conductivity, which are promising for use in photoelectrochemical converters as photocathodes.

Д.С. Пузикова, М.Б.Дергачева, Г.М. Хусурова

АҚ "Д.В. Сокольский атындағы жанармай,
катализ және электрохимия институты", Алматы, Қазақстан

ФОТОЭЛЕКТРОХИМИЯЛЫҚ ҚОЛДАНУҒА АРНАЛҒАН ЖҰҚА $CuBi_2O_4$ ПЛЕКАЛАРЫН АЛУ ӘДІСІ

Аннотоция. $CuBi_2O_4$ - су фотолиз процесін үлкен фототок тығыздығы мен үлкен асқын кернеумен қамтамасыз ете алатын материал болып табылады. Ол тыйым салынған аймағының энергиясы 1,6-1,8 эВ болатын р-типті металл-оксидті аралас жартылай өткізгіш болып табылады және стандартты сутекті электродқа қатысты потенциалы шамамен 1 В кезінде фототоқ басталады.

Қазіргі кезде қабықшаларды жасаудың түрлі әдістері белгілі және олардың әрқайсысына белгілі бір артықшылықтар мен кемшіліктер тән. Осы әдістердің көпшілігі күрделілігіне, жоғары температураны пайдалануына және нашар жаңғыртылуына байланысты кеңінен қолдануға болмайды.

Бұл жұмыста тұздардың су ерітінділерінен стандартты зертханалық жағдайларда жүргізілетін spinning coating әдісі қолданылады, үстіңгі беті бойынша жабынды біркелкі бөлу үшін центрифугалау артықшылық-тарын пайдаланады, аз материал сыйымдылығымен сипатталады, қалыңдығы белгілі жұқа нанокристалды қабаттарды қалыптастыруға мүмкіндік береді. $CuBi_2O_4$ қабықшаларының барлық бетіне ерітінді тамшыларын тозаңдануын жақсарту үшін полиэтиленгликоль (ПЭГ) қолданылады, бұл тығыз бір текті қабықшаларды тұндыруға мүмкіндік береді. Алынған $CuBi_2O_4$ жұқа қабықшалары фотоэлектрохимиялық қасиеттерін іргелі зерттеу үшін жақсы.

Қабықшаларды жағу үшін алдын ала тазартылған электродтар ретінде фторирленген қалайы оксиді (FTO) қабатымен жабылған оптикалық мөлдір шыны пластиналар қолданылды. Шөгу кезінде электродтың көлденең жазықтықта орналасуын арнайы ұстағыш қамтамасыз етті, оның конструкциясы айналғанда төсеніштің ығысуын болдырмауға және қабықшаның біркелкі жағылуына теріс әсер болдырмауға мүмкіндік берді. Айналу 90 секунд ішінде, минутына 500 айналым жиілігі кезінде жүзеге асырылды.

$CuBi_2O_4$ қабықшаларын жағуға арналған ерітіндіні дайындау бірнеше кезеңде өтті, ол мыс пен висмут азот тұздарын араластыру және концентрацияланған азот қышқылымен (65%) қышқылдандыру, ерітіндіні буландыру және температурасын бөлме температурасына дейін төмендету. Құрамында полиэтиленгликоль

(ПЭГ) бар ерітінділерден қабықшаларын тұндыру жөніндегі эксперименттер үшін ерітіндіге әрбір 5 мл ерітіндіге 0,25гр ПЭГ-2000 қосылды. Тиімді араластыру үшін ультрадыбыстық ванна қолданылды. Эксперимент нәтижелері дайындалған ерітіндіні тиімді пайдалану мерзімі дайындағаннан кейін бір тәуліктен артық болмауын көрсетті.

Соңғы кезекте муфельді пеште қабықшаларды 2 сағат бойы 600°C температурада күйдіру жүзеге асырылды.

Физикалық-химиялық зерттеулердің нәтижелері әртүрлі ПЭГ құрамы бар электролиттерден жасалған үлгілерде айтарлықтай айырмашылықтарды анықтады.

Сканерлі электрондық және атомдық-күш микроскопияның деректері $CuBi_2O_4$ бөлшектерінің өсуінің ретке келтіруін (көлемі $\approx$200 нм) және ерітіндіге полиэтиленгликоль қосылған кезде рельефтің кедір-бұдырлығының 1,5 есе төмендеуін көрсетеді. Микрофотографияда біркелкі өлшемді дөңгелек кристалдардың өсуі байқалады.

Бастапқы ерітіндіге ПЭГ енгізгенде үлгілердің XRD diagram салыстырмалы талдауында kusachiite ($CuBi_2O_4$) кристалдық фазасына сәйкес келетін шыңдар саны мен қарқындылығы көбейетіні байқалады.

Фотоэлектрохимиялық өлшеулердің нәтижелері негізінде электролитке полиэтиленгликольді қосу үлгілердің фотоактивтілігін 2 есеге арттыруға ықпал ететіні анықталды.

Осылайша, фотоэлектрохимиялық түрлендіргіштерде қолдану үшін перспективалы мыс-висмут $CuBi_2O_4$ күрделі оксидті жүйені тұндыру әдістемесі жоғары фотосезімталдығы р-типті поликристалды пленкаларды алуға мүмкіндік береді.

Тірек сөздер: күн энергиясы материалдары, spin coating, $CuBi_2O_4$, полиэтиленгликоль.

Д.С. Пузикова, М.Б. Дергачева, Г.М. Хусурова

АО "Институт топлива, катализа и электрохимии
им. Д.В. Сокольского", Алматы, Казахстан

СПОСОБ ИЗГОТОВЛЕНИЯ ТОНКИХ ПЛЕНОК $CuBi_2O_4$ ДЛЯ ФОТОЭЛЕКТРОХИМИЧЕСКИХ ПРИМЕНЕНИЙ

Аннотация. $CuBi_2O_4$ является материалом, который может обеспечить большую плотность фототока и большое перенапряжение процесса фотолиза воды. Он представляет собой смешанный металл-оксидный полупроводник *p*-типа с энергией запрещенной зоны 1,6-1,8 эВ и потенциалом начала фототока около 1 В относительно стандартного водородного электрода.

На сегодняшний день известны различные методы нанесения пленок и, каждому из них присущи определенные преимущества и недостатки. Большинство из этих методов не находит широкого применения из-за сложности, использования высоких температур и низкой воспроизводимости.

В данной работе используется метод spinning coating, который проводится при стандартных лабораторных условиях из водных растворов солей, использует преимущества центрифугирования для равномерного распределения покрытия по поверхности, характеризуется низкой материалоемкостью, позволяет формировать тонкие нанокристаллические слои с заданной толщиной. Полиэтиленгликоль (ПЭГ) используется для улучшения распыления капель раствора по всей поверхности пленки $CuBi_2O_4$, что позволяет осаждать плотные однородные пленки. Полученные тонкие пленки $CuBi_2O_4$ хорошо подходят для фундаментальных исследований фотоэлектрохимических свойств.

Для нанесения пленок использовали электроды, представляющие собой предварительно очищенные оптически прозрачные стеклянные пластины, покрытые слоем фторированного оксида олова (FTO). Положение электрода в горизонтальной плоскости при осаждении обеспечивал специальный держатель, конструкция которого позволила избежать смещения подложки при вращении и исключить влияние положения на равномерность нанесения пленки. Вращение осуществлялось при частоте 500 оборотов в минуту в течение 90 секунд.

Приготовление раствора для нанесения пленок $CuBi_2O_4$ происходило в несколько этапов, включающих смешивание азотных солей меди и висмута с подкислением концентрированной (65%) азотной кислотой, выпаривание и снижение температуры раствора до комнатной. Для экспериментов по осаждению пленок из растворов с содержанием полиэтиленгликоля (ПЭГ), в раствор добавляли 0,25 гр ПЭГ-2000 на каждые 5 мл раствора. Для эффективного перемешивания использовали ультразвуковую ванну. Результаты экспериментов показали, что оптимальный срок использования приготовленного раствора не более суток после приготовления.

В последнюю очередь осуществлялся отжиг пленок в муфельной печи в течение 2 часов при температуре 600 ˚С.

Результаты физико-химических исследований выявили значительные отличия в образцах, изготовленных из электролитов с различным содержанием ПЭГ.

Данные сканирующей электронной и атомно-силовой микроскопии демонстрируют упорядочивание роста частиц $CuBi_2O_4$ (размер ≈200 нм) и снижение в 1,5 раза шероховатостей рельефа при добавлении в раствор полиэтиленгликоля. На микрофотографиях виден рост равноразмерных округлых кристаллитов.

При сравнительном анализе XRD diagram образцов, наблюдается увеличение количества и интенсивности пиков, соответствующих кристаллической фазе Kusachiite ($CuBi_2O_4$) при введении ПЭГ в исходный раствор.

На основании результатов фотоэлектрохимических измерений установлено, что добавление в электролит полиэтиленгликоля способствует увеличению фотоактивности образцов в 2 раза.

Таким образом, разработанная методика осаждения сложнооксидной системы медь-висмут $CuBi_2O_4$ позволяет получать поликристаллические пленки p-типа проводимости с высокой фоточувствительностью, перспективные для использования в фотоэлектрохимических преобразователях.

Ключевые слова: материалы для солнечной энергии, spin coating, $CuBi_2O_4$, полиэтиленгликоль.

Information about authors:

Puzikova Darya Sergeevna – PhD student, master’s degree, researcher in electrochemical laboratory of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry, d.puzikova@ifce.kz, https://orcid.org/0000-0001-5275-4769

Dergacheva Margarita Borisovna - doctor of chemical science, professor, chief researcher in electrochemical technology laboratory of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry”, m_dergacheva@mail.ru, http://orcid.org/0000-0002-8490-1601

Khussurova Gulinur Marsovna - master’s degree, Junior Researcher in electrochemical technology laboratory of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry, gulinur_k@bk.ru, https://orcid.org/0000-0001-8700-7472

REFERENCES

[1] Bayeshova A.K., Molagain S., Bayeshov A.B. (2018). Hydrogen energetics current state and hydrogen production methods, News of NAS RK, 5: 107-116. https://doi.org./10.32014/2018.2518-1491.14 (in Eng.).

[2] Arai T. et al., (2007). Throughput Screening Using Porous Photoelectrode for the Development of Visible-Light-Responsive Semiconductors, J. Comb. Chem, 9:574. (in Eng.).

[3] Licht S. et al., (2001) Over 18% solar energy conversion to generation of hydrogen fuel; theory and experiment for efficient solar water splitting, Int. J. Hydrogen Energy, 26: 653-659 (in Eng.).

[4] Urazov K., Dergacheva M.B., Gremenok V.F., Zaretskaya E.P. (2019). Structure and photoelectrochemical properties of electrodeposited $Cu_2ZnSn(S,Se)_4$ films, News of NAS RK, Chemistry and Technology Series, 2:12-20 (in Eng.).

[5] Arai T., Konishi Y., Iwasaki Y., Sugihara H., Sayama K. (2007). High-throughput screening using porous photoelectrode for the development of visible-light-responsive semiconductors, J. Comb. Chem, 9:9574-581 (in Eng.).

[6] Malashchonak M.V., Streltsov E.A., Mazanik A.V., Korolik O., Kulak A. (2020). Puzikova D.S, Dergacheva M.B, Selskiss A. Effective p-type photocurrent sensitization of n-Bi_2O_3 with p-$CuBi_2O_4$ and p-CuO: Z-scheme photoelectrochemical system., Journal of Solid State Electrochemistry. https://doi.org/10.1007/s10008-020-04494-5 (in Eng.).

[7] Choi Y.H., Kim D.H., Joo W., Han B.S., Shin S.S., Yoo H.I., Hong S.H., Hong K.S. (2013). Synthesis and structural characteristics of p-type semi- conducting $CuBi_2O_4$ as a new gas sensor material, International Symposium on Defects, Transport and Related Phenomena, Materials Science and Technology (in Eng.).

[8] Hashzumze T., Yamamoto K., Sonoda T., Taniguchi M. (2011). Study on visible-light activity of photocatalytic composites composed of foreign semiconductors, Rapport de recherche, Kitakyushu Collège national.

[9] Elaziouti A., Laouedj N., Bekka A. (2012). Synthesis, characterization and UV-A light photocatalytic activity of 20 wt% SrO–$CuBi_2O_4$ composite, Appl Surf Sci, 258: 5010–5024 (in Eng.).

[10] Deng Y., Chen Y., Chen B., Ma J. (2013). Preparation, characterization and photocatalytic activity of $CuBi_2O_4/NaTaO_3$ coupled photocatalysts, J. Alloys Compd, 559:116–122 (in Eng.).

[11] Nishikawa M., Hiura S., Mitani Y., Nosaka Y. (2013). Enhanced photocat- alytic activity of $BiVO_4$ by co-grafting of metal ions and combining with $CuBi_2O_4$, J. Photochem. Photobiol A Chem, 262: 52–56 (in Eng.).

[12] Patil R. et al., (2014). Low temperature grown $CuBi_2O_4$ with flower morphology and its composite with CuO nanosheets for photoelectrochemical water splitting, J. Mater. Chem. A, 2:3661-3668 (in Eng.).

[13] Park H.S. (2014). Photoelectrochemical reduction of aqueous protons with a CuO|$CuBi_2O_4$ heterojunction under visible light irradiation, Phys. Chem, 16:22462 – 22465(in Eng.).

[14] Cao D. et al., (2016). P-type $CuBi_2O_4$: an Easily Accessible Photocathodic Material for High-efficient Water Splitting. J. Mater. Chem, A.4:8995-9001 (in Eng.).

[15] Berglund S.P., Abdi F.F., Bogdanoff P., Chernseddine A., Friedrich van de Krol R. (2017). Gradient self-doped $CuBi_2O_4$ with highly improved charge separation efficiency, J. Amer. Chem. Soc., 28:4231-4242. http://doi 10.1021/jacs7b07847 (in Eng.).

[16] Wang F., Chemseddine A., Abdi F., van de Krol R. (2017). Spray pyrolysis of $CuBi_2O_4$ photocathodes: improved solution chemistry for highly homogeneous thin films, J. Mater. Chem., A.5:12838-12847. http://doi10.1039/C7TA03009F (in Eng.).

[17] Liu W., Chen S., Zhang S., Zhao W., Zhang H., Yu X. (2018). Self-Assembly of Active Bi_2O_3/TiO_2 Visible Photocatalyst with Ordered Mesoporous Structure and Highly Crystallized Anatase, J. Phys. Chem. 112:16:6258-6262 https://doi.org/10.1021/jp800324t (in Eng.).

[18] Wei L., Shifu C., Sujuan Z., Wei Z., Huaye Z., Xiaoling Y. (2010). Preparation and characterization of p–n heterojunction photocatalyst p-$CuBi_2O_4$/n-TiO_2 with high photocatalytic activity under visible and UV light irradiation, J. Nanopart. Res., 12:1355−1366 (in Eng.).

[19] Zhu L., Basnet P., Larson S.R., Jones L.P., Howe J.Y., Tripp R.A., Zhao Y. (2016). Visible Light- Induced Photoeletrochemical and Antimicrobial Properties of Hierarchical $CuBi_2O_4$ by Facile Hydrothermal Synthesis, Chemistry Select, 1:1518–1524. https://doi.org/10.1002/slct.201600164 (in Eng.).

[20] Walter M.G., Warren E.L., Mc Kone J.R., Boettcher S.W., Mi Q., Santori E.A., Lewis N.S. (2010). Solar Water Splitting Cells, Chem.Rev., 110:6446−6473 (in Eng.).

[21] Sharma G., Zhao Z., Sarker P., Nail B.A., Wang J., Huda M.N., Osterloh F.E. (2016). Electronic structure, photovoltage, and photocatalyti c hydrogen evolution with p-$CuBi_2O_4$ nanocrystals, J. Mater. Chem., 3:2936–2942(in Eng.).

[22] Doi A., Obata K., Matsushima S. (2013) Preparation and characterization of $CuBi_2O_4$ powders by organic acid complex method, Research report, Kitakyushu National College, 46:39–4 (in Eng.).

[23] Zhao Y., Anderson N.C., Zhu K., Aguiar J.A., Seabold J.A., Lagemaat J., Branz H.M., Neale N.R., Oh J. (2015). Enhanced Photoelectrochemical Hydrogen Production from Silicon Nanowire Array Photocathode, Nano Lett., 15:2517−2525 (in Eng.).

[24] Anandan S., Lee G., Yang C.K., Ashokkumar W. (2012). Sonochemical synthesis of Bi_2CuO_4 nanoparticles for catalytic degradation of nonylphenol ethoxylate, ChemEng J., 183:46–52 (in Eng.).

[25] Hahn N.T., Holmberg V.C., Korgel B.A., Mullins C.B. (2012). Electrochemical synthesis and characterization of p-$CuBi_2O_4$ thin film photocathodes, J. Phys.Chem C., 116:6459–6466 (in Eng.).

[26] Liu W., Chen S., Zhang H., Yu X. (2011). Preparation, characterization of p-n heterojunction photocatalyst $CuBi_2O_4/Bi_2WO_6$ and its photocatalytic activities, J. Exp Nanosci., 6:102–120 (in Eng.).

[27] Herak M., Miljak M., Guy D. (2010). Revcolevschi A, Easy plane anisotropy in Bi_2CuO_4, J. Phys. Condens.Matter., 22:1–13 (in Eng.).

[28] Zhang J., Jiang Y. (2015). Preparation, characterization and visible photo- catalytic activity of $CuBi_2O_4$ photocatalyst by a novel sol–gel method, J. Mater. Sci. Mater. Electron, 26:4308–4312 (in Eng.).

[29] Wang M., Zai J., Wei X., Chen W., Liang N. (2015). N-type hedgehog-like $CuBi_2O_4$ hierarchical microspheres: room temperature synthesis and their photoelectrochemical properties, Cryst. Eng.Com, 17:21. http://doi 10.1039/C5CE0004OH (in Eng.).

[30] Yamamoto K., Fukuda R., Yamamoto T., Sonoda T., Yamada K. (2012). Preparation of n/p Tandem Type Dye Sensitized Solar Cell Utilizing Plasma Sputtering Method, Plasma Chem Plasma Process, 32:409. http://doi 10.1007/s11090-012-9379-7 (in Eng.).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.30**
Volume 2, Number 440 (2020), 107 – 114

UDC: 665.644.2 -404;665.74/75
IRSTI: 61.51.17

L.D. Volkova[1], N.N. Zakarina[1], O.K. Kim[1], A.K. Akurpekova[1],
D.A. Zhumadullaev[1], V.I. Yaskevich[1], V.P. Grigorjeva[1], A.V. Gabdrakipov [2]

[1]"D.V. Sokolskiy IFCE" JSC, Almaty, Kazakhstan;
[2] Scientific chemical analytical center, Almaty, Kazakhstan,
volkova_ld@rambler.ru, nelly_zakarina@rambler.ru, avgab@mail.ru, kimolya82@mail.ru

KAOLINITE MODIFIED BY ALUMINUM IN THE CRACKING OF VACUUM GASOIL AND IT'S MIXTURE WITH FUEL OIL

Abstaract. The data of the cracking of vacuum gas oil (VG) and a mixture of VG with fuel oil (M-100) on HLaY zeolite catalyst based on acid-activated kaolinite of the Pavlodar deposit modified by aluminum are presented. The synthesis of the kaolinite matrix and the HLaY zeolite catalyst with its use, the physicochemical and acid characteristics of the catalyst and its constituent components, and the fractional and hydrocarbon compositions of vacuum gas oil are described. High mesoporosity of the H-form of the used kaolinite (86.2%), modified by aluminum of the H-form (84.1) and the HLaY catalyst (80.1%), which provide the activity of the sample in cracking of the mixture with a yield of 32.6% gasoline and 25.9% light gas oil (LG) at 450^{0}C and in cracking of VG a yield of 38.2% gasoline and 29.4% LG at 500^{0}C. The gasolines of cracking of LG contain an increased content of iso paraffins (up to 20.2%) and a low content of aromatic hydrocarbons (24.1%), which makes the catalyst attractive for cracking a mixture of VG with fuel oil.

Key words: catalytic cracking, kaolinite, vacuum gas oil, fuel oil, zeolite, modification.

Introduction

Recently it is known that the main direction in the development of the oil refining industry is an increase in the production of motor fuels due to the involvement of heavy oil residues in the technology |1-3|. Fuel oil, which consists of about 50% of oil, is the main reserve for in-depth processing of oil raw materials. For the practical implementation of the process, it is interest to prepare catalysts using natural mineral raw materials – kaolinite and montmorillonite clays |1-7| and industrial waste - energy evils for example |2, 8|.

Among the many natural clays, leading foreign companies in the preparation of microspherical industrial cracking catalysts widely use kaolin |4-7, 9|, while in Russian catalysts, natural montmorillonite is preferred | 10 |.

Kaolinites belong to the class of layered silicates |4, 5,11,12| with continuous layers of silicon-oxygen tetrahedrons: 1 layer of octahedra and 1 layer of tetrahedrons. The bags are firmly adjacent to each other, as a result of which water molecules and metal cations cannot enter the interpackage space of minerals. Kaolinite is a hard aluminosilicate. It does not swell in a mixture with water, has a low cationic capacity. There are no noticeable isomorphic substitutions of aluminum with atoms of other metals. Changes in the structural and other physicochemical characteristics of kaolinites in catalytic and adsorption processes can be achieved by acid and alkaline activation of clays |12-15|.

An important property of kaolinite clay catalysts is their ability to remain active in the presence of heavy metals |16|, which is of considerable interest for cracking of residual crude oil. Large reserves of kaolinites in Kazakhstan |17| determine the attention to the study of the adsorption and catalytic properties of modified kaolinites.

Previously |18-19| we studied the activity of HCeY - zeolite catalysts on aluminum-modified kaolinites of the Ermakov and Sarymsak deposits in cracking of heavy vacuum gas oil and adsorption water purification from heavy metal cations on sorbents based on these clays |20-21|. It has been shown that cracking activity and adsorption capacity in water treatment depend on the chemical composition of the initial kaolinites. The catalyst based on Ermakov kaolinite showed great activity in the cracking. And an adsorbent based on the Sarymsak kaolinite – in the water treatment,.

The aim of the work was synthesis of matrix based on aluminum modified Pavlodar kaolinite, HLaY zeolite, the preparation of HLaY zeolite-containing catalyst and the determination of the activity of the synthesized catalyst in cracking of vacuum gas oil and its mixture with fuel oil.

Experimental part

For preparation of the catalyst, the kaolinite clay of the Pavlodar deposit RK was subjected to grinding and “elutriation”. Clay was activated by acid with a 20% sulfuric acid solution according to the standard procedure for 6 hours in a boiling water bath. After activation, the clay was washed from SO_4^{2-} ions, sequentially dried at room temperature (day), at 150^0C (2 hours) and calcined for 2 hours at 500^0C. Subsequent modification of kaolinite by aluminum was carried out by slow introduction of synthesized according to the method |19| hydroxocomplex with concentration of aluminum of 2.5 mmol Al^{3+} / g kaolinite. Calcination at 500 ° C is accompanied by the decomposition of the hydroxocomplex to alumina. The matrix of the prepared catalyst is designated as Al (2.5) HPK.

For preparation of the catalyst we used HY zeolite in the rare earth form — HLaY, which was obtained from NaY zeolite by ion exchange with NH_4Cl followed by the exchange of NH_4 ion to lanthanum. The content of HLaY zeolite in the catalyst is 15%. The elemental composition of the catalyst samples and their components was determined by X-ray fluorescence analysis on a “Niton XRF Analyzers” instrument manufactured by “Thermo Scientific” and using X-ray fluorescence spectroscopy in an energy dispersive microanalysis system “INCA-ENERGY 450” mounted on a JSM6610LV JEOL scanning electron microscope, Japan. The average value of three measurements was used.

The catalysts were characterized by BET, X-ray phase analysis performed on a DRON 4 * 0.7 device with CuKα radiation, and TPD (temperature-programmed desorption) of ammonia.

The activity of the synthesized catalysts in cracking was determined with using of vacuum gas oil of Pavlodar Petrochemical Plant (PPCP) with e.b. 532^0C and mixture of vacuum gas oil (70%) with fuel oil (30%).

The products of cracking and raw feed were analyzed chromatographically. For analysis of gasoline and the gas phase of cracking, Chromos GH-100 chromatograph with a 100 m capillary column with a stationary phase HP-1 (ASTM D 6729-04) was used. The carrier gas is helium. The analysis of vacuum gas oil components was carried out on an Auto System XL SIMIDS chromatograph with a Perkin Elmer SIMIDS -100% column (polymethylsiloxane), 30 m long with a helium flow of 40 cm^3/ min (ASTM D2887).

Results and discussions

Fractional and hydrocarbon composition of VG are presented in tables 1 and 2, and the chromatogram of the initial VG in figure 1.

Table 1 - the Fractional composition of the VG PPCP

The percentage of distillate, %	Distillation temperature by weight, °C	The percentage of distillate, %	Distillation temperature by weight, °C
5	258	55	407.5
10	290.1	60	415.7
15	312.0	65	422.9
20	323.1	70	430.7
25	338.6	75	440.1
30	383.6	80	450.1
35	365.7	85	461.6
40	377.4	90	474.7
45	388.4	95	498.2
50	398.5	100	532.0

Table 2 - Hydrocarbon Composition of the VG PPCP

Класс углеводородов	Content, % weight.
Paraffin hydrocarbons	66.2
Isoparaffin hydrocarbons	13.2
Aromatic HC	6.0
Olefins	0.4
Naphthenes	3.4
Oxygen containing compounds	2.9
Unidentified compounds	7.9
Total	100

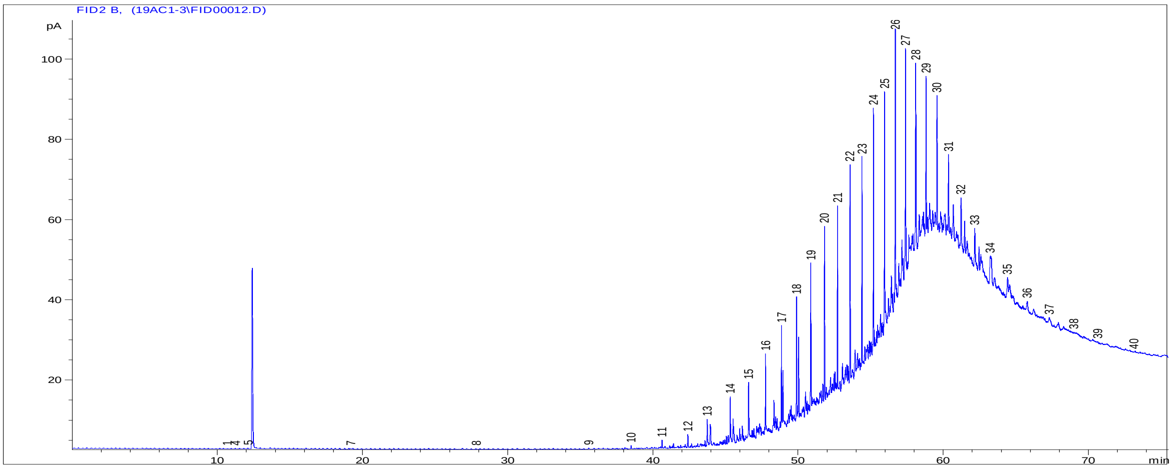


Figure 1 - Chromatogram of PPCP vacuum gas oil with e.b. 532^{0}C

According to the data of X-ray fluorescence spectroscopy, the composition of the used fuel oil M-100 PPCP includes 2.5% sulfur, 0.07% vanadium and 0.02% nickel.

The chemical composition of the used Pavlodar kaolinite PK, its H-form (HPK), aluminum modified Al (2.5) HPK and HLaY zeolite catalyst are shown in table 3.

Table 3 - The chemical composition of K, HK, Al (2.5)HPK and HLaY-zeolite catalyst

Sample	Content, weight %								
	Na_2O	MgO	Al_2O_3	K_2O	SiO_2	CaO	TiO_2	Fe_2O_3	La_2O_3
K	0.18	0.08	34.86	0.1	59.52	0.15	1.25	3.83	-
HK	0.03	0.03	32.81	0.08	63.11	0	1.38	2.57	-
Al(2.5)HPK	0.12	0.12	35.00	0.14	59.8	0.14	1.2	4.5	-
Al(2.5)HPK +HLaY	0.10	0.10	35.9	0.08	57.67	0.11	0.85	3.44	1.70

An analysis of the data in the table shows that acid activation leads to a decrease of the Al_2O_3 content (by ≈3%), which was compensated by the introduction of an aluminum hydroxocomplex. The initial kaolinite contains a small amount of 0.18% Na_2O and its amount decreases during the processing of the catalyst. The iron content in the initial sample is 3.83%, in the aluminum-modified sample - 4.50% and in the HLaY zeolite-containing catalyst - 3.44%. The amount of La_2O_3 in the catalyst is 1.7%.

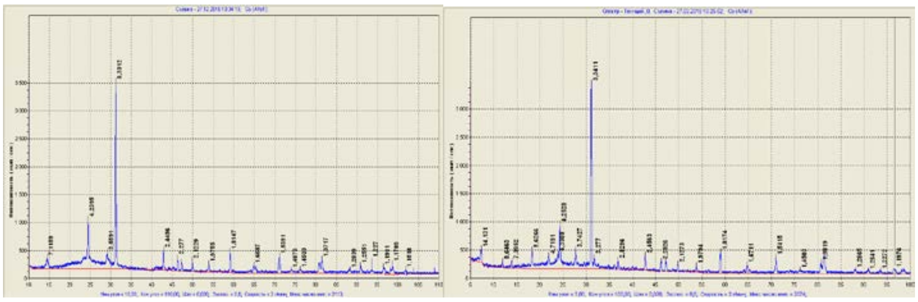
The textural characteristics of Al(2.5)HPK matrix and Al(2.5)HPK + HLaY samples are illustrated in table 4.

Table 4 - Characterization of aluminum-modified kaolinite sample and HLaY-catalyst by BET

Catalyst	S_{ss}, m^2/g	Total volume of pores,sm^3/g	R, nm	Relative content, %	
				Micropores <2 nm	Mesopores 2-8 nm
Al(2.5)HPK	28.8	0.09	2.0-8.0	16.0	84.0
Al(2.5)HPK+HLaY	131.8	0.15	2.0-8.0	19.9	80.1

When the H-form of Pavlodar kaolinite is modified by aluminum, the specific surface increases from 28.8 m^2/g to 131.8 and the number of mesopores, on the contrary, decreases to 80.1%.

X-ray diffraction diffractograms of the HK matrix and HLaY zeolite catalyst on aluminum-modified kaolinite are shown in figure 2. Reflex 2.02 is assigned to the lanthanum present on the surface.



a b

Figure 2 - The diffractograms of HPK (a) и Al(2.5)HPK +HLaY (b)

The activity of aluminosilicate contacts in cracking, as it is known, it is primarily associated with their acidity. The acid characteristics of the initial, acid-activated and aluminum-modified kaolinite, as well as the HLaY catalyst based on it are shown in table 5.

Table 5 - Acid characteristics of kaolinites of the studied samples

Sample	Content of a.c.	Weak a.c. < 200^0C	Medium a.c. 200-300^0C	Strong a.c. >350^0C	Total acidity
NK	%	47.8	45.2	7.0	100
	mcmole NH_3/g	20.9	19.8	3.0	43.8
HPK	%	38.9	38.7	22.3	100
	mcmole NH_3/g	45.1	44.9	10.0	115.9
Al(2.5)HPK	%	24.3	51.7	24.0	100
	mcmole NH_3/g	29.2	62.0	28.8	120.0
Al(2.5)HPK+ HLaY	%	23.0	47	30.0	100
	mcmole NH_3/g	30.2	61.7	39.4	131.3

The lowest acidity (43.8 mcmole/g) and the number of strong acid centers (a.c.) - 7% is the difference between the initial PK sample. Activation by acid and modification with aluminum lead to an increase of the total acidity and the number of strong a.c. The highest acidity (131.3 mcmole/g) and the number of strong a.c. -30% Al(2.5)HPK + HLaY

Data on the activity of the catalyst Al(2.5)HPK + HLaY in the cracking of VG and its mixture with fuel oil are shown in table 6.

Table 6 - Cracking VG and mixtures of VG with fuel oil on Al(2.5)HPK+HLaY

The yield of cracking products, % weight	VG			VG+ Fuel oil	
	450^0C	500^0C	550^0C	450^0C	500^0C
Gas	4.0	9.4	11.2	7.5	10.0
Gasoline	22.1	38.2	18.5	32.6	24.3
Coke	7.1	8.0	8.1	10.4	9.1
Light gas oil	40.0	29.4	25.0	25.9	23.2
Heavy gas oil	24.8	27.8	37.2	21.3	30.9
Losses	2.0	2.2	2.1	2.3	2.5
Conversion	73.2	85.0	62.8	73.4	64.6
Sum of light products	62.1	67.6	43.5	58.6	46.5
Octane number	85	85	85	85	85
Total	100	100	100	100	100

In VG cracking on a synthesized catalyst (table 6), the optimum temperature is 500^{0}C. At this temperature, the yield of gasoline was 38.2%, the amount of light gas oil - 29.4%, the yield of light products - 67.6% and the conversion of raw materials - 85%. The decrease of the cracking temperature to 450^{0}C and increasing to 550^{0}C leads to a decrease in gasoline yields. In the cracking of a mixture of VG with fuel oil, the best results were obtained at 450^{0}C: gasoline yield - 32.6%, light gas oil - 25.9%, the amount of light products - 58.6%. The gasoline yield during cracking of a mixture of VG with fuel oil is lower at 500°C, and at 450 ° C higher compared with VG cracking. When the mixture is cracked, coke formation is more intense than in the VG cracking: 10.4% at 450^{0}C. The rather high activity of the synthesized catalyst is probably determined by the high content of strong acid centers and increased mesoporosity of catalyst.

The hydrocarbon compositions of the gasoline cracking gasoline and a mixture of gasoline with fuel oil are shown in table 7.

Table 7 - The hydrocarbon composition of VG cracking gasoline
and a mixture of VG + fuel oil on aluminum-modified kaolinite

Catalyst	Raw	T^0,C	Paraffins	Iso paraffins	Aromatic PC	Naph thenes	Ole finns	∑
Al(2.5)HPK+HLaY	VG	450	6.9	22.9	2,3	15.0	32.9	100
	VG	500	5.7	20.4	2.5	14.4	34.9	100
	VG+Fuel oil	450	7.1	19.9	20.8	18.1	34.1	100
	VG+Fuel oil	500	6.0	20.2	23.0	18.3	32.5	100

In the composition of cracking gasolines the attention is drawn to the low content of aromatic hydrocarbons, which even in the cracking of a mixture of vacuum gas oil and fuel oil does not exceed 23% at 500°C with the benzene content (1.3 and 1.5% wt). The gasoline obtained on the HLaY catalyst based on aluminum-modified kaolinite in the cracking of VG and a mixture of VG with fuel oil, can be recommended for practical use in reducing of the amount of olefins in gasoline by hydro processing.

The hydrocarbon composition of the VG cracking gases and the mixture of VG with fuel oil on the sample are illustrated in table 8.

Table 8 - Hydrocarbon composition of gases of VG cracking and mixtures thereof with fuel oil on Al (2.5) HPK + HLaY

Hydrocarbons	VG		VG+Fuel oil	
	500^{0}C	450^{0}C	450^{0}C	500^{0}C
Methane	14.0	18.9	19.5	21.2
Ethane	10.3	12.7	13.0	14.1
Ethylene	15.0	13.7	19.5	19.1
Propane	9.8	9.0	4.5	6.4
Propylene	22.7	20.1	13.3	19.6
Iso butane	4.3	3.3	2.3	3.0
Butane	1.2	0.8	0.8	1.4
Butylene	12.5	10.8	3.2	7.8
∑C$_5$+C$_{5+}$	7.4	23.9	10.7	10.2
∑C$_2$-C$_3$ alkenes	37.7	33.8	32.8	38.7
∑C$_2$-C$_4$ alkenes	50.2	44.6	36.0	46.5

The compositions of the gaseous phase in the cracking of VG gases and the mixture of VG with fuel oil gases on an aluminum-modified kaolinite sample are quite close. VG cracking takes place with the release of significant quantities of dry gas (methane + ethane). At 450 and 500^{0}C these values are 24.3 and 31.6%. The yield of C$_2$ - C$_4$ alkenes at these temperatures is 50.2 and 44.6%. the most yield of propylene - 22.7% and butylene - 12.5% is formed during of the cracking of VG. When cracking of mixture of fuel oil with VG, less formation of propylene and butylenes was noted. The total amount of C$_2$-C$_4$ alkenes in VG cracking is 36.0 and 46.5% at 450 and 500^{0}C. In the composition of the cracking gases of the mixture of VG with fuel oil the content of dry gas 32.5 and 35.3% at 450 and 500 ° C and a significant (up to 46.5%) amount of C$_2$-C$_4$ alkenes is more than in the case of VG cracking.

Conclusion

The results of a study of the cracking of a mixture of VG with fuel oil and VG showed that the HLaY zeolite-containing catalyst based on aluminum-modified acid-activated Pavlodar kaolinite shows a rather high activity in the formation of light oil products of 32.6% gasoline and 25.9% LG at 450^0C with a raw conversion of 73.4%. The more active (38.2% gasoline and 29.4% LG) catalyst is in VG cracking. A distinctive feature of cracking gasolines on an HLaY catalyst modified with aluminum kaolinite is an increased content of isoparaffins (22.9% in cracking of VG at 450°C and 20.2% in cracking of a mixture of fuel oil with VG at 500°C) and a reduced amount of aromatic hydrocarbons not exceeding 2.5% in cracking of VG and 23.0% - in the cracking of a mixture of VG with fuel oil. The content of benzene is 1.3 - 1.5% wt. for every kind of raw. The increased content of olefinic hydrocarbons in the gasoline (32.5 – 34.9%) indicates the need for practical use of hydrotreating of the resulting gasoline.

An assumption was made about the effect of acidity and the mesoporous structure of the synthesized catalyst on the efficiency of work in the fuel direction to produce gasoline and light gas oil.

Acknowledgment

This work was supported by a grant of the Ministry of Education and Science of the Republic of Kazakhstan (project no. AP05132064).

Л.Д. Волкова[1], Н.А. Закарина[1], О.К. Ким[1], А.К. Акурпекова[1],
Д.А. Жумадуллаев [1], В.И. Яскевич[1], В.П. Григорьева[1], А.В. Габдракипов[2]

[1] «Д.В. Сокольский атындағы ЖКЭИ» АҚ, Алматы, Қазақстан;
[2]Ғылыми химико-аналитикалық орталық, Алматы, Қазақстан

ВАКУУМДЫҚ ГАЗОЙЛЬ ЖӘНЕ ОНЫҢ МАЗУТПЕН ҚОСПАСЫНЫҢ КРЕКИНГІНДЕГІ АЛЮМИНИЙМЕН ТҮРЛЕРНДІРІЛГЕН КАОЛИНИТ

Аннотация. Алюминимен түрлендіріліп, қышқылдық белсендірілген Павлодар кен орнының каолиниті негізіндегі HLaY-цеолитті катализаторындағы вакуумдық газойль (ВГ) және ВГ мазутпен (М-100) қоспанының крекингі бойынша мәліметтер келтірілген. Кіріспе бөлімінде каолинитті саз-балшықтар пайдаланылған катализаторлардағы крекингтің ерекшеліктері айтылған. Саз-балшықты қышқылды өңдеуден өткізіп, артынан SO_4-иондарынан жылыстататын каолинитті матрицаның синтезі, сирек кездесетін аралас формадағы HY–цеолитінің және HLaY-цеолитті катализаторларының синтездері сипатталған. Цеолит құрамы 15%мас құрады. Катализаторлар мен оны құраушы компоненттері БЭТ, рентгенфазалық анализ және аммиактың термобағдарламалық десорбциясы әдістері арқылы сипатталған. Үлгілердің элементтік құрамы анықталды. Хроматографиялық әдіспен анықталған вакуумдық газойльдың фракциялық және көмірсутектік құрамы, крекинг бензині мен газ фазасының көмірсутектік құрамы келтірілген.

Қышқылдық өңдеу кезіндегі алюминий оксиді құрамының төмендеуі 2.5ммоль $Al^{3+/}$г/каолинит концентрлі алюминий гидрокомплексін енгізіп, қыздырғанда Al_2O_3 дейін ыдырау арқылы орнына келтірілді.

Алюминиймен түрлендірілген Н-формалы каолиниттің меншікті бетінің мөлшері HLaY цеолитін енгізгенде 28.8 -ден 131.8 м^2/г дейін үлкейеді. Каолинит қолданылған Н-форма (86.2%), алюминиймен түрлендірілген Н-форма (84.1%) және HLaY-катализатор (80.1%) жоғары мезокеуектілік көрсетті, шамасы сол шикізатты белсендіріп мен катализатордың белсенділігін арттыратын сияқты.

ВГ мен мазут қоспасының крекингінде 450^0С кезінде бензин шығымы (32.6%) ВГ крекингінен көбірек (22.1%) шығады, ал 500^0С кезінде ВГ крекингінде бензин шығымының нәтижесі жоғары (38.2%) болады. Жеңіл газойль ВГ крекингінде ең жоғары нәтиже (450^0С кезінде 40.0%) көрсетеді. 450 және 500^0С кезінде ВГ крекингінің түсті өнімдері (62.0 және 67.6%) қоспадан қарағанда (58.5 және 47 5%) жоғары болды. ВГ крекингінде шикізаттың ең үлкен конверсиясы байқалады.

Каолинитті қышқылмен өңдеу, алюминиймен түрлендіру және HLaY цеолитті енгізу жалпы қышқылдық пен күшті және орта қышқылдығының артуына әкеледі, Al(2.5)НПК+HLaY катализаторы үшін сәйкесінше 131.3 мкмоль NH_3/г, 30 және 47%.

ВГ мен ВГ мазутпен қоспасы крекингінің бензиндері изо-парафиндер құрамының жоғарылауымен ерекшеленеді (ВГ үшін 450^0С кезінде 22.9% және қоспа үшін 500^0С кезінде 20.2%). 450^0С кезіндегі ВГ бензинінің ароматты көмірсутектер құрамы 2.3-2.5%, ал қоспада 20.8% болды. Каолиниткұрамды катализаторындағы ВГ мен ВГ мазутты қоспасының крекинг бензиндері 1.3-1.5% аспайтын бензол құрамының аз болуымен және қанықпаған көмірсутектердің көп болуымен ерекшеленеді. Крекинг бензинінің құрамындағы изо-парафиндер құрамының (20.2% дейін) артуы және ароматты көмірсутектер құрамының (24.1%) төмендеуі ВГ мазутпен қоспасының крекингі үшін катализаторды тартымды етеді.

Қышқылдық пен мезокеуекті құрылымның Бензин мен жеңіл газойль алынатын отындық бағыт бойынша жұмыстар тиімділігіне әсері туралы ұсыныстар айтылды.

Түйін сөздер: катализдік крекинг, каолинит, вакуумдық газойль, мазут, цеолит, түрлендіру.

Л.Д. Волкова[1], Н.А. Закарина[1], О.К. Ким[1], А.К. Акурпекова[1],
Д.А. Жумадуллаев[1], В.И. Яскевич[1], В.П. Григорьева[1], А.В. Габдракипов[2]

[1]АО «ИТКЭ им. Д.В. Сокольского», Алматы, Казахстан;
[2] Научный химико-аналитический центр, Алматы, Казахстан

МОДИФИЦИРОВАННЫЙ АЛЮМИНИЕМ КАОЛИНИТ В КРЕКИНГЕ ВАКУУМНОГО ГАЗОЙЛЯ И ЕГО СМЕСИ С МАЗУТОМ

Аннотация. Приведены данные по крекингу вакуумного газойля (ВГ) и смеси ВГ с мазутом (М-100) на HLaY-цеолитном катализаторе на основе модифицированного алюминием кислотно-активированного каолинита Павлодарского месторождения. В разделе «Введение» отмечены особенности крекинга на катализаторах с использованием каолинитовых глин. Описаны синтез каолинитовой матрицы, включающий кислотную обработку глины с последующим отмыванием от SO_4-ионов, HY –цеолита в замещенной редкоземельной форме и HLaY-цеолитного катализатора. Содежание цеолита составляло 15%мас. Катализаторы и составляющие его компонененты охарактеризованы методами БЭТ, рентгенофазового анализа и термопрограммированной десорбции аммиака. Определен элементный состав образцов. Приведен фракционный и углеводородный составы вакуумного газойля, углеводродные составы бензинов крекинга и газовой фаз, определенные. хроматографическим методом.

Уменьшение содержания оксида алюминия при кислотной активации компенсировали введением гидроксокомплекса алюминия с концетрацией 2.5ммоль Al^{3+}/г каолинита с последующим разложеним до Al_2O_3 при прокаливании.

Величина удельной поверхности модифицированной алюминием Н- формы каолинита при введениии цеолита HLaY увеличивается от 28.8 до 131.8 м^2/г. Показана высокая мезопористость Н-формы использованного каолинита (86.2%), модифицированной алюминием Н-формы (84.1%), и HLaY-катализатора (80.1%), которая, по-видимому, влияет на активацию сырья и активность катализатора.

Показано, что при 450^{0}С в крекинге смеси ВГ с мазутом выход бензина (32.6%) больше, чем при крекинге ВГ (22.1%), а при 500^{0}С лучшие результаты по выходу бензина (38.2%) получены для ВГ. Больше всего легкого газойля (40.0% при 450^{0}С) образуется при крекинге ВГ. Выход светлых продуктов при 450 и 500^{0}С для ВГ (62.0 и 67.6%) превышает этот показатель для смеси (58.5 и 47 5%). В крекинге ВГ отмечена и самая большая (85%) конверсия сырья..

Активирование каолинита кислотой, модифицирование алюминием и введение цеолита HLaY приводят к росту общей кислотности и увеличению числа сильных и средних кислотных центров, которые для катализатора Al(2.5)НПК+HLaY составляют 131.3 мкмоль NH_3/г, 30 и 47%, соответственно.

Бензины крекинга ВГ и смеси ВГ с мазутом отличаются повышенным содержанием изо-парафинов (22.9% при 450^{0}С для ВГ и 20.2% при 500^{0}С для смеси).. Содержание ароматических углеводородов в бензине из ВГ 2.3-2.5% и 20.8% из смеси при 450^{0}С. Бензины крекинга ВГ и смеси ВГ с мазутом, полученные на каолинит-содержащем катализаторе, отличаются малым содержанием бензола, не превышающем 1.3-1.5%, и высоким содержанием непредельных углеводородов. Это, по-видимому, определяет необходимость дополнительной гидроочистки бензинов, получаемых на модифицированных алюминием каолинит-содержащих катализаторах, при практическом использовании. Повышенное содержание изо-парафинов (до 20.2%) и пониженное содержание ароматических углеводородов (24.1%) делают катализатор привлекательным для крекинга смеси ВГ с мазутом

Высказано предположение о влиянии кислотности и мезопористой структуры синтезированного катализатора на эффективность работы по топливному направлению с получением бензина и легкого газойля

Ключевые слова: каталитический крекинг, каолинит, вакуумный газойль, мазут, цеолит, модифицирование.

Information about authors:
Volkova L.D. - “D.V. Sokolskiy IFCE” JSC, volkova_ld@rambler.ru, https://orcid.org/0000-0002-8017-5059;
Zakarina N.N. - “D.V. Sokolskiy IFCE” JSC, nelly_zakarina@rambler.ru, https://orcid.org/0000-0002-5895-8110;
Kim O.K. - “D.V. Sokolskiy IFCE” JSC, kimolya82@mail.ru, https://orcid.org/0000-0001-5110-2523;
Akurpekova A.K. - “D.V. Sokolskiy IFCE” JSC, https://orcid.org/0000-0002-8021-4644;

Zhumadullaev D.A. - “D.V. Sokolskiy IFCE” JSC;
Yaskevich V.I. - “D.V. Sokolskiy IFCE” JSC, https://orcid.org/0000-0001-9342-8337;
Grigorjeva V.P. - “D.V. Sokolskiy IFCE” JSC, https://orcid.org/0000-0002-1807-8530;
Gabdrakipov A.V. - Scientific chemical analytical center, Almaty, Kazakhstan, https://orcid.org/0000-0002-8016-4819

REFERENCES

[1] Gordievskaya Yu. I. (2017) Advances in chemistry and chem. technology [Uspekhi himii i him. tekhnologii] 31:67-69. (In Russ.).

[2] Kopytov M. A., Golovko A.K. (2009). News of Tomsk Polytechnic University. Chemistry [Izvestiya Tomskogo Politekhnicheskogo universiteta. Himiya] 315:83-86. (In Russ.).

[3] Nefedov B K (2010) Catatalysis in industry [Kataliz v promyshlennosti] 4: 39-50. (In Russ.).

[4] Murray H.H. (1999) Applied clay mineralogy today and tomorrow. Clay Minerals. 34:39-49. Doi:10.1180/000985599546055 (in Eng).

[5] Murray H.H. (2000) Traditional and new applications for Kaolin, smectite, and polyqorskite: a general overview. Appl. Clay Sci. 17:207-221. Doi: 10.1016/S0169-1317(00)00016-8 (in Eng).

[6] Zheng Sh. Q., Sun Sh. H., Wang Zh. F., Gao X. H., Xu. X. L. (2005) Suzhou kaolin as a FCC catalyst. Clay minerals 40:303-310. DOI:10.1180/0009855054030175. (in Eng).

[7] Eman A. E. (2013). Clays as Catalysts in Petroleum Refining Industry. ARPN J. of science and Technol. 3: 356-375 (in Eng).

[8] Sharonova O. M., Anshic N. N., Oruzhejnikov A.I., Akimochkina G.V., Salanov A.N., Nizovskij A.I., Semenov O.N., Anshic A.G. (2003) Chemistry for Sustainable Development [Himiya v interesah ustojchivogo razvitiya]11:673-682 (In Russ.).

[9] Rong T.J., Xiao J. (2002). The catalytic cracking activity of the kaolin-group minerals. Mater. Lett.57: 297-301(in Eng).

[10] Finevich V.P., Allert N. A., Karpova T.R., Duplyakin V.K. (2007) Russian Chem. journal [Ros. Him. zhurn] 60: 69-74(In Russ.).

[11] Shapkin N.P., Razov V.I., Majorov V.I., Hal'chenko I.G., Shkuratov A.L., Korochencev V.V. (2016). J. of inorganic chemistry [Zh. neorg. Himii] 61:1519-1528. DOI: 1078681S0044457X17090124 (In Russ.).

[12] Shapkin N.P., Leont'ev L.B., Hal'chenko I.G., Panasenko A.E., Majorov V.I., Razov V.I., Kajdalova T.A., Papanov E.K. (2017) J. of inorganic chemistry [Zh. neorg. Himii] 62:1217-1223. DOI: 1078681S0044457X17090124 (In Russ.).

[13] Silva-Valenzuela M.G., Matos Z.M., Shach L.A., Carvalho F.M.C., Sayeg L.J., Valenzuela-Diaz F.R. (2013) Engineering Properties of Kaolinite Clay with potencial Use in Drugs and Cosmetics. Int. Journ of Modern Engineering Research(IJMER).3: 163-165(in Eng).

[14] Belver C., Munor M.A., Vicente M.A. (2002). Chemical Activation of a Kaolinite under Acid and Alkaline Conditions. Chemistry of Materials. 14: 2033-2043. Doi: 10.1021/cm0111736 (in Eng).

[15] Panda A.K., Mishra B.G., Mishra D.K., Singh R.K. (2010). Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay. Colloids and Surfaces Physicochemical and Engineering Aspects. 363: 98-104. (in Eng).

[16] Dzhaksybaev S.I. (2012) Mineral raw materials of Pavlodar region.PSU after S. Torajgyrova, Kasakhstan (In Russ.).

[17] Liu C., Deng G., Pan G., Zheng Sh., Gao (2004) Interaction between heavy mttals and clay matrix in fluid catalytic cracking catalysts. Applied Catal. A: General.257:145-150. Doi: 10.1016/j.apcata.2003.07.008 (in Eng).

[18] Zakarina N.A., Volkova L.D., Akurpekova A.K., Kornauchova N.A., Kim O.K., Malimbaeva M.M. (2011) Removal of Fe, Ni, Cr, Zn ions from waste water by pillared clays on the Kazakhchstan deposits. In book; World Congress on Engineering and Technology. Shanghai: 787-791. (in Eng).

[19] Kim O.K., Volkova L.D., Zakarina N.A. (2011) Bashkir chem. Journal [Bashkirskij him. zhurnal]. 3:62-65. (In Russ.).

[20] Volkova L.D., Zakarina N.A., Akurpekova A.K. (2014) Petroleum chemistry [Neftekhimiya] 54:38-42. (In Russ.).

[21] Volkova L.D., Mahatova G.M., Shchukina O.V., Zakarina N.A. (2006). News of NAS RK. Chemical Series [Izvestiya NAN RK. Seriya himicheskaya] 4: 6-10 (In Russ.).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.31**
Volume 2, Number 440 (2020), 115 – 119

UDC 549.641:544.478

G.D. Jetpisbayeva, B.K. Massalimova, A.B. Daulet

M.Kh. Dulaty Taraz State University, Taraz, Kazakhstan;
massalimova15@mail.ru

SYNTHESIS OF PEROFSKITE-LIKE Co-CONTAINING CATALYST

Abstract. There are several approaches to the preparation of catalysts with a developed surface based on oxides with a perovskite structure. Perovskites, due to the possibility of easy variation of chemical composition, make it possible to choose the optimal composition of the catalyst and surface area, and as a result it is possible to influence effectively the selectivity.

Perovskite-like LaMeO3 oxides are one of the most promising catalysts for many oxidation processes due to their high activity in oxidative reactions and the stability in aggressive environment. Pekini method (polymer complexes method) and its simplified variant - citrate method are the most widely used for the synthesis of perovskite-like oxides.

This article reports about the synthesis of perovskite-like complex oxide $LaCoO_3$ obtained in two ways: hydrothermal, using ethylene glycol, and the citrate method using the template – mesoporous silica KIT-6. The structure of the samples obtained was determined by the XRD method. As a result, it was found that the catalysts have a perovskite structure.

Key words: $LaCoO_3$, perovskite, KIT-6.

Introduction. Cobalt catalysts are preferred for Fischer-Tropsch synthesis. The catalytic properties of cobalt catalysts are usually influenced by chemical interactions between the carriers and the metal, the texture of the catalysts and the morphology of crystals. Therefore, the balance of interactions between carriers and cobalt is very important [1-2]. It was previously shown that the type of precursor compound affects the physicochemical and catalytic properties of the reduced Co nanoparticles [3]. Such stable Co-containing compounds are mixed oxides with spinel, delafossite or perovskite structures.

Perovskites, due to the possibility of easy variation of the chemical composition, make it possible to choose the optimal composition of the catalyst and surface area, and as a result it is possible to influence effectively the selectivity for products. Perovskites have a flexible structure and are able to undergo significant changes with a possible decrease in symmetry or the formation of defects, while remaining within the framework of a perovskite structural type. There are several approaches to the preparation of catalysts with a developed surface based on oxides with a perovskite structure.

Perovskite-like $LaMeO_3$ oxides are one of the most promising catalysts for many oxidation processes due to their high activity in oxidative reactions and the stability in aggressive environment. Pekini method (polymer complexes method) and its simplified variant - citrate method are the most widely used for the synthesis of perovskite-like oxides [4]. The method of polymer complexes is a method for the synthesis of highly homogeneous and highly dispersed material oxides by using a complexing agent and the intermediate production of a polymer gel. Citric acid is usually used as the complexing agent, and ethylene glycol as the copolymer. However, the method of polymer complexes has its drawbacks, since the cations of some metals, for example, silver and platinum can’t stabilize in the resulting compound: they can be easily reduced by an organic complexing agent. Another possible way to obtain perovskite-like oxides is the hydrothermal method and template synthesis, which is the introduction of a template with a developed surface at the stage of deep interaction of the components [5].

This article reports the synthesis of perovskite-like complex oxide LaCoO3 obtained in two ways: hydrothermal, using ethylene glycol, and the citrate method using the template — mesoporous silica KIT-6. The proposed methods for the synthesis of catalysts ensure the homogenization of cations in the synthesized precursor compound and the homophasis of the compound obtained.

The structure of the samples obtained was determined by the XRD method. As a result, it was found that the catalysts have a perovskite structure. As a result, it was found that the catalysts have a perovskite structure.

Materials and methods. The following reagents were used in the work: $La(NO_3)_3x6H_2O$ (хч, Реахим, ТУ 6-09-4676-83), $Co(NO_3)_2x6H_2O$ (ч, Реахим, ГОСТ 4528-78), NaOH (хч, Экрос, ГОСТ 4328-77), HNO_3 (осч, ГОСТ-11125-84), ethylene glycol (хч, Реахим, ГОСТ 19710-83), citric acid (чда, Экрос, ГОСТ 36-52-69), C_2H_5OH (Реахим, ГОСТ Р 51999-2002). HCl (Гранхим, ГОСТ 3118-77), butanol-1 (Реахим, ГОСТ 6006-78), Pluronic P123 (Aldrich, MW 5800 O20PO70EO20), ethanol (ГОСТ Р 51999-2002), tetraethoxysilane (TEOS) (Компонент реактив, СТП ТУ КОМП 2-312-11) For the preparation of solutions, distilled water was used.

Two samples of $LaCoO_3$ with different ratios La:Co were obtained by the hydrothermal method [6] in the presence of ethylene glycol. The first sample of $LaCoO_3$ (LCO-1) was obtained by solvation of 0.06 mol of lanthanum nitrate and 0.06 mol of cobalt nitrate in 80 ml of water. Then 0.16 mol of ethylene glycol was added to the salt solution.

Separately, 120 ml of a 4M sodium hydroxide solution was prepared in a polypropylene beaker. Then, salt solution with a soft template was added drop wise to the sodium hydroxide solution. The pH of the solution changed from 3.0 to 13 with the formation of a thick purple precipitate of a mixture of cobalt alcoholates and lanthanum hydroxide. Then, nitric acid was added drop wise to the solution until pH = 10, the resulting suspension was stirred for 2 hours. Next, a propylene beaker with a suspension was closed tightly with a lid and placed in a heating oven for 24 hours at a temperature of 100^0C. Slow oxidation of templates by NO_3^- anions which are present in the solution occurs at 100^0C followed by the release of nitrogen or nitrous oxide. Formation of a mixture of carboxylic acids undergoing further degradation with the gradual separation of terminal carboxyl groups is observed in this process (figure 1).

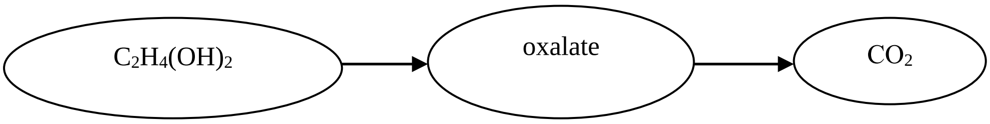


Figure 1 - The scheme of the oxidation of ethylene glycol in hydrothermal conditions

A slow decrease of pH is observed due to the isolation of oxidation products, which leads to an increase in the concentration of cobalt and lanthanum cations in the solution. At the end of the synthesis, the brown suspension was washed with 5 L of distilled water on a filter and dried under an infrared lamp. The obtained powder was calcined in air at 500°C for 3 hours and 750 °C for 4 hours. The second sample LCO-2 was obtained in a similar way, the amount of metal cations in this synthesis was 0.06 mol of lanthanum nitrate and 0.08 mol of cobalt nitrate. This ratio was chosen due to the fact that part of cobalt is lost due to its better solubility in comparison with lantanum [6].

According to published data [7], the mesoporous silicon carrier KIT-6 has a developed specific surface. On the one hand, its use in the synthesis of $LaCoO_3$ by the citrate method can significantly increase the surface of the forming perovskite. On the other hand, the use of citric acid and, as a consequence, the creation of an acidic environment under synthesis conditions prevents the chemical participation of SiO_2 in the formation of the sample.

The synthesis of the mesoporous silicon carrier KIT-6 was performed according to the procedure [7]. The following ratios of TEOS / P123 / HCl / H_2O / Butanol = 1 mol / 0.017 mol / 1.83 mol / 1.95 mol / 1.31 mol were used to calculate the weights. The synthesis procedure is as follows: 9 g of P123 and 17.40 g of HCl (35%) were dissolved in 325 g of water, mixed until the solution was completely homogenized. Next, 9 g of butanol was added and stirred at 35 ° C for 1 hour. Then, 19.35 g of TEOS was added. In this case, significant heat release was observed. The resulting solution was stirred at 35 ° C for 24 hours. In the last step, the mixture was hydrothermally treated at 100 ° C for 24 hours. Next, the resulting precipitate was filtered, washed with alcohol and dried under an infrared lamp. The obtained precursor was subjected to heat treatment for 4 hours at 500 ° C, during which the organic components of the precursor were removed and the desired template KIT-6 was formed.

A sample of $LaCoO_3$/KIT-6 (LCO / KIT-6) was obtained by the citrate method. Samples of salts of ($Co(NO_3)_3 \times 6H_2O$ (0.02 mol) 5.83 g and $La(NO_3)_3 \times 6H_2O$ (0.02 mol) 8.67 g and citric acid were dissolved in 60 ml of ethanol. 6 g KIT-6 was mixed with 60 ml of water and allowed to mix for 30 minutes. Then, a solution of salts was added dropwise into the resulting suspension. The resulting mixture was kept for 24 hours with continuous stirring at 35 °C, and then, evaporated in a rotary evaporator at 95 °C to form a gel, which was dried under an infrared lamp, grinded into powder and calcined at 500 °C for 3 hours and at 700 °C - 4 hours. Then, a sample with KIT-6 was kept in 500 ml of a 7% NaOH solution at 70 °C for 15 minutes, filtered and washed on a filter with 2 L of distilled water at a temperature of 75 °C four times, then dried under an infrared lamp.

In the synthesis by the citrate method, an excess of citric acid over the NO_3^- anions, calculated on the conversion of the latter into nitrogen, provides an amorphous gel [4], from which a single-phase LaCoO3 oxide was formed during heat treatment. The resulting powder contains in its structure lanthanum and cobalt as part of complex chelate complexes that decompose in stages during heat treatment at 1800C and 3500C with the release of water vapor, NO2 and CO2. At the limiting stage, cobalt is oxidized with air oxygen at 7000 ° C and a perovskite structure is formed:

$$3CoO + H_2O \rightarrow Co_3O_4 + 2H^+ + 2e \quad \mathrm{E^0=0.99\ B\ [8]} \tag{1}$$

$$2Co_3O_4 + H_2O \rightarrow 3Co_2O_3 + 2H^+ + 2e \quad \mathrm{E^0=1.02\ B\ [8]} \tag{2}$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \quad \mathrm{E^0=1.23\ B} \tag{3}$$

The phase composition of the samples was determined by X-ray phase analysis (XRD) on a D-8 diffractometer (Bruker) using Cu-Kα radiation by point-to-point scanning method with an interval of 0.050 in the angle range 2θ from 20 ° to 80 °.

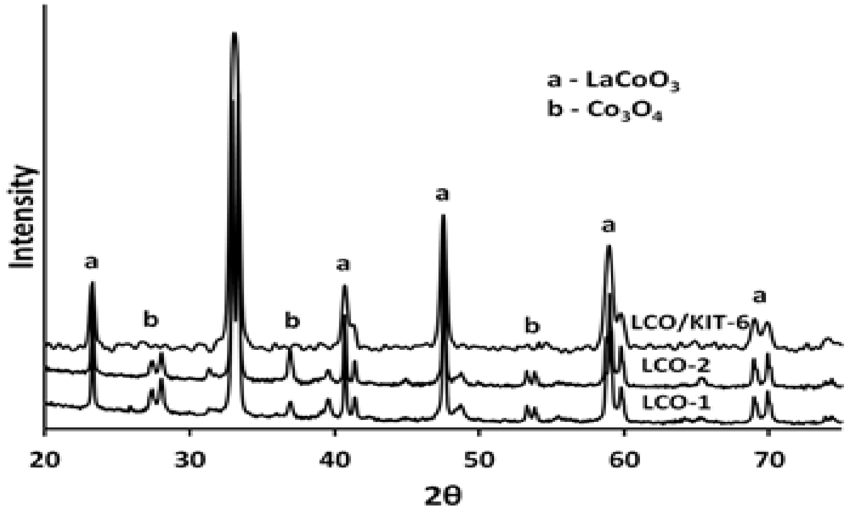


Рисунок 2 - Данные рентгенофазового анализа синтезированных образцов

According to the XRD data (Fig. 2), the samples obtained are represented by the $LaCoO_3$ perovskite phase (JCDD PDF2 00-025-1060) with the inclusion of the Co_3O_4 phase (JCDD PDF2 00-009-0418) and a small admixture of the La_2O_3 phase (JCDDPDF2 00-022-0641).

The results of the XRD analysis show that the samples obtained are represented by the perovskite phase. The resulting catalysts with perovskite structure are of great interest for the Fischer-Tropsch synthesis. Perovskites, due to the possibility of easy variation of the chemical composition, allow to choose the optimal composition and surface of the catalyst, as a result it is possible to influence effectively the selectivity. In this regard, further study the obtained Co-containing catalysts with the perovskite structure by other physicochemical methods is planned and the possibility of using them for Fischer-Tropsch synthesis is considered.

Source of research funding. Initiative project “Conversion of hydrocarbon raw materials of Kazakhstan” Department of “Chemistry and Chemical technology” of M.Kh.Dulaty Taraz State University.

Г.Д. Джетписбаева, Б.К. Масалимова, А.Б. Даулет

М.Х. Дулати атындағы Тараз мемлекеттік университеті, Тараз, Қазақстан

Со-ҚҰРАМДЫ ПЕРОВСКИТ ҚҰРЫЛЫМДЫ $LACOO_3$ КАТАЛИЗАТОРЫН СИНТЕЗДЕУ

Анотация. Перовскит құрылымы бар оксидтерге негізделген, беттік ауданы үлкен катализаторларды дайындаудың бірнеше тәсілдері бар. Перовскиттер, химиялық құрамының икемді өзгеруінің мүмкіндігіне байланысты катализатордың құрамын және оның беттік ауданын оңтайлы таңдауға мүмкіндік береді, нәтижесінде өнімнің селективтілігіне әсер етуі мүмкін.

Перовскит құрылымды оксидтер $LaMeO_3$ тотығу реакцияларындағы белсенділігі мен агрессивті ортаға тұрақтылығына байланысты көптеген тотығу процестерінің перспективті катализаторларының бірі болып табылады. Перовскит құрылымды оксидтерді синтездеу үшін Пекини әдісі (полимерлі кешендер әдісі) және оның жеңілдетілген нұсқасы цитратты әдіс кеңінен қолданылады. Бұл мақалада $LaCoO_3$ перовскит құрылымды күрделі оксид екі жолмен синтезделді: этиленгликоль қолдана отырып, гидротермалды әдіспен және қатты темплат мезопорлы кремнезем KIT-6 қатысында, цитрат әдісі. Алынған үлгілердің құрылымы РФА әдісімен анықталды. Нәтижесінде катализаторлардың перовскиттік құрылымға ие екендігі анықталды.

РФА мәліметтеріне сәйкес алынған үлгілердің фазалық құрамы $LaCoO_3$ перовскиттік фазасына (JCDD PDF2 00-025-1060) сай келеді. .Құрамында аз мөлшерде Co_3O_4 фазасының (JCDD PDF2 00-009-0418) және La_2O_3 фазасының (JCDDPDF2 00-022-0641) елемеуге болатын қоспалары бар.

РФА талдау нәтижелері алынған үлгілердің құрылымында перовскиттік фаза түзілгендігін көрсетеді. Перовскиттік құрылымға ие Со-құрамды катализаторлар Фишер-Тропш синтезінде қолдануңа үлкен қызығушылық тудырады. Себебі, перовскиттердің, химиялық құрамының икемді өзгеру мүмкіндігіне байланысты, олар катализатордың оңтайлы құрамы мен беттік ауданын ұлғайтуға мүмкіндік береді, нәтижесінде селективтілікке тиімді әсер етуі мүмкін. Осыған байланысты алынған перовскиттік құрылымы бар Со құрамды катализаторларды болашақта басқа физика-химиялық әдістермен зерттеу және Фишер-Тропш синтезінде қолдану мүмкіндігі қарастырылады.

Түйін сөздер: $LaCoO_3$, перовскит, KIT-6

Г.Д. Джетписбаева, Б.К. Масалимова, А.Б. Даулет

Таразский государственный университет им. М.Х.Дулати, Тараз, Казахстан

СИНТЕЗ ПЕРОВСКИТОПОДОБНОГО Со-СОДЕРЖАЩЕГО КАТАЛИЗАТОРА

Анотация. Существует несколько подходов к получению катализаторов с развитой поверхностью на основе оксидов со структурой перовскита. Перовскиты, благодаря возможности гибкого варьирования химического состава позволяет подобрать оптимальный состав катализатора и поверхности, вследствие чего возможно эффективно влиять на селективность по продуктам.

Перовскитоподобные оксиды $LaMeO_3$ являются одними из наиболее перспективных катализаторов для многих процессов окисления, благодаря своей высокой активности в окислительных реакциях и стабильности агрессивной среде. Для синтеза перовскитоподобных оксидов наибольшее распространение получил метод Пекини (мотод полимерных комплексов) и его упращенный вариант – цитратный метод. В этой статье было синтезировано перовскитоподобный сложный оксид $LaCoO_3$ двумя способами: гидротермальным, с применением этиленгликоля, и цитратным способом с внесением темплата – мезопористого кремнезёма KIT-6. Структуры полученных образцов было определено РФА методом. В результате было установлено, что катализаторы имеют перовскитную структуру.

Согласно данным РФА полученные образцы представлены фазой перовскита $LaCoO_3$ (JCDD PDF2 00-025-1060) с включением фазы Co_3O_4 (JCDD PDF2 00-009-0418) и небольшой примесью фазы La_2O_3 (JCDDPDF2 00-022-0641).

Результаты РФА анализа показывают, что полученные образцы представлены фазой перовскита. Полученные катализаторы со структурой перовскита представляют большой интерес в синтезе Фишера-Тропша. Так как, перовскиты, благодаря возможности гибкого варьирования химического состава позволяет подобрать оптимальный состав и поверхности катализатора, вследствие чего возможно эффективно влиять на селективность. В связи с этим полученные Со- содержащие катализаторы со структурой перовскита в будущем планируется исследовать другими физико-химическими методами и рассмотреть возможность использования в синтезе Фишера-Тропша.

Ключевые слова: $LaCoO_3$, перовскит, KIT-6.

Information about authors:

Jetpisbayeva Gulim Danebaevna –PhD student of 6D060600- Chemistry of the Department of “Chemistry and Chemical technology” of M.Kh.Dulaty Taraz State University, e-mail: gulim_86@mail.ru

Massalimova Bakytgul Kabykenovna – candidate of chemical sciences, associated professor, manager of the Department of “Chemistry and Chemical technology” of M.Kh.Dulaty Taraz State University, e-mail: massalimova15@mail.ru

Daulet Assel Baktybaikyzy - master student of 6D060600- Chemistry of the Department of “Chemistry and Chemical technology” of M.Kh.Dulaty Taraz State University, e-mail: daulet_asel@mail.ru

REFERENCES

[1] Davis B.H. (2005) Fischer-Tropsch synthesis: Overview of reactor development and future potentialities. *Topics in catalysis*, Vol. 32. P. 143-168.

[2] Massalimova, B.K., Altynbekova, D.T., Nauruzkulova, S.M., Atakozhaeva, A.A., Sadykov, V.A. (2019). Low-percentage co/clay catalysts in the process of oxidative conversion of C3-C4 saturated hydrocarbons. *News of the Academy of Sciences of the Republic of Kazakhstan. Series of Chemistry and Technology.* Vol. 2. P. 6-11. https://doi.org/10.32014/2019.2518-1491.11

[3] Pan X., Fan Zh., Chen W., Luo H., Bao X. (2007) Enhanced ethanol production inside carbon-nanotube reactors containing catalytic particles. *Nature Materials.* Vol. 6. P. 507-511.

[4] Taran O.P., Ayusheeva A.B., Ogorodnikova O.L., Prosvirin I.P., Isupova L.A. (2013) Perovskitopodobnyie katalizatory tipa dlya glubokogo jidkofaznogo okislenija fenola peroksidomvodoroda. *Jurnal sibirskogo federalnogo universiteta*. Himiya 3. P.26-285.

[5] Predoana, L., Malic, B., Kosec, M., Scurtu, M., Caldararu, M., Zaharescu, M. (2009) Phase formation and electrical properties of the $LaCoO_3$ obtained by water-based sol-gel method with citric acid. *Processing and Application of ceramics.* Vol. 1-2. P. 39-42.

[6] Dokuchits E.V., Tafilevich A.N., Shtertser N.V., Minyukova T.P. (2019) Synthesis of $LaCoO_3$ in mild hydrothermal conditions. *Journal of Siberian Federal University. Chemistry 2.* Vol. 12. P. 178-185. DOI: 10.17516/1998-2836-0117

[7] Tuysuz H., Lehmann C. W., Bongard H., Tesche B., Schmidt R., Schu F. (2009) Direct Imaging of Surface Topology and Pore System of Ordered Mesoporous Silica (MCM-41, SBA-15, and KIT-6) and Nanocast Metal Oxides by High Resolution Scanning Electron Microscopy. *J. AM. CHEM. SOC.* Vol.130 (34). P. 11510-11517.

[8] Porthault H., Le Cras F., Baddour-Hadjean R., Pereira-Ramos J.P., Franger S. (2011). One step synthesis of lamellar R-3m $LiCoO_2$ Thin films by an electrochemical-hydrothermal method. *Electrochimica Acta.* Vol. 56(22). P. 7580-7585.

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.32**
Volume 2, Number 440 (2020), 120 – 128

UDC 621.742.4
IRSTI 29.19.23

E.S. Abdrakhmanov [1], B.T. Yermagambet[2],
Zh.M. Kassenova[2], M. K. Kazankapova[2], A. Sairanbek [2]

[1] "Pavlodar State University named after S. Toraygyrov", Pavlodar, Kazakhstan;
[2] "Institute of Coal Chemistry and Technology" LLP, Nur-Sultan, Kazakhstan.
E-mail: erai1512@mail.ru, bake.yer@mail.ru, zhanar_k_68@mail.ru, maira_1986@mail.ru, asi_48@mail.ru

INVESTIGATION OF RELIABILITY OF THE SCREW UNIT OF THE COAL-ROLL PRESS BT-3M

Abstract. In the article we propose the method of calculation of parameters of stress state and rigidity of screw blade at bending in one plane, screw-piston press of BT-3M grade for production of coal briquettes is simultaneously mixing, transporting and pressing unit. The blade is regarded as a thin axially endless helicoid shell rigidly attached to the shaft along an internal helical boundary. Considering that the presence of the blade does not affect the deformation of the constant-section shaft during bending, we examine the effect of the presence of the blade on the bending stiffness of the screw. Invention covers the problem of screw blade deformations at preset displacements at inner boundary caused by shaft bending considering that its axis has curvature.

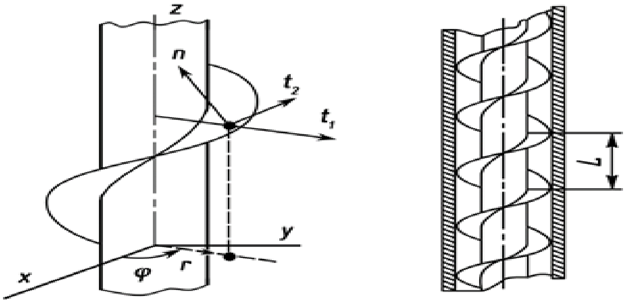
In the second stage of calculation we construct a compensating solution, which eliminates inconsistencies in differential equilibrium equations and static boundary conditions, and on the inner contour of the shell we set conditions of rigid pinching. As a result, the screw was calculated using the developed method. Blade is calculated with parameters r1 = 0.04 m, r2 = 0.1 m, r3 = 0.03 m, screw blade thickness d = 0.005 m, L = 0.2 m, total length of hollow shaft 1, 2 m. Calculations have shown that at such screw parameters and created specific pressure of material on the screw Ore = 8.5 · 10^5 Pa, the rigidity of the blade is the stiffness 11% of the tubular shaft.

Keywords: screw, press, calculation, briquette, extras, equations.

Introduction. For a number of years, the company Briquette Technologies LLC (Barnaul, Russian Federation) has been manufacturing equipment, improving and introducing it [1]. In particular, BT-type equipment is manufactured for the production of coal briquettes (figure 1).

The operation of this equipment was studied taking into account the technological parameters of its knot. The screw is at the same time a mixing, conveying and pressing knot. The screw knot (figure 2) consists of a tubular shaft and a helical tape of welded construction.

Figure 1 - Industrial screw piston press BT - 2.5-3 t/h



а) б)

Figure 2 - To the calculation of the screw knot: a) design scheme, b) auger in the trench

In this case, the screw knot experiences bending of the shaft during operation, wear of the helicoid tape and alternating loads caused by the uneven density of the mixed mass. In these cases, it can be argued that the blades and shaft of the screw will always be under high voltage.

We propose a method for calculating the parameters of the state under voltage and rigidity of a screw blade of auger during bending in one plane. We consider the blade as a thin helical shell endless in the axial direction, rigidly fastened to the shaft along the internal helical boundary (figure 2b).

Assuming that the presence of the blade does not affect the nature of the deformation of the shaft of constant cut during bending, we study the effect of the presence of the blade on the bending rigidity of the screw.

Consider the problem of the deformation of a screw blade for a given displacement on the inner boundary due to bending of the shaft, assuming that its axis has a curve $1/\rho$.

Middle surface of the helicoid shell is assigned (figure 1) to the coordinates r, ϕwhich define the orthogonal coordinate lines system on it (figure 2), with Lame parameters [6]:

$$A = 1,\ B = \sqrt{r^2 + (0{,}5L/\pi)^2},$$

where L - is the step of the helicoid.

The unit vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ of the coordinate lines r and the normal n to the middle surface [5] (see figure 2) are related to the unit vectors of the Cartesian coordinate system by the formulas:

$$\mathbf{t}_1 = \cos\varphi\,\mathbf{i} + \sin\varphi\,\mathbf{j};$$

$$\mathbf{t}_2 = \frac{r}{B}(-\sin\varphi\,\mathbf{i} + \cos\varphi\,\mathbf{j}) + \frac{L}{2\pi B}\mathbf{k}; \tag{1}$$

$$\mathbf{n} = \frac{L}{2\pi B}(\sin\varphi\,\mathbf{i} - \cos\varphi\,\mathbf{j}) + \frac{r}{B}\mathbf{k}.$$

The next is to determine the displacements of the points of the interface line between the shell and the shaft. When the shaft bends in the YOZ plane, the movement of its points along the directions of the X, Y, Z axes is

$$\xi = 0; \quad \eta = -0{,}5\cdot\frac{z^2}{\rho}; \zeta = \frac{yz}{\rho}; \tag{2}$$

$$x = r_1 \cos\varphi;\ y = r_1 \sin\varphi\ ;\ z = 0{,}5\,L\,\frac{\varphi}{\pi}$$

wherer_1 is the radius of the shaft, and passing using formulas (1) to the projections of displacement on the axis of the local basis of the shell, we obtain

$$u = -C\cdot\frac{\varphi^2}{2}\cdot\sin\varphi; \quad v = C\cdot\frac{r_1}{B_1}\cdot\left(\varphi\cdot\sin\varphi - \frac{\varphi^2}{2}\cdot\cos\varphi\right); \tag{3}$$

$$w = C \cdot \left(\frac{L}{2\pi B_1} \frac{\varphi^2}{2} \cdot \cos\varphi + \frac{2\pi r_1^2}{L B_1} \cdot \varphi \cdot \sin\varphi \right),$$

where $C = (0{,}5L/\pi)^2/\rho$; B_1 is the value of the Lame parameter of the ϕ -line at the inner boundary of the shell.

In addition to displacement (3), the values of the angle of rotation of the normal **n** or, equivalently, the unit vector $\mathbf{t}_1$ in the plane perpendicular to the boundary of the shell border must be specified. When the shell is rigidly bonded to the shaft, its unit t1 rotates with the shaft transverse cross of shaft through an angle

$$\theta = \frac{z}{\rho} \mathbf{i}.$$

It follows that the rotation angle in the plane **n**, $\mathbf{t}_1$ is equal to

$$\vartheta_1 = \theta \mathbf{t}_2 = \mathbf{i} \cdot \mathbf{t}_2 \frac{L\varphi}{2\pi\rho} = -\mathrm{C} \frac{2\pi r_1}{LB_1} \cdot \varphi \cdot \sin\varphi \ . \tag{4}$$

So, the kinematic boundary conditions on the inner edge of the shell are established. There is no voltage on the outer free edge.

To calculate the helicoids the equations of the general theory of shells [6], [8], [9] written in the orthogonal system of curvilinear coordinates of the surface that do not coincide with the lines of the main curvatures are used. In this case, we take into account that the curvatures of the normal cross of the helicoid passing through the r - and ϕ - lines are equal to zero, and the surface torsion is

$$\frac{1}{R_{12}} = -\frac{L}{2\pi B^2} \ .$$

As a result, we obtain the following system of equations:

– equation of equilibration:

$$\frac{\partial[BT_1]}{\partial r} + \frac{\partial}{\partial\varphi}\left(S - \frac{M_2}{R_{12}}\right) - \frac{r}{B}T_2 - \frac{BQ_2}{R_{12}} + Bq_1 = 0; \ \frac{\partial}{\partial r}\left[B\left(S - \frac{M_1}{R_{12}}\right)\right] + \frac{\partial T_2}{\partial\varphi} + \frac{r}{B}\left(S - \frac{M_2}{R_{12}}\right) - \frac{BQ_1}{R_{12}} + Bq_2 = 0; \tag{5}$$

$$\frac{\partial(BQ_1)}{\partial r} + \frac{\partial Q_2}{\partial\phi} + \frac{B}{R_{12}}\left(2S - \frac{M_1 + M_2}{R_{12}}\right) + B\, q_n = 0; \ \frac{\partial(BM_1)}{\partial r} - \frac{r}{B}M_2 + \frac{\partial H}{\partial\phi} - BQ_2 = 0;$$

$$\frac{\partial(BH)}{\partial r} + \frac{r}{B} \cdot H + \frac{\partial H}{\partial\varphi} - B \cdot Q_2 = 0;$$

– geometric ratio:

$$\varepsilon_1 = \frac{\partial u}{\partial r}; \quad \varepsilon_2 = \frac{\partial v}{B\partial\varphi} + \frac{ru}{B^2}; \quad \gamma_{12} = \frac{\partial u}{B\partial\varphi} + B\frac{\partial}{\partial r}\left(\frac{v}{B}\right) - \frac{2\omega}{R_{12}};$$

$$\theta_1 = -\frac{v}{R_{12}} - \frac{\partial w}{\partial r}; \quad \theta_2 = -\frac{u}{R_{12}} - \frac{\partial w}{B\,\partial\varphi}; \ \Omega_n = \frac{1}{2B}\left[\frac{\partial(Bv)}{\partial r} - \frac{\partial u}{\partial\varphi}\right]; \ \nu_1 = \frac{\partial\theta_1}{\partial r} - \frac{\Omega_n}{R_{12}}; \tag{6}$$

$$v_2 = \frac{\partial\theta_2}{B\partial\varphi} + \frac{r\theta_1}{B^2} + \frac{\Omega_n}{R_{12}}; \quad \eta = \frac{\partial\theta_1}{B\partial\varphi} - \frac{r\theta_2}{B^2} + \frac{\varepsilon_2}{R_{12}};$$

– ratio of elasticity:

$$T_1 = \frac{E\,h}{1-\nu^2}(\varepsilon_1 + \nu\varepsilon_2) \quad (1 \leftrightarrow 2)\,; \quad S = \frac{E\,h}{2(1+\nu)}\varphi_{12}\,;$$

$$M_1 = D\,(\chi_1 + \nu\,\chi_2) \;\; (1 \leftrightarrow 2);\; H = D\,(1-\nu)\,\eta\,. \tag{7}$$

We write the static boundary conditions on the external contour of the helicoid in the form [8]

$$T_1^* = T_1 - \frac{H}{R_{12}} = 0;\quad T_{12} = S - \frac{M_1}{R_{12}} = 0;\; Q_1^* = Q_1 + \frac{\partial H}{B\partial\varphi} = 0;\;\; M_1 = 0. \tag{8}$$

In this screw bending problem, the distributed loads q_1, q_2, q_n are absent, all blade turns are in the same stressed state, so internal forces and deformations are periodic coordinate functions. Displacements u, v, w and rotation angles ϑ_1, ϑ_2, Ω_n have no periodicity property.

The blade is calculated in two stages.

First, we set an approximate law for changing the movements of the blade points assuming that its radial sections passing through the horns t₁, n (figure 2) do not deform. It is assumed that kinematic boundary conditions (3) and (4) are satisfied.

In the second stage of calculation we build a compensating solution, which eliminates inconsistencies in differential equations of equilibrium (5) and static boundary conditions (8), and on the inner contour of the shell we set conditions of rigid pinching.

Thus, all components of stress-strain state are represented as sums $f = f^{(1)} + f^{(2)}$, where $f^{(1)}$ - components of approximate solution satisfying kinematic boundary conditions of shell with shaft, and $f^{(2)}$ - components of compensating solution.

In the first solution, the movement functions according to the conditions (5) have the form:

$$u = -C\frac{\varphi^2}{2}\sin\varphi;\quad v = C\frac{r_1}{B_1}\left(\varphi\sin\varphi - \frac{\varphi^2}{2}\cos\varphi\right);w = C\cdot\left(\frac{L}{2\pi B_1}\frac{\varphi^2}{2}\cdot\cos\varphi + \frac{2\pi r_1^2}{L\,B_1}\cdot\varphi\cdot\sin\varphi\right). \tag{9}$$

Using ratios (6), we find membrane deformation components

$$\varepsilon_1^{(1)} = 0;\; \varepsilon_2^{(1)} = C\cdot\frac{r}{B^2}\cdot\sin\varphi\;;\quad \gamma_{12}^{(1)} = 0 \tag{10}$$

and parameters for changing the curvature and torsion of the middle surface $\chi_1^{(1)} = 0$;

$$\chi_2^{(1)} = -C\cdot\frac{2\pi}{LB}\cdot\left(1+\frac{r^2}{B^2}\right)\cdot\cos\varphi;\;\; \tau^{(1)} = -C\cdot\frac{Lr}{\pi B^4}\cdot\sin\varphi\,. \tag{11}$$

using elastic ratios (7) we determine internal forces and moments $T_1^{(1)} = \nu\cdot T_2^{(1)}$;

$$M_2^{(1)} = -D\cdot C\cdot\frac{2\pi}{L\cdot B}\cdot\left(1+\frac{r^2}{B^2}\right)\cdot\cos\varphi; \tag{12}$$

$$H^{(1)} = -D\cdot C\cdot(1-\nu)\cdot\frac{L\cdot r}{\pi\cdot B^2}\cdot\sin\varphi;$$

from the fourth and fifth equations of equilibrium of moments from (5), we get transverse forces

$$Q_1^{(1)} = \frac{D\cdot C\cdot r}{B^5}\cdot\left(\frac{4\pi r^2}{L} - \frac{L}{2\pi}\right)\cdot\cos\varphi;$$

(13)

$$Q_2^{(1)} = \frac{D \cdot C}{B^2} \cdot \left[\frac{2\pi}{L} \left(1 + \frac{r^2}{B^2} \right) + (1-\nu) \cdot \frac{L}{\pi B^2} \left(\frac{2r^2}{B_2} - 1 \right) \right] \cdot \sin\varphi \ .$$

By substituting the forces found into the first three equilibrium equations (5), we find surface loads

$$q_1^{(1)} = \frac{EhC}{1-\nu^2} \left[(1+\nu) \cdot \frac{r^2}{B^4} - \frac{\nu}{B^2} \right] \cdot \sin\varphi \ ;$$

$$q_2^{(1)} = -\frac{EhC}{1-\nu^2} \cdot \frac{r}{B^2} \cdot \cos\varphi ; \qquad (14)$$

$$q_3^{(1)} = -\frac{DCL}{2\pi B^2} \left[16r^2 + (3\nu - 1) \left(\frac{L}{2\pi} \right)^2 \right] \cdot \cos\varphi \ ;$$

In the expressions for loads $\boldsymbol{q_1^{(1)}}$ and $\boldsymbol{q_2^{(1)}}$ and omitted the components having order $(h/B)^2$.

As can be seen from the dependencies (12), forces exist on the outer contour of the blade

$$T_1^{*(1)} = \frac{\nu \cdot EhC}{1-\nu^2} \cdot \frac{r_2}{B_2^2} \cdot \sin\varphi ; \quad T_{12}^{(1)} = -\frac{\nu \cdot DC}{B_2^2} \cdot \left(1 + \frac{r_2^2}{B_2^2} \right) \cdot \cos\varphi \ ; \qquad (15)$$

$$Q_1^{*(1)} = \frac{DCr_2}{B_2^5} \cdot \left[\frac{4\pi\, r_2^2}{L} - (3 - 2\nu) \cdot \frac{L}{2\pi} \right] \cdot \cos\varphi \ ; M_1^{(1)} = -\nu\, D\, C \cdot \frac{2\pi}{L\, B_2} \cdot \left(1 + \frac{r_2^2}{B_2^2} \right) \cdot \cos\varphi \ ,$$

Where r_2 – is the outer radius of the blade; B_2 - is the value of the Lame parameter at this radius.

Thus, the inconsistencies in equilibrium equations generated by approximate solutions are established.

Let 's look at the problem of finding a solution that compensates for mischief. This solution must satisfy equations (5) - (7) at loads

$$q_1^{(2)} = -q_1^{(1)} \ ; \ q_2^{(2)} = -\ q_2^{(1)} ; \ q_n^{(2)} = -q_n^{(1)} , \qquad (16)$$

boundary conditions of the specified rigid fixation on the inner contour

$$u^{(2)} = v^{(2)} = w^{(2)} = \vartheta_1^{(2)} = 0, \qquad (17)$$

and conditions of specified loading on external circuit free in relation to displacements

$$T_1^{*(2)} = -T_1^{*(1)} ; \ T_{12}^{(2)} = -T_{12}^{(1)} ; \ Q_1^{*(2)} = -Q_1^{*(1)} \ ; \ M_1^{(2)} = -M_1^{(1)} . \qquad (18)$$

The formulated task allows for the separation of variables. This procedure differs from the same procedure in the related task of calculating *rotation shells*.

Accepting that functions

$$u^{(2)}, \ \varepsilon_1^{(2)}, \ \varepsilon_2^{(2)}, T_1^{(2)}, T_2^{(2)}, \ \vartheta_1^{(2)}, \kappa^{(2)}, H^{(2)}, Q_2^{(2)}$$

change along helical lines r = const by the law of the sinus, i.e.

$$f^{(2)} = \tilde{f}(r) \cdot \sin\varphi , \qquad (19)$$

Where $f^{(2)}$ – is any of the functions listed.

Each of functions

$$v^{(2)},\ \gamma_{12}^{(2)},\ \Omega_n^{(2)},\ S^{(2)},\ w^{(2)},\vartheta_1^{(2)},\kappa_1^{(2)},\kappa_2^{(2)},M_1^{(2)},M_2^{(2)},Q_1^{(2)}$$

imagine in the form

$$g^{(2)}=\tilde{g}\cdot\cos\varphi\ . \tag{20}$$

Unlike the shells of rotation in the helicoid, normal forces and bending moments are functions of different parity. The same can be said of shear forces and torques. As a result of substitution of expressions (19), (20) in equations (5) - (7) and separation of angular coordinate ϕ functions, we obtain a system of ordinary differential equations, which can be represented as

$$\frac{d}{dr}Y = F\,Y + G\,Z + g\,;\ \ Z = M\,Y, \tag{21}$$

where

$$Y = \left\{\tilde{u},\ \tilde{v},\ \tilde{w},\ \tilde{\vartheta}_1,\ \tilde{B}\left(\tilde{T}_1-\frac{\tilde{H}}{R_{12}}\right),\ \tilde{B}\left(\tilde{S}-\frac{M_1}{R_{12}}\right),\ B\left(\tilde{Q}_1+\frac{\tilde{H}}{B}\right),\ B\tilde{M}_1\right\}.$$

A vector of basic variables (order 8), $Z=\{\tilde{\kappa}_1,\ \tilde{\tau}\}$ - a vector of complementary variables (order 2); F, G, M – are coefficient matrices.

$$F=\begin{pmatrix}
-\frac{\nu\kappa}{B^2} & \frac{\nu}{B} & 0 & 0 & \frac{1-\nu^2}{EhB} & 0 & 0 & 0\\
-\frac{1}{B} & \frac{r}{B^2} & \frac{2}{R_{12}} & 0 & 0 & \frac{2(1+\nu)}{EhB} & 0 & \frac{2(1+\nu)}{EhBR_{12}}\\
0 & -\frac{1}{R_{12}} & 0 & -1 & 0 & 0 & 0 & 0\\
-\frac{(1-2\nu)}{BR_{12}} & \frac{(1-\nu)r}{B^2R_{12}} & -\frac{\nu}{B^2}+\frac{1-\nu}{R_{12}^2} & -\frac{\nu r}{B^2} & 0 & \frac{2(1+\nu)}{EhBR_{12}} & 0 & \frac{1}{BD}\\
\frac{Ehr^2}{B^3} & -\frac{Ehr}{B^2} & 0 & 0 & \frac{\nu r}{B^2} & \frac{1}{B} & 0 & \frac{(1-2\nu)}{BR_{12}}\\
-\frac{Ehr}{B^2} & \frac{Eh}{B} & 0 & 0 & -\frac{\nu}{B} & -\frac{r}{B^2} & \frac{1}{R_{12}} & -\frac{(1-\nu)\cdot r}{B^2R_{12}}\\
0 & 0 & 0 & 0 & 0 & -\frac{2}{R_{12}} & 0 & \frac{\nu}{B^2}-\frac{1-\nu}{R_{12}^2}\\
0 & 0 & 0 & 0 & 0 & 0 & 1 & \frac{\nu\cdot r}{B^2}
\end{pmatrix}$$

$$G^{\mathrm{T}}=\begin{pmatrix}
0 & 0 & 0 & 0 & -\frac{2D\left(1-\nu^2\right)}{R_{12}} & \frac{D\left(1-\nu^2\right)\cdot r}{B\,R_{12}} & D\left(1-\nu^2\right)\left(\frac{B}{R_{12}^2}+\frac{1}{B}\right) & \frac{D(1-\nu)\cdot r}{B}\\
\frac{(1-\nu)h^2}{12\,R_{12}} & 0 & 0 & 0 & \frac{(3+\nu)(1-\nu)r\,D}{B\,R_{12}} & -\frac{D\left(1-\nu^2\right)}{R_{12}} & -\frac{2(1-\nu)\,r\,D}{B^2} & -2D(1-\nu)
\end{pmatrix}$$

$$M=\begin{pmatrix}
-\frac{2}{B\,R_{12}} & \frac{r}{B^2R_{12}} & \frac{1}{R_{12}^2}+\frac{1}{B^2} & \frac{r}{B^2} & 0 & 0 & 0 & 0\\
\frac{2r}{B^2R_{12}} & -\frac{1}{B\,R_{12}} & -\frac{r}{B^2} & -\frac{1}{B} & 0 & 0 & 0 & 0
\end{pmatrix}.$$

The edge problem for the system of equations is solved numerically by the method of orthogonal Godunov run. With known blade deformations, its effect on screw bending stiffness can be determined by Lagrange 's theorem. For this purpose we calculate deformation energy of one blade turn [5]

$$U=\frac{1}{2}\int_{r_1}^{r_2}\int_{0}^{2\pi}\left\{\begin{array}{l}\frac{Eh}{1-\nu^2}\left[(\varepsilon_1+\varepsilon_2)^2+2(1-\nu)\left(\frac{\gamma_{12}^2}{4}-\varepsilon_1\varepsilon_2\right)\right]+\\ +\quad D\left[(\kappa_1+\kappa_2)^2+2(1-\nu)\left(\tau^2-\kappa_1\cdot\kappa_2\right)\right]\end{array}\right\}B\,d\varphi\,dr \qquad (22)$$

Each deformation component in expression (22) defines the superposition of two solutions, for example: $\varepsilon_2=\varepsilon_2^{(1)}+\varepsilon_2^{(2)}$ etc. In so much as the deformations are proportional to either sin or cos, in you (22) it is necessary to calculate only a one-dimensional integral by the pen r, in which the deformations are replaced by their amplitude functions.

Bending stiffness of the blade is found by formula $K = \frac{2U}{\theta^2}$, where $\theta = \frac{L}{\rho}$

- Mutual rotation angle of shaft sections spaced apart by screw L pitch.

When calculating the screw as a bending rod, the rigidity of the blade (23) is added to the stiffness of the shaft *EI/L*. Figure 3 shows the dependence of the bending stiffness of the blade *K/(Eh)* 3 on the pitch L, *mm*.

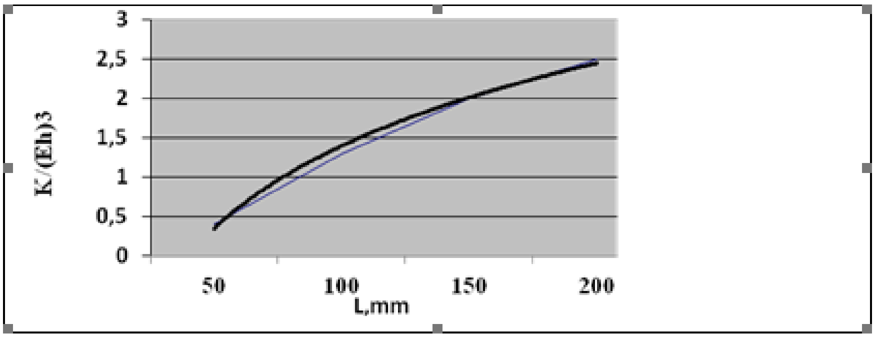


Figure 3 - Graphic dependence of bending stiffness of blade K/(Eh) 3 on pitch L, mm of screw line

Conclusion. According to the developed method, the screw of the auger press BT-3M for the production of coal briquettes was calculated. Calculation of the blade with r_1=0,04м parameters of m, r_1=0,04 м, r_2=0,1 м, r_3=0,03 м, thickness of the screw piston δ=0.005 blade of m, *L*=0.2 m, total length of a hollow shaft 1, 2 m is executed.

Calculations have shown that at such screw parameters and created specific pressure of material on the screw Ore = 8,5·10^5 Pa, the rigidity of the blade is the stiffness 11% of the tubular shaft. Reliability by capacity criterion P = 0.667, which is structurally insufficient.

In order to increase reliability, one-piece version of the screw with the developed casting technology can be offered.

Е.С. Абдрахманов[1], Б.Т. Ермағамбет[2],
Ж.М. Касенова[2], М.К. Казанкапова[2], А. Сайранбек[2]

[1] «С. Торайгыров атындағы Павлодар мемлекеттік университеті», Павлодар, Қазақстан;
[2] «Көмір химиясы және технология институты» ЖШС, Нұр-Сұлтан, Қазақстан

ИССЛЕДОВАНИЕ НАДЕЖНОСТИ ШНЕКОВОГО УЗЛА УГЛЕБРИКЕТНОГО ПРЕССА БТ-3М

Аннотация. Мақалада бір жазықтықта иілу кезінде шнектің бұрандалық алағының кернеулі күйі мен қаттылығының параметрлерін, бірмезгілде араластырып,тасымалдайтын және нығыздаушы түйін болып табылатын көмір брикеттерін өндіру үшін БТ-3М маркалы шнек-поршенді престің параметрлерін есептеу әдісін ұсынамыз. Ішкі бұрандалы шекара бойынша білікпен қатты бекітілген қалақты, осьтік бағытта жіңішке шексіз геликоид қабық ретінде қарастырамыз. Қалақтың болуы иілу кезінде тұрақты қима білігінің деформациясының сипатына әсер етпейді деп есептейміз, қалақтың бар болуын шнектің иілу қаттылығына әсері зерттелді. Осінің $1/\rho$ қисықтығы бар деп есептей отырып, біліктің майысуымен байланысты ішкі шекарада берілген орын ауыстырулар кезінде бұрандалы қалақтың деформациясы туралы тапсырма қаралды. Бұл ретте шнек торабы жұмыс істеген кезде біліктің майысуын, геликоид таспасының тозуын және аралас массаның біркелкі емес тығыздығымен туындататын белгісіздік жүктемелерді сынайды. Әрине, бұл жағдайларда шнектің қалақтары мен білігі әрдайым жоғары кернеумен болады деп айтуға болады. Қарастырылып отырған тапсырмада иілу шнектің бөлінген жүктемелер q_1, q_2, q_n жоқ, жауырынның барлық орамдары бірдей кернеулі күйде, сондықтан ішкі күш пен деформациялар ϕ координатаның периодтық функциялары болып табылады. Жылжыту U, V, w және бұрылу бұрыштарында ϑ_1, ϑ_2, Ω_n, мерзімділік қасиет жоқ. Екінші кезеңде дифференциалдық теңдеулерінде және статикалық шекаралық жағдайларда таңғыштарды жоятын компенсациялық шешім құралды, сонымен қатар қабықтың ішкі контурында қатты қысымның шарттарын қойылды. Нәтижесінде әзірленген әдістеме бойынша шнекті есептеу жүргізілді. r_1=0,04 м, r_2=0,1 м, r_3=0,03 м м параметрлер арқылы қалақты есептеу орындалды, шнекті қалақтың қалыңдығы δ=0,005 м, L=0,2 м, қуыс біліктің жалпы ұзындығы 1, 2 м. Есептеу нәтижесінде, шнектің белгіленген параметрлерінде және кен шнектерінде материалда пайда болатын меншікті қысым $P_{уд}$=8,5•10^5Па, қалақтың қаттылығы құбырлы біліктің қаттылығының 11% құрайтынын көрсетті. Ең алдымен, қалақ нүктелерінің жылжу өзгерісінің жақын заңын белгілейміз, бұл оның t_1 , n орталары арқылы өтетін радиалды қималары деформацияланбауын көрсетеді (сурет 2).Бұл ретте кинематикалық шекаралық жағдайлар (3) және (4) қанағаттандырылады. Есептеудің екінші кезеңде дифференциалдық теңдеулерінде тепе-теңдік (5) және статикалық шекаралық жағдайларда (8) таңғышты жоятын компенсациялық шешім түземіз, сонымен қатар қабықтың ішкі контурында қатты қысым шарттарын қоямыз. Сонымен, кернеулі-деформацияланған күйдің барлық компоненттерін $f = f^{(1)} + f^{(2)}$ қосындылары түрінде елестетеміз , мұнда $f^{(1)}$ – қабықшаның білікпен жанасуының кинематикалық шекаралық шарттарын қанағаттандыратын, жақындатылған шешімнің компоненттері, ал $f^{(2)}$ – компенсациялық шешімнің компоненттері.

Түйін сөздер: шнек, пресс, есептеу, брикет, қалақ, теңдеу.

Е.С. Абдрахманов[1], **Б.Т. Ермағамбет**[2],
Ж.М. Касенова[2], **М.К. Казанкапова**[2], **А.Сайранбек**[2]

[1] «Павлодарский государственный университет им. С. Торайгырова», Павлодар, Казахстан;
[2]ТОО « Институт химии угля и технологии», Нур-Султан, Казахстан

ИССЛЕДОВАНИЕ НАДЕЖНОСТИ ШНЕКОВОГО УЗЛА УГЛЕБРИКЕТНОГО ПРЕССА БТ-3М

Аннотация. В статье предлагается метод расчета параметров напряженного состояния и жесткости винтовой лопасти шнека при изгибе в одной плоскости, шнекопоршневого пресса марки БТ-3М для производства угольных брикетов являющего одновременно смешивающим, транспортирующим и прессующим узлом. Лопасть рассматриваем как тонкую бесконечную в осевом направлении геликоидную оболочку, жестко скрепленную с валом по внутренней винтовой границе. Считая, что наличие лопасти не влияет на характер деформаций вала постоянного сечения при изгибе, исследуем влияние наличия лопасти на изгибную жесткость шнека. Рассмотрена задача о деформациях винтовой лопасти при заданных перемещениях на внутренней границе, обусловленных изгибом вала, считая, что его ось имеет кривизну

При этом шнековый узел испытывает при работе изгиб вала, износ геликоидной ленты и знакопеременные нагрузки, вызываемые неравномерной плотностью смешиваемой массы. Естественно, в рассмотренных этих случаях, можно утверждать, что лопасти и вал шнека всегда будет находиться под высоким напряжением. В рассматриваемой задаче изгиба шнека распределенные нагрузки q_1, q_2, q_n отсутствуют, все витки лопатки находятся в одинаковом напряженном состоянии, поэтому внутренние усилия и деформации являются периодическими функциями координаты. Перемещения u, v, w и углы поворота, свойством периодичности не обладает. Во втором этапе расчета строим компенсирующее решение, которое устраняет невязки в дифференциальных уравнениях равновесия и статических граничных условиях, причем на внутреннем контуре оболочки ставим условия жесткого защемления. В результате по разработанной методике проведены расчеты шнека. Выполнен расчет лопасти с параметрами r_1=0,04 м, r_2=0,1 м, r_3=0,03 м, толщина шнековой лопасти δ=0,005 м, L=0,2 м, общая длина полого вала 1, 2м. Расчеты показали, что при таких параметрах шнека и создаваемом удельном давлении материала на шнек $P_{уд}=8,5\bullet10^5$ Па , жесткость лопасти составляет 11% жесткости трубчатого вала. Сначала задаем приближенный закон изменения перемещений точек лопасти в предположении, что ее радиальные сечения, проходящие через орты $\mathbf{t}_1$, $\mathbf{n}$ (рис. 2), не деформируются. При этом предполагается, что удовлетворяются кинематические граничные условия (3) и (4).Во втором этапе расчета строим компенсирующее решение, которое устраняет невязки в дифференциальных уравнениях равновесия (5) и статических граничных условиях (8), причем на внутреннем контуре оболочки ставим условия жесткого защемления. Итак, все компоненты напряженно-деформированного состояния представим в виде сумм $f = f^{(1)} + f^{(2)}$, где $f^{(1)}$ – компоненты приближенного решения, удовлетворяющего кинематическим граничным условиям сопряжения оболочки с валом, а $f^{(2)}$ – компоненты компенсирующего решения.

Ключевые слова: шнек, пресс, расчет, брикет, лопасти, уравнения.

Information about the authors:

Abdrakhmanov Ermagambet Seisenbekovich - Candidate of technical sciences, Professor "Pavlodar State University of S. Toraygyrov", Pavlodar, Kazakhstan, e-mail: erai1512@mail.ru, https://orcid.org/0000-0001-9726-1642;

Yermagambet Bolat Toleukhanuly– Doctor of Chemical Science, Professor, Director of LLP "Institute of Coal Chemistry and Technology", Nur-Sultan, Kazakhstan, e-mail:bake.yer@mail.ru; https://orcid.org/0000-0003-1556-9526;

Kassenova Zhanar Muratbekovna – Master of Chemical Sciences and Technology, Deputy Director of LLP "Institute of Coal Chemistry and Technology", Nur-Sultan, Kazakhstan, e-mail: zhanar_k_68@mail.ru;https://orcid.org/0000-0002-9497-7319;

Kazankapova Maira Kuttybaevna - PhD in Philosophy, LLP "Institute of Coal Chemistry and Technology", Nur-Sultan, Kazakhstan, e-mail: maira_1986@mail.ru; https://orcid.org/0000-0001-9016-3062;

Sairanbek Asiya – Master of Chemical Sciences and Technology, Junior researcher of LLP "Institute of Coal Chemistry and Technology", Nur-Sultan, Kazakhstan, e-mail: asi_48@mail.ru, https://orcid.org//0000-0001-7763-2450

REFERENCES

[1] Nikishanin M.S., ZagrutdinovR.Sh., Senachin P.K. (2016) Briquetting of local fuels and waste for energy supply systems in rural areas [Briketirovaniye mestnykh topliv i otkhodov dlya sistem energoobespecheniya v sel'skoy mestnosti] 1:88-95 (in Russ.).

[2] Sabyrov T., Abdrakhmanov E. S. (2004) Calculation and study of the hydro-mechanical and hydrodynamic characteristics of the mixing apparatus with mixers. Part I [Raschet i issledovaniye gidromekhanicheskikh i gidrodinamicheskikh kharakteristik smeshivayushchego apparata meshalkami. ch. I] 1:49 – 58 (in Russ.).

[3] Sabyrov T., Abdrakhmanov E.S (2005) Calculation and study of the hydro-mechanical and hydrodynamic characteristics of the mixing apparatus with stirrers. Part II [Raschet i issledovaniye gidromekhanicheskikh i gidrodinamicheskikh kharakteristik smeshivayushchego apparata meshalkami. ch. II] 3:98-110 (in Russ.).

[4] Vodnev V. T., Naumovich A. F., Naumovich N. F. (1984) Mathematical Dictionary of Higher Education. Vysh. School, Minsk. ISBN: 978-00-1296937-0

[5] Ilyin V. A., Poznyak E. G. (2002) Fundamentals of mathematical analysis. Part II. Science, Moscow. ISBN: 5-9221-0131-5

[6] Goldenweiser A. L. (1976) The theory of elastically thin shells. Science, Moscow.

[7] Novozhilov V. V., Chernykh K. F., Mikhailovsky E. I. (1991) Linear theory of thin shells. Polytechnic , Leningrad. ISBN: 5-7325-0127-4

[8] Alexandrov A.V., Potapov V.D. (1990) Fundamentals of the theory of elasticity and plasticity. High school, Moscow. ISBN: 5-06-000053-2

[9] Bauman V.A., Klushantsev B.V., Martynov V.D. (1981) Mechanical equipment of building materials and products enterprises. Engineering, Moscow.

[10]Gorsky A.I. (1978) Calculation of machines and mechanisms of automatic foundry production lines. Engineering, Moscow.

[11]Kuznetsova V.I., Barzilovich E.Yu. (1990) Reliability and efficiency in technology. Volume 8, Engineering, Moscow.

[12]Vygodsky M.I. (2002) Handbook of Higher Mathematics. Science, Moscow. ISBN: 5-271-03651-0

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.33**
Volume 2, Number 440 (2020), 129 – 137

UDC 541.13:669.537
IRSTI 31.15.35

A.B. Bayeshov[1], A.K. Mamyrbekova[2], M.K. Kassymova[3],
A.D. Mamitova[3], A.K. Mamyrbekova[2], O.N. Chechina[4]

[1]D.V. Sokolsky institute of fuel, catalysis and electrochemistry, Almaty, Kazakhstan;
[2]Khoja Akhmet Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan;
[3]M. Auezov South Kazakhstan state university, Shymkent, Kazakhstan;
[4]Samara state technical university, Samara, Russia.
E-mail: bayeshov@mail.ru; aizhan.mamyrbekova@ayu.edu.kz; mahabbat_67@mail.ru;
a-mamitova@mail.ru; aigul.mamyrbekova@ayu.edu.kz; chechinao@yandex.ru

EFFECT OF SURFACTANTS ON THE REDUCTION OF LEAD(II) IONS ON LEAD ELECTRODE

Abstract. The effect high molecular weight water-soluble surfactants with different functional groups have on the electroreduction of lead(II) ions on a lead electrode in various electrolytes is studied. A copolymer of methacryloylaminophenol with acrylic acid, a leather waste hydrolyzate, and a copolymer of monoethanolamine with vinyl ether acetate are used as surfactants. The electrolytes that are used are 1 M KCl, KBr, KNO_3, HCOONa, NH_2SO_3H, 0.5 M Na_2SO_4, and 0.35 M $Na_3C_6H_5O_7\cdot 2H_2O$. It is shown that in 1.0 M KCl or KBr solutions, there is no inhibition of the electroreduction of lead(II) ions by the adsorption layers of surfactants. It is found that the inhibitory effect of polymers on the electroreduction of lead(II) ions in different background electrolytes increases in the order KCl > KBr > $Na_3C_6H_5O_7\cdot 2H_2O$ > Na_2SO_4 > KNO_3 > HCOONa > NH_2SO_3H.

Key words: lead ions, electroreduction, surfactants, electrolyte, lead electrode, exchange current.

Introduction. Surfactants are widely used to improve the cathodic deposits of metals and alloys, to obtain coatings with desired physicochemical properties, and as additives to electrolytes for metal refining and corrosion inhibitors [1–3].

A great many studies have recently been devoted to the effect surfactants have on electrode processes. Most of them reflect the effect low-molecular compounds have on electrode processes, and only a few discuss the effects of high-molecular compounds [4–7].

In recent years, there has been growth of interest in studies on additions of water-soluble polymers with several functional groups with different properties, which provide high adsorption capacity on electrodes and have an appreciable effect on the electrode reactions [8, 9].

It is known that the presence of surfactants makes it difficult for electrode processes to proceed, as it produces an inhibitory effect explained by the blocking of the electrode’s surface [10, 11]. The inhibitory effect of organic additives also depends on a number of other factors, including the composition of the electrolyte [12–15]. The inhibitory effect of the additive depends on the nature of the anions of the electrolyte, so it is impossible to predict continuation of the effect of inhibition in different electrolytes. If we know the general patterns of the effect organic substances have on the anions of a background electrolyte and their interaction with them, we can interpret the mechanism of electrode processes, and in some cases adjust the rate of electrochemical reactions [16-18].

Therefore, investigation of the electroreduction of metal ions on electrodes in the presence of polymer additives with several functional groups that provides the necessary physicochemical properties of the electrolyte (scattering power, viscosity, electric conductivity, etc.) is very important from both theoretical and practical viewponits.

The aim of this work was to study the effect a number of organic compounds have on the rate of lead electroreduction on a lead electrode in electrolytes, in the presence of different anions of the background electrolyte.

Methods. The effects of a number of surfactants were studied:a copolymer of ethacryloylaminophenol with acrylic acid (CMAAP-AA) (Mr = 15000–20000), a hydrolyzate of leather industry waste (HLIW), and a monoethanolamine vinyl ether acetate copolymer (VEMEA) (Mr = 50000–100000). Electrolytes of the following composition were studied: 1 M KCl, KBr, KNO_3, HCOONa, NH_2SO_3H, 0.5 M Na_2SO_4, and 0.35 M $Na_3C_6H_5O_7 \cdot 2H_2O$.

KCl and KBr were chosen as the background electrolytes,due to their strong adsorption activity. The accelerating effect halogen ions have on electrode processes is well known. $Na_3C_6H_5O_7 \cdot 2H_2O$ and HCOONa were chosen from among the organic acids, since they are inert; the NO_3^- ion is a weakly adsorbable anion. It was of interest to use 1.0 M NH_2SO_3H as the background electrolyte for purposes of comparison against other electrolytes, since the inhibitory effect of the SO_3H - ion in the presence of surfactants is strong. It was of particular interest to study Na_2SO_4 as the background electrolyte, since the SO_4^{2-} anion does not participate in adsorption. We studied the electrochemical behavior of lead(II) ions in the 0.067×10^{-2} to 1.33×10^{-2} wt % range of surfactant concentrations at 298–328 K. The kinetics of the discharge of lead(II) ions on a polycrystalline lead electrode was studied by measuring the polarization curves using a P-5827M potentiostat.

Results and discussions. Our studies of the electroreduction of lead(II) ions on a solid electrode against a background of 1.0 M KCl, 1.0 M KBr, 1.0 M KNO_3 and 0.35 M $Na_3C_6H_5O_7 \cdot 2H_2O$ showed surfactants had no effect on the discharge of lead ions(II). This was due to the high specific adsorption of halogen ions on the surface of a lead electrode, which can compete with the adsorption of adsorbate molecules. The result is that no inhibition is observed. The depolarizing effect halogen ions have on inhibition could be due to two phenomena. The first is the altered structure of the adsorption layer, caused by the adsorption of both halogen ions and surfactant molecules. The second is associated with the catalytic action of halogen ions; their low content in solution accelerates the electrode process.

Figure 1 shows the polarization curves of the electroreduction of lead(II) ions on a lead electrode against 0.5 M Na_2SO_4 with and without a surfactant at T = 298 K. Adding a surfactant to the solution greatly inhibits the discharge of lead(II) ions, which is apparent from the falling reduction current and a substantial increase in polarization. When the content of the surfactant in the solution is increased, the degree of inhibition grows and the drop in the limiting current becomes greater in the region of negative potentials. The polarization curves of the electroreduction of lead(II) ions in the presence of HLIW are N-shaped, which is characteristic of the discharge of lead(II) ions in the presence of nitrogen-containing surfactants.

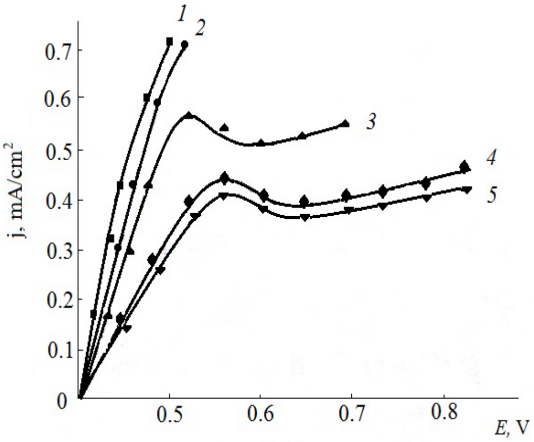


Figure 1 - Polarization curves for the electroreduction of lead(II) ions on a lead electrode obtained at T = 298 K on the background of 0.5 M Na_2SO_4 in the presence of surfactants and without them HLIW. Csurf $\times 10^3$, wt %: (*1*) 0.00, (*2*) 2.00, (*3*) 5.30, (*4*) 13.30

A similar study was conducted in the presence of CMAAP-AA and VEMEA. The introduction of polymer surfactants into the solution accelerates the electrode process. With increasing surfactant content in the solution, the discharge of lead(II) ions accelerates. This is manifested in an increase in recovery currents and a decrease in polarization.

Polarization curves of lead(II) ion discharge in the HCOONa solution in the absence and presence of polymer surfactants at T=298 K indicate that the introduction of CMAAP-AA and VEMEA into the solution leads to inhibition of the lead(II) ion discharge process. With increasing concentration of additive CMAAP-AA and VEMEA in solution increases the slump of the limiting current and increases the polarization. With the increase in the content of these surfactants in solution inhibitory action CMAAP-AA and VEMEA diminished In the case of HLIW the introduction of surfactant in the solution leads to inhibition of the process of discharge of ions of lead(II), accompanied by a reduction in currents reconstruction and zoom eniem polarization. With an increase in the concentration of the HLIW additive in the solution, the degree of inhibition increases, the decline of the limiting current increases.

In the presence of HLIW, a similar picture is observed in 1.0 M NH_2SO_3H and 1.0 M KNO_3 solutions. It should be noted that in the presence of CMAAP-AA and VEMEA in a solution of 1.0 M NH_2SO_3H, the addition of copolymers leads to inhibition of the process, manifested in a decrease in the limiting reduction current. At the same time, there is a slight increase in polarization. With increasing concentration of surfactant additives in the solution, the degree of inhibition increases. However, at surfactant concentration above 1.33.10-2 wt. % there is some weakening of the inhibitory effect of surfactants.

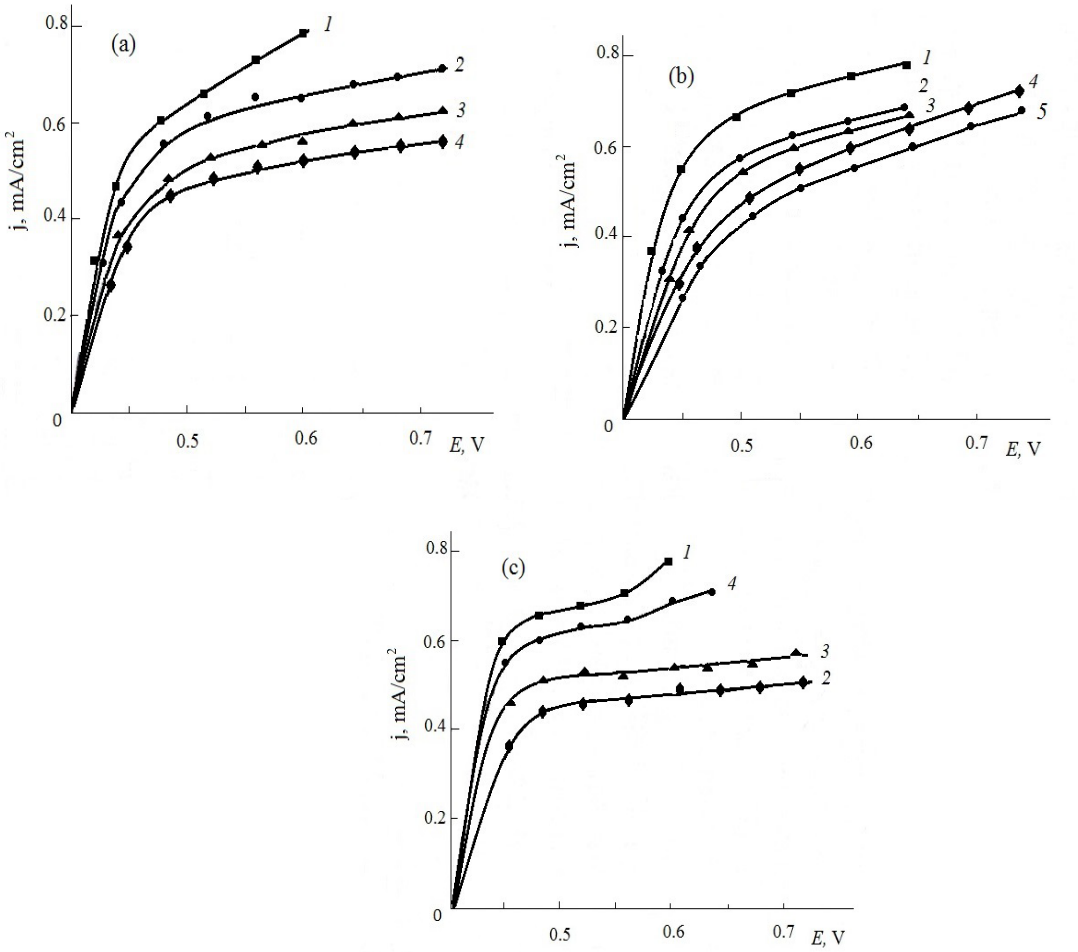


Figure 2 - Polarization curves for the electroreduction of lead(II) ions on a lead electrode obtained at T = 298 K on the background of 1.0 M HCOONa in the presence of surfactants and without them:
(a) CMAAP-AA, C_{surf} $\times 10^3$, wt %: (*1*) 0.00, (*2*) 2.00, (*3*) 5.30, (*4*) 13.30.
(b) HLIW, C_{surf} $\times 10^3$, wt %: (*1*) 0.00, (*2*) 2.00, (*3*) 5.30, (*4*) 6.70, (*5*) 13.30.
(c) VEMEA. C_{surf} $\times 10^3$, wt %: (*1*) 0.00, (*2*) 2.00, (*3*) 5.30, (*4*) 6.70, (*5*) 13.30

The obtained polarization curves were analyzed as described in [19], and the dependences for the electroreduction of lead(II) ions were constructed:

$$\ln i/(1-e^{(nF\eta/RT)})-\eta$$

where i is the current density, n is the number of electrons transmitted, F is the Faraday constant, η is the overvoltage, R is the universal gas constant, and T is the absolute temperature. In the investtigated region of polarization (figure 3), the dependences were linear and parallel to one another, testifying to the constant value of the transfer coefficient. The data are presented in table 1.

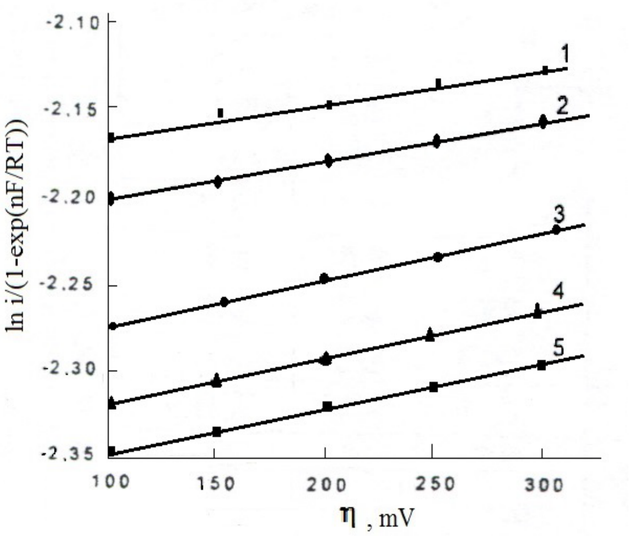


Figure 3 - Semi-logarithmic dependences of electroreduction of lead(II) ions at T=298 K in the absence and presence of HLIW. C_{surf} ×10^3, wt %: 1 – 0.00; 2 – 2.00; 3 – 5.30; 4 – 6.70; 5 – 13.30

The data are presented in table 1.

Table 1 - Values of transfer coefficients α for electroreduction of lead ions (II) in various electrolytes in the presence of surfactants and without them at T=298 K

surfactants background	without surfactants	CMAAP-AA	HLIW	VEMEA
KNO_3	0.33+0.01	0.33	0.33	0.33
NH_2SO_3H	0.62+0.01	0.62	0.62	0.62
HCOONa	0.22+0.01	0.22	0.22	0.22

The electroreduction of lead(II) ions proceeds in two stages:

$$Pb^{2+} \rightarrow Pb_s^{2+} + 2e \rightarrow Pb$$

Table 2 - Exchange currents (jo × 10^3, A/cm^2) of the electroreduction of lead(II) ions in different electrolytes in the presence of CMAAP-AA at T = 298–328 K

Electrolyte	T, K	C_{surf} ×10^3, wt %					
		0	2.0	4.0	5.3	7.0	13.3
1.0 M NH_2SO_3H	298	5.0	4.6	3.7	3.3	3.2	3.7
	308	5.1	5.4	5.3	4.4	3.9	3.8
	318	6.8	5.3	4.6	3.8	4.1	3.9
	328	6.3	6.3	4.2	4.7	4.7	4.7
1.0 M HCOONa	298	5.9	5.3	4.9	4.3	4.1	3.9
	308	6.4	5.9	5.7	5.6	5.8	5.7
	318	6.3	-	-	-	-	-
	328	6.7	-	-	-	-	-

The slowing of the electron transfer stage does not affect the adsorption of Pb^{2+} ions on the electrode. The constant transfer coefficient testifies to the uniform mechanism of the discharge of Pb^{2+} ions. Exchange currents jo for the discharge of lead ions(II) were calculated from dependences. The exchange currents (jo × 10^3, A/cm^2) of the electroreduction of lead(II) ions in different electrolytes in the presence of surfactants are given in tables 2,3.

Table 3 - Exchange currents (jo × 10^3, A/cm^2) of the electroreduction of lead(II) ions in different electrolytes in the presence of VEMEA at T = 298–328 K

Electrolyte	T, K	C_{surf} ×10^3, wt %					
		0	2.0	4.0	5.3	7.0	13.3
1.0 M NH_2SO_3H	298	5.0	4.8	4.7	4.6	3.4	4.1
	308	5.4	4.9	4.8	4.7	4.5	4.5
	318	6.3	6.3	6.2	5.4	4.5	4.7
	328	6.3	6.4	5.9	5.8	4.8	4.8
1.0 M HCOONa	298	5.9	4.6	4.2	3.9	5.4	5.4
	308	6.4	5.4	5.4	5.2	5.1	7.0
	318	6.3	5.9	5.7	5.5	5.4	7.1
	328	6.7	6.9	6.2	5.9	5.5	7.4

Analysis of the data presented in the tables shows that depending on the background anion when there are no surfactants, the rate of the electroreduction of lead(II) ions slows in the order

$$KCl > KBr > Na_3C_6H_5O_7 \cdot 2H_2O > Na_2SO_4 > KNO_3 > HCOONa > NH_2SO_3H.$$

Adding a surfactant lowers jo, indicating that this process is slowed. It should be noted that in a solution of 0.5 M Na_2SO_4, the electroreduction of lead(II) ions is strongly inhibited in the presence of a surfactant. This is because an adsorption surfactant film forms on the electrode’s surface. The inhibitory effect of the surfactant additive depends on the nature of the electrolyte anions and is enhanced in the presence of CMAAP-AA in the order

$$KNO_3 > HCOONa > NH_2SO_3H > Na_2SO_4$$

while with HLIW and VEMEA we have

$$Na_2SO_4 > KNO_3 > HCOONa > NH_2SO_3H.$$

The dependences obtained for the discharge of lead(II) ions with and without surfactants are linear and parallel to one another; i.e., the mechanism behind the inhibition of the electrore-duction of lead(II) ions in the presence of surfactants at high temperatures remains unchanged.

The values of transfer coefficient α for the discharge of lead(II) ions at on a lead electrode remain constant. The constancy of α suggests that the mechanism of the discharge of lead(II) ions was not changed in the presence of surfactants. It is inhibited at the stage where depolarizer ions penetrate into the surface layer. The analysis of tables 2,3 shows that in solutions of 1.0 M NH_2SO_3H and 1.0 M HCOONa with increasing temperature the inhibitory effect of CMAAP-AA and VEMEA weakens. The inhibitory effect of HLIW persists at T=328 K. In solutions 1.0 M KNO_3 and 0.5 M Na_2SO_4 inhibition of electricoreduction of lead ions (II) adsorption surfactant film is not observed.

A temperature-kinetic analysis of the polarization curves in the range T = 298–328 K with no surfactants was performed using the technique proposed in [20]. The temperature–kinetic curves for the discharge of lead ions(II) without surfactants and with surfactants are linear and independent of the overvoltage. Using these data, we calculated the effective energies of activation of the electroreduction of lead(II) ions in different electrolytes with and without surfactants. Our findings are listed in table 4.

Table 4 - Effective energy of activation (A_{eff}, kJ/mol) of the electroreduction of lead(II) ions in different electrolytes

Electrolyte	With no surfactants	CMAAP-AA	HLIW	VEMEA
NH_2SO_3H	11.5	9.6	15.3	19.1
HCOONa	11.5	45.0	-47.5	6.8
KNO_3	11.5	-	2.3	-

Conclusion. Thus, the obtained experimental data allow to conclude that on the background of 1.0 M KCl, KBr 1.0, 0.35 M $Na_3C_6H_5O_7 \cdot 2H_2O$ 2O inhibition of the electroreduction of lead ions(II) adsorption of the surfactant film at the studied temperatures was observed.

In other cases, the rate of electrical recovery of lead ions (II) in dependence on surfactants decreases in a row:

HLIW > CMAAP-AA > VEMEA.

Temperature studies show that the discharge of lead(II) ions in the presence of surfactants is inhibited at T=328 K. It was found that the inhibitory effect of polymers on the electrical recovery of lead(II) ions in electrolytes increases in the following sequence:

$$KCl > KBr > Na_3C_6H_5O_7 \cdot 2H_2O > Na_2SO_4 > KNO_3 > HCOONa > NH_2SO_3H.$$

А.Б. Баешов[1], А.К. Мамырбекова[2], М.К. Касымова[3],
А.Д. Мамитова[3], А.К. Мамырбекова[2], О.Н. Чечина[4]

[1]Д.В. Сокольский атындағы жанармай, катализ және электрохимия институты, Алматы, Казахстан;
[2]Қ.А. Ясауи атындағы Халықаралық қазақ-түрік университеті, Түркістан, Қазақстан;
[3]М. Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент, Қазақстан;
[4]Самара мемлекеттік техникалық университеті, Самара, Россия

ҚОРҒАСЫН ЭЛЕКТРОДЫНДА ҚОРҒАСЫН ИОНДАРЫН(II) ТОТЫҚСЫЗДАНУЫНА БЕТТІК-АКТИВТІ ЗАТТАРДЫҢ ӘСЕРІ

Аннотация. Беттік-активті заттар (БАЗ) металдардың катодты тұнбалары мен құймаларды жақсарту үшін, берілген физикалық-химиялық қасиеттері бар жабындыларды алу үшін, металдарды рафинирлеу электролиттеріне және коррозия ингибиторларына қоспалар ретінде кеңінен қолданылады.

Электродты процестеріне БАЗ-дың әсерін зерттеуге көптеген зерттеулер арналған, олардың көпшілігі төмен молекулалық қосылыстардың электродтық процестеріне әсерін және тек аз ғана жұмыстар саны - жоғары молекулалық қосылыстардың әсерін қарастырылған. Соңғы уақытта ғалымдардың назарын электродтарда жоғары адсорбциялық қабілетті қамтамасыз ететін және электродты реакцияларға елеулі әсер ететін, қасиеттері бойынша ерекшеленетін функционалдық топтары бар, суда еритін полимерлердің қоспалары бойынша зерттеулер қызықтырады. Электролиттің қажетті физико-химиялық қасиеттерін (шашырату қабілеті, тұтқырлығы, электрөткізгіштігі және т.б.) қамтамасыз ететін бірнеше функционалдық топтары бар полимерлік қоспалардың қатысуымен электродтарда металл иондарын электртотықсыздануы өте өзекті мәселе болып табылады, сонымен бірге теориялық және практикалық маңызы бар.

Әртүрлі функционалдық топтармен (акрил қышқылы бар метакрилоиламинофенолдың сополимері (АҚ-МААФС), Mr=15-20 мың, былғары өнеркәсібі қалдықтарының гидролизаты (БӨҚГ) және моноэтаноламин винил эфирінің ацетатының сополимері (МЭАВЭ), Mr =50-100 мың) суда еритін жоғары молекулалы беттік-активті заттардың (БАЗ) аттас электродта қорғасын иондарының(II) әртүрлі электролиттерде электртотық-сыздануына әсері зерттелді.

Жұмыста келесі электролиттер зерттелді: 1 М KCl, KBr, KNO_3, HCOONa, NH_2SO_3H, 0.5 M Na_2SO_4, 0.35 M $Na_3C_6H_5O_7 \cdot 2H_2O$. Фондық электролит ретінде күшті адсорбциялық белсенділікке байланысты KCl және KBr таңдалған. Галоидты иондардың электродтық процестерге жеделдейтін әсері белгілі. $Na_3C_6H_5O_7 \cdot 2H_2O$, HCOONa органикалық қышқылдардан инертті болғандықтан таңдалған. NO_3^- ион аз адсорбцияланатын аниондарға жатады.

Фондық электролит ретінде басқа электролиттермен салыстыру үшін 1.0 М NH_2SO_3H зерттелген, өйткені БАЗ қатысуымен SO_3H- ионның тежеуіш әсері үлкен. Анион SO_4^{2-} адсорбциялық белсенділігі төмен болғандықтан, фондық электролит ретінде Na_2SO_4 зерттеуі де белгілі бір қызығушылық тудырды.

Қорғасын иондарының(II) қорғасын электродында электрохимиялық қасиеттері қарастырылатын БАЗ-дың концентрация интервалында $6.7 \cdot 10^{-4} \div 1.33 \cdot 10^{-2}$ масс. % және температура 298-328 К аралығында зерттелді.

Эксперименталды нәтижелерді талдау кезінде қорғасын иондарының(II) электртотықсыздану жылдамдығы БАЗ болмаған кезде фонның анионына байланысты келесі қатар бойынша (барлық зерттелген температураларда) анықталды: HCOONa > KNO_3 > NH_2SO_3H > $Na_3C_6H_5O_7$ > Na_2SO_4. АҚ-МААФС қатысуымен зерттелген электролиттерде оның ингибирлеуші әсері келесі қатарда күшейтіледі: KNO_3 > HCOONa > NH_2SO_3H > Na_2SO_4, БӨҚГ қатысында келесі қатарға Na_2SO_4 > KNO_3 > HCOONa > NH_2SO_3H ие.

Алынған тәжірибелік нәтижелер бойынша фон ретінде қарастырылған 1.0 М KCl, 1.0 KBr, 0.35 M $Na_3C_6H_5O_7 \cdot 2H_2O$ ерітінділерде зерттелген температураларда адсорбциялық БАЗ пленкасымен қорғасын иондарының электртотықсыздануының тежеу байқалмайды. Қалған жағдайларда қорғасын(II) иондарының электртотықсыздану жылдамдығы БАЗ-ға байланысты келесі қатарда: БӨҚГ > АҚ-МААФС > МЭАВЭ.

Температуралық зерттеулер қорғасын иондарының(II) разряды қарастырылатын БАЗ қатысуымен T=328 K кезінде де тежеуді көрсетеді. Электролиттерде қорғасын иондарын(II) электртотықсыздануына полимерлердің ингибирлеуші әсері келесі ретпен өседі: KCl > KBr > $Na_3C_6H_5O_7 \cdot 2H_2O$ > Na_2SO_4 > KNO_3 > HCOONa > NH_2SO_3H. Температура 298-328 K аралығында поляризациялық қисықтардың температура-лық-кинетикалық талдау жүргізілді. БАЗ қатысуында н қорғасын(II) иондар разрядының температуралық-кинетикалық қисықтар түзу сызықты болып келеді.

Электролиттерде БАЗ қатысуында және қатысуыңсыз температура 298-328 K кезінде қорғасын (II) иондарының электртотықсыздану үшін ауысу коэффициенттерінің (α) шамалары есептелген.

Әртүрлі электролиттерде БАЗ қатысуында және қатысуыңсыз температура 298-328 K кезінде қорғасын (II) иондарының электртотықсыздану үшін алмасу токтарының мәндері ($j_o \cdot 10^3$ А/см^2) есептелген.

Электролиттерде БАЗ қатысуымен қорғасын(II) иондар разрядының тиімді активтендіру энергиясының шамалары есептелген. БАЗ қатысуымен үш негізгі жағдайды көрсетуге болады. Активтендіру энергиясы артады. Бұл құбылыс қосымша потенциалды кедергінің пайда болуын көрсетеді, яғни тежеудің активациялық механизмі орын алады. Активтендіру энергиясы азаяды, яғни қорғасын(II). иондарының разряды жеңілдетіледі Активтендіру энергиясы теріс мәнге ие, температуралық-кинетикалық қисық кері тәуелділікке ие. Бұл, электрод бетін толтыру дәрежесінің өзгеруімен температураның жоғарылауы кезінде компенсациялық әсер құбылысымен байланысты.

Жұмыста зерттелген БАЗ қорғасын электродында адсорбцияланады және максималды адсорбция аймағы- 0.4 ÷ -1.0 В интервалында орналасқан. Қорғасынның нөлдік зарядының потенциалы $E_{q=0}$ = - 0.56 В, ал тепе-теңдік потенциалы E_p = - 0.126 В тең. БАЗ қатысуыңсыз қорғасын(II) иондарының разряды электродтың оң зарядталған бетінде өтеді.

Түйін сөздер: қорғасын иондары, электртотықсыздану, беттік-активті заттар, электролит, қорғасын электродыы, алмасу тогы.

А.Б. Баешов[1], А.К. Мамырбекова[2], М.К. Касымова[3],
А.Д. Мамитова[3], А.К. Мамырбекова[2], О.Н. Чечина[4]

[1]Институт топлива, катализа и электрохимии им. Д.В. Сокольского, Алматы, Казахстан;
[2]Международный казахско-турецкий университет им. Х.А. Ясави, Туркестан, Казахстан;
[3]Южно-Казахстанский государственный университет им. М. Ауэзова, Шымкент;
[4]Самарский государственный технический университет, Самара, Россия

ВЛИЯНИЕ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ НА ВОССТАНОВЛЕНИЕ ИОНОВ СВИНЦА(II) НА СВИНЦОВОМ ЭЛЕКТРОДЕ

Аннотация. Поверхностно-активные вещества (ПАВ) нашли широкое применение для улучшения катодных осадков металлов и сплавов, получения покрытий с заданными физико-химическими свойствами, в качестве добавок в электролиты рафинирования металлов и ингибиторов коррозии.

Изучению действия ПАВ на электродные процессы посвящено большое количество исследований, большинство из которых отражает влияние на электродные процессы низкомолекулярных соединений и только незначительное число работ - действие высокомолекулярных соединений. В последнее время все большее внимание ученых привлекают исследования по добавкам водорастворимых полимеров с несколькими различающимися по свойствам функциональными группами, которые обеспечивают высокую адсорбционную способность на электродах и оказывают заметное влияние на электродные реакции. Электровосстановление ионов металлов на электродах в присутствии полимерных добавок с несколькими функциональными группами, которое обеспечивает необходимые физико-химические свойства электролита (рассеивающая способность, вязкость, электропроводность и др.) очень актуально и имеет как теоретическое, так и практическое значение.

Исследовано влияние высокомолекулярных, растворимых в воде поверхностно-активных веществ (ПАВ) с различными функциональными группами (сополимер метакрилоиламинофенола с акриловой кислотой, Mr=15-20 тыс, гидролизат отходов кожевенной промышленности и сополимер ацетата винилового эфира моноэтаноламина, Mr =50-100 тыс.) на электровосстановление ионов свинца(II) на одноименном электроде в различных электролитах.

Исследованы электролиты следующего состава: 1 M KCl, KBr, KNO_3, HCOONa, NH_2SO_3H, 0.5 M Na_2SO_4, 0.35 M $Na_3C_6H_5O_7 \cdot 2H_2O$. В качестве фонового электролита выбраны KCl и KBr ввиду сильной адсорбционной активности. Известно ускоряющее действие галоидных ионов на электродные процессы.

$Na_3C_6H_5O_7 \cdot 2H_2O$, HCOONa выбраны потому, что являются инертными из числа органических кислот. NO_3^- ион относится к малоадсорбирующимся анионам.

В качестве фонового электролита изучен 1.0 М NH_2SO_3H для сравнения с другими электролитами, так как тормозящее действие SO_3H- иона в присутствии ПАВ велико. Определенный интерес представляло также изучение Na_2SO_4 в качестве фонового электролита, так как анион SO_4^{2-} адсорбционно малоактивен.

Исследовано электрохимическое поведение ионов свинца(II) на свинцовом электроде в присутствии выбранных ПАВ в области концентрации $6.7 \cdot 10^{-4} \div 1.33 \cdot 10^{-2}$ масс. % в интервале температур T = 298-328 К.

Анализ экспериментальных данных показывает, что скорость электровосстановления ионов свинца(II) в зависимости от аниона фона в отсутствие ПАВ убывает в ряду (при всех исследованных температурах): HCOONa > KNO_3 > NH_2SO_3H > $Na_3C_6H_5O_7$ > Na_2SO_4 . В присутствии СМААФ-АК его ингибирующее действие в исследованных электролитах усиливается в следующем ряду: KNO_3 > HCOONa > NH_2SO_3H > Na_2SO_4, в случае ГОКП имеет вид: Na_2SO_4 > KNO_3 > HCOONa > NH_2SO_3H

Полученные экспериментальные данные позволяют сделать заключение, что на фоне 1.0 М KCl, 1.0 KBr, 0.35 М $Na_3C_6H_5O_7 \cdot 2H_2O$ ингибирования электровосстановления ионов свинца(II) адсорбционной пленкой ПАВ при изученных температурах не наблюдается. В остальных случаях скорость электровосстановления ионов свинца(II) в зависимости от ПАВ убывает в ряду: ГОКП > СМААФ-АК > ВЭМЭА.

Температурные исследования показывают, что разряд ионов свинца(II) в присутствии полученных ПАВ ингибируется и при T=328 К. Установлено, что ингибирующее действие полимеров на электровосстановление ионов свинца(II) в электролитах возрастает в следующей последовательности: KCl > KBr > $Na_3C_6H_5O_7 \cdot 2H_2O$ > Na_2SO_4 > KNO_3 > HCOONa > NH_2SO_3H.

Проведен температурно-кинетический анализ поляризационных кривых для интервала температур T=298-328 К. Температурно-кинетические кривые разряда ионов свинца(II) в присутствии ПАВ прямолинейны.

Установлены величины коэффициентов переноса α для электровосстановления ионов свинца (II) в различных электролитах в отсутствие и в присутствии ПАВ при T=298-328 К.

Рассчитаны величины токов обмена ($j_o \cdot 10^3$ А/см^2) для электровосстановления ионов свинца(II) в различных электролитах в отсутствие и в присутствии ПАВ при T=298-328 К.

Определены величины эффективной энергии активации разряда ионов свинца(II) в присутствии ПАВ в различных электролитах. В присутствии ПАВ можно выделить три основных случая. Энергия активации возрастает. Увеличение $A_{эфф}$ свидетельствует о возникновении дополнительного потенциального барьера, т.е. имеет место активационный механизм торможения. Энергия активации уменьшается, т.е. облегчается разряд ионов свинца(II). Энергия активации имеет отрицательное значение, температурно-кинетическая кривая имеет обратную зависимость. Это, вероятно, связано с явлением компенсационного эффекта при повышении температуры с изменением степени заполнения поверхности электрода. Изученные нами ПАВ адсорбируются на свинцовом электроде и область максимальной адсорбции находится в интервале – 0.4 ÷ - 1.0 В. Потенциал нулевого заряда свинца $E_{q=0}$ = - 0.56 В, а равновесный потенциал E_p = - 0.126 В. Разряд ионов свинца(II) в отсутствие ПАВ протекает на положительно заряженной поверхности электрода.

Ключевые слова: ионы свинца, электровосстановление, поверхностно-активные вещества, электролит, свинцовый электрод, ток обмена.

Information about authors

Bayeshov A.B. – Doctor of Chemistry, Professor, academician of NAS RK, D.V. Sokolsky institute of fuel, catalysis and electrochemistry, 87017741973, Almaty, Shevchenko street, 28, bayeshov@ mail.ru, https://orcid.org/0000-0002-4482-9430;

Mamyrbekova Aizhan – candidate of chemical science, associate professor, Khoja Akhmet Yassawi International Kazakh-Turkish University, Medicine Faculty, 87029244575, Turkistan, B. Sattarkhanov avenue, 29, aizhan.mamyrbekova@ayu.edu.kz, https://orcid.org/0000-0003-2798-9755;

Kassymova M.K. – candidate of chemical science, associate professor, M. Auezov South Kazakhstan state university, Textile and Food Engineering higher school, 87784680233, Shymkent, Tauke khan avenue, 5, mahabbat_67@ mail.ru, https://orcid.org/0000-0002-4789-7148;

Mamitova A.D. – candidate of technical science, associate professor, M. Auezov South Kazakhstan state universty, Department of Biotechnology, 87057179333, Shymkent, Tauke khan avenue, 5, a-mamitova@mail.ru, https://orcid.org/0000-0002-4582-9743;

Mamyrbekova Aigul – candidate of chemical science, associate professor, Khoja Akhmet Yassawi International Kazakh-Turkish University, Medicine Faculty, 87017741973, Turkistan, B. Sattarkhanov avenue, 29, aigul.mamyrbekova@ayu.edu.kz, https://orcid.org/0000-0002-4482-9430;

Olga N. Chechina – Doctor of chemistry sciences, professor of Chair of Food Production Technology and Perfumery-Cosmetic Products, Samara State Technical University, Samara, Russia, Samara, Russia, chechinao@ yandex.ru, https://orcid.org/0000-0003-8974-5223

REFERENCES

[1] Damaskin BB, Petryy OA, Tsirlina GA (2006) Electrochemistry. Chemistry: ColosS, Moscow. ISBN 5–98109–011–1 (in Russ.).

[2] Tufa, LT, Siraj K, Soreta TR (2013) Electrochemical determination of lead using bismuth modified glassy carbon electrode, Russ J Electrochem,49: 59–66. DOI:10.1134/S1023193512090121 (in Eng.).

[3] Kuznetsov VV, Skibina LM, Geshel' SV (2003) Lead Electroplating from Sulfate Electrolytes Containing Crown Ethers, Protection of Metals 39:145–149. DOI:10.1023/A:1022994827528 (in Eng.).

[4] Loshkaryov MA, Loshkaryov YM Some trends in the influence of surface-active substances on electrode processes Some trends in the influence of surface-active substances on electrode processes**,** Surface Technology, 6:397-408. DOI:10.1016/0376-4583(78)90010-9 (in Eng.).

[5] Demeev BB, Dauletbay A, Nauryzbaiev MK (2016) The Effect of Organic Surface-Active Additives Upon the Kinetics of Electrodeposition of Ultrafine Copper Powder,Chem Eng Trans, 47: 211-216. DOI: 10.3303/CET1647036 (in Eng.).

[6] Nekrasov LN, Vykhodtseva LN, Korotayeva LM, Gultyai VP The ambident behaviour of aromatic carbonyl compounds in the reaction of electrochemical dimerization, J. Electroanal. Chem., 138:177-183. DOI: 10.1016/0022-0728(82)87137-4 (in Eng.).

[7] Nieszporek J (2014) The Inhibiting or Accelerating Effect of Different Surfactants on Electroreduction of Zn2+, S Afr J Chem., 67: 1–5 (in Eng.).

[8] Ivonina TA (2010) Investigation of the effect of a high-frequency electromagnetic field on the electrochemical behavior of heavy metal ions in the presence of surfactants, Russ J Electrochem, 310: 18-328 (in Russ.).

[9] Dalbanbay A, Nefedov A, Nurmanova R, Nauryzbayev M (2017) Study of the influence of surface-active substances on the initial stage of copper electrodeposition, Chemical Bulletin of Kazakh National University, 4:12-19. DOI: 10.15328/cb890 (in Russ.).

[10] Joseph MJ (1982) Effect of surface active compounds on the redox reactions of some electroactive species , Ind J Chem, 23: 145-152. DOI: 10.3390/s100605308 (in Eng.).

[11] Muller E, Emous H, Porfler H, Lipkowsky JJ, J. Electroanalyt. Chem., 1982, 142: 39 (in Eng.).

[12] Kozybaev AK, Tusupova BB, Abdikarimova AD (2014) Electrochemical Reduction of Cadmium Ions(II) on Cadmium Electrode in the Presence of Polymeric Surfactants at different Temperatures, Advances in Environmental Biology, 8(16):252-257.

[13] Carla Gouveia-Caridade, Christopher MA Brett (2006) The influence of Triton-X-100 surfactant on the electroanalysis of lead and cadmium at carbon film electrodes – An electrochemical impedance study, J Electroanal Chem, 592: 113–120. DOI: 10.1002/elan.200603482

[14] Drweesh MA (2004) Effect of surfactants on the removal of copper from waste water by cementation, Alexandria Engineering Journal, 43: 917-925 (in Eng.).

[15] Kasymova MK, Bayeshov AB, Zhylysbayeva GN, Mamyrbekova AK, Chechina ON (2018) Kinetic researches and electrochemical behaviour of lead at polarization alternating current, Bulletin of the National Academy of Sciences of the Republic of Kazakhstan, 6, 376: 139 – 146. https://doi.org/10.32014/2018.2518-1467.37 (in Eng.).

[16] Bayeshov A, Abijanova DA, Abduvalieva UA, Zhurinov M (2019) Study of electrochemical properties of copper in solution of sulphuric acid with copper(II) ions and titan through potentiodynamic polarized curve, Bulletin of the National Academy of Sciences of the Republic of Kazakhstan, 2, 378: 241 – 248. https://doi.org/10.32014/2019.2518-1467.62 (in Eng.).

[17] Edgar Nagles, Verónica Arancibia, Roxana Ríos, Carlos Rojas (2012) Simultaneous Determination of Lead and Cadmium in the Presence of Morin by Adsorptive Stripping Voltammetry with a Nafion–Ionic Liquid–coated Mercury Film Electrode, Int J Electrochem Sci**,** 7: 5521 – 5533 (in Eng.).

[18] Ádám Golcs, Viola Horváth, Péter Huszthy and Tünde Tóth Fast (2018)Potentiometric Analysis of Lead in Aqueous Medium under Competitive Conditions Using an Acridono-Crown Ether Neutral Ionophore, Sensors, 18: 1407. DOI:10.3390/s18051407 (in Eng.).

[19] Mamyrbekova Aigul, Kassymova MK, Mamyrbekova Aizhan (2019) Effect of pH on the Electroreduction of Cadmium(II) and Lead(II) Ions on Electrodes in the Presence of Surfactants, Russ J Phys Chem, 93: 442–446. DOI: 10.1134/S0036024419030129 (in Eng.).

[20] Kassymova MK, Nauryzbaev MK, Mamyrbekova Aigul, Zhylysbayeva GN, Mamyrbekova Aizhan (2019) Effect of Surfactants on the Reduction of Cadmium(II) Ions on Cadmium Electrode, Russ J Phys Chem, 93: 980-985. DOI 10.1134/S0036024419050170 (in Eng.).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.34**
Volume 2, Number 440 (2020), 138 – 144

UDC 54.057:661.722

S.M. Naurzkulova[1], B.K. Massalimova[1], K.A. Shorayeva[1],
G.M. Dzhienbaeva[1], M.V.Arapova[2,3], V.A. Sadykov[2,3]

[1]M.Kh. Dulaty Taraz State University, 080000, Taraz, Kazakhstan;
[2] Novosibirsk State University, 630090, Novosibirsk, Russia;
[3] Institute of Catalysis named after G.K. Boreskov, 630090, Novosibirsk, Russia.
E-mail: simbat_3@mail.ru

SYNTHESIS AND STUDY OF STRUCTURAL PROPERTIES OF COMPOSITES BASED ON NI-RU FOR STEAM CONVERSION OF ETHANOL

Abstract. Catalyst precursors, substituted by rare-earth and transition metals, promoted with Ru nanoparticles using the modified Pechinimethod (Organic polymeric precursor) have been synthesized. To transform biofuel (ethanol) into hydrogen from the obtained active phases, three different methods were used to synthesize composites with the general formula [$LaMn1\text{-}xBxO_3 + \delta$ / $Ln_{1-y}Zr_yO_2$] (1: 1 by mass), B = Ni, Ru, Ln = Pr, Sm , Ce. Structural and surface properties of the obtained samples of complex oxides and composites were studied using the BET and XPA methods. The textural and structural characteristics of composites differing in the methods of their preparationare presented.

Key words: perovskite, fluorite, composites, biomass, hydrogen.

Introduction

Fossil fuels are widely used, but their resources are limited. Therefore, the development of new fuels is necessary, and currently much attention is paid to renewable energy sources [1]. Biomass as a renewable raw material is not only the subject of numerous scientific studies, but in some countries it largely replaces traditional fossil energy sources. To date, one of the most promising methods for transforming biomass into fuel and energy is catalytic steam conversion of the liquid products of biomass processing into hydrogen and synthesis gas [2].

In this regard, the need to create new catalysts for the steam conversion of ethanol to hydrogen and synthesis gas is of great interest. Well known catalysts for steam reforming of oxygen-containing compounds are usually noble [3-5] or transition metals [6-9] deposited on the surface of porous supports. The main problem that impedes their industrial application is the coke formation on the surface of catalysts and, as a consequence, their deactivation [6-10].

Nanocrystalline oxides with the structure of fluorite, perovskite and spinel and their nanocomposites containing cations of rare-earth and transition metals, capable of changing their oxidation state, have high mobility and reactivity of oxygen. Such oxides are one of the most promising carriers resistant to coke formation for catalysts for the conversion of hydrocarbons or oxygen-containing compounds into synthesis gas [11,12].

There are several approaches to the preparation of oxide nanocomposites with the structure of perovskite and fluorite. The method of synthesis of nanocomposite materials should provide high chemical uniformity of the obtained complex oxides along with their high dispersion. Among many methods for preparing catalysts, the high spatial uniformity of the distribution of cations in mixed oxides is ensured by the method of the so-called ester polymer precursors (Pechini method) with the addition of chelating agents such as citric acid, ethylene diamine (ED) and ethylene glycol [13].

Based on this, the aim of this work is to synthesize and study the texture properties of Ni-Ru-based composites intended for ethanol steam reforming.

Experimental part

Preparation of active ingredients

To prepare the samples $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ and $LaMn_{0.45}Ni_{0.4}5Ru_{0.1}$ according to the Pechinimethod, we used crystalline hydratesPr $(NO_3)_3 \cdot 6H_2O$(pur.), Sm $(NO_3)_2 \cdot 6H_2O$ (puriss), Ce $(NO_3)_2 \cdot 6H_2O$ (p.a.), $ZrOCl_2$ (puriss),La $(NO_3)_3 \cdot 6H_2O$ (puriss), $Ni(NO_3)_2 \cdot 6H_2O$ (p.a.),$RuOCl_3$ (p.a.), $Mn(NO_3)_2 \cdot 6H_2O$ (puriss), citric acid (LA, puriss), ethylene glycol (EG, p.a.), ethylenediamine (ED, pur).

The exact molar masses of nitrates were determined by thermal analysis. Ethylene glycol and citric acid were used as complexing agents. Ethylene diamine is added to further polymerization of the system. Reagents were taken in molar ratios of LC: EG: EDA: Σν (metals) = 3.75: 11.25: 3.75: 1. Citric acid was dissolved in ethylene glycol with vigorous stirring and gentle heating (60-80 ° C). Crystalline hydrates of metal nitrates were added to the resulting solution cooled to room temperature with vigorous stirring, then ethylenediamine was added dropwise. Full homogenization was expected in 2 h. The resulting mixture was evaporated with stirring to obtain a viscous polymer, calcined in a muffle furnace at 700 ° C during 5 hours.

Synthesis of Nanocomposites

Nanocomposites based on $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ $LaMn_{0.45}Ni_{0.4}Ru_{0.1}$complex oxides at a 1: 1 ratio were synthesized using a modified Pechini polymeric precursor method, followed by calcination with 700°C for 4 hours.

Physico-chemical studies of the samples obtained

The phase composition of the samples was determined by x-ray phase analysis (XRD). Diffraction patterns were obtained using a Bruker Advance D8 diffractometer with CuKα radiation. Scanning was carried out in the angle range of 20-80 (2Θ) with a scan step of 0.05 (2Θ). Identification of the phases obtained and quantitative calculations were obtained using the ICDD X-ray file cabinet.

The specific surface area of the synthesized samples was measured by the express version of the BET method for thermal desorption of argon on a SORBI-M device.

Results and discussion

Using the method of low-temperature nitrogen adsorption, the specific surface area of the obtained oxides and nanocomposites was calculated.

Table 1 -Textural properties of complex oxides and synthesized composites

№	Composition of Composites	Method of preparation	Calcination,°C	Surface, m^2/g	Bulkdensity, kg/m^3
1	$Pr_{0.15}$ $Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$	Pechini	700	75	-
2	$LaMn_{0.45}Ni_{0.45}$ $Ru_{0.1}O_3$	Pechini	700	8	-
3	$Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ и $LaMn_{0.45}Ni_{0.45}Ru_{0.1}O_3$	Polymer	700	36	1,3621
4	$Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ и $LaMn_{0.45}Ni_{0.45}Ru_{0.1}$ O_3	one-pot synthesis	700	49	1,4691
5	$Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ и $LaMn_{0.45}Ni_{0.45}Ru_{0.1}O_3$	Ultrasonic dispersion	700	61	1,1174

From the results presented in table 1, it is seen that the fluorite-like complex oxide with the composition $Pr_{0.15}$ $Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$prepared by thePechinimethod has the largest specific area - 75 m2/g. The composite prepared by the method of ultrasonic dispersion is distinguished by a high specific surface as well. The composites prepared by the Polymer and One-pot synthesis methods showed 36 and 49 m^2/g, respectively. The lowest specific surface index has a perovskite-like complex oxide with the composition $LaMn_{0.45}Ni_{0.45}Ru_{0.1}O_3$prepared by the Pechinimethod. It is known thatperovskites generally have a low specific surface area [14, 15].

The phase composition of the sample of complex oxide $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$prepared by the Pechini method and calcinedat 700 ° C in the angle range 2θ, 20-80 ° C is shown in figure 1.

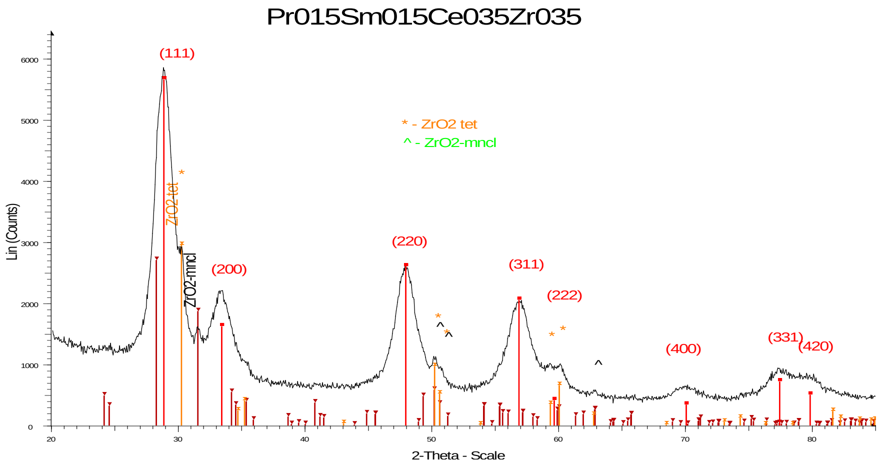


Figure 1 - Diffraction pattern of the $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$sample

According to X-ray diffraction data (figure 1), a sample of the complex oxide $Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_2$ is a single-phase well crystallized system, which is a solid fluorite-like solution of cubic type PrSmCeZrO (Fm3m) with a small admixture of phases of monoclinic and tetragonal zirconium oxides.

Using the XRD method, the phase composition of the complex oxide sample $LaMn_{0.45}Ni_{0.45}Ru_{0.1}O_3$prepared by the Pechini method, calcined at 700 ° C in the angle range 2θ, 20-80 ° C (figure 2) was determined.

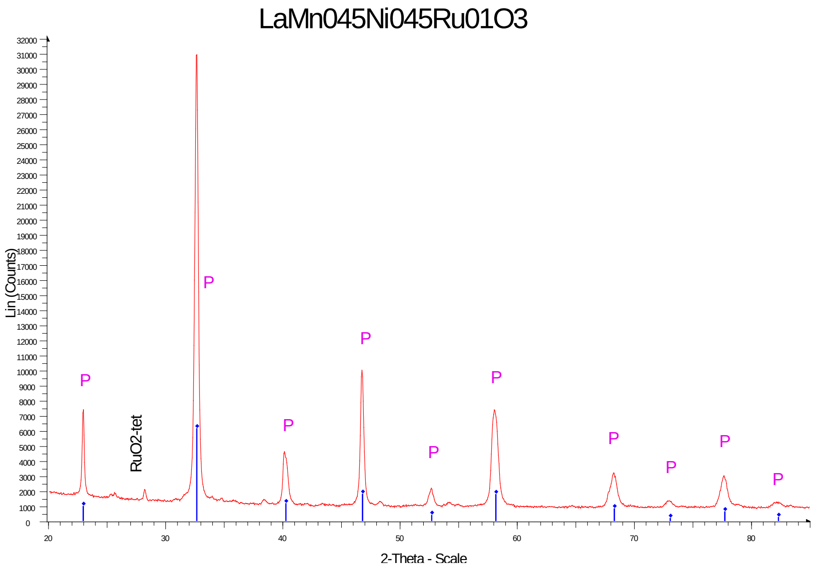


Figure 2 - Diffraction pattern of the $LaMn_{0.45}Ni_{0.4}Ru_{0.1}O_3$sample

According to the XRD data (figure 2), the phase composition of the LaMnNiRuOnanocomposite is crystallized in the structural type of perovskite with orthorhombic symmetry.

Next, the phase compositions of composites synthesized by the Polymer and One-pot synthesis methods and the ultra dispersion method (figure 3) based on complex oxide precursors were determined.

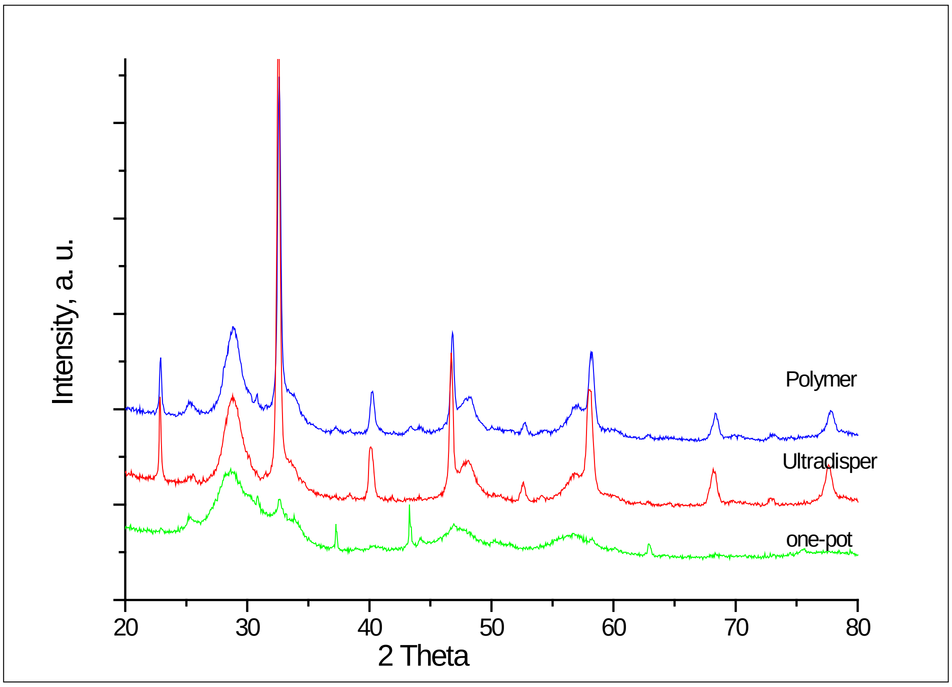


Figure 3 - X-ray diffraction patterns of composites

From the data presented (figure 3) it can be seen that upon application of various active components, such as Ni, Mn, Ru, the fluorite-like structure of composites obtained using the Polymer and ultradispersion methods is preserved. Whereas in a composite synthesized by the One-pot method, the fluorite-like structure is deformed. The crystalline phase — NiO was identified in composite, obtained using the Polymer method.

Surface promotion of the support by rare-earth elements inhibits the growth of nickel crystallites, preventing the formation of large particles necessary for the formation of coke, and also complicates the reoxidation of metallic nickel during the reaction [16,17,18,19]

Complex oxides with a perovskite structure in addition to high oxygen mobility have a number of additional unique properties. Due to this, they are sometimes called "replacement of noble metals" in the application to catalysis [20]. Catalysts based on substituted precursors for the ethanol steam reforming process based on perovskites $LaFeNiO_3$ [21], $La_{1-x}AxFe_{1-y}NiyO_3$ (A = Ca, Sr) [22.23], $La1\text{-}xSrxFe_{1-y}Co_yO_3$ [24], $La_{1-x}CaxFe_{1-x}Co_xO_3$ [25] and $LaXCoO_3$ (X = Mg, Ca, Sr, Ce) [26] are well known.

The results of this work are of particular interest in the field of modern catalysis in obtaining renewable energy sources, and also require further research. The data obtained contribute to the solution of the development of domestic catalyst production

Conclusions

This study presents the results of the synthesis of single-phase nanocrystalline complex oxides with the general formula [LaMn1-xBxO3 + δ / Ln1-yZryO2] (1: 1 by mass), B = Ni, Ru, Ln = Pr, Sm, Ce, with fluorite (doped cerium-zirconium oxide) and perovskite structures by thePechinimethod.

Synthesis methods are proposed that lead to the formation of a complex perovskite-fluorite system with cations uniformly distributed in one structure and a developed interphase phase. The influence of the synthesis method on the structural properties of the oxide system is shown. The results of the study showed that in the synthesis of composite structures, the most effective is the method of ultrasonic dispersion.

Acknowledgments

This work was financially supported by M.Kh. DulatiTaraz State University, Taraz, Kazakhstan. Research work was carried out in the scientific laboratory of "Chemistry and Chemical Technology"

department of TarSU and "Deep Oxidation Catalysts" laboratory of G.K. Boresky institute of catalysis SB RAS, Novosibirsk, Russia.

С.М. Наурызкулова[1], Б.К. Масалимова[1], К.А. Шораева[1],
Г.М.Джиенбаева[1], М.В. Арапова[2,3], В.А. Садыков[2,3]

[1] М.Х. Дулати атындағы Тараз мемлекеттік университеті, 080000, Тараз, Қазақстан;
[2]Новосібір мемлекеттік университеті, 630090, Новосібір, Ресей;
[3]Г.К. Боресков атындағы катализ институты, 630090, Новосібір, Ресей

ЭТАНОЛДЫҢ БУ АЙНАЛЫМЫ ҮШІН NI-RU НЕГІЗІНДЕГІ КОМПОЗИТТЕРДІ СИНТЕЗДЕУ ЖӘНЕ ОЛАРДЫҢ ҚҰРЫЛЫМДЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

Аннотация. Қазба отындары кеңінен қолданылады, бірақ олардың ресурстары шектеулі. Сондықтан отынның жаңа түрлерін жасау қажет. Қазіргі уақытта жаңартылатын энергия көздеріне көп көңіл бөлінуде. Биомасса- шикізат ретінде көптеген ғылыми зерттеулердің тақырыбы ғана емес, сонымен қатар, кейбір елдерде дәстүрлі қазба энергия көздерін алмастыруда. Бүгінгі таңда биомассаны отын мен энергияға айналдырудың перспективті әдістерінің бірі – биоотынды сутегі мен синтез газына булы каталитикалық айналдыру болып табылады.

Осыған байланысты этанолды сутегі мен синтез газына бу айналымына қажетті жаңа катализаторларды жасау қажеттілігі үлкен қызығушылықты тудырды. Құрамында оттегі бар қосылыстардың булы айналымының катализаторлары әдетте кеуекті тасымалдағыштарға қондырылған асыл немесе ауыспалы металдар болып табылады. Оларды өнеркәсіпте қолдануға кедергі келтіретін негізгі мәселе, катализаторлардың көмірленуі және соның салдарынан олардың жарамсыздығы болып табылады.

Құрамында сирек кездесетін және ауыспалы металдардың катиондары бар флюорит, перовскит және шпинель құрылымды нанокристалды оксидтер мен олардың нанокомпозиттері тотығу күйін өзгертуге қабілетті және оттегінің жоғары қозғалғыштығы мен реакцияласу қабілетіне ие. Мұндай оксидтер көмірсутектерді немесе оттегі бар қосылыстарды синтез газы мен сутегіне айналдыруға қажетті катализаторлардың көмірленуіне тұрақты тиімді катализаторлардың бірі болып табылады.

Осыған сәйкес, бұл жұмыстың мақсаты - этанолдың бу айналымындағы Ni-Ru негізіндегі композиттерді синтездеу және олардың құрылымдық қасиеттерін зерттеу болып табылады.

Ru нанобөлшектерімен промоторланған, сирек кездесетін және ауыспалы металдармен алмастырылған катализаторлардың прекурсорларының синтезі, полимерлі органикалық прекурсорлардың модифицирленген әдісімен (Пекини) жүргізілді. Биоотыннан (этанол) сутегі алу үшін, алынған белсенді фазалардан үш түрлі әдіспен жалпы формуласы [$LaMn_{1-x}B_xO_{3+\delta}/Ln_{1-y}Zr_yO_2$] (1:1 масса бойынша), B = Ni, Ru, Ln = Pr, Sm, Ce композиттер синтезделді.Синтездеу әдістерінің үлгілердің құрылымдық және беттік қасиеттеріне әсерін рентгендік фазалықжәне BET әдістерімен зерттелді.Синтездеу әдістерінің ерекшелігіне байланысты композиттердіңқұрылымдық және беттік қасиеттері сипатталды.

Бұл жұмыстың нәтижелері заманауи катализ саласында жаңартылатын энергия көздерін алуда ерекше қызығушылық тудырады, осыған орай, одан әрі зерттеуді қажет етеді. Алынған мәліметтер катализаторлардың отандық өндірісін дамыту мәселелерін шешуге ықпал етеді.

Түйін сөздер: перовскит, флюорит, нанокомпозиттер, биомасса, сутегі.

С.М. Наурызкулова[1], Б.К. Масалимова[1], К.А. Шораева[1],
Г.М.Джиенбаева[1], М.В. Арапова[2,3], В.А. Садыков[2,3]

[1] Таразский государственный университет имени М.Х. Дулати, 080000, Тараз, Казахстан;
[2]Новосибирский государственный университет, 630090, Новосибирск, Россия;
[3] Институт катализа имени Г.К. Борескова, 630090, Новосибирск, Россия

СИНТЕЗ И ИЗУЧЕНИЕ СТРУКТУРНЫХ СВОЙСТВ КОМПОЗИТОВ НА ОСНОВЕ NI-RU ДЛЯ ПАРОВОЙ КОНВЕРСИИ ЭТАНОЛА

Аннотация. Ископаемые виды топлива широко используются, однако их ресурсы ограничены. Поэтому разработка новых видов топлива необходима, и в настоящее время большое внимание уделяется возобновляемым источникам энергии. Биомасса как возобновляемое сырье не только является предметом многочисленных научных исследований, но в некоторых странах в значительной мере заменяет традиционные ископаемые источники энергии. На сегодняшний день одним из самых перспективных методов трансформации биомассы в топливо и энергию является каталитическая паровая конверсия жидких продуктов переработки биомассы в водород и синтез-газ.

В этой связи необходимость создания новых катализаторов для паровой конверсии этанола в водород и синтез-газ вызывает большой интерес. Известные катализаторыдля паровой конверсии кислородсодержащих соединений обычно представляют собой благородные или переходные металлы, нанесенные на поверхностьпористых носителей. Основной проблемой, затрудняющей их промышленное применение, является зауглероживание катализаторов икак следствие - их дезактивация.

Нанокристаллические оксиды со структурой флюорита, перовскита и шпинели и их нанокомпозиты, содержащие катионы редкоземельных и переходных металлов, способные изменять свою степень окисления, обладают высокой подвижностью и реакционной способностью кислорода. Такие оксиды являются одними из наиболее перспективных носителей, устойчивых к зауглероживанию катализаторов, для превращения углеводородов или кислородсодержащих соединений в синтез-газ и в водород.

Исходя из этого,цельюданной работы является синтез и изучение текстурных свойств композитов на основе Ni-Ru, предназначенных для паровой конверсии этанола.

Синтезированы предшественники катализаторов, замещенные редкоземельными и переходными металлами промотированных наночастицами Ru с помощью модифицированного метода organic polymeric precursor (метод Пекини). Для трансформации биотоплива (этанола) в водород, из полученных активных фаз тремя разными методами синтезированы композиты с общей формулой [$LaMn_{1-x}B_xO_{3+\delta}/Ln_{1-y}Zr_yO_2$] (1:1 по массе), B = Ni, Ru, Ln = Pr, Sm, Ce.. Структуные и поверхностные свойства полученных образцов сложных оксидов и композитов изучены с помощью методов БЭТ и РФА. Представлены текстурные и структурные характеристики композитов, отличающиеся в зависимости от методов его приготовления.

Результаты настоящей работыпредставляют особый интерес в области современного катализа приполучении возобновляемых источников энергии, а также требуют дальнейшее исследование. Полученные данные способствуют решению вопросов развития отечественного производства катализаторов.

Ключевые слова: перовскит, флюорит, композиты, биомасса, водород.

Information about authors:

Naurzkulova Symbat Muratbekovna – 2-year PhD student of specialty chemistry, M.Kh. DulatiTaraz State University, Tole bi str. 60, Taraz, Kazakhstan, simbat_3@mail.ru, https://orcid.org/0000-0002-2144-233X;

Massalimova Bakytgul Kabykenovna – candidate of chemical sciences, associated professor, manager of the department of “Chemistry and chemical technology”, M.Kh. DulatiTaraz State University, Tole bi str. 60, Taraz, Kazakhstan, massalimova15@mail.ru, https://orcid.org/0000-0003-0135-9712;

Shorayeva Kamshat Abitkhanovna – 3-year PhD student of specialty chemistry, M.Kh. DulatiTaraz State University, Tole bi str. 60, Taraz, Kazakhstan, k.a.shorayeva@mail.ru;

Dzhienbaeva GulbanuMaksetovna – 2-year master’s student of specialty chemistry, M.Kh. DulatiTaraz State University, Tole bi str. 60, Taraz, Kazakhstan,Dzhienbaeva.G.@mail.ru;

Arapova M.V. - candidate of chemical sciences,Boreskov Institute of Catalysis, Novosibirsk, Russia, arapova@catalysis.ru;

Sadykov V.A. – doctor of chemical sciences, professor, Boreskov Institute of Catalysis, Novosibirsk, Russia, vasadykov@mail.ru, sadykov@catalysis.ru, https://orcid.org/0000-0003-2404-0325

REFERENCES

[1] Miyazawa T., Kimura T., Nishikawa J., Kado S., Kunimori K., Tomishige K. (2006) Catalytic performance of supported Ni catalysts in partial oxidation and steam reformingof tar derived from the pyrolysis of wood biomass, Catal. Today 115 254–262. (in Eng).

[2] Арапова М.В. Синтез и свойства Ni-содержащих катализаторов на основе сложных оксидов для процессов паровой конверсии этанола и глицерина // Диссертация 2017. с. 6-7.

[3] Pakhare D., Spivey J. (2014) A review of dry (CO_2) reforming of methane over noble metal catalystsChemical Society Reviews,V. 43. P. 7813.(in Eng).

[4] Al-Fatesh A.S., Ibrahim A.A., Haider S., Fakeeha A.H. (2013) Sustainable Production of Synthesis Gases via State of the Art Metal Supported Catalytic Systems: An Overview. journal of chinese chemical societyV.60. P. 1297.(in Eng).

[5] Li D., Li X.,. Gong J (2016)Catalytic Reforming of Oxygenates: State of the Art and Future Prospects//Chemical reviews. V. 116. P. 11529.(in Eng).

[6] Ma J., Sun N., Zhang X., Zhao N., Xiao F., Wei W., Sun, Y. (2009)A short review of catalysis for CO_2conversion.Catalysis Today. V. 148. P. 221(in Eng).

[7]Usman M., WanDaud W.M.A., Abbas H.F. (2015)Dry reforming of methane: Influence of process parameters – A review, Renewable and Sustainable Energy,V. 45. P. 710.(in Eng)

[8] Kumar N., Shojaee M., Spivey J.J. (2015) Methanol production by bi-reforming,Current Opinion in Chemical Engineering, V. 9. P. 8.(in Eng).

[9] Tomishige K., Li D., Tamura M., Nakagawa Y. (2017) Nickel–iron alloy catalysts for reforming of hydrocarbons: preparation, structure, and catalytic properties ,CatalysisScience and Technology V. 7. P. 3952.(in Eng).

[10] Vaidya P.D., Rodrigues A.E. (2006)Insight into steam reforming of ethanol to produce hydrogen for fuel cells, Chemical Engineering Journal, V. 117. P. 39.(in Eng).

[11] Sadykov V., Bobrova L., Pavlova S., Simagina V., Makarshin L., Parmon V., Ross J. R. H., Van Veen A. C.,. Mirodatos C. (2012)Syngas Generation from Hydrocarbons and Oxygenates with Structured Catalysts. Nova Science Publishers, Inc, New York, P. 140. (in Eng).

[12] Sadykov V.A., Pavlova S.N., Alikina G.M., Sazonova N.N., Mezentseva N.V., Arapova M.V, Rogov V.A., Krieger T.A., Ishhenko A.V., Gulyaev R.V., Zadesenets A.V., Roger A.-C., Chan-Thaw C.E., Smorygo O. (2013)Perovskite-Based Catalysts for Transformation of Natural Gas and Oxygenates into Syngas. Chapter in book Perovskite: Crystallography, Chemistry and Catalytic Performance, ed. J. Zhang and H. Li. Nova Science Publishers, Inc, New York, 2013. P.1.(in Eng).

[13] Pechini M.P. (1967)Pat.3330697, Sprague Electric Co, (in Eng).

[14] V. Sadykov, N. Mezentseva, M. Simonov, E. Smal, M. Arapova, S. Pavlova,Y. Fedorova, O. Chub, L. Bobrova, V. Kuzmin, A. Ishchenko, T. Krieger, A.-C. Roger,K. Parkhomenko, C. Mirodatos, O. Smorygo, J. Ross, (2015) Int. J. Hydrogen Energy 407511–7522.(inEng).

[15]V.A. Sadykov, S.N. Pavlova, G.M. Alikina, N.N. Sazonova, N.V. Mezentseva,M.V. Arapova, V.A. Rogov, T.A. Krieger, A.V. Ishchenko, R.V. Gulyaev,A.V. Zadesenets, A.-C. Roger, C.E. Chan-Thaw, O.L. Smorygo, Perovskite-based catalysts for transformation of natural gas and oxygenates into syngas, in: J. Zhang,H. Li (Eds.), Perovskite: Crystallography, Chemistry and Catalytic Performance,

Nova Science Publishers, Inc, New York, 2013, pp. 1–58.(in Eng).

[16]Yurdakul M., Ayas N., Bizkarra K., El Doukkali M., Cambra J.F. Preparation of Ni-based catalysts to produce hydrogen from glycerol by steam reforming process // International Journal of Hydrogen Energy. 2016. V. 41. P. 8084-8091. (in Eng).

[17] Calles J.A., Carrero A., Vizcaino A.J. Ce and La modification of mesoporous Cu–Ni/SBA-15 catalysts for hydrogen production through ethanol steam reforming // Microporous and Mesoporous Materials. 2009. V. 119. P. 200–207. (inEng).

[18] Sánchez-Sánchez M.C., Navarro R.M., Fierro J.L.G. Ethanol steam reforming over Ni/MxOy–Al2O3 (M = Ce, La, Zr and Mg) catalysts: influence of support on the hydrogen production // International Journal of Hydrogen Energy. 2007. V. 32. P. 1462–1471. (inEng).

[19]Bednarczuk L., Ramirez de la Piscina P., Homs N. Efficient CO2-regeneration of Ni/Y2O3-La2O3-ZrO2 systems used in the ethanol steam reforming for hydrogen production // International Journal of Hydrogen Energy. 2016. V. 41. P. 19509-19517. (inEng).

[20] Royer S., Duprez D., Can F., Courtois X., Batiot-Dupeyrat C., Laassiri S., Alamdari H. Perovskites as Substitutes of Noble Metals for Heterogeneous Catalysis: Dream or Reality // Chemical Reviews. 2014. V. 114. P. 10292−10368.(inEng).

[21] Chen S.Q., Liu Y. LaFeyNi1-yO3 supported nickel catalysts used for steam reforming of ethanol // International Journal of Hydrogen Energy. 2009. V. 34. P. 4735. (inEng).

[22] Chen S.Q., Wang H., Liu Y. Perovskite La–St–Fe–O (St = Ca, Sr) supported nickel catalysts for steam reforming of ethanol: The effect of the A site substitution // International Journal of Hydrogen Energy. 2009. V. 34. P. 7995.(inEng).

[23] Zhao L., Wei Y., Huang Y., Liu Y. La1−xKxFe0.7Ni0.3O3 catalyst for ethanol steam reforming. The effect of K-doping // Catalysis Today. – 2016. – V. 259. – P. 430–437.(inEng).

[24] Natile M.M., Poletto F., Galenda A., Glisenti A., Montini T., De Rogatis L., Glisenti P. La0.6Sr0.4Co1-yFeyO3-δPerovskites: Influence of the Co/Fe Atomic Ratio on Properties and Catalytic Activity toward Alcohol Steam-Reforming // Chemical Materials. 2008. V. 20. P. 2314.(inEng).

[25] Wang Z., Wang H., Liu Y. La1-xCaxFe1-xCoxO3 – a stable catalyst for oxidative steam reforming of ethanol to produce hydrogen // RSC Advances. 2013. V. 3. P. 10027-10036(in Eng).

[26] Ma F., Ding Z., Chu W., Hao S., Qi T. Preparation of LaXCoO3 (X = Mg, Ca, Sr, Ce) catalysts and their performance for steam reforming of ethanol to hydrogen // Chinese Journal of Catalysis. 2014. V. 35. P. 1768–1778.(inEng).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.35**
Volume 2, Number 440 (2020), 145 – 152

UDC 620.193.4

K.A.Mammedov

SOCAR “Oil Gas Scientific Research Project” Institute OGPI, Baku, Azerbaijan.
E-mail: k.a.mammedov@gmail.com

STUDY OF THE EFFECT OF A NEW COMBINED INHIBITOR AND A PERMANENT MAGNETIC FIELD ON CORROSION AND SALT DEPOSITION

Abstract. This academic article encompasses the investigation results concerning, the composite acquired from the mixture of hydrated technical phosphatide, cubic thickness of polypropylene glycol, and sodium hexametaphosphate. According to the outcomes of laboratory researches, it was determined that the developed new composite provides not only prevention of equipment from corrosion, but also protection of those from salt deposition. Furthermore, as a result of the joint effect of a stable magnetic field of 280 kA/m, high protective efficiency was determined. Thus, the optimum consumption was found to be 150 mg/l. In this case, the protection effectiveness against corrosion and salt deposition accounted for 93% and 85% accordingly.

Commercial tests of the combined action of the reagent and the permanent magnetic field were carried out on the cooling system of compressors “Bibiheybatneft” OGED (Oil and Gas Extraction Department). In the field with the combined use of a magnetic field and inhibitors the protective effect is 90%, and the protective effect of salt deposition is 73%.

Keywords: oilfield equipment, salt deposition, inhibitor, aggression, composite, corrosion.

Introduction

At the oil and gas refineries and petrochemical plants, when water is heated due to the super saturation of water with salts, primarily calcium carbonate, on the heat exchange surfaces of the heat supply and hot water supply systems, circulating cooling systems, distillation desalination plants and evaporators, low-pressure steam boilers. Operation of the listed equipment is also hampered by the formation of iron oxide deposits with high corrosive water aggressiveness. Similar problems arise in oilfield equipment in oil production. Therefore, the development of a multifunctional reagent that effectively inhibits corrosion and salt deposition is an urgent task.

Corrosion and salt sedimentation processes occurring in oil extraction create difficulties in exploitation of wells and consequently this causes an increase in the cost of the extracted oil.

Salt deposits form on the exploitation line, pump-compressor tubes, valves, and pumps, as well as oil preparation equipment and therefore entirely cover the internal surface of the facilities, restrict flow of stream or bring to whole limitation in movement of steam [1, 2]. Furthermore, salt sediments inevitably contribute to corrosion and its enhancement [3, 4].

The feasible causes for salt sedimentations can become chemical incompatibility of the waters flowing into wells from various horizons (mixture of alkaline and hard waters), and excessive saturation of water-salt system throughout the period of change in hydraulic pressure and thermodynamic conditions. From this reason, the improvement of exploitation efficiency of wells operating in circumstance in which corrosion and salt deposition take place is one of the pressing issues [5,6].

Firstly, inhibitors against salt sedimentation are applied in preservation of submersible pumps operating in wells because precipitation of salts inside working pieces of facilities will have a profoundly negative impact on the operation of the equipment, the facilities will be out of order prematurely, and thereby the work of the equipment will extremely aggravate. Unambiguously, salt deposition decreases operation time of pumps by virtually three-five times [6]. Recently, an inhibitor against salt deposition are applied in oil reserves for protection of oilfield equipment from mineral salts mainly comprising calcium and magnesium carbonates [7]. A fundamental study of scale formation of calcium carbonate ($CaCO_3$) for producing oil wells has been carried out [8, 9].

It is imperative to select an effective inhibitor in accordance with the operating parameters of the wells and the chemical composition of layer water once choosing technology for prevention from corrosion and salt precipitation [10-12]. From this reason, production of effective inhibitors prepared from multicomponent mixtures for prevention against corrosion and salt deposition becomes necessary. To obtain synergetic effective composite, combination of inhibitors is investigated on the basis of certain principles and optimal analyses.

Even though each of these inhibitors made from several components have a certain power of influence, combination of those results in formation of synergetic effect and make an opportunity to deteriorate different influences simultaneously and have complex effects.

Results of laboratory researches

As a result of laboratory researches, new complex effective composite was prepared from the mixture of hydratedtechnical phosphatide (TP), sodium hexametaphosphateand $(NaPO_3)_6$,cubic thickness of polypropylene glycol (PPG).

In order to investigate protection effectiveness from corrosion of new complex effective composition, according to laboratory tests was conducted on U-shaped device with using aggressive layer water within the period of six hours and at temperature of $25C^0$.

The corrosion rate is computed by the expression given below:

$$CR = \frac{m - m_1}{St} \tag{1}$$

where, CR – corrosion rate, $g/m^2 \cdot hour$; m – mass of the test specimen before the test, g; m_1 – mass of the test specimen after the test, g; S – the surface area of the witness specimen, m^2; t – test time, hours.

The effectiveness of the protective action of the inhibitor was characterized by the degree of protection IE, %.

$$IE = \frac{CR - CR_1}{CR} 100\% \tag{2}$$

where, CR and CR_1 –corrosion rates of the sample without inhibitor and with inhibitor.

Research methodology of composites against salt sedimentation principally consists of examination of precipitation of carbonate salts in laboratory conditions. On the other hand, protection effectiveness of composite against salt deposition is dependent upon amount of consumption in aggressive environment.

In order to determine intensity of salt deposition investigations were performed in underground water environment during the period of six hours and at the temperature of $65C^0$. Consumption rate of the composite was in the range of 50 and 250 mg/l.

Intensity of salt deposition is determined by precipitation of calcium ion. Concentration of calcium ion is detected by means of titration method. As an aggressive environment, underground water containing abundant minerals was utilized.

The effectiveness of the reagent is defined by reduction in an amount of calcium carbonate present in the reagent solution for precluding precipitation of calcium carbonate into solid surface.

Reagent effectiveness is expressed with the assistance of the formula given in the following.

$$E_r = \frac{DR_0 - DR_1}{DR_0} \cdot 100\%$$

E_r – effectiveness of reagent in, %; DR_o – speed of salt deposition in water, $mg/cm^2 \cdot hour$; DR_1 – speed of salt deposition in the water containing reagent, $mg/cm^2 \cdot hour$.

The research results are shown in figure 1.

As it can be seen from figure1, results of laboratory researches have determined that optimal consumption of the composite in the environment is 200 mg/l. In this case, protection effectiveness values against corrosion and salt deposition are 94% and 87% respectively (0.73-0.044 $g/m^2 \cdot hour$ and 0.0127-0.0016 $mg/sm^2 \cdot hour$).

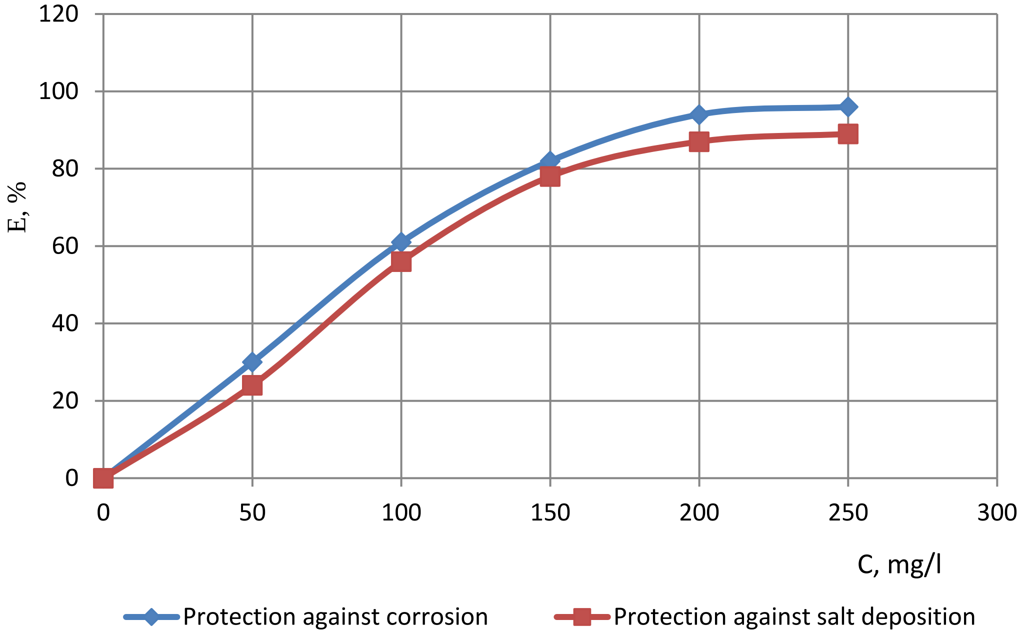


Figure 1 – Intensity of salt deposition and corrosion rate in underground water

To study the mechanism of the protective action of the reagent, a potentiostatic method of obtaining polarization curves of 1020 steel was also used. The research results are shown in figure 2.

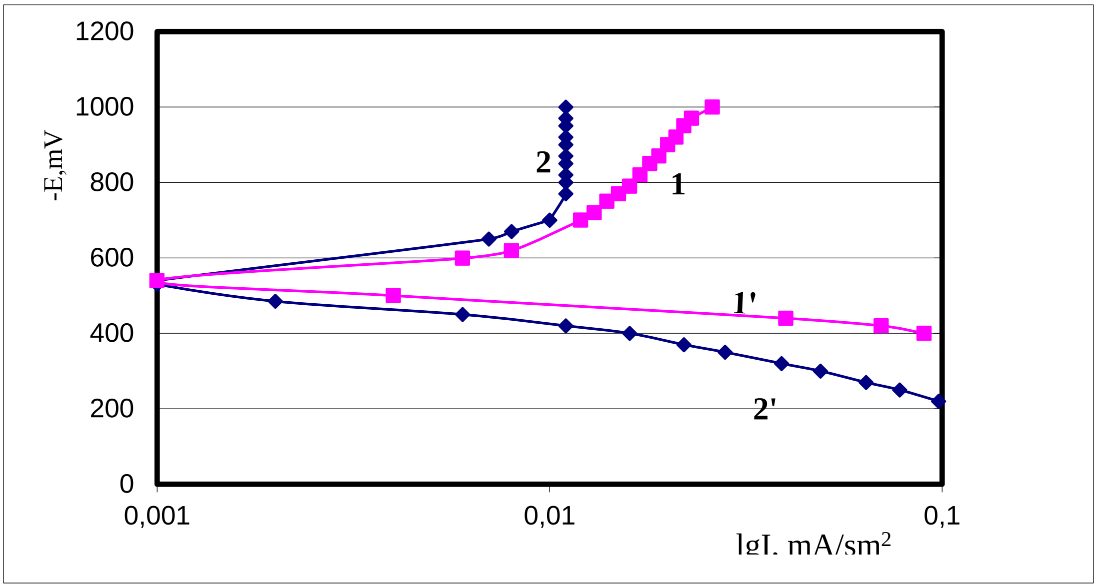


Figure 2 – Cathode (1-2) and anodic (1^1-2^1) potentiostatic polarization curves
1,1^1- cathode and anode curves without reagent
2, 2^1 - cathode and anode curves with a reagent (200 mg/l)

As can be seen from figure 2, a mixed-type reagent is capable of equally effectively inhibiting both electrochemical reactions on an electrode at a concentration of 200 mg/l, which is consistent with gravimetric tests.

In recent years, the use of physical fields encompassing fixed and variable magnetic fields has been widely used in various industrial sectors. Magnetic, like any other effect, has negative and positive sides [13-20].

Therefore, in order to examine the joint influence of the different voltage stable magnetic inductors and the developed new composite, the investigations were performed in laboratory circumstances.

To inspect the effectiveness of stable magnetic field in preservation from salt deposition and corrosion, the laboratory experiments were performed in magnetized and non-magnetized ground water throughout the period of six hours. 30x50x3 mm samples prepared from 1020 brand steel and 40, 120, 200, 280, 360, and 400 kA/m voltage stable magnetic inductors were utilized in the tests. A laboratory setup for studying the effect of a constant magnetic field on the corrosion rate in formation waters is shown in Figure 3.

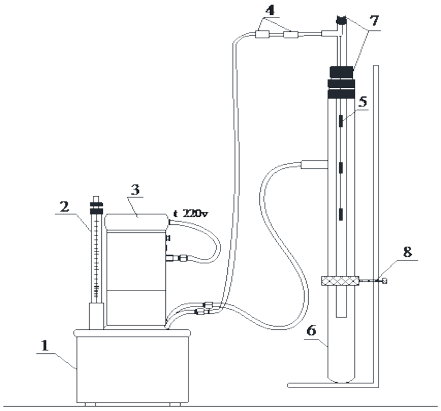


Figure 3 - Laboratory installation for studying the effect of magnetic fields on the corrosion rate in formation waters
1-thermostat u1, MLW, 2-contoct thermometer, MLW PGW, 3- Medingen/silz freital,4- magnetic inductors,5-tests coupon (samples),6- well model,7- laboratory cork, 8-laboratory tripod

The effect of stable magnetic field can vary depending upon the static regime of the exploited environment, the duration of the effect of magnetic field on the environment, the intensity of the field. Considering these, to determine the optimum effect conditions of magnetic field, the velocity of the water used in the investigations and the outcomes of the water magnetized by different voltage magnetic fields are demonstrated in figure 4 and 5.

As depicted in figure 4 and 5, in the magnetized underground water flowing at the velocity of 0.5 m/sec during the period of six hours corrosion rate and intensity of salt deposition of 1020 brand steel were 0.73 $g/m^2 \cdot hour$ and 0.0127 $mg/sm^2 \cdot hour$ accordingly. Once the environment was affected by stable magnetic field having different voltage, it was revealed that there was reduction in corrosion and salt deposition to certain extent. The maximum effect against corrosion and salt deposition was acquired in 280 kA/m voltage stable magnetic field. Therefore, when the undeground water flowed at the speed of 0.5 m/sec through 280 kA/m voltage stable magnetic field, corrosion rate and protection effectiveness against corrosion decreased up to 0.59 $g/m^2 \cdot hour$ and 19% respectively. In the meantime, intensity of salt deposition and protection effectiveness against salt deposition comprised 0.0097 $mg/sm^2 \cdot hour$ and 24% accordingly.

The influence of the magnetic field on the concentration of cations of magnesium, calcium, and iron was studied in well formation water № 117 deposits of Gunashli. The results of the study are shown in figure 6.

As can be seen from the figure, after 200-300 hours of exposure to formation water with a magnetic field of 280 kA/m, the concentration of Ca^{2+} and Mg^{2+} ions decreases, a particularly active decrease is observed in Ca^{2+}. Subsequently, with increasing time of exposure to a magnetic field, the concentration of these ions does not change. In contrast to calcium and magnesium ions, the concentration of iron ions in the first 120 hours of exposure to a magnetic field increases as a result of corrosion processes. In the range of 120-200 hours, the amount of dissolved iron stabilizes, and after 200 hours of exposure is reduced. A decrease in the concentration of iron ions in the formation water is a sign that under the influence of a constant magnetic field, the corrosion of the metal is inhibited. This assumption is confirmed by measurements of the corrosion rate made by the gravimetric method in laboratory conditions.

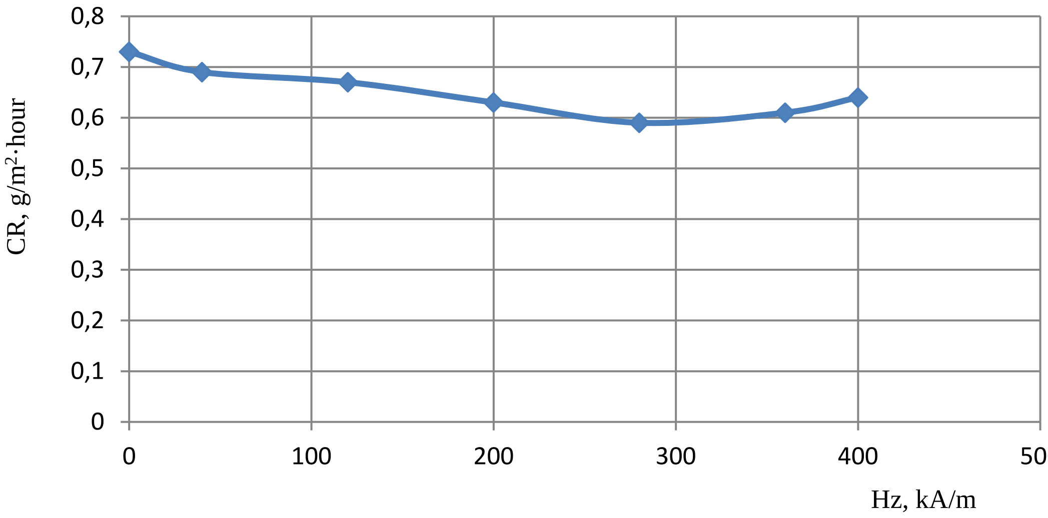


Figure 4 – Effect of stable magnetic field on corrosion rate of layer water

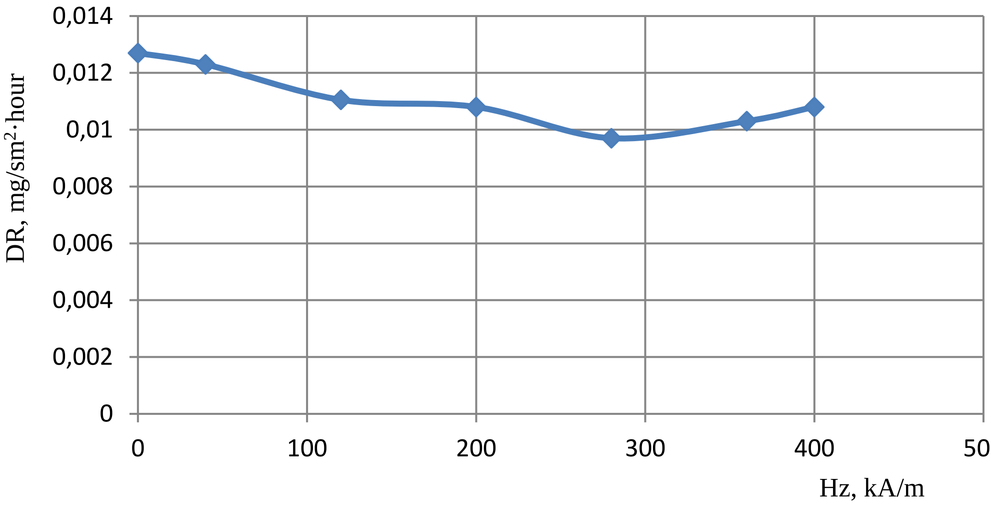


Figure 5 – Effect of stable magnetic field on intensity of salt depostion of underground water

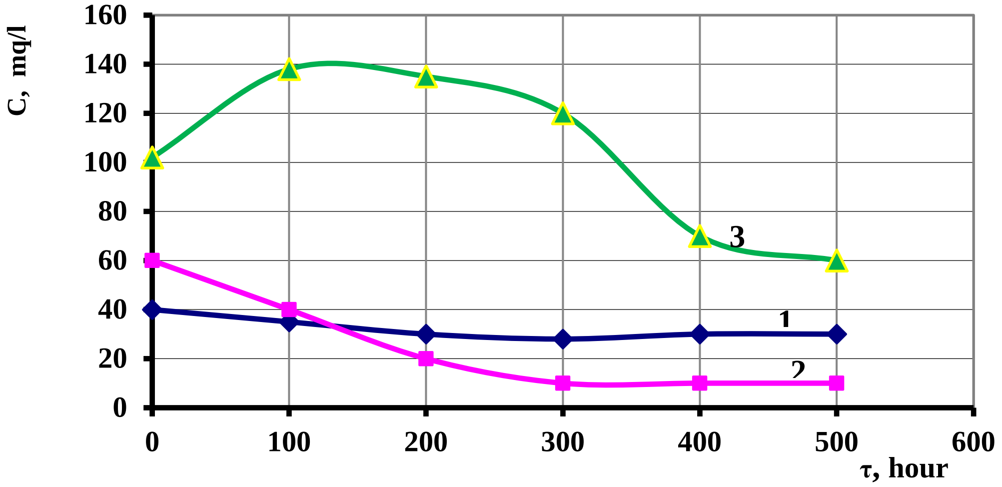


Figure 6 – Dependence of the concentration of cations of magnesium, calcium and iron in produced water of wells №117 of the Guneshli fields from the time of exposure to a magnetic field of 280 kA / m (1 - Mg^{2+}, 2 - Ca^{2+}, 3 - Fe^{2+} + Fe^{3+})

A constant magnetic field affects not only the chemical composition of the produced water, but also the number of microorganisms contained in the well's production. In laboratory conditions, the effect of a constant magnetic field of 280 kA / m on the number of SRB was studied. After 200 hours of exposure to a magnetic field, the amount of SRB decreased from 10^7bacteria/ml to 10^3bacteria/ml , indicating a biostatic effect. Thus, laboratory studies have shown that when a magnetic field of 280 kA/m is exposed to formation water, its corrosiveness decreases.

Inside aggressive environment, for researching the joint influence of 280 kA/m voltage fixed magnetic field with the prepared new composite the conducted investigation results are represented in figure 7.

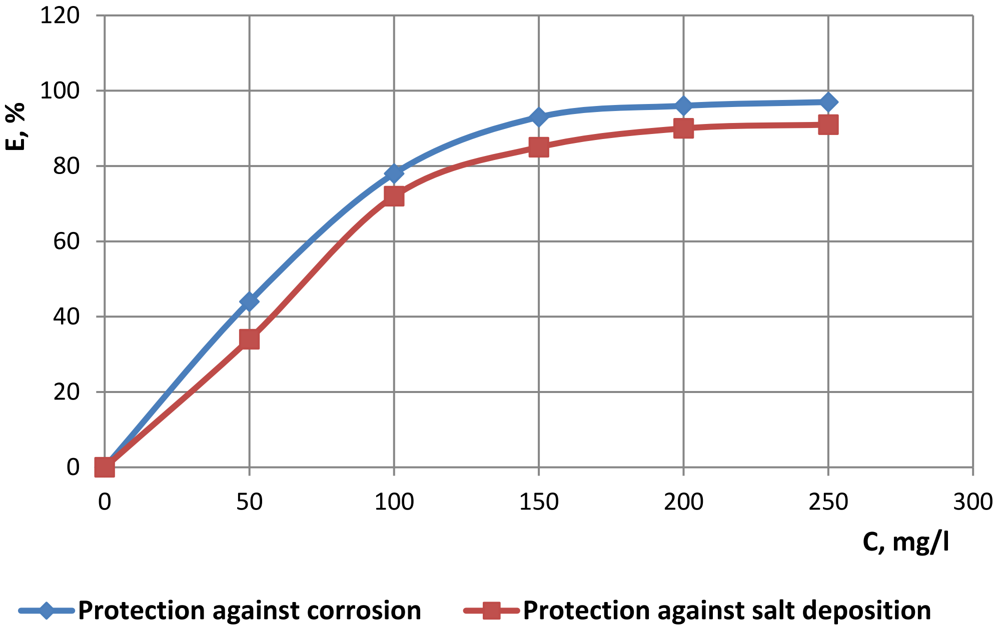


Figure 7 – Joint effect of fixed magnetic field with prepared composite on intensity of salt deposition and corrosion rate in layer water

It can apparently seem from figure 7 that the existence of protective effect is noticed as a consequence of the joint effect of 280 kA/m voltage fixed magnetic field with the prepared reagent. Thereby, it is concluded from the obtained outcomes during carrying out the laboratory experiments the optimum consumption of the composite with the fixed magnetic field is equal to 150 mg/l. In this condition, protection effectiveness against salt deposition and corrosion constitute 85% and 93% respectively. As seen from the comparative analysis of the results obtained that co-application of composition with fixed magnetic field is efficient with respect to economy. In this case, 25% of the reagent is saved.

Conducted researches have shown that the new composite can be utilized in oil wells, petrochemical plants, internal transportation systems of mines and also against corrosion and salt deposition in preservation system of layer pressure.

Production tests

Commercial tests of the combined action of the reagent and the permanent magnetic field were carried out on the cooling system of compressors“Bibiheybatneft” OGED (Oil and Gas Extraction Department).

To determine the corrosion rate by gravimetric method and assess the braking effect of the inhibitor, control specimens were installed for 30 days before and after injection of the reagent. The samples were made from steel grade 1020.

Fishing tests showed that with the use of the reagent, the corrosion rate decreased on average from 0.0815 g/m^2·hour to 0.0082 g/m^2·hour, with a protective effect of 90%. Tests have shown that treating water with a permanent magnetic field inhibitor significantly (up to 10 times) reduces the rate of corrosion.

The rate of scale deposition decreased on average from 0.0097 to 0.0026 mg/sm^2·hour and the protective effect of scaling was 73%.

Using the composite has not only expanded lifetime of pipelines and equipment and time needed for corrosion and salt deposition to be occurred, but also provided ecological safety in by decreasing the number of accidents.

Conclusions

1. A new composite has been generated from the mixture of technical phosphatide, cubic thickness of polypropylene glycol, and sodium hexametaphosphates a result of laboratory researches.
2. Optimal consumption of the composite has been determined as 200 mg/l in an aggressive environment. In this case, protection effectiveness values against corrosion and salt deposition are accounted for 94% and 87%, respectively.
3. Has been determined by means of the joint protective effect of 280 kA/m voltage fixed magnetic field with the prepared new composite. Hence, the optimal consumption has been diminished by 200 mg/l, constituting 150 mg/l. In this case, protection effectiveness against corrosion and salt deposition has been accounted for 93% and 85% accordingly.
4. The results obtained showed that the combined use of the composition with a fixed magnetic field is effective from the point of view of economy. In this case, the reagent consumption is reduced by 25%.
5. In the field with the combined use of a magnetic field and inhibitors the protective effect is 90%, and the protective effect of salt deposition is 73%.

Information about authors:

Mammedov K.A. – Ph.D, Laboratory supervisor SOCAR “Oil Gas Scientific Research Project” Institute (OGPI); к.a.mammedov@gmail.com; https://orcid.org/0000-0002-4330-0500

REFERENCES

[1] Moghadasi J. et al.(2004) Model Study on the Kinetics of Oil Field Formation Damage Due to Salt Precipitation from Injection, Journal of Petroleum Science and Engineering , 43(3-4): pp. 201–217(in Eng.).

[2] PerekupkaA. G., ElizarovaY.S.(2003)Efficiency and prospects of application of multicomponent mixtures of scale inhibitors// Technique and technology of oil production, 6: (pp. 82-84). [in Russian].

[3] Osokogwu U, Oghenekaro E. (2010) Evaluation of Corrosion Inhibitors Effectiveness in Oil Field Production Operation. International Journal of Scientific & Technology Research, 1(4): 19–23. (in Eng.).

[4] Brondel D, Edwards R., Hayman A., Hill D., Mehta S, Semerad T. (1994) Corrosion in the Oil Industry, Oilfield Review, April ,pp.4-18. (in Eng.).

[5] Orynbayev S. , Amanbayev E., Alimbayev B., Manapbayev B., Beglerova S., Myktybekov B., (2019). Internal corrosion propagation in curved sections of steel pipes//News of the national academy of sciences of the republic of Kazakhstan series of geology and technical sciences// volume 4, number 436, 213-221 https://doi.org/10.32014/2019.2518-170x.116(in Eng.).

[6] Bikchantayeva N.V., MonakhovaN.V., AleshkinaIV.(2000) Investigation of the properties of the new scaling inhibitor SNPCH-5312// Technique and technology of oil production, 11: (pp. 39-40). [in Russian].

[7] Khormali A.and Petrakov D. (2014) Scale Inhibition and its Effects on the Demulsification and Corrosion Inhibition, International Journal of Petroleum and Geoscience Engineering (IJPGE), Vol. 2, No. 1, p. 22-33(in Eng.).

[8] Khormali A, Petrakov D.G., Shcherbakov G.Y. (2014) An In-depth Study of Calcium Carbonate Scale Formation and Inhibition. Iranian Journal of Oil & Gas Science and Technology, Vol. 3, No. 4: pp. 67-77. (in Eng.).

[9] Mavredaki E. and Neville A. (2014) Prediction and Evaluation of Calcium Carbonate Deposition at Surfaces. Paper SPE 169796 presented at the SPE International Oilfield Scale Conference and Exhibition, Aberdeen, UK, 14-15 May, DOI: http://dx.doi.org/10.2118/169796-MS(in Eng.).

[10] Levanyuk O., (2012) A 3-Year Results of Application a Combined Scale Inhibition and Hydraulic Fracturing Treatments using a Novel Hydraulic Fracturing Fluid, Russia. Presented at the SPE International Conference and Exhibition on Oilfield Scale. 30–31 May, Aberdeen, UK. (in Eng.).

[11] Ketrane R., Saidani B., GilO.,(2009) Efficiency of Five Scale Inhibitors on Calcium Carbonate Precipitation from Hard Water: Effect of Temperature and Concentration. Desalination 249 (3): 1397-1404. DOI: http://dx.doi.org/10.1016/j.desal.2009.06.013 (in Eng.).

[12] Brzeszcz J., Turkiewicz A., (2015) Corrosion inhibitors - application in oil industry. NAFTA-GAZ, ROK LXXI, Vol. 2. pp. 67-75 (in Eng.).

[13] Alison J. Davenport, Yee Chin Tang, Miguel Gonzalez-Torreira, Seungeun Yang, Rex Harris., Effects of Magnetic Fields on Corrosion. The University of Birmingham Metallurgy and Materials Edgbaston, Birmingham B15 2TT, UK.https://www.electrochem.org/dl/ma/203/pdfs/0635.pdf (in Eng.).

[14] GhabashyM.A.,(1988) Effect of magnetic field on the rate of steel corrosion in aqueous solutions. Anti-Corrosion Methods and Materials, Vol. 35, Issue 1: 12-13. (in Eng.).

[15] Davenport A. J., Isaacs H. S., Kendig M.W.(1991) The Application of Surface Analysis Methods to Environmental Material Intertactions, pV 91-7, The Electrochemical Society Proceedings Series, Pennington, NJ. 433 p. (in Eng.).

[16] Botello-Zubiate M.E., Alvarez A., Martinez-Villafane A., Almeraya-Calderon F., Matutes-Aquino J.A. (2004)Influence of magnetic water treatment on the calcium carbonate phase formation and the electrochemical corrosion behavior of carbon steel. Journal of Alloys and Compounds 369. pp. 256–259. (in Eng.).

[17] Alimi F., Tlili M., Ben Amor M., Maurin G., Gabrielli C.(2009) Influence of magnetic field on calcium carbonate precipitation in thepresence of foreign ions Surface. Engineering and Applied Electrochemistry. V. 45, no. 1. pp. 56–62.(in Eng).

[18] Botello-Zubiate M.E., Alvarez A., Martinez-Villafane A., Almeraya-Calderon F.,Matutes-Aquino J.A.(2004) Influence of magnetic water treatment on the calcium carbonate phase formation and the electrochemical corrosion behavior of carbon steel. Journal of Alloys and Compounds 369. pp. 256–259 (in Eng.).

[19] Atherton D.L., Jiles D.C.(1986) Effects of Stress on Magnetization. *NDT International*, Vol. 19, pp. 15–19. (in Eng.)

[20] Jiles D.C. (1988)The Effect of Compressive Plastic Deformation on the Magnetic Properties of AISI 4130 Steels with Various Microstructures. *J. Phys. D: Appl. Phys.*, pp. 1196-1204. (in Eng.).

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2020.2518-1491.36**
Volume 2, Number 440 (2020), 153 – 155

ЮОЖ 547.94:577.15/.17

А.Х. Жакина[1], Д.С. Абдрахманова[2]

[1]ҚР ЖШС Органикалық синтез және көмірхимиясы институты, Қарағанды, Қазақстан;
[2] Қарағанды мемлекеттік техникалық университеті, Қазақстан.
E-mail: alzhakina@mail.ru, abdrahmanova-damira@mail.ru

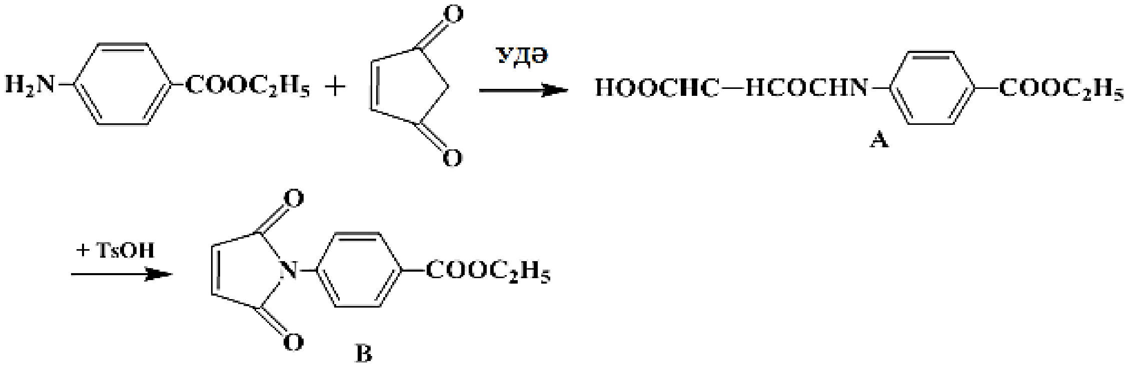
УЛЬТРАДЫБЫС ЖАҒДАЙЫНДА 4-АМИНОБЕНЗОЙ ҚЫШҚЫЛЫНЫҢ МОДИФИКАЦИЯЛАНҒАН ТУЫНДЫСЫН СИНТЕЗДЕУ

Аннотация. Қысқаша хабарламада 3-[(4-этоксикарбонил)фенилкарбамойл]-2-пропен қышқылынан этил 4-(2,5-диоксо-2,5-дигидро-1Н-пирролил)бензоатты ультрадыбыстық белсендендіруді пайдалана отырып, оны одан әрі циклдендіру кезінде, фуран циклін ашу сатысы арқылы синтездеу мүмкіндігі қарастырылған. Бастапқы реагенттер ретінде *п*-аминобензой қышқылының этил эфирі және малеин ангидриді қолданылды. Реакция бастапқы реагенттердің эквимольдік қатынасында бірқалыпты жүреді. Ультрадыбыстық қондырғы ретінде 22 кГц жиіліктегі және магнитострикциялық түрлендіргіші бар ультрадыбыстық генератормен жабдықталған ИЛ-10 ультрадыбыстық құрылғы қолданылды. Ультрадыбысты қолдану химиялық процесті қарқынды жүргізуге, реакция жылдамдығын арттыруға және соңғы өнімнің шығымдылығын арттыруға мүмкіндік береді. Алынған қосылыстың құрылымы мен құрамы ИҚ- және ЯМР ^{1}Н спектроскопиясы арқылы расталды.

Түйін сөздер: ультрадыбыс, *п*-аминобензойной қышқылының этил эфирі, малеин ангидриді, циклдену.

Биологиялық белсенді қасиеттері бар жаңа тиімді препараттарды іздеу – фармацевтика ғылымының өзекті мәселелерінің бірі. Соңғы уақытта бұл препараттарды синтездеу процесін жандандыру және химиялық реакциялардың тиімділігін арттыру үшін, толқындық химия қолданылып келеді. Ультрадыбыстық әсер (УДӘ) әдісін қолдана отырып, биологиялық белсенді қасиеттері бар қосылыстардың синтезін зерттеу ғалымдардың қызығушылығын арттырып отыр [1, 3]. Ультрадыбыс химиялық реакциялардың жылдамдығы мен бағытына айтарлықтай әсер етеді. Бағалы биологиялық белсенді заттар синтезінің негізінде жатқан реакция қабілетін арттыру үшін ультрадыбыстық әсер етуді кеңінен пайдалану өзекті мәселе болып саналады.

Зерттеушілер конденсирленген азот және оттекқұрамдас гетероцикл синтезіне жіті назар аударады. Олардың бірі – белгілі дәрілердің фармакофорты фрагменттері болса, бірі табиғи биологиялық белсенді қосылыстардың құрамына кіреді. Ғылыми деректерден n-аминобензой қышқылының туындылары мен олардың эфирлері – табиғи қосылыстардың синтетикалық аналогтары болатыны, ал пирролидон туындыларының жаңа биологиялық белсенді қосылыстардың синтезін ынталандыратын жоғары гипнозды, антиконвульсантты, антиаритмиялық белсенділігі [4-5] бар екендігі белгілі. Пирролидон ядросы бар n-аминобензой қышқылының жаңа туындыларын алу үшін ультрадыбыстық жағдайда этил 4-(2,5-диоксо-2,5-дигидро-1Н-пирролил)бензоаты синтезделді. Ультрадыбыс көзі ретінде магнитострикциялық түрлендіргішпен жабдықталған, жұмыс жиілігі 22 кГц, максималды қуаттылығы 1200 Вт және цилиндрлік толқын қондырғысы бар ИЛ-100-6 / 2 ультрадыбыстық аппараты пайдаланылды. Бұл процесс n-аминобензой қышқылының этил эфирінің малеин ангидридпен бөлме температурасында ультрадыбыстық аппарат көмегімен схема бойынша өзара әрекеттесуімен жүзеге асырылды:



Реакция бірқалыпты жүреді. Ультрадыбыстық құрылғының әсер ету уақыты 10 минутты құрады. Синтез уақыты 60 минутта 92 % шығымды құрады. Ультрадыбыс реакция жылдамдығын едәуір жеделдетіп, соңғы өнімнің шығымдылығын арттырады. Қалыпты жағдайда синтездеу уақыты 180 минутты құрады. Алынған қосылыстың құрылымы мен құрамы ИҚ-және ЯМР ^{1}H спектроскопиясы арқылы расталды.

Алынған қосылыс – 3-[(4-этоксикарбонил)фенилкарбамоил]-2-пропен қышқылы, одан әрі циклдендіру кезінде, фуран циклінің ашылу сатысын зерттеуге мүмкіндік берді. Суды азеотропты айдау арқылы толуолсульфоқышқылының ДМФА – толуол қоспасында шығымы 89 %-ды құрайтын этил 4-(2,5-диоксо-2,5-дигидро-1Н-пирролил)бензоат алынды. Алынған қосылыстың құрылымы мен құрамы ИҚ-және ЯМР ^{1}H спектроскопиясы арқылы расталды.

Тәжірибелік бөлім

3-[(4-этоксикарбонил)фенилкарбамоил]-2-пропен қышқылы (А). Ультрадыбыстық құрылғының қатысында *п*-аминобензой қышқылының этил эфирі және 20 мл. ацетон ерітіндісіне біртіндеп малеин ангидридтің 7,5 мл. эквимолярлы мөлшерін қосады. Ультрадыбыстық құрылғының әсер ету уақыты 10 минутты құрайды. 1 сағаттан кейін пайда болған тұнба сүзіледі және ацетоннан қайта кристалдандырылады. Өнімнің шығымы – 92 %-ға, балқу температурасы 192-193 °С-қа тең. Алынған қосылыстың құрылымы мен құрамы ИҚ- және ЯМР ^{1}H спектроскопиясы арқылы расталды. Алынған қосылыстың ИҚ спектрінде амид тобының (NHCO) сіңіру жолақтары 3280, 3190 см$^{-1}$ аймағында, карбонил тобының (С = О) сіңіру жолақтары 1670 см$^{-1}$ аймағында, (СОС) сіңіру жолағы 1230 см$^{-1}$аймағында байқалды.

Этил-4-(2,5-диоксо-2,5-дигидро-1Н-пирролил)бензоат (В). 3-[(4-этоксикарбонил)фенилкарбамоил]-2-пропен қышқылы толуолсульфоқышқылының қатысында және 40 мл. ДМФА-толуол қоспаларын су бөлінуінің тоқталуына дейін Дин-Старк саптамасымен қыздырады. Содан кейін буландырылады, кристалданған тұнбаны спирттен қайта кристалдандырады. Өнімнің шығымы 89 %-ға, балқу температурасы 114-115 °С-қа тең. Алынған қосылыстың құрылымы мен құрамы ИҚ-және ЯМР ^{1}H спектроскопиясымен элементтік талдау арқылы расталды. Алынған қосылыстың ИҚ спектрлерінде НС=СН тобының валентті тербеліс қарқындылығы төмен көрінеді, бірақ 3100-3090 см$^{-1}$ кезінде сипаттамалық сигнал байқалады, С=О тобының валентті тербелісі 1700-1680 см$^{-1}$ аймағында қарқынды жолақтар түрінде және әлсіз обертон түрінде 3465-3450 см$^{-1}$ аймағында, СОС тобының валентті тербелісі 1245 см$^{-1}$ аймағында байқалады. Этил 4-(2,5-диоксо-2,5-дигидро-1Н-диррил) бензоат қосылысын ЯМР ^{1}H спектрлік талдауында ароматты төрт протон сигналы H_1 – H_2 ($4H_{аром.}$, $^3J_{HH}$ 8 Гц) әлсіз өрістер аймағында көрінеді: 7,51 м.д. болғанда, дублет H_1 және 8,05 м.д. болғанда. Этил фрагментінің сигналдары: (3Н, CH_3 , $^3J_{HH}$ 8 Гц) 1,43 м.д. болғанда, синглет ретінде және (2Н, CH_2, $^3J_{HH}$ 8 Гц) 4,34 м.д. болғанда, квадруплет ретінде байқалады. (2Н, СН = СН) имид циклiндегі СН тобының протондары 7,11 м.д. болғанда, синглет түрінде байқалады.

A.Kh. Zhakina[1], D.S. Abdrakhmanova[2]

[1]Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan;
[2]Karaganda State Technical University, Kazakhstan

SYNTHESIS OF A MODIFIED 4-AMINOBENZOIC ACID DERIVATIVE UNDER ULTRASOUND CONDITIONS

Abstract. The search for new effective drugs with biologically active properties is one of the urgent problems. Recently, to intensify the process of their synthesis and increase the efficiency of chemical reactions, wave chemistry has been used. Increased interest of researchers is caused by the synthesis of compounds with biologically active properties using the method of ultrasonic treatment (US). It is known that derivatives of p-aminobenzoic acid and their esters are synthetic analogues of natural compounds, and pyrrolidone derivatives have high hypnotic, anticonvulsant, antiarrhythmic activity, which stimulates the synthesis of new biologically active compounds. In a brief report, the possibility of synthesizing ethyl-4-(2,5-dioxo-2,5-dihydro-1H-pyrrolyl) benzoate from 3-[(4-ethoxycarbonyl) phenylcarbamoyl]-2-propenoic acid using ultrasonic activation through a step is considered disclosure of the furan cycle with further cyclization. Ethyl ester p-aminobenzoic acid and maleic anhydride were used as starting reagents. An ultrasound device IL-100-6/2, equipped with a magnetostrictive transducer, with an operating frequency of 22 kHz, with a maximum power of 1200 W and a cylindrical waveguide, was used as a source of ultrasound. The synthesis of 3-[(4-ethoxycarbonyl) phenylcarbamoyl]-2-propenoic acid was carried out by reacting the starting reagents at equimolar ratios and room temperature. The US time was 10 minutes. The reaction proceeds smoothly. Ultrasound has a significant effect on the rate of chemical reactions and can increase the yield of the final product. Under classical conditions, the synthesis time was 180 minutes; using ultrasound, the synthesis time was reduced by 3 times. The product yield was 92%. The structure and composition of the obtained compound was confirmed by IR- and H^1 NMR-spectroscopy. In the IR-spectra of the obtained compound, there are absorption bands of the amide group (NHCO) in the region of 3280, 3190 cm^{-1}, absorption bands of the carbonyl group (C=O), characteristic in the region of 1670 cm^{-1}, absorption band (COC) in the region of 1230 cm^{-1}.

The resulting compound, 3-[(4-Ethoxycarbonyl) phenylcarbamoyl]-2-propenoic acid, made it possible to study the step of opening the furan ring, with further cyclization. Ethyl 4-(2,5-dioxo-2,5-dihydro-1H-pyrrolyl) benzoate was obtained in 89% yield by azeotropic distillation of water in the presence of toluenesulfonic acid in a DMFA-toluene mixture. The resulting product is a light yellow powder with melting point 114-115°C. The structure and composition of the obtained compound was confirmed by IR-and H^1 NMR-spectroscopy. In the IR-spectra of the obtained compound, the stretching vibrations of the HC=CH group manifest themselves in the form of a low-intensity but characteristic signal at 3100-3090 cm^{-1}, stretching vibrations of the C=O group as intense bands in the region of 1700-1680 cm^{-1} and a weak overtone at 3465-3450 cm^{-1}, stretching vibrations of the COC group in the region of 1245 cm^{-1}. When analyzing the H^1 NMR-spectrum of a compound, ethyl 4-(2,5-dioxo-2,5-dihydro-1*H*-pyrrolyl) benzoate, the signals of aromatic four protons H_1- H_2 ($4H_{aryl}$, $^3J_{HH}$ 8 Hz) are recorded in the field of weak fields: H_1 doublet at 7.51 ppm. and a doublet at 8.05 ppm. Signals of the ethyl fragment: (3H, CH_3, $^3J_{HH}$ 8 Hz), appear as a singlet at 1.43 ppm. and (2H, CH_2, $^3J_{HH}$ 8 Hz) quadruplet at 4.34 ppm. The protons of the CH group of the imide cycle (2H, CH=CH) appear as a singlet at 7.11 ppm.

Keywords: ultrasound, ethyl ether p-aminobenzoic acid, maleic anhydride, cyclization.

Information about authors:

Zhakina Alma Khasenovna – candidate of Chemical Sciences, docent, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, e-mail: alzhakina@mail.ru, https://orcid.org/0000-0001-5724-2279;

Abdrakhmanova Damira Sagatzhanovna – master student in the specialty 6M072100 – "Chemical technology of organic substances", Karaganda State Technical University, e-mail: abdrahmanova-damira@mail.ru, https://orcid.org/0000-0002-5170-568X

REFERENCES

[1] Gravotto G., Cintas P. (2006) Power ultrasound in organic synthesis: moving cavitational chemistry from academia to innovative and large-scale applications. Chemical Society Reviews. Volume 35, Number 2 (2006), PP. 180-196. https://doi.org/10.1039/B503848K

[2] Saleh T.S., Abd EL-Rahman N.M. (2009) Ultrasound promoted synthesis of substituted pyrazoles and isoxazoles containing sulphone moiety. Ultrasonics Sonochemistry. Volume 16, Number 2 (2009), PP. 237-242. https://doi.org/10.1016/j.ultrasonch.2008.07.012

[3] Mokhtar M., Saleh T.S., Ahmed N.S., Al-Thabaiti S.A., Al-Shareef R.A. (2011) An eco-friendly N-sulfonylation of amines using stable and reusable Zn-Al-hydrotalcite solid base catalyst under ultrasound irradiation. Ultrasonics Sonochemistry, Volume 18, Number 1, PP. 172-176. https://doi.org/10.1016/j.ultrasonch.2010.05.001

[4] Zhakina A.Kh., Gazaliev A.M., Nurkenov O.A., Kurapova M.Y. (2007) Synthesis and modification of new derivatives of 4-aminobenzoic acid ethyl ether. News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technical sciences, Number 6, (2007), PP. 88-91.

[5] Kolyamshin O.A., Danilov V.A., Koltsov N.I. (2007) 4-(3-Dialkylamino-2,5-dioxopyrrolidin-1-yl)benzoic acid esters. Russian Journal of Organic Chemistry, Volume 43(3), (2007), PP. 393-396. https://doi.org/10.1134/S1070428007030104

МАЗМҰНЫ

Жакина А.Х., Арнт О.В., Василец Е.П., Животова Т.С., Мулдахметов З.М., Газалиев А.М., Семенова С.А. Көмір өндіру қалдықтары негізіндегі композиттік материалдың синтезі мен қасиеттері........ 6

Нурлыбаева А.Н., Рустем Е.И., Садиева Г.Р., Сейтбекова Г.А., Дарменбаева А.С., Калмаханова М.С., Егисинова А.М., Отыншиева У.Т. Акрил үлдірлерін синтездеу және лак-бояу материалдарына қолдану........ 14

Файзуллаев Н., Акмалайұлы К., Каржавов А. Ацетон линиясының катетикалық синтезі........ 23

Баешов А.Б., Тулешова Э.Ж., Баешова А.К., Өзлер М. Калий ферроцианиді ерітіндісіндегі күмістің электрохимиялық қасиеті 31

Ташимбетова А.Б., Умбетова А.К., Халменова З.Б., Ихсанов Е.С., Чоудхари М.И., Абилов Ж.А., Бурашева Г.Ш. *Lavandula fertilizer*-дің химиялық зерттеуі........ 39

Естемесов З.А., Садыков П.И., Барвинов А.В., Сарсенбаев Н.Б., Естемесов М.З., Уралханова А.У., Тулаганов А.А. Түйіршіктелген фосфор қождары үйінділерінде болатын физикалық-химиялық процестер........ 47

Жұмаділлаева С.А., Баешов Ә.Б., Колесников А.В. Жоғары майлы қышқылдардың каталиттік гидразинолизін зерттеу........ 56

Фазылов С.Д., Нұркенов О.А., Сейлханов Т.М., Аринова А.Е., Газалиев А.М., Ибраев М.К., Фазылов А.С. N-метил-2-(пирид-4-ил)-3,4-фуллеропирролидиннің синтезі және қасиеттері........ 62

Ихсанов Е.С., Тасмагамбетова Г.Е., Литвиненко Ю.А., Сейтимова Г.А., Бурашева Г.Ш. *Rosa Canina L.* өсімдік жемістерінің липофильді фракциясынын фитохимиялық құрамы........ 69

Касымова М.К., Кобжасарова З.И., Орымбетова Г.Э., Нурынбетова Г., Блиджа Анита. «Шымкентмай» АҚ шығаратын күнбағыс майын пайдаланып эмульсиялық тұздық технологиясын өңдеу........ 75

Куатбаева Т.К., Наширалиев Ж. Т., Жамбакина З. М., Бруяко М. Г., Орынова А. Т. Мұнай битуминозды жыныстар мен оларды өңдеудің қалдықтарыпайдаланып және өңдеп силикатты материалдардын жасау........ 83

Абильмагжанов А.З., Иванов Н.С., Малимбаев М.С., Адельбаев И.Е., Нуртазина А.Е., Алтынбек А.Д., Шокобаев Н.М. Уранды шаймалау тиімділігін арттыру үшін бивалентті темірді каталитикалық тотығуы........ 92

Пузикова Д.С., Дергачева М.Б., Хусурова Г.М. Фотоэлектрохимиялық қолдануға арналған жұқа $CuBi_2O_4$ плекаларын алу әдісі........ 99

Волкова Л.Д., Закарина Н.А., Ким О.К., Акурпекова А.К., Жумадуллаев Д.А., Яскевич В.И., Григорьева В.П., Габдракипов А.В. Вакуумдық газойль және оның мазутпен қоспасының крекингіндегі алюминиймен түрлерндірілген каолинит........ 107

Джетписбаева Г.Д., Масалимова Б.К., Даулет А.Б. Со-құрамды перовскит құрылымды $LACOO_3$ катализаторын синтездеу........ 115

Абдрахманов Е.С., Ермағамбет Б.Т., Касенова Ж.М., Казанкапова М.К., Сайранбек А. Исследование надежности шнекового узла углебрикетного пресса БТ-3М........ 120

Баешов А.Б., Мамырбекова А.К., Касымова М.К., Мамитова А.Д., Мамырбекова А.К., Чечина О.Н. Қорғасын электродында қорғасын иондарын(II) тотықсыздануына беттік-активті заттардың әсері........ 129

Наурызкулова С.М., Масалимова Б.К., Шораева К.А., Джиенбаева Г.М., Арапова М.В., Садыков В.А. Этанолдың бу айналымы үшін NI-RU негізіндегі композиттерді синтездеу және олардың құрылымдық қасиеттерін зерттеу........ 138

Мамедов К.А. Жаңа құрама ингибитор мен тұрақты магнит өрісінің коррозияға және тұзға әсерін зерттеу........ 145

Қысқаша ғылыми хабарламалар

Жакина А.Х., Абдрахманова Д.С. Ультрадыбыс жағдайында 4-аминобензой қышқылының модификацияланған туындысын синтездеу........ 153

СОДЕРЖАНИЕ

Жакина А.Х., Арнт О.В., Василец Е.П., Животова Т.С., Мулдахметов З.М., Газалиев А.М., Семенова С.А. Синтез и свойства композитного материала на основе отходов угледобычи 6
Нурлыбаева А.Н., Рустем Е.И., Садиева Г.Р., Сейтбекова Г.А., Дарменбаева А.С., Калмаханова М.С., Егисинова А.М., Отыншиева У.Т. Синтез и применение акриловых пленок в лакокрасочных материалах..... 14
Файзуллаев Н., Акмалайұлы К., Каржавов Б. Каталитический синтез линии гидратацией ацетилена..... 23
Баешов А.Б., Тулешова Э.Ж., Баешова А.К., Өзлер М. Электрохимическое поведение серебра в растворе ферроцианида калия..... 31
Ташимбетова А.Б., Умбетова А.К., Халменова З.Б., Ихсанов Е.С., Чоудхари М.И., Абилов Ж.А., Бурашева Г.Ш. Химическое исследование *Lavandula fertilizer*..... 39
Естемесов З.А., Садыков П.И., Барвинов А.В., Сарсенбаев Н. Б., Естемесов М.З., Уралханова А.У., Тулаганов А.А. Физико-химические процессы, происходящие в отвалах гранулированных фосфорных шлаков..... 47
Джумадуллаева С.А., Баешов А.Б., Колесников А.В. Исследование каталитического гидразинолиза высших жирных кислот..... 56
Фазылов С.Д., Нуркенов О.А., Аринова А.Е., Сейлханов Т.М., Газалиев А.М., Ибраев М.К., Фазылов А.С. Синтез и свойства N-метил-2-(пирид-4-ил)-3,4-фуллеропирролидина..... 62
Ихсанов Е.С., Тасмагамбетова Г.Е., Литвиненко Ю.А., Сейтимова Г.А., Бурашева Г.Ш. Фитохимический состав липофильной фракции плодов растения *Rosa Canina L.* рода шиповник (*Rosa*)..... 69
Касымова М.К., Кобжасарова З.И., Орымбетова Г.Э., Нурынбетова Г., Блиджа Анита. Использование подсолнечного масла, выпускаемой АО «Шымкентмай» при разработке технологии эмульсионного продукта…..... 75
Куатбаева Т.К., Наширалиев Ж. Т., Жамбакина З. М., Бруяко М. Г., Орынова А. Т. Использование нефтебитуминозных пород и отходов их переработки в создании композиционных силикатных материалов…..... 83
Абильмагжанов А.З., Иванов Н.С., Малимбаев М.С., Адельбаев И.Е., Нуртазина А.Е., Алтынбек А.Д., Шокобаев Н.М. Каталитическое окисление двухвалентого железа для повышения эффективности выщелачивания урана..... 92
Пузикова Д.С., Дергачева М.Б., Хусурова Г.М. Способ изготовления тонких пленок $CuBi_2O_4$ для фотоэлектрохимических применений..... 99
Волкова Л.Д., Закарина Н.А., Ким О.К., Акурпекова А.К., Жумадуллаев Д.А., Яскевич В.И., Григорьева В.П., Габдракипов А.В. Модифицированный алюминием каолинит в крекинге вакуумного газойля и его смеси с мазутом..... 107
Джетписбаева Г.Д., Масалимова Б.К., Даулет А.Б. Синтез перовскитоподобного Co-содержащего катализатора..... 115
Абдрахманов Е.С., Ермағамбет Б.Т., Касенова Ж.М., Казанкапова М.К., Сайранбек А. Исследование надежности шнекового узла углебрикетного пресса БТ-3М..... 120
Баешов А.Б., Мамырбекова А.К., Касымова М.К., Мамитова А.Д., Мамырбекова А.К., Чечина О.Н. Влияние поверхностно-активных веществ на восстановление ионов свинца(II) на свинцовом электроде 129
Наурызкулова С.М., Масалимова Б.К., Шораева К.А., Джиенбаева Г.М., Арапова М.В., Садыков В.А. Синтез и изучение структурных свойств композитов на основе NI-RU для паровой конверсии этанола ……..... 138
Мамедов К.А. Изучение влияния нового комбинированного ингибитора и постоянного магнитного поля на коррозию и солеотложение 145

Краткие научные сообщения

Жакина А.Х., Абдрахманова Д.С. Синтез модифицированного производного 4-аминобензойной кислоты в условиях ультразвука..... 153

CONTENTS

Zhakina A.Kh., Arnt O.V., Vassilets Ye.P., Zhivotova T.S., Muldahmetov Z.M., Gazaliev A.M., Semenova S.A. Synthesis and properties of a composite material based on coal mining waste...... 6

Nurlybayeva A.N., Rustem E.I., Sadiyeva H.R., Seitbekova G.A., Darmenbayeva A.S., Kalmakhanova M.S., Egisinova A.M., Otinshieva U.T. Synthesis and application of acrylic films in paint and varnish materials...... 14

Fayzullayev N., Akmalaiuly K., Karjavov A. Catalytic synthesis of a line by acetylene hydration…...... 23

Bayeshov A.B., Tuleshova E.Zh., Baeshova A.K., Ozler M.A. Electrochemical behavior of silver in a potassium ferrocyanide solution...... 31

Tashimbetova A.B., Umbetova A.K., Halmenova Z.B., Ikhsanov Y.S., Choudhary M.I., Abilov Zh.A., Burasheva G.Sh. Chemical study of *Lavandula fertilizer*...... 39

Estemesov Z.A., Sadykov P.I., Barvinov A.V., Sarsenbaev N. B., Estemesov M.Z., Uralkhanova A.U., Tulaganov A. A. Physical and chemical processes occurring in the granulated phosphorus slag dumps...... 47

Dzhumadullaeva S.A., Bayeshov A.B., Kolesnikov A.V. Study of the catalytic hydrazinolysis of higher fatty acids...... 56

Fazylov S.D., Nurkenov O.A., Arinova A.E., Seilkhanov T.M., Gazaliev A.M., Ibraev M.K., Fazylov A.S. Synthesis of properties N-methyl-2-(pyrid-4-yl)-3,4-fulleropyrrolidine 62

Ikhsanov Y.S., Tasmagambetova G.E., Litvinenko Y.A., Burasheva G.Sh., Seitimova G.A. Phytochemical composition of lipophilic fraction of plants of the plant *Rosa Canina L.* genus Rosa...... 69

Kassymova M.K., Kobzhasarova Z.I., Orymbetova G.E., Nurynbetova G., Blija Anita. Use sunflower oil produced by JSC «Shymkentmay» at the development of technology of emulsion product 75

Kuatbayeva T.K., Nashiraliyev Zh. T., Zhambakina Z. M., Bruyako M. G., Orynova A. T. Use of oil and bituminous rocks and waste from their processing in creation of composite silicate materials...... 83

Abilmagzhanov A.Z., Ivanov N.S., Malimbaev M.S., Adelbayev I.Y., Nurtazina A.E., Altynbek A.D., Shokobayev N.M. Catalytic oxidation of ferrous iron to increase the efficiency of uranium leaching...... 92

Puzikova D.S., Dergacheva M.B., Khussurova G.M. Method for manufacturing thin films of cubi$_2$O$_4$ for photoelectrochemical applications...... 99

Volkova L.D., Zakarina N.N., Kim O.K., Akurpekova A.K., Zhumadullaev D.A., Yaskevich V.I., Grigorjeva V.P., Gabdrakipov A.V. Kaolinite modified by aluminum in the cracking of vacuum gasoil and it's mixture with fuel oil…...... 107

Jetpisbayeva G.D., Massalimova B.K., Daulet A.B. Synthesis of perofskite-like Co-containing catalyst...... 115

Abdrakhmanov E.S., Yermagambet B.T., Kassenova Zh.M., Kazankapova M. K., Sairanbek A. Investigation of reliability of the screw unit of the coal-roll press BT-3M...... 120

Bayeshov A.B., Mamyrbekova A.K., Kassymova M.K., Mamitova A.D., Mamyrbekova A.K., Chechina O.N. Effect of surfactants on the reduction of lead(II) ions on lead electrode...... 129

Naurzkulova S.M., Massalimova B.K., Shorayeva K.A., Dzhienbaeva G.M., Arapova M.V., Sadykov V.A. Synthesis and study of structural properties of composites based on NI-RU for steam conversion of ethanol...... 138

Mammedov K.A. Study of the effect of a new combined inhibitor and a permanent magnetic field on corrosion and salt deposition...... 145

Brief Scientific Messages

Zhakina A.Kh., Abdrakhmanova D.S. Synthesis of a modified 4-aminobenzoic acid derivative under ultrasound conditions...... 153

Publication Ethics and Publication Malpractice in the journals of the National Academy of Sciences of the Republic of Kazakhstan

For information on Ethics in publishing and Ethical guidelines for journal publication see http://www.elsevier.com/publishingethics and http://www.elsevier.com/journal-authors/ethics.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the described work has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see http://www.elsevier.com/postingpolicy), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct (http://publicationethics.org/files/u2/New_Code.pdf). To verify originality, your article may be checked by the Cross Check originality detection service http://www.elsevier.com/editors/plagdetect.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of Sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of Sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации
в журнале смотреть на сайте:

www:nauka-nanrk.kz

http://chemistry-technology.kz/index.php/en/arhiv

ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: *М. С. Ахметова, Г. Б. Халидуллаева, Д. С. Аленов*
Верстка на компьютере *А.М. Кульгинбаевой*

Подписано в печать 02.04.2020.
Формат 60х881/8. Бумага офсетная. Печать – ризограф.
10 п.л. Тираж 300. Заказ 2.

Национальная академия наук РК
050010, Алматы, ул. Шевченко, 28, т. 272-13-18, 272-13-19