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

Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75

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**T.S. Baizhumanova¹, S.A. Tungatarova^{1,3}, G. Xanthopoulou²,
Z.T. Zheksenbaeva^{1,3}, R. Sarsenova¹, K. Kassymkan¹,
G. Kaumenova³, A.O. Aidarova⁴, A. Erzhanov³**

¹D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan;

²Institute of Nanoscience and Nanotechnology, NCSR Demokritos, Athens, Greece;

³Al-Farabi Kazakh National University, Almaty, Kazakhstan;

⁴Taraz State Pedagogical University, Taraz, Kazakhstan

baizhuma@mail.ru

CATALYTIC OXIDATION OF A C₃-C₄ MIXTURE ON POLYOXIDE CATALYSTS

Abstract. The results of a study of the activity of polyoxide catalysts based on molybdenum, chromium and gallium supported on natural clays for the catalytic oxidation of light alkanes to industrially important chemical products are presented. The developed three-component catalytic systems based on molybdenum, chromium and gallium showed catalytic activity in the reactions of gas-phase and liquid-phase oxidation of linear hydrocarbons to aldehydes, alcohols, ketones and olefins. Studies of the oxidative conversion of a propane-butane mixture on molybdenum, chromium and gallium polyoxometallates supported on natural clays allowed to determine that the predominant composition of the products is determined by the temperature of the process. A sequential and combined method of introducing the active components into the composition of the developed catalysts was studied. It has been determined that the sequential introduction of one or two components negatively influence on the efficiency of catalyst. It is assumed that the metals begin to react with each another (as observed visually during preparation of catalysts) and eliminates the additional separate drying and calcination of each supported subsequent element separately at co-supporting process of active phase of catalyst on carrier. It was determined that the simultaneous introduction of all components into the impregnating solution is optimal. It was found that the production of a number of products with high yields: acetaldehyde - at 673-723 K, acetone - at 823 K, methanol - at 673-723 K, MEK - at 773-823 K, ethanol - at 823 K, ethylene - at 673 -723 K, H₂ - at 823 K is possible at oxidative conversion of propane-butane mixture at GHSV = 450 h⁻¹ on the developed three-component supported Mo-Cr-Ga catalysts. It has been determined that 5 and 10% Mo-Cr-Ga catalysts are optimal for obtaining of products in both the liquid and gas phase, and 1% Mo-Cr-Ga catalyst is more favorable for the synthesis of products in the gas phase.

Key words: catalytic oxidation, catalysts, C₃-C₄ mixture.

Introduction

Natural and oil gases are the most important alternative sources of raw materials, capable in the long term to compete with oil. The problem of rational use of C₁-C₄ alkanes, included in their composition, is particularly relevant in countries rich in this type of raw materials. Despite the huge reserves of hydrocarbon raw materials in the Republic of Kazakhstan, it is mainly spent in the form of domestic, industrial and motor fuel, and the remaining raw materials are burned as part of exhaust gases, or again pumped into oil reservoirs. In this regard, the processing of alkanes (the main components of natural gas and oil) for the purpose of obtaining industrially important chemical products is one of the most urgent environmental problems in Kazakhstan.

Formation of synthesis gas, unsaturated hydrocarbons, aldehydes, acids and alcohols should be expected at incomplete oxidation of methane, ethane, propane and butane. Only the optimal selection of catalysts can purposefully to carry out the process with preferential formation one of the listed products.

However, the development of new effective catalysts for selective oxidation of light alkanes is still at the stage of research and development [1-11].

In the process of oxidative conversion of propane-butane mixture on various types of catalysts is possible to obtain a range of products such as oxygenates [12-16], olefins [16-20], hydrogen [21,22], synthesis gas [23-25] and $\text{CO}_2 + \text{H}_2\text{O}$ [26].

Experimental

Catalyst preparation

Preliminary preparation was carried out for the preparation of catalysts on natural carriers. The natural carriers were dried at 473 K for 2 h, calcined at 773 K for 2 h and then treated in a solution of 10% HCl and calcined again at 773 K for 2 h. The catalysts were prepared by the capillary impregnation method of mixed aqueous solutions of nitrate salts of metals, supported on preformed natural clays.

Characterization techniques

The analysis of the initial mixture and reaction products was carried out using a chromatograph "Chromos GC-1000" with the "Chromos" software and on a chromatograph "Agilent Technologies 6890N" (USA) with computer software. Chromatograph "Chromos GC-1000" is equipped with packed and capillary columns. The packed column is used for the analysis of H_2 , O_2 , N_2 , CH_4 , C_2H_6 , C_2H_4 , $\text{C}_3\text{-C}_4$ hydrocarbons, CO and CO_2 . A capillary column is used to analyze liquid organic substances, such as alcohols, acids, aldehydes, ketones and aromatic hydrocarbons. Temperature of the detector by thermal conductivity – 200°C, evaporator temperature – 280°C, column temperature – 40°C. Carrier gas velocity $\text{Ar} = 10$ ml/min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve $V = f(S)$ was constructed, where V - amount of substance in ml, S - peak area in cm^2 . Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was $\pm 3.0\%$.

Physico-chemical research

The phase composition of catalysts was determined on X-ray diffractometer DRON-4-7 with Co-anode (25 kV, 25 mA, $2\theta = 15\text{-}80^\circ$).

Determination of the surface was conducted by low-temperature adsorption of nitrogen by the BET method on the "Accu Sorb" installation from Micromeritics produced in the USA.

Morphology, particles size, chemical composition of initial and worked out catalysts were performed on transmission electron microscope TEM-125K with enlargement up to 66000 times by replica method with extraction and micro diffraction. Carbonic replicas were sputtered in vacuum universal station, and carrier of catalysts was dissolved in HF. Identification of micro diffraction patterns was carried out by means of ASTM card index (1986).

Results and discussion

The results of a study of activity of the Mo-Cr-Ga catalysts supported on natural clays of different content in the process of partial oxidation of propane-butane mixture at $\text{C}_3\text{-C}_4 : \text{O}_2 : \text{N}_2 : \text{Ar} = (33.33 : 7.0 : 26.34 : 33.33, \%)$, $\text{GHSV} = 450 \text{ h}^{-1}$ and a temperature range of 673-823 K are presented. As can be seen from Figure 1, the formation of C_2H_4 , H_2 , and CO_2 was observed at oxidative conversion of propane-butane mixture on the developed 1% MoCrGa catalyst. A 39.2% yield of ethylene passed through a maximum at 773 K. The formation of 1.0 – 2.6% H_2 was also observed. 39.5% of CO_2 is formed by raising the reaction temperature to 773 K and up to 823 K in reaction mixture. With increasing temperature, the process proceeds towards the formation of a deep oxidation product (CO_2) along with oxidative dehydrogenation (C_2H_4 , H_2).

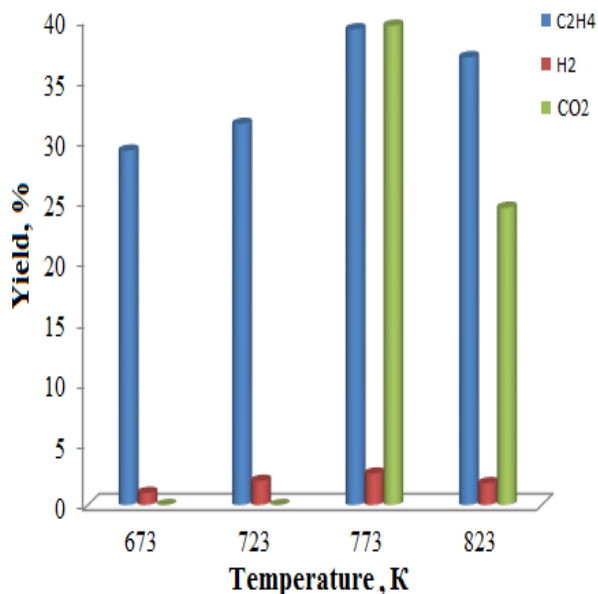


Figure 1 - Oxidative conversion of propane-butane mixture on 1% MoCrGa catalyst

Figure 2 shows the activity of 5% MoCrGa/TWC catalyst at oxidative conversion of propane-butane mixture. The greatest yields of acetaldehyde and methanol were obtained at relatively low temperatures of 673-723K. The yield of acetaldehyde decreased from 33.3% to 11.5% with an increase in temperature from 673 K to 823 K, and methanol - from 13.8% to 10.7% at 773 K. Methanol was not detected in product at higher temperatures. A different picture was observed for acetone and methyl ethyl ketone. The maximum yields for these products were observed at 823 K. The yield of acetone at this temperature was 50.9%, and methyl ethyl ketone - 37.6%. It was determined that content of ethylene at all temperatures decreased compared with 1% catalyst. However, the yield of hydrogen increased from 5.7 to 18.8%. The formation of products of deep oxidation was not observed.

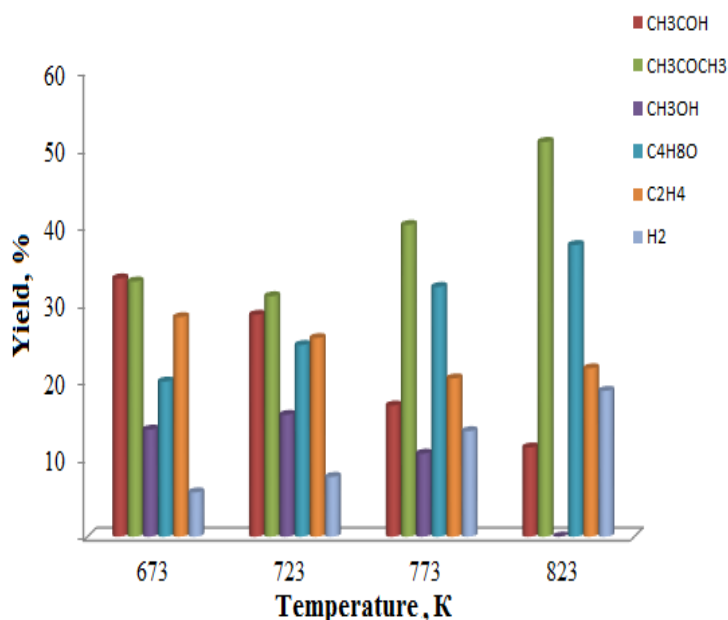


Figure 2 - Oxidative conversion of propane-butane mixture on 5% MoCrGa catalyst

The same trend of reduction of gaseous substances in reaction products was observed at a further increase in the content of MoCrGa on the carrier to 10%. The yield of ethylene did not exceed 8.6%. A new product - ethanol appeared in the liquid phase, the yield of which was 66.0% at 823 K.

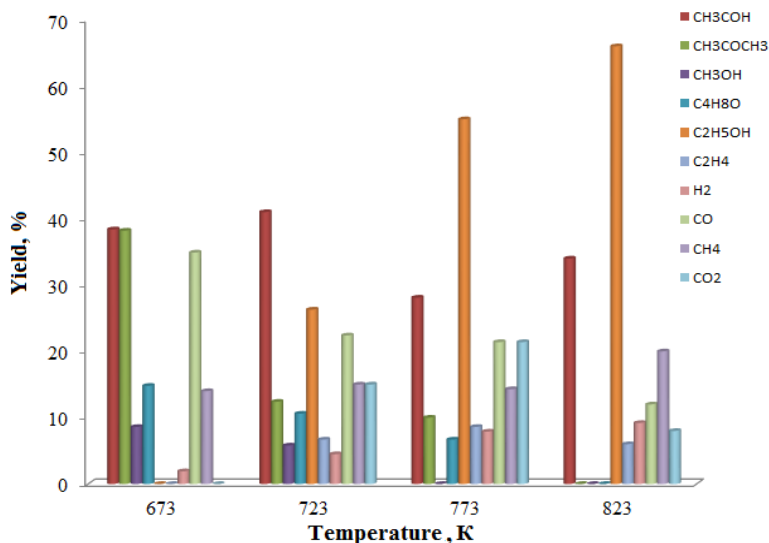


Figure 3 - Oxidative conversion of propane-butane mixture on 10% MoCrGa catalyst

It can be seen from the data in Figure 3 that the decrease in the formation of acetaldehyde, acetone, methanol, MEK, ethylene and hydrogen compared to the 5% catalyst composition was observed on this catalyst composition.

Thus, the production of a number of products with high yields: acetaldehyde - at 673-723 K, acetone - at 823 K, methanol - at 673-723 K, MEK - at 773-823 K, ethanol - at 823 K, ethylene - at 673- 723 K, H₂ - at 823 K is possible during the oxidative conversion of propane-butane mixture at GHSV = 450 h⁻¹ on 1-10% MoCrGa catalysts. It was determined that 1% MoCrGa/TWS catalyst is more suitable for the synthesis of gaseous products. It has been established that 5% MoCrGa catalyst is optimal for obtaining of high yields as liquid products of partial oxidation and oxidative dehydrogenation products (33.3% acetaldehyde, 50.9% acetone, 15.7% methanol, 37.6% MEK, 28.3% ethylene and 18.8% H₂).

The polyoxide MoCrGa catalysts supported on natural clays investigated in the oxidative conversion of propane-butane mixture were studied by physical-chemical methods. The specific surface and porosity of the studied sorbent samples were determined by the BET method for low-temperature nitrogen adsorption. It was established that the clay surface is 10-16 m²/g, and the change in the optimum pore radius was observed from 20 to 50 Å. Elemental analysis of the initial and processed samples of sorbents with 10% HCl showed that the oxide compounds of Si, Al, as well as Ca, Mg, Fe, and Na are predominantly present in clay samples. The ratio of SiO₂/Al₂O₃ (silicon module) was 5-0.4. The silicon module increased after acid treatment, but the phase composition remained practically unchanged. In the course of work, it was determined that the yields of target products on the catalysts pretreated with 10% HCl exceed analogous yields on the untreated catalysts. It is assumed that acid treatment of sorbents contributed to the development of surface and increase in the pore radius, which led to increase in the yield of target products of the oxidative conversion of propane-butane mixture.

It was established by the XRD method that the kaolinite Al₂[OH]₄Si₂O₅ (JCPDS-29-1488), α-quartz SiO₂ (JCPDS 5-490) and the X-ray amorphous component (short-range order 4.20 Å) are the main phase of natural clay. The diffractograms of spent catalysts under reaction conditions at 573 and 773 K are identical. The 3.62, 2.66, and 2.48 reflexes, relating to the phase of Cr₂O₃ (JCPDS 6-504) and the 3.52, 2.67, 2.38 reflexes, relating to the phase of Cr₃O₁₂ (JCPDS 18-390) were detected. The 3.52 reflex refers, perhaps, to textured kaolinite. The structural elements relating to Ga and Mo were not detected because of their dispersity.

Electron microscopic studies have shown that the presence of a large number of insoluble components, which make it difficult to decipher the deposited phases is characteristic for carrier. Large particles and aggregates from large dense particles are characteristic for the initial samples of MoCrGa. Their microdiffraction pattern is represented by separate rare reflections attributed to Cr₂O₃ (JCPDS, 6-508) and CrO (JCPDS, 6-532), as well as to semitransparent plate-like particles, the microdiffraction pattern from which is represented by reflexes located on a hexagonal motif referred to CrMoO₄ (JCPDS,

34-474). The presence of combined chromium-molybdenum-gallium phases is characteristic for samples processed under experimental conditions.

Figure 4a shows small clusters composed by particles with a size of 30-50 Å and big plate-like particles. A mixture of rings and separate reflexes presents the microdiffraction. The rings correspond to CrMoO_4 phase (JCPDS, 29-452) - dispersed particles. The big plate crystals correspond to CrMoO_6 (JCPDS, 33-401).

Figure 4b shows an aggregate of dense particles with signs of cutting with a minimum dimension of $\sim 200^\circ$. The microdiffraction pattern is presented by reflexes arranged along the rings, and corresponds to a mixtures of $\text{Cr}_{0.17}\text{Mo}_{0.83}\text{O}_2$ (JCPDS, 34-473) and CrO (JCPDS, 6-532).

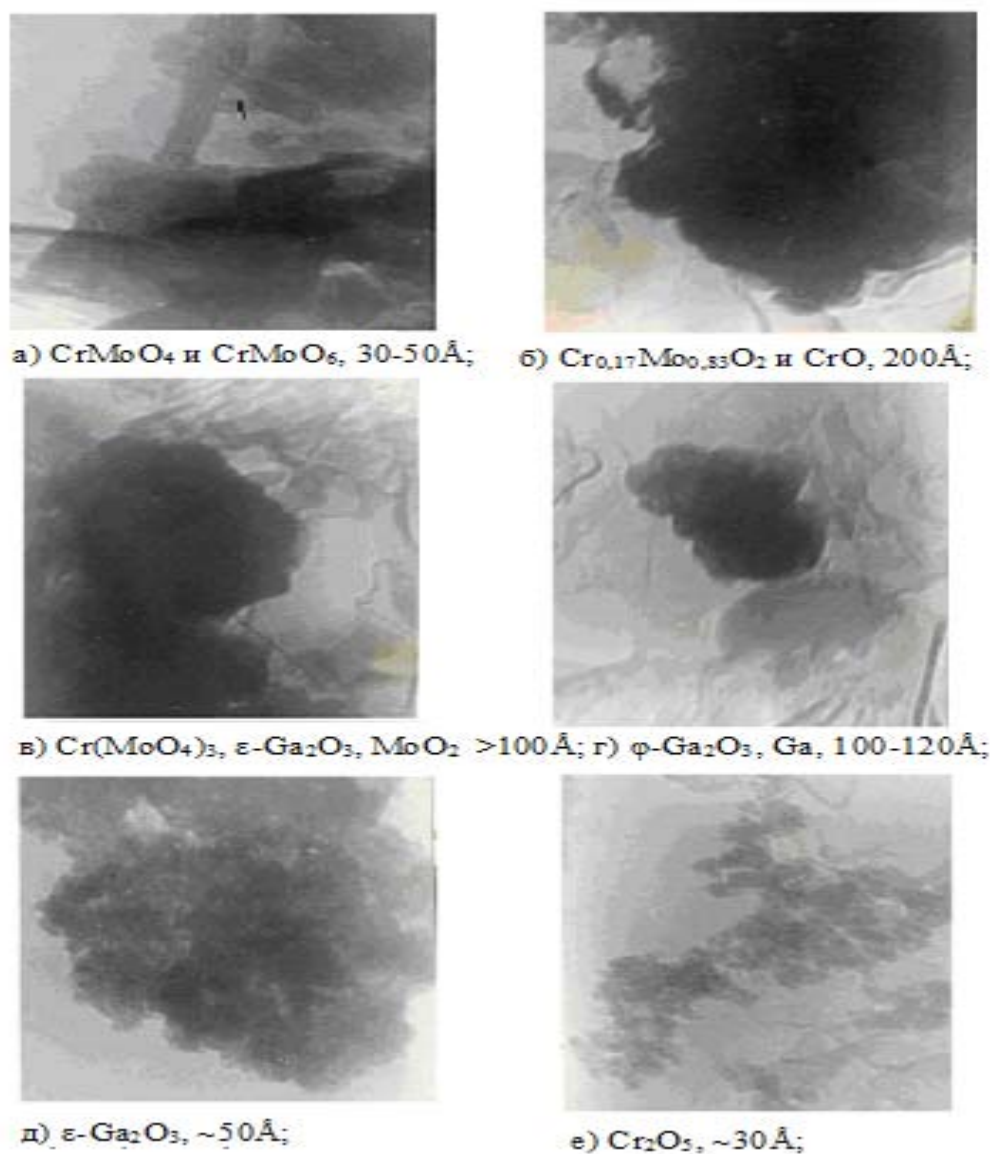


Figure 4 – Electron microscopic images of the 5%MoCrGa (x 66000)

The microdiffraction pattern of aggregate (Figure 4c) is presented by rings and reflexes which are located by series and corresponds to a mixture of $\text{Cr}(\text{MoO}_4)_3$ (JCPDS, 20-309), MoO_2 (JCPDS, 9-209) and, possibly, $\varepsilon\text{-Ga}_2\text{O}_3$ (JCPDS, 6-503) phases, where there are aggregates with a size more than 100 Å and individual large particles. A small aggregate (Figure 4d) with a particle size of 100-120 Å is presented in a microdiffraction pattern by separate reflexes and corresponds to $\varphi\text{-Ga}_2\text{O}_3$ (JCPDS, 20-426) in a mixture with Ga (JCPDS, 31-539). The extensive aggregation (Figure 4e) from dispersed particles of size

$\sim 50\text{Å}$ corresponds to $\varepsilon\text{-Ga}_2\text{O}_3$ (JCPDS, 6-509). Smaller dispersed particles (Figure 4f) size of $\sim 30\text{Å}$ are assigned to Cr_2O_5 (JCPDS, 36-1329).

Comparison EM images of the 1-10% MoCrGa samples showed that the set of phases is significantly reduced at simultaneous enlargement of particles with increasing the content of active component on the carrier.

$\text{CrMoO}_2 + \text{CrO}$ spinels with a particle size of 600Å and Ga_2O_3 of various modifications (α and ϕ) as well as Cr^{5+} remain on the surface of the 5% MoCrGa sample treated at 623 K. The Cr^{5+} , CrOOH phases disappear on the surface. The phases corresponding to Ga^{3+} and Cr^{3+} are present in all catalysts, becoming somewhat larger in size. The appearance of spinel (CrMoO_6) with a size of 500Å , which was absent at 573 K, and also Cr^{2+} is a distinguishing feature of the highly active optimal 5% MoCrGa catalyst heated at 823 K. This facilitates the process both towards partial oxidation and towards oxidative dehydrogenation with optimum production of the desired reaction products.

Conclusion

Thus, developed three-component catalytic systems based on Mo, Cr and Ga showed catalytic activity in gas-phase and liquid-phase oxidation of linear hydrocarbons to aldehydes, alcohols, ketones and olefins. The research of oxidative conversion of propane-butane mixture on polyoxide catalysts based on molybdenum, chromium and gallium supported on natural clay allowed to determine that preferential composition of products is determined by temperature of process. It was found that 5% MoCrGa catalyst in which by varying the reaction temperature was obtained up to 33% acetaldehyde, 50.9% acetone, 38% MEK, 15.7% methanol, 28.3% ethylene and 18.8% hydrogen is most active when the content of active phase of catalyst varies from 1 to 10% on a carrier.

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**Т.С. Байжуманова¹, С.А. Тунгатарова^{1,3}, Г. Ксандопуло², З.Т. Жексенбаева^{1,3},
Р. Сарсенова¹, К. Касымхан¹, Г. Кауменова³, А.О. Айдарова⁴, А. Ержанов³**

¹Д.В.Сокольский атындағы «Жанармай, катализ және электрохимия институты» АҚ, Алматы, Қазақстан;

²Нанотехнология және наноғылым институты, «Демокрит» ҰҒЗО, Афины, Греция;

³Әл-Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан;

⁴Тараз мемлекеттік педагогикалық университеті, Тараз, Қазақстан

ПОЛИОКСИДТІ КАТАЛИЗАТОРЛАРДА C₃-C₄ ҚОСПАСЫНЫҢ КАТАЛИТИКАЛЫҚ ТОТЫҒУЫ

Аннотация. Жеңіл алкандарды каталитикалық тотықтыру үрдісінде өндірістік маңызды химиялық өнімдер алу үшін табиғи сазбалшыққа отырғызылған молибден, хром және галлий негізіндегі полиоксидті катализаторлардың белсенділігін зерттеу нәтижелері ұсынылған. Газды және сұйық фазада сызықты көмірсутектердің альдегидтерге, спирттерге, кетондарға және олефиндерге тотығу реакцияларының каталитикалық жүйесінде молибден, хром және галлий негізінде жасалынған үш компонентті катализаторлар каталитикалық белсенділікті көрсетті. Пропан-бутан қоспасының тотығу конверсиясын зерттеуде табиғи сазбалшыққа отырғызылған молибден, хром және галлийдің полиоксометаллаттарынан алынған өнімдердің құрамын анықтауда температуралық үрдістің қолайлылығы анықталды. Жасалынған катализаторлардың құрамына белсенді компоненттерді сатылы және біріккен әдістермен енгізуге зерттеулер жүргізілді. Бір немесе екі құрамды сатылы енгізу әдісі катализаторлардың тиімділігіне кері әсер ететіні анықталды. Біріккен әдісте катализаторға белсенді фазаны тасымалдағышқа отырғызғанда металдар бір-бірімен реакцияға түседі (катализаторды дайындау үрдісі кезінде байқауға болады) және әрбір енгізілген элементтерге жеке-жеке құрыштау мен кептіру қосымша жүргізілмеуіне болжам жасалынды. Барлық құрамды бір мезгілде сіңіретін ерітіндіге енгізу қолайлы болатындығы анықталды. Пропан-бутан қоспасын тотықтыра айналдыру үрдісі V= 450 сағ⁻¹ кезінде Мо-Сг-Ga негізінде жасалынған енгізілген катализаторларда жоғары шығымды өнімдердің келесі қатарын: 673-723 К-де ацетальдегид, 823 К-де ацетон, 673-723 К-де метанол, 773-823 К-де МЭК, 823 К-де этанол, 673-723 К-де этилен,

823 К-де H_2 алуға болады. Сонымен қатар, 5 және 10% Мо-Сг-Ga жасалған катализаторлар сұйық және газды фазада да өнімдер алу үшін, ал 1% Мо-Сг-Ga катализаторы тек газды фазада өнімдерді синтездеу үшін оңтайлы болып табылатындығы анықталды.

Түйін сөздер: каталитикалық тотығу, катализаторлар, C_3 - C_4 қоспасы.

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Т.С. Байжуманова¹, С.А. Тунгатарова^{1,3}, Г. Ксандопуло², З.Т. Жексенбаева^{1,3},
Р. Сарсенова¹, К. Касымхан¹, Г. Кауменова³, А.О. Айдарова⁴, А. Ержанов³

¹ Институт топлива, катализа и электрохимии им. Д.В. Сокольского, Алматы;

² Институт нанонауки и нанотехнологий, ИЦНИ Демокрит, Афины, Греция;

³ Казахский национальный университет им. аль-Фараби, Алматы, Казахстан;

⁴ Таразский государственный педагогический университет, Тараз, Казахстан;

КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ C_3 - C_4 СМЕСИ НА ПОЛИОКСИДНЫХ КАТАЛИЗАТОРАХ

Аннотация. Представлены результаты исследования активности нанесенных на природные глины полиоксидных катализаторов на основе молибдена, хрома и галлия для проведения процесса каталитического окисления легких алканов в промышленно важные химические продукты. Разработанные трехкомпонентные каталитические системы на основе молибдена, хрома и галлия проявили каталитическую активность в реакциях газофазного и жидкофазного окисления линейных углеводородов в альдегиды, спирты, кетоны и олефины. Исследования окислительной конверсии пропан-бутановой смеси на нанесенных на природные глины полиоксометаллатах молибдена, хрома и галлия позволили определить, что преимущественный состав продуктов определяется температурой процесса. Проведено исследование последовательного и совместного способа введения активных компонентов в состав разработанных катализаторов. Определено, что последовательное введение одного или двух компонентов отрицательно влияет на эффективность катализатора. Предполагается, что при совместном способе нанесения активной фазы катализатора на носитель металлы начинают вступать в реакцию друг с другом (что наблюдается визуально в процессе приготовления катализаторов) и исключается дополнительная раздельная сушка и прокалка каждого нанесенного последующего элемента по отдельности. Определено, что оптимальным является одновременное введение всех компонентов в пропиточный раствор. Установлено, что в процессе окислительного превращения пропан-бутановой смеси при $V = 450 \text{ ч}^{-1}$ на разработанных трехкомпонентных нанесенных катализаторах на основе Мо-Сг-Ga возможно получение ряда продуктов с высокими выходами: ацетальдегида - при 673-723 К, ацетона - при 823 К, метанола - при 673-723 К, МЭК - при 773-823 К, этанола - 823 К, этилена - при 673-723 К, H_2 - при 823 К. Определено, что 5 и 10% Мо-Сг-Ga нанесенные катализаторы являются оптимальными для получения продуктов как в жидкой фазе, так и газовой, а 1% Мо-Сг-Ga катализатор более благоприятен для синтеза продуктов в газовой фазе.

Ключевые слова: каталитическое окисление, катализаторы, C_3 - C_4 смесь.

Information about authors:

T.S. Baizhumanova - Leading Researcher, Candidate of Chemical Sciences, Laboratory of Organic Catalysis, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan. Tel: +77272916632, e-mail: baizhuma@mail.ru

S.A. Tungatarova - Chief Researcher, Doctor of Chemical Sciences, Laboratory of Organic Catalysis, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Al-Farabi Kazakh National University, Almaty, Kazakhstan. Tel: +77272916632, e-mail: tungatarova58@mail.ru

G. Xanthopoulou - Professor, PhD, DSc, Laboratory of Modern Ceramics, Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Athens, Greece. e-mail: g.xanthopoulou@inn.demokritos.gr

Z.T. Zheksenbaeva - Leading Researcher, Candidate of Chemical Sciences, Laboratory of Organic Catalysis, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Al-Farabi Kazakh National University, Almaty, Kazakhstan. Tel: +77272916632, e-mail: zheksenbaeva07@mail.ru

R. Sarsenova - Junior Researcher, Laboratory of Organic Catalysis, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan. Tel: +77272916632, e-mail: rabinur@mail.ru

K. Kassymkhan - Junior Researcher, Laboratory of Organic Catalysis, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan. Tel: +77272916632, e-mail: kaysar_007@mail.ru

G.N. Kaumenova - PhD Doctoral Student, Al-Farabi Kazakh National University, Laboratory of Organic Catalysis, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan. e-mail: kaumenova.gulnar@mail.ru

A.O. Aidarova - senior teacher of the Taraz State Pedagogical University, Taraz, Kazakhstan, Taraz, Kazakhstan. e-mail: aitkul1128@mail.ru

A. Erzhanov - Graduate Student, Al-Farabi Kazakh National University, Almaty, Kazakhstan. e-mail: ar_man.e@mail.ru

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**M.S. Kalmakhanova¹, B.K. Massalimova¹, H.G. Teixeira^{2,3},
J.L. Diaz de Tuesta^{2,3}, I.G. Tsoy¹, A.O. Aidarova⁴**

¹M.K.H. Dulati Taraz State University, Department of Chemistry and Chemical Engineering, Taraz, Kazakhstan;

²Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal;

³Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM),
Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal;

⁴Taraz State Pedagogical University, Department of Chemistry and methods of teaching chemistry,
Taraz, Kazakhstan

E-mail: marjanseitovna@mail.ru, jl.diazdetuesta@ipb.pt, hgtgomes@ipb.pt, massalimova15@mail.ru,
tsoyirinagen@mail.ru, aitkul1128@mail.ru

OBTAINING OF ZIRCONIUM CATALYSTS BASED ON PILLARED CLAYS FOR PEROXIDE OXIDATION OF 4-NITROPHENOL

Abstract. Natural resources, including abundant and cheap natural clays in the southern region are one of the main wealth of the Republic of Kazakhstan. The chemical industry in Kazakhstan is being developed rapidly in recent years and there is an urgent need to find solutions for the treatment of wastewaters. This work aims to explore natural clays for the synthesis of low-cost pillared clays that can be used as catalysts in oxidation technologies for the treatment of wastewaters. Nitrophenols are commonly found in many types of wastewaters (plastic, pharmaceutical, paper or pesticide production). The purification of such specific wastewater according to classical schemes does not always ensure a safe level of pollution in waters discharged into water ponds. Thus, further development of the chemical industry will inevitably be associated with the need for more effective disposal of wastewater containing toxic products. 4-nitrophenol was used as a representative model compound in catalyst screening studies. Catalysts based on pillared clays modified with Zr^{4+} cations were synthesized from natural clays of Karatau and Kokshetau deposits and investigated for the catalytic wastewater peroxide oxidation (CWPO) of 4-nitrophenol (4-NP) at 323⁰K. Pillared clays with Zr^{4+} showed the higher catalytic activity in the removal of 4-NP and Total organic carbon (TOC) by CWPO and selectivity for the formation of CO_2 and H_2O than natural clays. The best 4-NP and TOC conversion results were obtained by using the pillared clay from Karatau deposit as a catalyst. A complete removal of the contaminant was achieved after 2 hours with 97.3 % conversion.

Keywords: natural clays, pillared clays, catalytic wet peroxide oxidation, 4-nitrophenol, wastewater.

1. Introduction

4-nitrophenol is a dangerous toxic, non-biodegradable industrial pollutant, discharged by various enterprises. 4-nitrophenol is widely used in the production of medicines, fungicides, dyes and dark leather products [1]. This is a reason of a serious threat to the environment and health: ingestion causes drowsiness and nausea. Usually, in order to remove 4-nitrophenol from wastewater physicochemical and biological methods are used, but they are not sufficiently effective. Thus, there is a need to develop a process that can effectively degrade 4-nitrophenol using a safe and inexpensive technique. Every year large volumes of wastewater are produced by chemical, petrochemical and pharmaceutical enterprises. Such wastewater polluted with organic components can be purified with a help of catalysts. The use of catalysts is a true alternative to the chemical or biological oxidation of phenols in aqueous medium [2]. Pillared clay prepared from natural mineral is one of these catalysts. Pillared clays have received increased interest due to their texture and catalytic activity for various reactions [3]. Pillared clay is an interesting type of porous material used as a sorbent and catalyst [4]. There are examples of their use in various

reactions as catalysts for wastewater treatment [5-7]. To solve the problems aimed to increase of the catalytic activity of clays, a lot of studies were carried out on their modification by active metals, such as zirconium [8]. Zirconium easily penetrates to the structure of pillared clay and provides conditions for the complete oxidation of organic contaminants with hydrogen peroxide [9].

In this work, we report the investigation results of 4-nitrophenol oxidation as a model pollutant by CWPO with pillared clays modified by zirconium tetrachloride. The raw materials used were natural clays of the Kazakh deposits of Karatau and Kokshetau.

2. Materials and methods

2.1. Materials and reagents

Two types of natural clays with different characteristics from the Kazakh deposits of Karatau (Zhambyl region) and Kokshetau (North Kazakhstan region) were taken as raw materials. For the preparation of pillared clays the raw materials were washed with water and 2M HCl successively at 50°C. According to available sources [10-11] 1M sodium chloride solution was used in most cases. Further, the clays were treated with a solution of $ZrCl_4$ as a source of zirconium cations. The modification reagent was prepared by slow adding of 0.2M NaOH to zirconium tetrachloride solution at room temperature up to pH = 2.8. The resulting solution was kept at room temperature for 24 hours. The described procedure provides a total metal content of 10 mmol per gram of clay. The samples obtained were dried at 350°C, and then calcined during 2 hours at 823 °K at a heating rate of 275°C/min.

2. Characterization

To determine the physico-chemical characteristics of the nature clays the X-ray spectral analysis method was used. An electron probe microprobe of the Superprobe 733 (Super Probe 733) brand from JEOL (Jael, Japan), was used for determination of the angular position and intensity of reflexes. Analyses of the elemental composition of samples and photography in various types of radiation were performed using the Inca Energy with dispersive spectrometer from Oxford Instruments, England. UV-Vis absorption spectra were obtained using the T70 Spectrophotometer (PG Instruments, Ltd.) in the wavelength range of 200-660 nm with a scan interval of 1 nm. SEM was performed on the FEIQuanta 400FEG ESEM/EDAX Genesis X4M instrument equipped with the Energy Dispersive Spectrometer (EDS). Transmission electron microscopy (TEM) was performed with LEO 906E instrument operating at 120 kV, equipped with a 4 Mpixel 28 × 28 mm CCD camera from TRS.

2.3. Catalytic oxidation

Catalytic oxidation of 4-NP in an aqueous medium was carried out in a 250 ml glass reactor equipped with a stirrer at 323°C at constant stirring. The reactor was charged with 100 ml of an aqueous solution of 4-NP with a concentration of 5.0 g/L. Then the pH of the solution was adjusted to 3 with solutions of H_2SO_4 and NaOH. The experiment was carried out without additional pH adjustment. In order to achieve the stoichiometric quantity of H_2O_2 in the media (17.8 g/l) 6.6 ml of 30% (w/v) hydrogen peroxide solution was added for mineralization. Then 2.5 g of catalyst were added to the reactor. The moment of complete homogenization of the resulting solution was taken as the initial point ($t_0 = 0$ h). In order to differentiate adsorption of 4-NP and catalytic oxidation pure adsorption runs were also performed under the same operating conditions, replacing H_2O_2 by an equal volume of distilled water. The experiment was carried out during 24 h. The 4-NP conversion and the appearance of the oxidized intermediates was fixed by taking samples from reaction media at regular intervals.

3. Results and discussion

3.1 Characteristics of natural and pillared clays

The results of elemental composition of natural clays were obtained by using EMP analysis. Table 1 presents the content of elements in the original natural clays.

After pillaring treatment of clays with $ZrCl_4$ solution the amount of zirconium in a sample obtained on the basis of natural clay of the Kokshetau deposit was only 4.75%, and based on the Karatau clay - 35.07%. The chemical composition analysis shows that Si content is higher than other elements (Table 1). The amount of zirconium absorbed by Karatau clay is larger than by Kokshetau one. In fact, the Zr content

for Karatau and Kokshetau clays is 35.07% and 4.75% subsequently. These results prove a modification of the zirconium pillars by hydrolysis and polymerization [12].

The results of elemental analysis

Pillared clays	Mass of the metals (%)									
	Na	Mg	Al	Si	K	Ca	Ti	Zr	Fe	Total
Zr-Karatau	2.51	2.50	9.99	41.83	4.27	0.87	0.31	35.07	2.66	100
Zr- Kokshetau	0.85	1.50	22.98	53.43	3.69	0.23	2.14	4.75	10.42	100

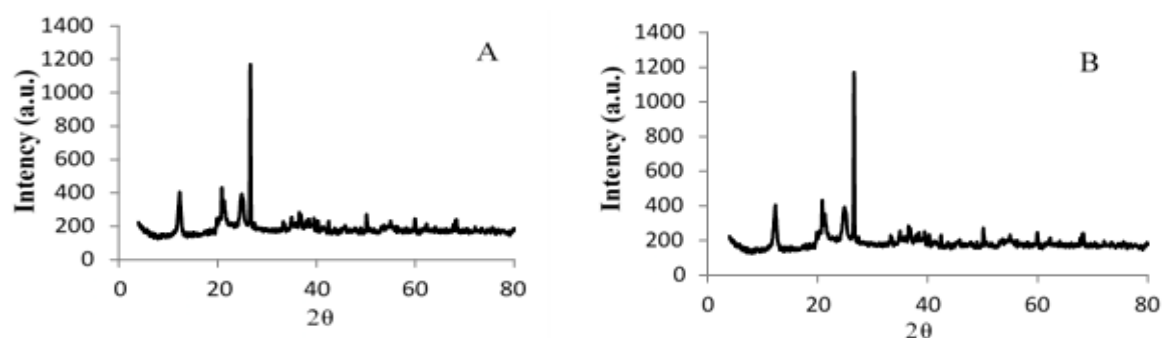


Figure 1 - X-ray diffraction spectra of natural clays by EMP; (A) Karatau, and (B) Kokshetau

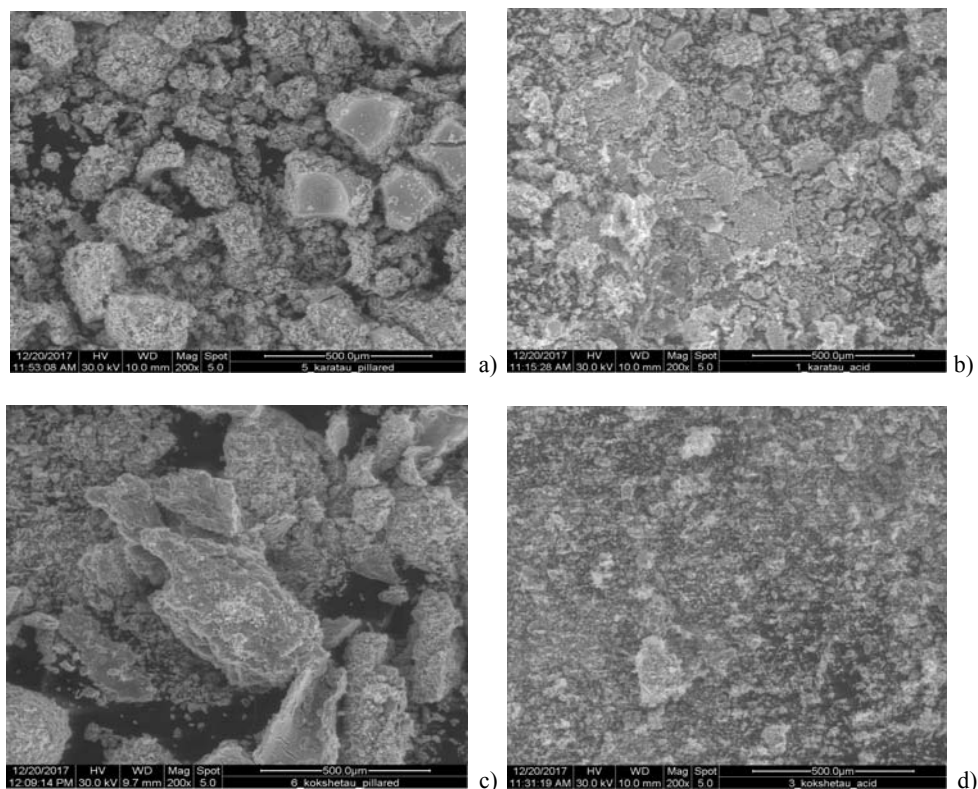


Figure 2 - SEM images: (a) Zr-Karatau PILC, (b) natural Karatau clay and (c) Zr-Kokshetau PILC, (d) natural Kokshetau clay

In addition the X-ray diffraction spectra were investigated. The signals associated with the montmorillonite phases are clearly seen on the X-ray patterns (Fig. 1). Studies of the mineralogical composition of clay confirm that the clay of the Karatau deposit is a representative of polymineral clay. To determine the quantitative ratio of crystalline phases, clay samples were subjected to X-ray diffractometric analysis. The polymineral composition was confirmed by the appearance of the corresponding signals on the X-ray patterns: montmorillonite ($d = 14.73\text{-}14.56, 4.98\text{-}4.39, 2.54\text{-}2.60 \text{ \AA}$), muscovite ($d = 2.59, 2.38 \text{ \AA}$), kaolinite ($d = 7.09\text{-}7.04, 3.54\text{-}3.24, 2.56 \text{ \AA}$) with the formula $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot x\text{H}_2\text{O}$. Kokshetau clay showed the presence of kaolinite ($d = 7.18 \text{ \AA}$) and muscovite ($d = 4.45, 2.37 \text{ \AA}$).

In the process of pillared structures production, natural clays washed with 2M HCl showed better results than those washed with water only. After treatment with a solution of zirconium chloride, the clay was washed with water at 50°C up to pH 7.35 was achieved in the washings. The obtained clay samples were examined on a scanning electron microscope. The chemical composition of clay was determined by X-ray analysis.

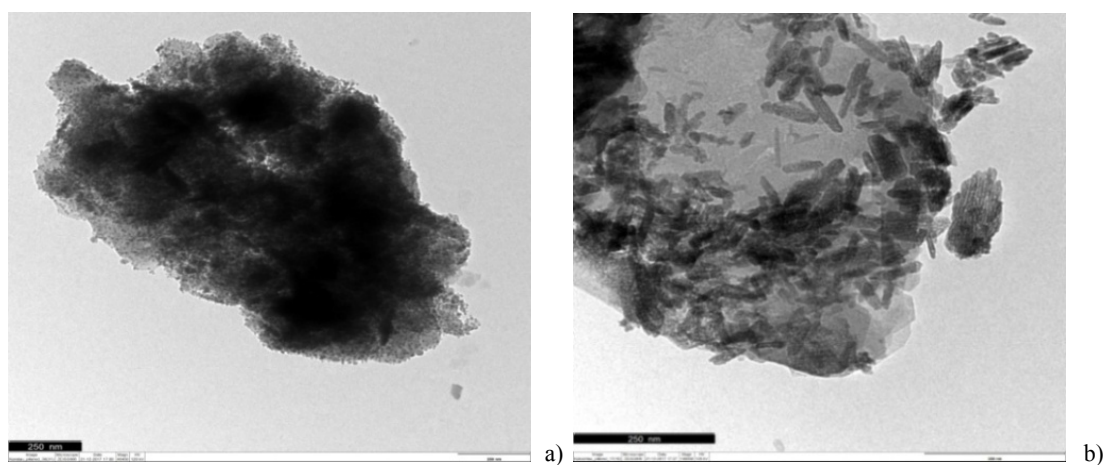


Figure 3 - TEM images: (a) Zr-Karatau PILC and (b) Zr-Kokshetau PILC

The morphology of the pillared clay surface is shown in Figures 2. A layered and smooth surface is visible on the micrographs of natural clays, but the surface becomes more prominent and porous after obtaining pillared clay. The developed surface of pillared clay indicates an increase in the number of active sites on the surface of zirconium bars, which makes the catalyst more active [13-15]. TEM results of pillared clays are shown on Figure 3. The results presented demonstrate the location of Zr points on the surface of clays more clearly. Modified pillared clay combines the availability, ease of preparation with a large surface area and high catalytic activity.

3.2. CWPO of 4-NP

The results of oxidation of 4-NP in the presence of the catalysts obtained, performed by HPLC, are presented below (Fig. 6-7). The pillared clays modified with zirconium cations showed excellent catalytic activity in the 4-NP oxidation reaction, with the best results obtained for the modified pillared clay of the Karatau deposit after washing with an acid solution.

According to the results shown in Fig. 4, complete removal of the pollutant is achieved after 2 hours of reaction by using the pillared clay of Karatau as catalyst. The Kokshetau clay allows removing the contaminant after 6 hours of oxidation reaction (Fig. 5). It was noted that with the increase in time, the rate of degradation was rapid during the first hours. After 120 minutes (FIG. 4) degradation of 4-nitrophenol was 97.3 %, further degradation change was constant.

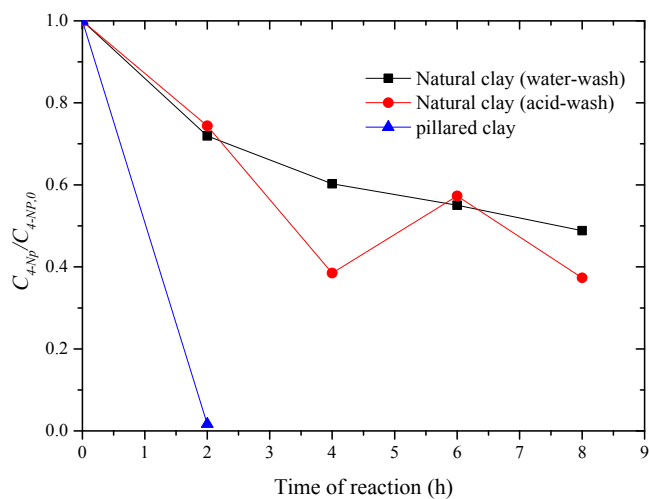


Figure 4 - Catalytic peroxide oxidation of 4-NP with Karatau clay (4-NP 5 g/L, H₂O₂ 17.8 g/L, 2.5g clays, pH= 3.0, 50°C)

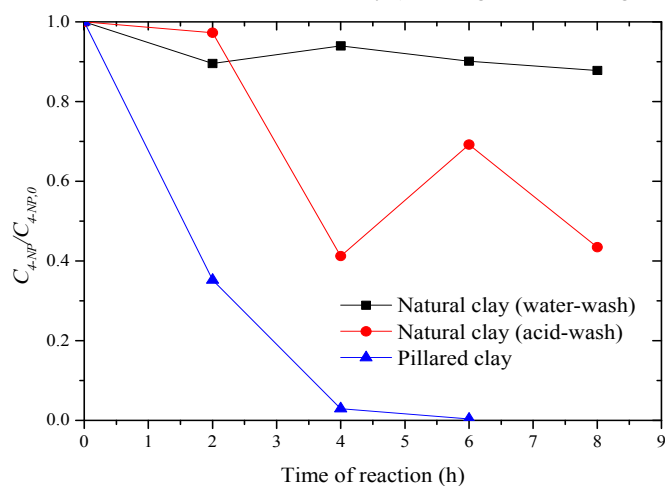


Figure 5 - Catalytic peroxide oxidation of 4-NP with Kokshetau clay (4-NP 5 g/L, H₂O₂ 17.8 g/L, 2.5g clays, pH=3.0, 50°C)

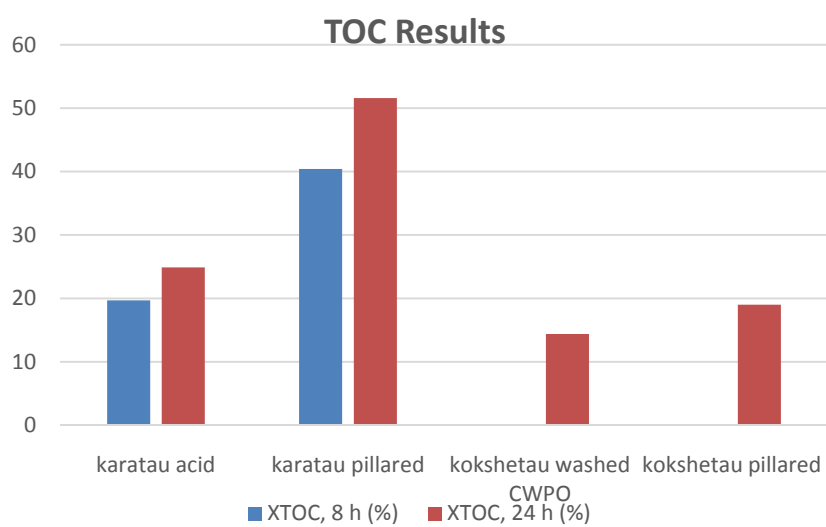


Figure 6 - Conversion of TOC in the removal of 4-nitrophenol by CWPO with natural and pillared clays from Karatau and Kokshetau catalysts at 8 and 24 hours of reaction time.

The highest activity was observed when Karatau clay was used as catalyst: the total organic carbon conversion was 40.4%, and 51%, whereas with the pillared Kokshetau clay conversion didn't overcome 0% and 20% after 8 and 24 hours, respectively. Thus, it can be stated that the modification of pillared clay by zirconium leads to excellent results. Previously published results on the oxidation of phenol using zirconium pillared clays also indicate the best TOC values [16-18].

The pillaring process is followed by the development of porosity of natural clay, that leads to increase of the surface area of the clays and, hence, more active sites may be available for the 4-NP molecules in CWPO process [19-20].

4. Conclusions

Pillared clays were obtained on the basis of natural clays of Karatau and Kokshetau deposits. Catalysts obtained by modification of pillared clays with Zr^{4+} ions have a high efficiency in the oxidation of 4-nitrophenol in dilute aqueous medium under very mild conditions (323⁰K and atmospheric pressure). The best 4-NP and TOC conversion results were obtained by using the pillared clay from Karatau deposit as catalyst. A complete removal of the contaminant was achieved after 2 hours with 97.3 % conversion.

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**М.С. Калмаханова¹, Б.К. Масалимова¹, Х.Г. Тейшера^{2,3},
Ж.Л. Диас Туеста^{2,3}, И.Г. Цой¹, А.О. Айдарова⁴**

¹Таразский Государственный Университет им М.Х. Дулати, кафедра «Химия и химическая технология», Тараз, Казахстан;

²Исследовательский Центр Монтанха (CIMO), Политехнический Институт Браганса, 5300-253 Браганса, Португалия;

³Лаборатория технологии разделения и реакции - Лаборатория катализа и материалов (LSRE-LCM), Инженерный факультет Университета Порту, Руа Д-р Роберто Фриас, 4200-465 Порту, Португалия;

⁴Таразский Государственный Педагогический Университет, кафедра «Химия и методика преподавания химии», Тараз, Казахстан

ПОЛУЧЕНИЕ ЦИРКОНИЕВЫХ КАТАЛИЗАТОРОВ НА ОСНОВЕ СТОЛБЧАТЫХ ГЛИН ДЛЯ ПЕРОКСИДНОГО ОКИСЛЕНИЯ 4-НИТРОФЕНОЛА

Аннотация. Одним из основных богатств Республики Казахстан являются природные ресурсы, в том числе богатые и дешевые природные глины в южном регионе. Химическая промышленность Казахстана в последние годы быстро развивается, и существует настоятельная необходимость найти решения для очистки сточных вод. Эта работа направлена на изучение природных глин в синтезе низко затратных столбчатых глин, которые будут использоваться в качестве катализаторов в технологиях окисления для очистки сточных вод. Нитрофенолы обычно встречаются во многих типах сточных вод (производство пластмасс, фармацевтики, бумаги и пестицидов).

Очистка таких специфических сточных вод по классическим схемам не всегда обеспечивает безопасный уровень загрязнений в сбрасываемых водах. Поэтому дальнейшее развитие химической промышленности неизбежно связано с необходимостью более эффективного обезвреживания сточных вод, содержащих токсичные продукты. 4-нитрофенол использовался в качестве типичного модельного соединения в исследованиях скрининга катализатора. Катализаторы на основе столбчатых глин с катионами Zr^{4+} были синтезированы из природных глин месторождений Каратау и Кокшетау и исследованы при каталитическом окислении 4-нитрофенола при 323°K. Столбчатые глины, модифицированные Zr^{4+} , показали более высокую активность в окислении 4-NP и ТОС селективность в отношении образования CO_2 и H_2O , чем природная глина. Наилучшие результаты по конверсии 4-нитрофенола и по количеству углерода были получены при использовании столбчатых глин, полученных на основе глины Каратауского месторождения. Полное удаление загрязнения было достигнуто по истечении 2 часов со степенью конверсии 97.3%.

Ключевые слова: природные глины, столбчатые глины, каталитическое окисление, 4-нитрофенол, сточные воды.

М.С. Калмаханова¹, Б.К. Масалимова¹, Х.Г. Тейшера^{2,3},
Ж.Л. Диас Туеста^{2,3}, И.Г. Цой¹, А.О. Айдарова⁴

¹М.Х. Дулати атындағы Тараз Мемлекеттік Университеті, «Химия және химиялық технологиялар» кафедрасы, Тараз, Қазақстан;

²Монтанха Зерттеу Институты (СИМО), Браганса Политехникалық Институты, 5300-253 Браганса, Португалия;

³Реакция және бөлу технологиясы зертханасы – материалдар және катализ зертханасы (LSRE-LCM), Порту Университетінің инженерлік факультеті, Руа Д-р Роберто Фриас, 4200-465 Порту, Португалия;

⁴Тараз Мемлекеттік Педагогикалық Университеті, «Химия және химияны оқыту әдістемесі» кафедрасы, Тараз, Қазақстан

4-НИТРОФЕНОЛДЫ АСҚЫНТОТЫҚПЕН ТОТЫҚТЫРУ ҮШІН БАҒАНАЛЫ САЗБАЛШЫҚТАР НЕГІЗІНДЕГІ ЦИРКОНИЙ КАТАЛИЗАТОРЛАРЫН АЛУ

Аннотация. Қазақстан Республикасының негізгі байлықтарының бірі табиғи ресурстар, соның ішінде Оңтүстік өңіріндегі арзан және бай табиғи сазбалшықтар болып табылады. Соңғы жылдары Қазақстанда химия өнеркәсібі қарқын дамуда, сондықтан міндетті түрде ағынды суларды тазартудың шешу жолдарын табуда қажеттілік бар. Бұл жұмыс ағынды суларды тазарту үшін тотығу технологияларында қолданылатын катализатор ретінде арзан бағаналы сазбалшық синтезіндегі табиғи сазбалшықтарды зерттеуге бағытталған. Жалпы нитрофенолдар көптеген ағынды сулардың түрлерінде (пластмасс өндірісінде, фармацевтика, қағаз және пестицидтер) кездеседі. Осындай нақты ағынды суларды классикалық схемаларға сәйкес тазарту әрдайым сулардағы ластауыш заттардың қауіпсіз деңгейін қамтамасыз етпейді. Сондықтан, токсинді өнімдері бар ағынды суларды тиімді заласыздандыру химия өнеркәсібінің ары қарай дамуына септігін тигізетіні анық. Катализатор скринингіндегі зерттеулерге модельдік қосылыс ретінде 4-нитрофенол қолданылды. Zr^{4+} катионы бар бағаналы сазбалшық негізінде жасалған Қаратау және Көкшетау мекендерінің табиғи сазбалшықтарынан синтезделген катализаторлар 323 °K температурада 4-нитрофенолдың катализдік тотығуында зеріттелген. Zr^{4+} модификацияланған бағаналы сазбалшықтар табиғи сазбалшықтардан қарағанда 4-нитрофенол тотығуында және ТОС нәтижесіндегі CO_2 және H_2O түзілу көрсеткіші бойынша жоғары белсенділікті көрсетті. Қаратау мекенінің табиғи сазбалшық негізінде жасалған бағаналы сазбалшықты қолдану арқылы көміртек мөлшері және 4-нитрофенол конверсиясы бойынша жақсы нәтижелер алынды. 97,3% конверсия деңгейімен ластағыш заттар толық 2 сағат ішінде жойылды.

Түйін сөздер: табиғи сазбалшықтар, бағаналы сазбалшықтар, каталитикалық тотығу, 4-нитрофенол, ағынды сулар.

Information about authors:

M.S. Kalmakhanova – doctoral student of 2nd course 6D060600 – Chemistry. M.Kh. Dulati Taraz State University, Kazakhstan. marjanseitovna@mail.ru;

B.K. Massalimova – candidate of chemical science, head of “Chemistry and chemical technology” department of M. Kh. Dulati Taraz State University massalimova15@mail.ru;

J.L. Diaz de Tuesta – Ph.D, post-doctoral researcher at Instituto Politécnico de Bragança (IPB), Bragança, Portugal. j.l.diazdetuesta@ipb.pt;

H.T. Gomes – Adjunct professor at the Department of Chemical and Biological Technology, Instituto Politécnico de Bragança (IPB), Bragança, Portugal. htgomes@ipb.pt;

I.G. Tsoy – candidate of chemical science, department of “Chemistry and chemical technology”, M. Kh. Dulati Taraz State University. tsyovirinagen@mail.ru;

A.O. Aidarova – master of chemistry, Taraz State Pedagogical University. aitkul1128@mail.ru.

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Nurlybekova A.K.¹, Yang Ye², Dyusebaeva M.A.¹, Abilov Zh. A.¹, Jenis J.^{1*}

¹Al-Farabi Kazakh National University, Almaty, Kazakhstan;

²Shanghai Institute of Materia Medica, Chinese Academy of Science, Shanghai, China

*e-mail: janarjenis@mail.ru yve@mail.shnc.ac.cn Zharlykasyn.Abilov@kaznu.kz moldyr.dyusebaeva@mail.ru
nurl_al@mail.ru

INVESTIGATION OF CHEMICAL CONSTITUENTS OF *LIGULARIA NARYNENSIS*

Abstract. In this work, the quantitative and qualitative analysis of phytochemical constituents of medicinal plant *Ligularia narynensis* from Kazakhstan has been made for the first time. Total bioactive components of *L. narynensis* such as organic acids (0.64 %), flavonoids (0.52 %) and together with moisture content (5.14 %), total ash (13.24 %), and extractives content (27.7 %) were determined. Eleven macro-micro elements from the ash of plant were identified, main contents of them were K (2214.13 µg/ml), Ca (391.31 µg/ml), and Fe (311.73 µg/ml) by using the method of multi-element atomic emission spectral analysis. In addition, twenty amino and eight fatty acids were analyzed from the plant. The results showed that major contents of amino acids were glutamate (2452 mg/100g), aspartate (1238 mg/100g) and alanine (748 mg/100g), as well as in fatty acids were oleic (33.5 %) and linoleic (41.2 %) acids, respectively.

Key words: *Ligularia narynensis*, bioactive constituents, macro-micro elements, amino-, fatty acids.

Introduction

Ligularia is the genus of perennial herbs of the family Compositae, containing about 180 Eurasian species, 17 species growing in mountains of Kazakhstan [1]. Some species in this genus have been used for a long time as folk remedies for their antibiotic, antiphlogistic, and antitumor activities [2-5]. More than 27 *Ligularia* species have been used as traditional Kazakh and Chinese medicinal herbs for the treatment of fever, pain, inflammation, and intoxication, and to invigorate blood circulation [6-9]. Previous studies confirmed the presence of sesquiterpenes, triterpenes, sinapyl alcohol derivatives, lignans, alkaloids, and steroids in *Ligularia* [10]. Eremophilane sesquiterpenes are considered as the major secondary metabolites and taxonomic markers of *Ligularia* genus. More than 500 eremophilane sesquiterpenes have been reported from this genus [11, 12]. Additionally, oplopane sesquiterpenes have been reported from *L. narynensis* [13].

Amino acids are one of the most important classes of natural compounds. The content of amino acids in plants varies depending on the age of plants, the external conditions: from nutrition, temperature, day length, moisturizing and qualitative composition of amino acids. The number of free amino acids decreases with the age of the plant. In vegetative organs of plants, free amino acids are more than in reproductive. An increase in the total amount of free amino acids is observed with a reduced nutrition of plants with potassium, phosphorus, sulfur, calcium and magnesium. The same action occurs when a number of microelements are lacking: zinc, copper, manganese, iron. This is due to the weakening of the synthesis of proteins from amino acids under these conditions. An increase in the amino acids content is also observed with an improvement in nitrogen nutrition [14].

Fatty acids are structural components of lipoproteins of cell membranes and participate in the implementation of a number of important biochemical processes in the cell. The greatest biological

activity is observed in fatty acids with two or more double bonds. It is to such unsaturated fatty acids are linoleic, linolenic, arachidonic acids. Unsaturated fatty acids prevent the development of atherosclerosis, reduce blood clotting and reduce the possibility of thrombosis. They increase the protective properties of the organism and its resistance to infections, relevant to the development of many skin diseases. There are data on the ability of such acids to prevent the action of substances that cause the development of tumors [15].

This study has made the investigation of the chemical constituents from Kazakh medicinal plant of *L. narynensis* grown in Almaty region of Kazakhstan for the first time.

Materials and methods

Plant material. The root part of plant *L. narynensis* was collected in September 2017 from Butakovskoe gorge of the Zailiysky Alatau Mountains of Almaty region and identified by Dr. Alibek Ydyrys. Specimens (1217-БН-17) were deposited in the Herbarium of Laboratory Plant Biomorphology, Faculty of Biology and Biotechnology, Al-Farabi Kazakh National University, Almaty, Kazakhstan. The air dried roots of *L. narynensis* were cut into small pieces and stored at room temperature.

Experimental part. The quantitative and qualitative contents of biologically active constituents of underground part of the plant were determined according to methods reported in the State Pharmacopeia XI edition techniques.

In the "Center of Physico-Chemical methods and analysis", Republican State Enterprise Kazakh National Al-Farabi University, MON RK using the method of multi-element atomic emission spectral analysis in the ash of *L. narynensis* was analyzed elemental constituents. To determine the mineral composition of ashes was used Shimadzu 6200 series spectrometer.

Method for the determination of amino acids. 1 g of the analyte, hydrolyzed in 5 ml of 6N hydrochloric acid at 105 °C for 24 hours, in ampoules sealed under a stream of argon. The resulting hydrolyzate is evaporated three times to dryness on a rotary evaporator at a temperature of 40-50 °C and a pressure of 1 atm. The resulting precipitate is dissolved in 5 ml of sulfosalicylic acid. After centrifugation for 5 minutes, the packed liquid is passed through a column of ion exchange resin at a rate of 1 drop per second. After this, the resin is washed with 1-2 ml of deionized water and 2 ml of 0.5N acetic acid; then the resin is washed to neutral pH with deionized water. To elute the amino acids from the column, 3 ml of a 6N NH₄OH solution is passed through it at a rate of 2 drops per second. The eluate is collected in a round bottom flask together with distilled water, which is used to wash the column to a neutral pH medium. The contents of the flask are then evaporated to dryness on a rotary evaporator at a pressure of 1 atm and a temperature of 40-50 °C. After adding a drop of freshly prepared 1.5% SnCl₂ solution, 1 drop of 2,2-dimethoxypropane and 1-2 ml of propanol saturated with hydrochloric acid, it is heated to 110 °C, keeping this temperature for 20 minutes, and then the contents are again evaporated from the flask on a rotary evaporator. In the next step, 1 ml of freshly prepared acetyl reagent (1 volume of acetic anhydride, 2 volumes of triethylamine, 5 volumes of acetone) is introduced into the flask and heated at a temperature of 60 °C for 1.5-2 minutes. The sample is again evaporated on a rotary evaporator to dryness and 2 ml of ethyl acetate and 1 ml of a saturated NaCl solution are added to the flask. The contents of the flask are thoroughly mixed and as the two layers of liquids are clearly formed, an upper layer (ethyl acetate) is taken for gas chromatographic analysis.

To determine the amino acids composition was made erenow [16] of the raw material used GC/MS device. GC/MS analysis: the roots of *L. narynensis* were analyzed by Gas Chromatograph coupled to Mass Spectrometer using polar mixture of 0.31% carbowax 20 m, 0.28% silar 5 CP and 0.06% lexan in chromosorb WA-W-120-140 mesh., column (400 x 3 mm). The column temperature was programmed from 110°C (held for 20 min), at 6°C/min from 110°C to 180°C, at 32°C/min from 185°C to 290°C. When it reaches to 250°C, it should stay constant till finishing analysis of all existed amino acids. The chromatogram is counted according to an external standard.

Determination of the fatty acids composition of dried plant *L. narynensis* extracted with a chloroform-methanol mixture (2:1) for 5 minutes, the extract is filtered through a paper filter and concentrated to dryness. Then, to taked extract add 10 ml of methanol and 2-3 drops of acetyl chloride and further methylation at 60-70°C in a special system for 30 minutes. The methanol is removed by rotary evaporation and the samples are extracted with 5 ml of hexane and analyzed using a gas chromatograph.

As a result, chromatograms of methyl esters of fatty acids were obtained. By comparison with reliable samples by the time of exit from the column, eight fatty acids were identified. To determine the components was used the internal normalization method.

Results and discussion

The quantitative and qualitative analysis of biologically active constituents together with moisture content, total ash, and extractives contents were determined from roots of *L. narynensis*. The results are shown in Table 1.

Table 1 – Quantitative analysis of bioactive constituents of *L. narynensis*

Content, %				
Moisture content	Ash	Extractives	Organic acids	Flavonoids
5.14	13.24	27.7	0.64	0.52

In “Center of Physico-Chemical methods of analysis”, Republican State Enterprise Kazakh National Al-Farabi University, MES RK using the method of multi-element atomic emission spectral analysis in the ash of *L. narynensis* there were determined eleven macro- and microelements, shown in Table 2 and major of them was K (2214.13 µg/ml), Ca (391.31 µg/ml), Fe (311.73 µg/ml). Potassium is involved in the process of carrying out nerve impulses and transferring them to innervated organs, promotes better brain activity, is also necessary for the implementation of contractions of skeletal muscles. Calcium plays a very important role in many intra- and extracellular processes, including the contractile function of the cardiac and skeletal muscles, nerve conduction, regulation of enzyme activity, and the action of many hormones. It is also a cofactor of the activation of many enzymes or the formation of a number of enzyme complexes in complex, multistage processes of blood coagulation. Iron is a part of the hemoglobin of erythrocytes, myoglobin and many enzymes, participates in hematopoiesis [17].

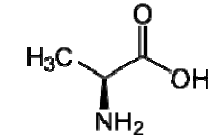
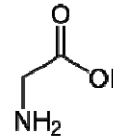
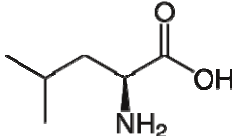
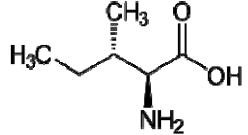
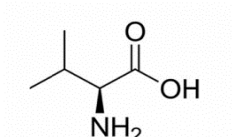
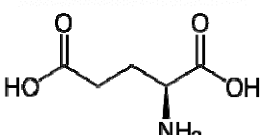
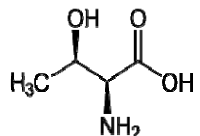
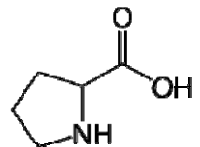
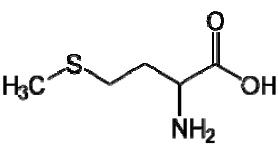
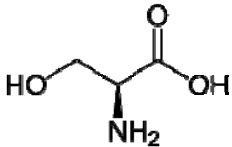
Table 2 – Composition of macro-micro elements in the ash of plant *L. narynensis*

Element	Cu	Zn	Cd	Pb	Fe	Ni	Mn	K	Na	Mg	Ca
µg/ml	1.57	2.58	0.05	0.66	311.73	0.36	11.73	2214.13	31.74	288.08	391.31

In the composition of amino acids mainly were glutamate (2452 mg/100g), aspartate (1238 mg/100g) and alanine (748 mg/100g). The results shown in Table 3. Glutamate is one of the most abundant of the amino acids. In addition to its role in protein structure, it plays critical roles in nutrition, metabolism and signaling. Post-translational carboxylation of glutamyl residues increases their affinity for calcium and plays a major role in hemostasis [18]. Aspartic acid increases immunity, metabolism, deactivates ammonia, participates in the formation of ribonucleic acids, promotes the removal of chemicals, including drugs, restores working capacity. Studies conducted by scientists have proved the effectiveness of taking asparaginic acid preparations for increasing testosterone levels. Aspartic acid is taken as an additive by bodybuilding athletes to improve strength, increase libido and testosterone in the blood [19]. Alanine also increases immunity and provides energy for brain and central nervous system, the muscle tissue. This amino acid protects against the development of cancer of the pancreas and prostate gland [20].

Quantitative composition of fatty acids in *L. narynensis* mostly contained in linoleic acid (41.2 %) and oleic acid (33.5 %), showed in Table 4. Linoleic acid is an essential fatty acid in nutrition and is used in the biosynthesis of prostaglandins and cell membranes [21]. Oleic acid can inhibit the progression of diseases affecting the brain and adrenal glands, as well as improve memory and reduce blood pressure, but there is evidence that the substance can provoke cancer, in particular breast cancer [22].

Table 3 – Amino acids contents of *L. narynensis*

№	Amino acids	Molecular formula	Structure	MW	Amount in plant, mg/100g
1	2	3	4	5	6
1	Alanine	$C_3H_7NO_2$		89	748
2	Glycine	$C_2H_5NO_2$		75	296
3	Leucine	$C_6H_{13}NO_2$		131	329
4	Isoleucine	$C_6H_{13}NO_2$		131	290
5	Valine	$C_5H_{11}NO_2$		117	278
6	Glutamate	$C_5H_9NO_4$		147	2452
7	Threonine	$C_4H_9NO_3$		119	275
8	Proline	$C_5H_9NO_2$		115	528
9	Methionine	$C_5H_{11}NO_2S$		149	80
10	Serine	$C_3H_7NO_3$		105	356

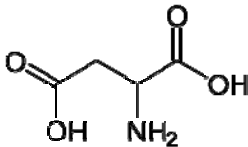
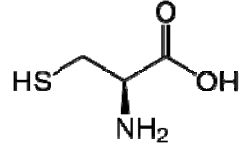
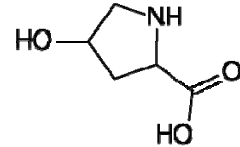
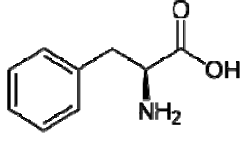
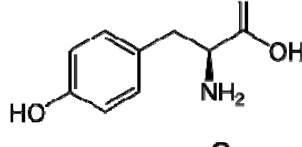
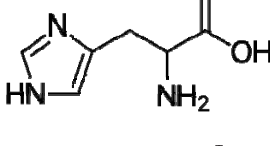
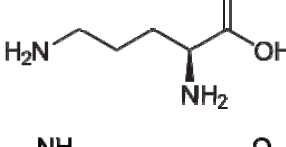
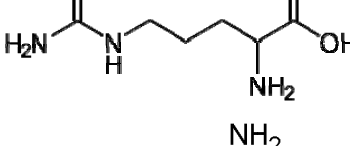
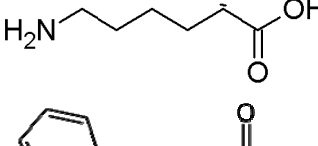
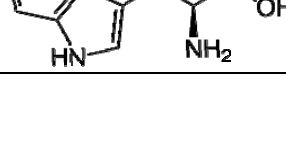
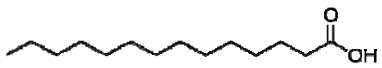
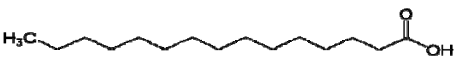
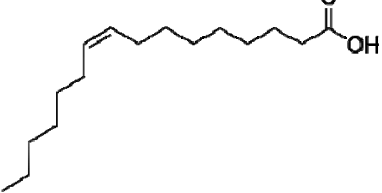
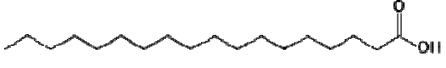
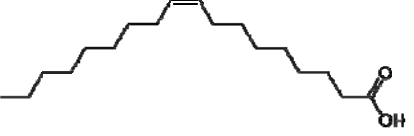
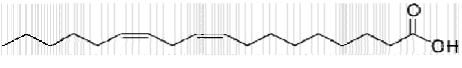
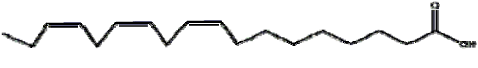
1	2	3	4	5	6
11	Aspartate	$C_4H_7NO_4$		133	1238
12	Cysteine	$C_3H_7NO_2S$		121	34
13	Oxyproline	$C_5H_9NO_3$		131	2
14	Phenylalanine	$C_9H_{11}NO_2$		165	290
15	Tyrosine	$C_9H_{11}NO_3$		181	345
16	Histidine	$C_6H_9N_3O_2$		155	218
17	Ornithine	$C_5H_{12}N_2O_2$		132	2
18	Arginine	$C_6H_{14}N_4O_2$		174	510
19	Lysine	$C_6H_{14}N_2O_2$		146	296
20	Tryptophan	$C_{11}H_{12}N_2O_2$		204	120

Table 4 – Fatty acids contents of *L. narynensis*

№	Fatty acids	Molecular formula	Structure	MW	Amount in plant, %
1	Meristic acid C _{14:0}	C ₁₄ H ₂₈ O ₂		228	2.5
2	Pentadecanoic acid C _{15:0}	C ₁₅ H ₃₀ O ₂		242	1.4
3	Palmitic acid C _{16:0}	C ₁₆ H ₃₂ O ₂		256	14.3
4	Palmitoleic acid C _{16:1}	C ₁₆ H ₃₀ O ₂		254	1.1
5	Stearin acid C _{18:0}	C ₁₈ H ₃₆ O ₂		284	5.2
6	Oleic acid C _{18:1}	C ₁₈ H ₃₄ O ₂		282	33.5
7	Linoleic acid C _{18:2}	C ₁₈ H ₃₂ O ₂		280	41.2
8	Linolenic acid C _{18:3}	C ₁₈ H ₃₀ O ₂	 Linolenic acid	278	0.8

Conclusion

In summary, the quantitative and qualitative analysis of phytochemical constituents from root of medicinal plant *L. narynensis* of Kazakhstan have been made for the first time. As the results of this study, total bioactive components of *L. narynensis* were determined, eleven macro-micro elements from the ash of plant were identified together with twenty amino and eight fatty acids were quantified from medicinal plant. Presence of these bioactive constituents, may indicative that the plant has substances capable of promote a better brain activity, the contractile function of the cardiac and skeletal muscles, nerve conduction, and the action of many hormones, which play major roles in nutrition, in protein structure, metabolism, signaling, in hemostasis, increase immunity, protect against the development of cancer of the pancreas and prostate gland. The plant *L. narynensis* has high research potential and demands multidimensional study.

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А.К. Нурлыбекова¹, Е. Янг², М.А. Дюсебаева¹, Ж.А. Абилов¹, Ж. Жеңіс^{1*}

¹ Өль-Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан;

² Shanghai Institute of Materia Medica, Chinese Academy of Science, Шанхай, Қытай

LIGULARIA NARYNENSIS ХИМИЯЛЫҚ ҚҰРАМЫН ЗЕРТТЕУ

Аннотация. Бұл жұмыста Қазақстанда өсетін дәрілік өсімдіктің *Ligularia narynensis* фитохимиялық құрамының сандық және сапалық талдауы бірінші рет жүргізілді. Өсімдіктің ылғалдылығы (5.14 %), күлділігі (13.24 %) және экстрактивтілігі (27.7 %), сонымен бірге органикалық қышқыл (0.64 %), флавоноидтар (0.52 %) сияқты биологиялық активті компоненттер құрамы анықталды. Атомдық эмиссия спектральды талдау әдісін қолдана отырып, өсімдіктің күліндегі он бір макро- және микроэлементтері

зерттелді және оның негізгі құрамы К (2214.13 мкг/мл), Са (391.31 мкг/мл), Fe (311.73 мкг/мл). Бұдан басқа, жиырма амин және сегіз майлы қышқыл анықталды. Алынған нәтижелер бойынша аминқышқылдардың негізгі құрамы глутамат (2452 мг/100г), аспартат (1238 мг/100г) және аланин (748 мг/100г), май құрамында – олеин (33.5 %) және линол (41.2 %) қышқылдары.

Түйін сөздер: *Ligularia narynensis*, биоактивті құрамдастар, макро-, микроэлементтер, аmino-, майлы қышқылдар.

А.К. Нурлыбекова¹, Е. Янг², М.А. Дюсебаева¹, Ж.А. Абилов¹, Ж. Женис^{1*}

¹Казахский национальный университет имени аль-Фараби, Алматы, Казахстан;

²Shanghai Institute of Materia Medica, Chinese Academy of Science, Шанхай, Китай

ИССЛЕДОВАНИЕ ХИМИЧЕСКОГО СОСТАВА *LIGULARIA NARYNENSIS*

Аннотация. В данной работе впервые был сделан количественный и качественный анализ фитохимических составляющих лекарственного растения Казахстана *Ligularia narynensis*. Определены биологически активные компоненты *L. narynensis*, такие как органические кислоты (0,64 %), флавоноиды (0,52 %) вместе с содержанием влаги (5,14 %), общей золы (13,24 %) и экстрактивных веществ (27,7 %). При использовании метода многоэлементного спектрального анализа атомной эмиссии в золе растения были идентифицированы одиннадцать макро-, микроэлементов, основными из которых являются К (2214,13 мкг/мл), Са (391,31 мкг/мл), Fe (311,73 мкг/мл). Кроме того, были проанализированы двадцать аминокислот и восемь жирных кислот, содержащихся в растении. Результаты показали, что основным составляющим аминокислот являются глутамат (2452 мг/100г), аспартат (1238 мг/100г) и аланин (748 мг/100г); жирных кислот – олеиновая (33,5 %) и линолевая (41,2 %) кислоты.

Ключевые слова: *Ligularia narynensis*, биоактивные компоненты, макро-, микроэлементы, аминокислоты, жирные кислоты.

Information about authors:

Jenis Janar, Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan, PhD, Associate Professor, janarjenis@mail.ru

Yang Ye, Chinese Academy of Science, Deputy Director-General of Shanghai Institute of Materia Medica, PhD, Professor, yue@mail.shcnc.ac.cn

Abilov Zharylkasyn A., Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan, Doctor of chemical Sciences, Professor, Zharlykasyn.Abilov@kaznu.kz

Dyusebaeva Moldyr A., Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan, Candidate of chemical Sciences, moldyr.dyusebaeva@mail.ru

Nurlybekova Aliya K., Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan, PhD student, nurl_al@mail.ru

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**Zh.T. Umirbekova¹, A.A. Atchabarova¹, K.K. Kishibayev¹,
R.R. Tokpayev¹, S.V. Nechipurenko¹, S.A. Efremov¹, A.R. Yergeshev¹, A.N. Gosteva²**

¹Center of Physico-Chemical Methods of Research and Analysis at the al-Farabi Kazakh National University
Almaty, Kazakhstan;

²I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Russian Academy of Sciences Kola Science Center, Apatity, Russia

E-mail: janna_umirbekova@mail.ru, azhar.atchabarova@mail.ru, kanagat_kishibaev@mail.ru,
rustamtokpaev@mail.ru, nechipurenkos@mail.ru, efremsa@mail.ru, akim9797@mail.ru

THE OBTAINING AND INVESTIGATION OF PHYSICAL AND CHEMICAL PROPERTIES OF CARBON MATERIALS BASED ON POWER-GENERATING RAW MATERIALS RK

Abstract. The method of obtaining activated and impregnated carbon sorbent based on the special coke of the Shubarkol field is described. Elemental and X-ray fluorescence spectroscopic analysis of the raw material was carried out. Physical and chemical characteristics were studied, the specific surface area of the raw material and the obtained carbon materials were determined. It is shown that the specific surface area rises from 14.44 m²/g to 361.4 m²/g when the coke is activated by water vapor, with additional impregnation up to 504.425 m²/g. The use of coke as a raw material simplifies the technology of obtaining a carbon support, reducing energy consumption and increasing the environmental purity of the process by eliminating the carbonization stage of the coal. The possibility of using impregnated coke for deep cleaning of furnace gas of the phosphorous industry from toxic substances was also investigated.

Key words: active coals, impregnation, power-generating coals, specific surface, phosphine.

Introduction. The phosphorous industry is one of the sources of pollution of atmospheric air of the environment, as in gas emissions contain toxic gases such as phosphine, phosphorus anhydride, hydrogen sulfide, etc. Only in the Zhambyl branch of LLC «Kazphosphate» NDFZ, in the production of 110.0 thousand tons of yellow phosphorus, 4969.36 tons/year of gaseous substances are released into the atmosphere. Specific output of furnace gas at phosphorous plants is 2800-3000 m³ per 1 ton of phosphorus [1].

The furnace gas of phosphorus production contains about 85-90% carbon monoxide [2], which can be used as a raw material in organic synthesis. However, the use of furnace gas is limited because the furnace gas the content of phosphine that is a potent catalyst poison [3]. Also currently an urgent problem for the phosphorous industry is an unsuccessful system for cleaning gas-dust emissions. The solution of these problems is the use of sorption and catalytic purification methods [4,5]. The advantages of these methods are the ability to remove contaminants to almost any residual concentrations. Moreover, lack of secondary pollution and the controllability of the process, the relatively low cost of construction of sewage treatment plants. Also high removal efficiency of low concentrated contaminants; the small footprint of the unit adsorption purification; the possibility of adsorption of substances in multicomponent mixtures.

Activated carbons are universal adsorbents and supports of catalysts due to their unique properties, high chemical and heat resistance, strength, high sorption capacity in relation to various substances, stability of its structure under the reaction conditions [6,7]. As is known, impregnation of activated carbons with oxides or chlorides of metals creates specific forces on their surface (hydrogen bonding, acid-base interactions or chemical reactions, complex formation, etc.) responsible for chemisorption. Based on the literature data, copper salts with additives of transition and rare-earth metals are the most

frequently used impregnating agents for purification from phosphine [8-12]. Therefore, copper, zinc and chromium salts were chosen as impregnates in this work.

The aim of this work is to obtain and study the physical and chemical properties of the carbon support and catalyst based on the special coke of the Shubarkol field for cleaning the furnace gas of a phosphorous plant from toxic substances such as phosphine, phosphoric anhydride, hydrogen sulphide, etc..

Materials and methods

In the present work, a special coke on the basis of coal "D" of the Shubarkol field was used as the carbon raw material.

Elemental and X-ray fluorescence spectral analysis of raw materials was carried out on the elemental analyzer "Vario Micro Cube", Germany and X-ray fluorescence spectrometer "Focus-2M", Russia, respectively.

Obtaining a carbon support on the basis of the special coke. Special coke on the basis of coal grade "D" Shubarkol field previously crushed to a fraction of 1.5-4 mm, then activated with water vapor at a temperature of 850-950°C. The activation process transforms the carbon material into a form that contains as many randomly distributed pores of various shapes and sizes as possible, thereby increasing the specific surface area of the sorbent [13].

Impregnation of carbon support with the metal salts. The impregnation of the sorbent was carried out with solutions of the following salts in a certain order: $\text{Zn}(\text{CH}_3\text{COO})_2$, $(\text{NH}_4)_2[\text{Cr}(\text{C}_2\text{O}_4)_2]$, $\text{Cu}(\text{NH}_4)_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$ to obtain the required concentrations of the oxides in the solid residue with further evaporation of the solution. The concentration of oxides in the solid residue was determined by atomic absorption spectroscopy on the spectrometer «AAnalyst 400», Perkin Elmer, Germany. Drying of impregnated sorbent was carried out at 120-140 °C for 20 minutes, then calcined at 260-295 °C for 10 hours with a heating rate of 10°C/min in the air at Teflon and steel trays on the muffle furnace SNOL 7,2/1100. As a result, a carbon-metal system with the following content of metal oxides was obtained: CuO 8.3-9.8 mass.%, ZnO 0.4-0.6 of the masses.%, Cr_2O_3 0.9-1.1 mass.% [14].

Humidity was determined by the difference between the masses of the original sample (its mass is ~1 g) and dried sample at 110°C for 1 h in the weighing bottle. Ash was also found by weighing a sample of sorbent with a mass of 1 g, heating it for 2-2.5 hours at 800 °C. In all cases, three parallel experiments were conducted [15].

When determining the sorption capacity for iodine, preliminary preparation of the sample was carried out, which consist in a 10-minute boiling of 20 g of sample in 200 cm³ of 0.2N solution of HCl, followed washing it with distilled water and drying for 1 hour at 110 °C. To determine 1 g of the sample shake 15-30 min with 100 cm³ 0.1N iodine solution in KI (25 g/dm³), then aliquot (10 cm³) titrated 0.1 N sodium thiosulfate solution (indicator – starch) [16].

The mass fraction of volatile substances and the total volume of pores is determined by RMG 6382-2001 and RMG 17219-71 [16, 17].

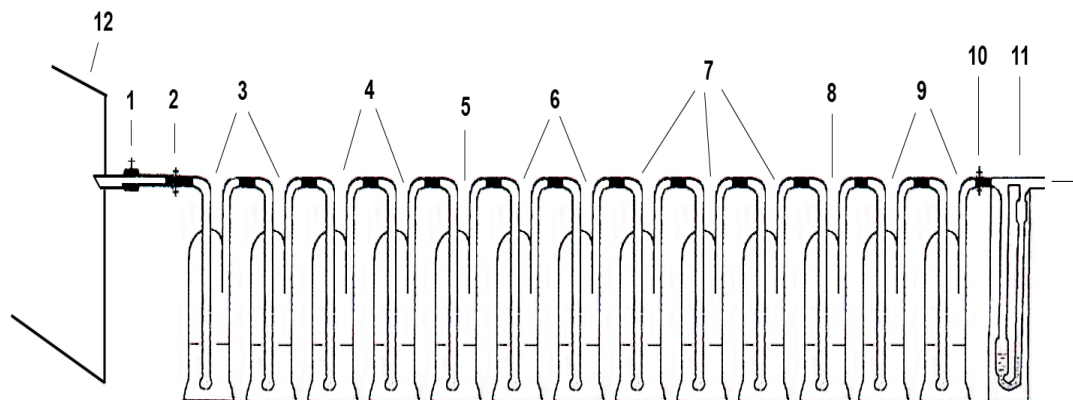
The pH of the aqueous extract was determined by the procedure of [18].

pH of the aqueous extract was determined at 3-minute boiling of 5 g of finely ground sorbent in 50 cm³ of distilled water with a reverse refrigerator, followed by rapid filtration of the suspension through a paper filter and cooling it before pH measurement [19].

The sorption capacity by methylene blue is determined for a dry sample weighing 1 g, which is in contact with the solution in static mode. The contact time is 24 hours. The sorption capacity E_{mg} of sorbent is calculated from the difference between the concentrations of methylene blue solution before and after the experiment. Analysis of the concentration of methylene blue was carried out on a photoelectrocolorimeter AR-101, Japan [20].

The specific surface area and the total pore volume were determined by the Brunauer–Emmet–Teller (BET) method using the standard procedure based on the data on the measurement of adsorption – desorption isotherms at 77 K using the surface area and pore size analyzer NOVA 3200E (Quantachrome Instruments, USA).

Methodology of sorption purification of furnace gas. The laboratory installation for the purification of furnace gas consisted of a series of connected Drexel flasks, the volumes of which are 50 ml, filled with 5% soda Na_2CO_3 and 25% solution of copper sulfate, benzene to absorb yellow phosphorus, and the flask filled with 207 g of impregnated sorbent (figure 1).



11 - the valve; 2,10 - clamps; 3 - Na_2CO_3 soda solution 5%; 4 - CuSO_4 - 25%, 5-8 - absorbers are empty; 6 - absorber with benzene for P_4 ; 7 - absorber with NaOH solution for P_2O_5 and HF ; 9 - impregnated adsorbent; 11 - rheometer; 12 - flue.
Figure 1- Scheme of deep cleaning of furnace gas from PH_3 , as well as other associated gases

From the flue is supplied furnace gas, which is passing through the cleaning flasks Drexel undergoes deep cleaning. The flow rate of the furnace gas was controlled with the rheometer and was $1 \text{ dm}^3/\text{min}$. The purification tests were carried out for 2.5 hours. Gas samples were taken at the beginning of the experiment and 2 hours after the start of the experiment. The concentrations of P_2O_5 and PH_3 before and after purification were determined by the photocolometric method [20,21], and concentrations of the associated gases were determined by the methods of [22-24].

Results and discussion

Visually, the special coke of the Shubarkol field used as a feedstock, solid, has a grayish-black color and a characteristic specific smell (velvet-black color on the fracture of the pieces). Fraction size from 0,1 to 10 mm. Elemental and component composition of the initial coke is presented in tables 1,2. As can be seen from the table, coke is characterized by a high content of carbon - 80.501%, a small amount of sulfur. The oxide composition of coke is dominated by oxides of silicon, aluminum, calcium and iron.

Table 1-Elemental composition of the special coke

Element	Content, %
Carbon	80.501
Hydrogen	3.971
Sulfur	0.054
Nitrogen	not found
Unidentified elements	15.474

Table 2 - Component (oxide) quantitative composition and total sulfur of the original special coke

Component	Content, %
Na_2O	0.01
MgO	0.03
Al_2O_3	1.09
SiO_2	2.14
P_2O_5	0.03
K_2O	0.06
CaO	0.63
TiO_2	0.06
MnO	<0.01
Fe_2O_3	0.14
п.п.п.	95.81
Total	100
S_{total}	0.03

As a result of activation of the special coke with water vapor, the specific surface area increases from 14,443 to 361, 377 m² / g, and the iodine number increases from 1.78 to 40.47%, this improves the sorption properties due to the burnout of unstructured amorphous carbon (Table 3). The mass fraction of volatile substances and moisture is significantly reduced.

Table 3-Physico-chemical characteristics of the initial and activated coke

№	Name of the indicator	Initial coke	Activated coke
1	Mass fraction of moisture, %	22.24	2.24
2	Mass fraction of ash, %	6.61	6.24
3	Mass fraction of volatile substances, %	9.98	0.1
4	Adsorption activity by iodine, %	1.78	40.47
5	Specific surface area, m ² /g	14.443	361.377

The total pore volume of activated coke is determined, which is equal to 0.59 cm³/g, and the sorption capacity for methylene blue is 114 mg/g and pH of aqueous extract 7.1. The data obtained indicate that the obtained carbon material is comparable to the known commercial BAU-A sorbent by sorption properties [25].

Impregnation of activated coke with solutions of salts Zn(CH₃COO)₂, (NH₄)₂[Cr(C₂O₄)₂], Cu(NH₄)₂[Cu(C₂O₄)₂] increases the sorbent ash content to 19.5-20.0%. Figure 2 shows the isotherm of adsorption and desorption of nitrogen in impregnated coke. The adsorption isotherm is of type I or Langmuir isotherm, inherent for microporous samples with a relatively small outer surface, where the limiting amount of adsorbate depends more on the available volume of micropores [26].

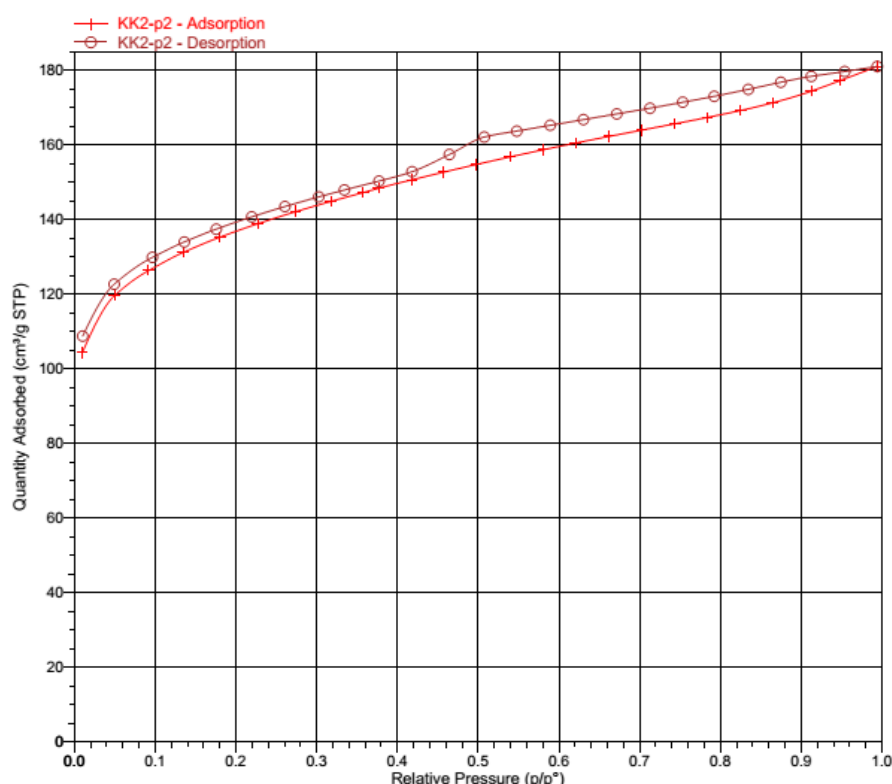


Figure 2 – The isotherm of adsorption and desorption of nitrogen on impregnated coke

The specific surface area determined by the BET method for the nitrogen adsorption isotherm is 504.425 m²/g, which is 1.4 times greater than the activated coke.

According to the analysis of the pore volume distribution, the sorbent obtained relates to fine-porous sorbents, the volume of mesopores (15-50 nm) is not more than 0.0118 cm³/g, the volume of micropores (0-15 nm) is 0.1380 cm³/g, macropores are absent.

In the central factory laboratory of LLC «Kazphosphate» NDFZ, in February 2018, laboratory tests were carried out on the technology of deep cleaning of furnace gas adopted at the plant using coke impregnated with salts of active metals. The purpose of the tests was to establish the possibility of using the developed adsorbent for deep purification of the furnace gas from phosphine and other associated gases. The average composition of the furnace gas is shown in Table 4.

Table 4 - Average composition of furnace gas of LLC «Kazphosphate» NDFZ

The composition of furnace gas										
P ₄ , мг/м ³	P ₂ O ₅ , мг/м ³	PH ₃ , мг/м ³	F, мг/м ³	S _{total} , мг/м ³	CO ₂ , % (об.)	PH ₃ , % (об.)	O ₂ , % (об.)	CO, % (об.)	H ₂ , % (об.)	CH ₄ , % (об.)
180	180	770	5,2	430	0,6	0,2	2,0	65,5	1,3	0,4

As a result of the studies, it was found that impregnated coke exhibits a high degree of purification with respect to phosphine, phosphoric anhydride and concomitant gases (HF, H₂S) throughout the experiment, and poorly adsorbs SO₂ (Table 5).

Table 5 – test Results for cleaning of furnace gas LLC «Kazphosphate» NDFZ

Date	Sampling point	Defined components	Before cleaning mg/m ³	After cleaning mg/m ³	the Purification efficiency, %	Temperature of sampling
16.02.18 1 sampling (at the beginning of the experiment)	the furnace №6 SUPG	P ₄	351,522	traces	100	27°C
		P ₂ O ₅	804,985	traces	100	
		PH ₃	1497,415	3,475	99,8	
		HF	Следы	traces	100	
		H ₂ S	488,225	traces	100	
		SO ₂	917,863	734,291	20,0	
2 sampling (after 2 hours)	the furnace №6 SUPG	P ₄	277,066	traces	100	31 °C
		P ₂ O ₅	634,481	traces	100	
		PH ₃	886,787	15,687	98,2	
		HF	Следы	traces	100	
		H ₂ S	494,761	traces	100	
		SO ₂	930,151	930,151	–	

Conclusion. As a result of the work, the sorbent activated and impregnated with salts of metals was obtained on the basis of the special coke of the Shubarkol field and their physical and chemical properties were determined. It is noted that the impregnated sorbent obtained has a fine-porous structure and a high specific surface area. The results of the study showed that the impregnated adsorbent exhibits high sorption characteristics in the purification of furnace gas LLC «Kazphosphate» NDFZ. The resulting carbon catalyst is a promising adsorbent for deep purification of furnace gases of the phosphorous industry and is recommended for research in semi-industrial and industrial conditions.

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Information about authors:

Umirbekova Zhanna Tanzharykovna - Center for Physical and Chemical Methods of Research and Analysis of the Kazakh National University Named after al-Farabi, Almaty, Kazakhstan, Doctoral Student, janna_umirbekova@mail.ru;

Atchabarov Azhar Aidarovna - Center for Physical and Chemical Methods of Research and Analysis of the Kazakh National University Named after al-Farabi, Almaty, Kazakhstan, Senior Researcher of Sorption and Catalytic Processes Laboratory, PhD (Chemistry), azhar.atchabarova@mail.ru;

Kishibayev Kanagat Kazhmukhanovich - Center for Physical and Chemical Methods of Research and Analysis of the Kazakh National University Named after al-Farabi, Almaty, Kazakhstan, Senior Researcher of the Composite Materials Laboratory, PhD (Chemistry), kanagat_kishibaev@mail.ru;

Tokpayev Rustam Rishatovich - Center for Physical and Chemical Methods of Research and Analysis of the Kazakh National University Named after al-Farabi, Almaty, Kazakhstan, the Head of Sorption and Catalytic Processes Laboratory, PhD (Chemistry), rustamtokpaev@mail.ru;

Nechipurenko Sergey Vitalievich - Center for Physical and Chemical Methods of Research and Analysis of the Kazakh National University Named after al-Farabi, Almaty, Kazakhstan, the Head of Composite Materials Laboratory, PhD (Engineering), nechipurenkos@mail.ru;

Efremov Sergey Anatolyevich - Center for Physical and Chemical Methods of Research and Analysis of the Kazakh National University Named after al-Farabi, Almaty, Kazakhstan, the Deputy Director of Innovation and Technological Activities, Dr. Sc. (Chemistry), Professor, efremsa@mail.ru;

Yergeshev Akim Ruslanovich - Center for Physical and Chemical Methods of Research and Analysis of the Kazakh National University Named after al-Farabi, Almaty, Kazakhstan, laboratory assistant of Sorption and Catalytic Processes Laboratory, akim9797@mail.ru;

Gosteva Alevtina Nikolaevna - I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Russian Academy of Sciences Kola Science Center, Apatity, Russia, PhD (Chemistry), junior researcher of the Powder Metallurgy Laboratory, fiona_tolk@bk.ru.

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A.O.Adilbekova, K.I.Omarova, Sh.Abdrakhmanova

Al-Farabi Kazakh National University, Almaty, Kazakhstan

Akbota.Adilbekova@kaznu.kz, omar_kainzhamal@mail.ru,

sholpan_kz@mail.ru

DEMULSIFICATION EFFECT OF NON-IONIC SURFACTANTS TWEEN-20, TWEEN-80 ON MODEL WATER-IN-OIL EMULSIONS

Abstract. Breaking of water-in-oil emulsions is a necessary part of crude oil preparation for processing and the development of new demulsifying compositions has importance for the Republic of Kazakhstan. In this research, the demulsification effect of non-ionic surfactants Tween-20, Tween-80 with a high value of hydrophilic-lipophilic balance (HLB) was considered. For thermal treatment of water-in-oil emulsion the model emulsions based on crude oil of North-West Konys with 30%, 40%, 50%, 60 % (vol.) of water phase concentration were studied. *The degree of oil emulsion dewatering in the presence of Tween-20* do not exceed 63% at temperature 60°C. The optimal term of thermal chemical breaking down by means of mixtures of non-ionic surfactants Tween-20, Tween-80 and anionic surfactant sulfanol at a ratio of 1:1 (vol.) was determined. The maximum demulsification equaled to 97.01% after 100 min for 30-50% water-in-oil emulsion was found out for Tween-20 – sulfanol mixture at a ratio of 1:1 at 60°C. The results confirm the opportunity of using of mixtures of Tweens with anionic surfactant sulfanol as demulsifying reagents.

Keywords: thermal chemical demulsification, non-ionic surfactants, Tween-20, Tween-80, sulphanol, water-in-oil emulsions, breaking of water-in-oil emulsions.

Introduction

Water-in-oil emulsions (microheterogeneous and ultradispersed water droplets suspended in crude oil) are formed as a result of oil production. The stability of water-in-oil emulsions varies from few minutes to several years and depends on the oil field and the physicochemical characteristics of the crude oil [1, 2]. Breaking of oil emulsions is an important part of oil preparation for processing, therefore the development of new demulsifying compositions has importance for the Republic of Kazakhstan.

Crude oil emulsions must be broken down because they make corrosion of pipelines and equipment used for oil refining due to the presence of water droplets with dissolved chloride salts. It favors an increase in the cost of transportation and refining of oil. In addition, the emulsified water causes changes the properties of crude oil, such as viscosity, density, etc. [3].

The high molecular weight nonionic surfactants are widely used for breaking of oil emulsions. They show a good demulsifying effect and do not leave any counter ions in crude oil and petroleum products [4].

In the research, polysorbates or so-called Tweens related to polymer surfactants were used to select highly effective destabilizers of water-in-oil-emulsions with the optimal composition and nature of components. Tweens are viscous, oily liquids and they are derivatives of polyethylene glycols – sorbitan esterified with fatty acids. Groups of ethylene oxide $-(CH_2CH_2O)-$ and polyester of carboxylic acid provide the hydrophilic properties to Tweens and polysorbitan favor the lipophilic properties. Tweens are widely used to stabilize the oil-in-water emulsions in practice [1]. Therefore, it was expected that this type of nonionic surfactants can be effective for breaking of the water-in-oil emulsion, i.e. they can be used for the breaking down the crude emulsions (reverse emulsions) [1, 5]. The polymeric demulsifiers with rather high value of hydrophilic-lipophilic balance (HLB) adsorb at the water/oil interface and destroy the adsorption layer of emulsifiers [1]. The presence of a developed hydrophilic part

contributes to a greater separation of water from oil. Tweens have a suitable HLB due to the large number of ethylene oxides. Oxyethylated groups interact with the aqueous phase due to hydrogen bonds and provide a strong hydrophilic part to the surfactant molecule.

It was shown in [6, 7] that a high molecular weight, an increase of the number of hydroxyl agents, and a percentage of nonionic polymers in demulsifier compositions improves the demulsifying effect of the surfactant. Studies have shown that an increase in the number of HLB is effective for demulsification [8]. Since Tweens have a high value of HLB, they can contribute to the breaking of crude oil emulsion.

At present, there is no detailed research on the demulsifying effect of Tweens and their compositions for the destruction of oil emulsions of local oil fields lacking effective demulsifiers.

Experimental

For demulsification investigation the non-ionic polymer surfactants Tween-20, Tween-80 and anionic surfactant Sodium dodecylbenzenesulfonates (sulfanol) were used.

Tween-20 – polyethylene (20) sorbitan monolaurate, $C_{58}H_{114}O_{26}$. Tween-80 – polyethylene (20) sorbitan monooleate, $C_{64}H_{124}O_{26}$.

Sulfanol is produced as a mixture of related sulfonates. It conforms to the formula $R-C_6H_4SO_3Na$, where R is a radical corresponding to C_nH_{2n+1} , $n=14-18$.

For preparation of a model emulsion the oil of North-West Konys oil field was used. Some physical-chemical properties were determined: density (833 kg/m^3), content of chloride salt (1.5 mg/L), mechanical impurities (0.067%), sulphur (0.163%) [9].

Water-in-oil emulsions of 30%, 40%, 50%, 60 % (vol.) concentration were prepared by mixing of oil with 20 % solution of sodium chloride in water. Emulsification was carried out using an IKA T 10 basic ULTRA-TURAX homogenizer (Germany) at 10000 rpm for 30 min. The prepared emulsion was left for a week to stabilize by adsorption of surface active components of the crude oil. The increase of the mixing time and the number of rotations did not have a significant effect on the oil emulsion stability.

The kinematic viscosity of the oil emulsions was measured by means of glass viscometer for oil and oil products by the time of the outflow of the oil emulsion.

The dispersion of water droplets was measured using an optical microscope. A drop of crude oil was placed on the glass slide and spread on it. The images were processed using a «Leica DM6000M» microscope of the National nanotechnology laboratory of al-Farabi Kazakh National University.

To determine the destabilizing ability of demulsifier 50 ml of crude oil in graduated glass test tubes and placed into a thermostat. The aqueous phase separation was visually monitored at regular time intervals. The water separation in percent (W, %) was calculated as relation of volume of separated water to the original volume of water in the emulsion.

To determine the demulsifying ability of the demulsifier, 50 ml of oil was placed in a graduated test tube, the required amount of demulsifier was added with a microdoser and mixed with a homogenizer for 5 minutes at 10000 rpm. Then the tube was placed into a thermostat at 40-60 °C and the volume of water separated was determined every 10 minutes. At the same time, the state of water layer and the interface were observed and assessed visually.

Results and discussion

Concentrations of model emulsions vary from 30% to 60% (vol.). The watering of crude oil emulsions corresponds to these concentrations for oil fields of Kazakhstan in average as a result of exploitation. Increasing of water content helps to model oil emulsion with different viscosity.

Emulsions with 10% and 20% of water are close to initial oil without water by their viscosity. Increasing of water content in oil till 50 % - 60 % effects on oil emulsion viscosity significantly (Fig. 1). The viscosity of 60 % (vol.) model emulsion increases by 50 times in comparison with dewatered oil.

It is known that naphthenic acids, fatty carbon acids and their salts, asphaltenes, resins and high molecular weight paraffins are the base natural stabilizers of oil emulsion [10, 11]. According to quantitative analysis of oil components (asphaltenes, resins and paraffins) the stable emulsions can form on the basis of the probe of North-West Konys oil [9]. Analysis of the dispersion degree of the model emulsion samples by means of the optical microscopy allows to relate them to highly dispersed system. Hence, it confirms that the water droplets cannot sediment under the gravity. The investigated water-in-oil emulsions

are characterized by droplets of spherical shape and polydispersity. The sizes of water droplets range from 0.91 μm to 19.1 μm (Fig. 2).

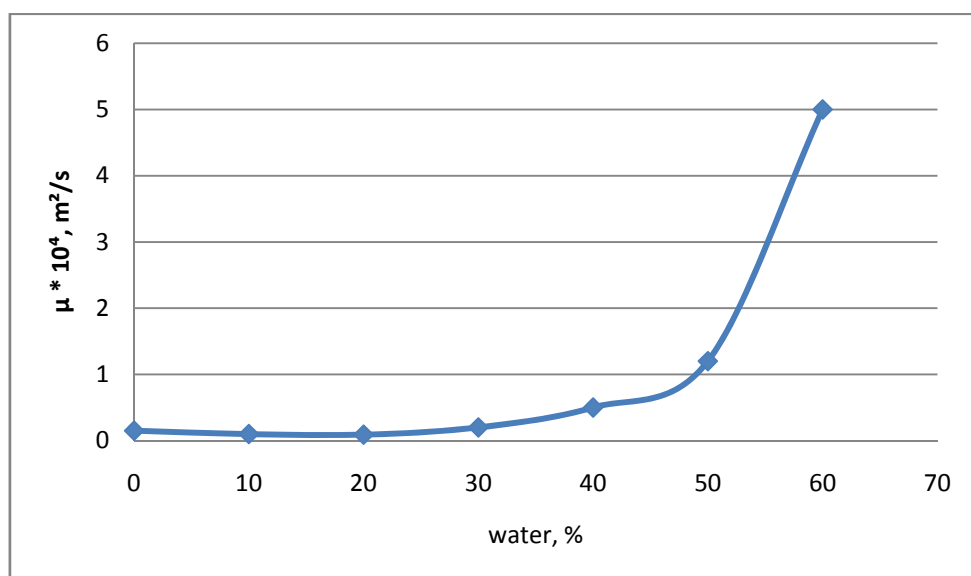
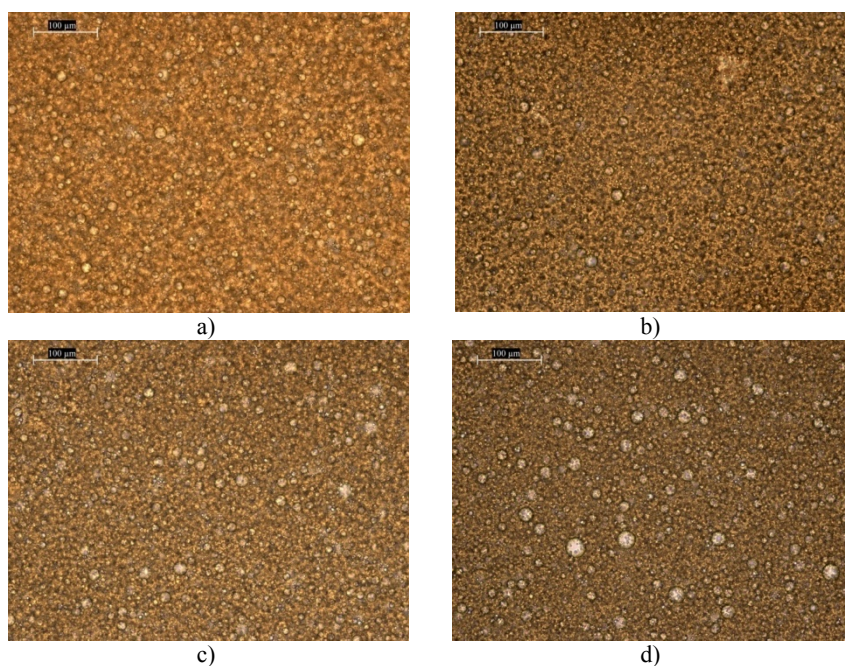


Figure 1– Influence of water concentration on kinematic viscosity of oil emulsion. $T=20^\circ\text{C}$

According to the optical microscopy images, the increasing of water concentration in the emulsions is accompanied by growth of the average diameter of the droplets (Fig. 2). It is obvious that the increasing the water droplet size in an emulsions results in an increase of watering degree and decreasing the emulsion stability. However, so-called "cold settling" of model emulsions, i.e. sedimentation without heating, and the thermal treatment of them from 40-60° C did not lead to the separation of water.



a) – 30% a – 30%; b) – 40%; c) – 50%; d) – 60%

Figure 2– Optical microscopy images of oil emulsions with different water concentration (resolution 100 μm)

To study the demulsification 1 ml of 1% aqueous solution of Tweens was introduced into model emulsions of different concentrations and then emulsions were mixed with Tween surfactant for 5 min using the homogenizer.

The addition of Tween-20 and Tween-80 solutions showed that there is no separation of water at 40° C and 50° C. The rise in the temperature to 60° C led to the separation of water within 10 minutes and reached a constant value after 120 minutes of observation.

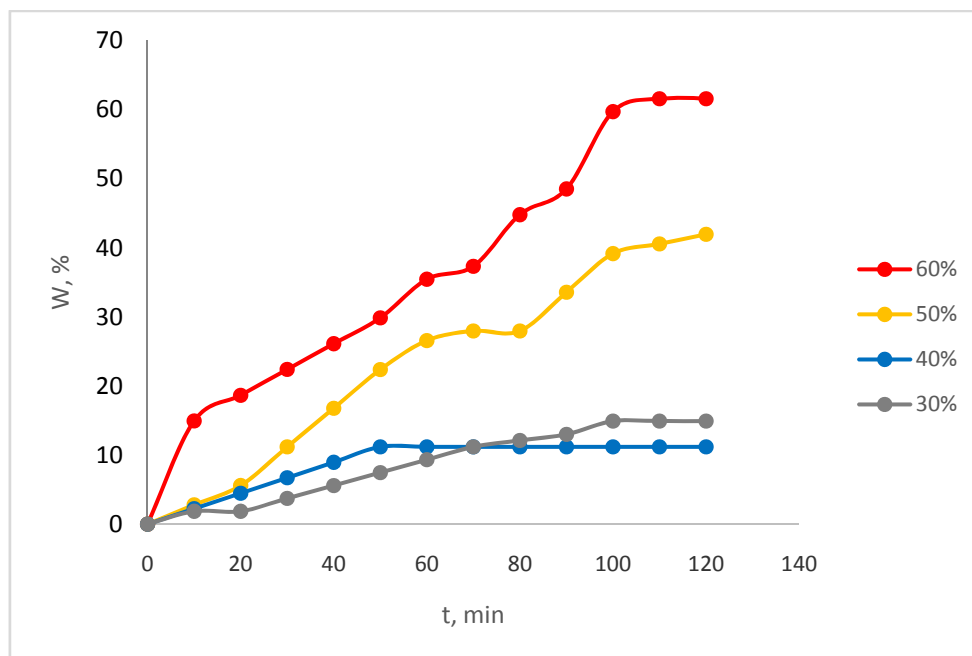


Figure 3— The amount of water separated from oil emulsions of different concentrations at the addition of Tween-20. T = 60°C

Fig.3 shows that water separation percentage increases with the growth of dispersed phase concentration of water-in-oil emulsions. For 60% emulsion, the water separation was 63 %.

The maximum degree of dewatering for Tween-80 was insufficient, about 12% for emulsions studied after the same observation time.

The greater demulsifying effect of Tween-20 can be explained by the difference of interfacial activity at the water/oil interface and different hydrophilic-lipophilic balance of their molecules (HLB for Tween-20 is 16.7, and for Tween-80 is 15.0) [1]. The higher the number of polysorbate, the higher the value of its HLB, the lower its value; the ability to create stable emulsions of o/w decreases. The use of Tweens for demulsification was interesting, since they are of natural origin, based on sorbitol and fatty acids from base oils: coconut oil for Tween-20, olive oil for Tween-80. Tweens have the property of easily decomposing in natural environments[12]. Therefore, they will not cause a deterioration of the quality of oil processed, in comparison with other chemical reagents.

In addition, the great amount of ethylene oxides, their number in Tweens equals to 20, favors the study of demulsifying action of them. They have developed hydrophilic part able to penetrate to an interfacial layer around the water droplet.

Heating to 60 °C reduces the viscosity of the oil medium and increases the difference between the density of the dispersed phase and the dispersion medium, facilitating the coalescence of water globules in accordance with the Stokes law when they collide. However, a further increase of temperature to increase the water separation is not advisable, since this can lead to volatilization of light oil fractions.

The demulsifying effect of compositions of Tweens with anionic surface-active substance sulfanol was studied. Sulfanol is a more hydrophilic surfactant than non-ionic Tween. Therefore, for increasing the hydrophilic-lipophilic balance the demulsifying effect of the Tween-sulfanol mixed composition was investigated. Composition Tween 20 – sulfanol was used in a ratio of 1: 1 (vol.). In addition, sulfanol refers

to a sufficiently accessible technical anionic surfactant because it is produced as a mixture of related sulfonates and can be obtained from wastes of petroleum industry.

At room temperature and with a temperature rise up to 40 °C in the presence of the surfactant composition, the water separation, as in the case of individual Tween-20 and Tween-80, was not observed. Starting from 50 °C, after 10 minutes of settling, the degree of dehydration was 60 % and reached 95.24% for 30-50 % of water-in-oil emulsions after 100 minutes of treatment. At 60 °C for 30-50 % emulsions the maximum degree of dehydration is 97.01%, and for 60% of emulsion - 83.96% (Fig. 4).

For Tween-sulfanol mixture in the difference with individual non-ionics it is seen that 60% emulsion has lower water separation in comparison with emulsions with small water concentration.

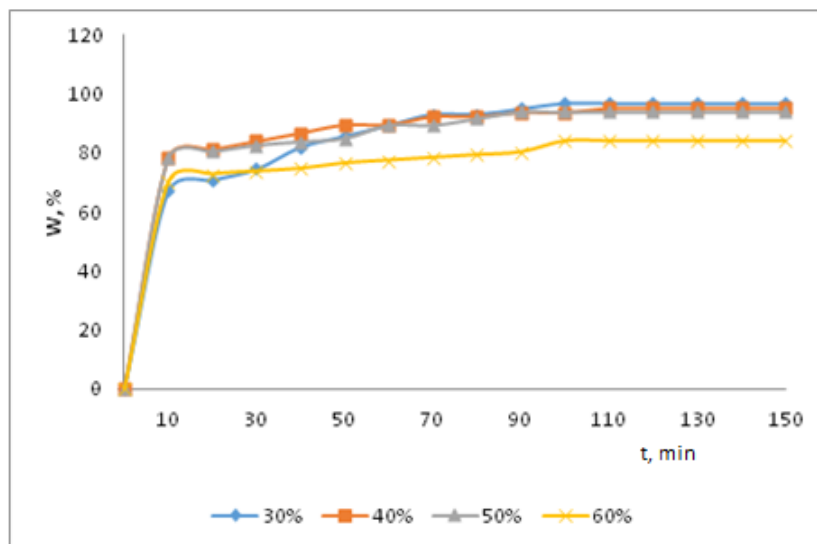


Figure 4 – Degree of dewatering of oil emulsions of different concentration in the presence of the composition Tween-20 - sulfanol. T = 60 °C

For aqueous mixtures of Tween 80 –sulfanol the degree of water separation at 50 °C for 30-40% of emulsions, the degree of dewatering was 78.43%. For 60% emulsion W = 63.43% at the same temperature. With an increase of temperature till 60 °C for water-oil emulsions of 30-40%, the maximal dehydration degree was 82.09% and 75.63% respectively, for 60% emulsion – 59.7% (Figure 5).

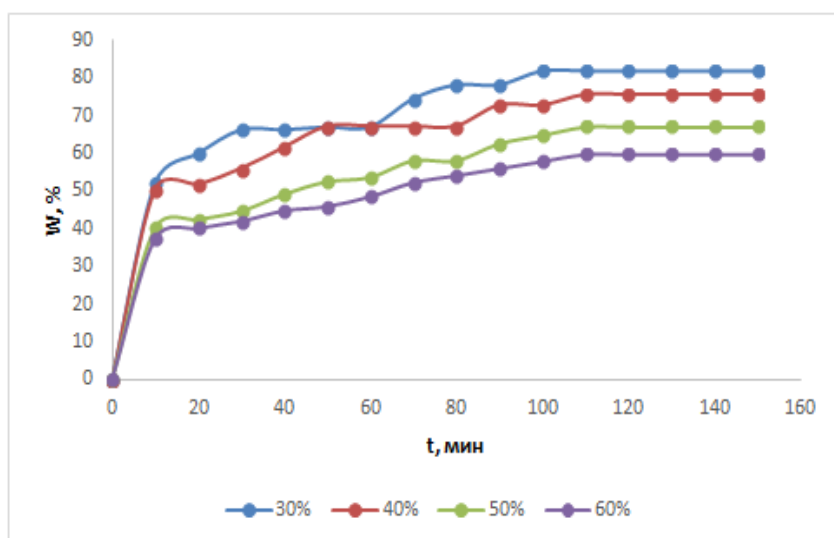


Figure 5– Degree of dehydration of water-in-oil emulsions of different concentrations in the presence of the composition Tween-80 –sulfanol. T = 60 °C

The Tween-20 – sulfanol formulation shows a greater demulsifying effect on oil emulsions in comparison with individual non-ionic surfactants. This occurs probably due to the greater interfacial activity of Tween-20 compared to Tween-80 and higher HLB value and the Tween-20 – sulfanol has an additive demulsifying effect, displacing the natural stabilizers from oil/water interface.

Conclusion

The demulsifying action of nonionic surfactants Tween-20, Tween-80 with high HLB value and their mixtures with anionic sulfanol was studied on model emulsions based on the crude oil of North-Western Konys oil field.

The use of Tween-20 for breaking down the oil emulsions did not exceed 63% at 60 °C. The mixture of 1% water solution of anionic and non-ionic surfactants at a ratio of 1:1 (vol.) shows a better demulsifying action. According to results, the maximum demulsification was observed for the composition of Tween 20 – sulfanol at 60 °C and equals to 97.01% after 100 minutes of thermochemical treatment of artificial water-in-oil emulsions with water content of 30-50%. The research results showed the opportunity of using Tweens mixtures with anionic surfactants sulfanol as effective demulsifying agents.

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А.О.Адилбекова, Қ.И.Омарова, Ш.Абдрахманова

Әл-Фараби атындағы Қазақ ұлттық университеті

МОДЕЛЬДІ МҰНАЙ ЭМУЛЬСИЯЛАРЫНА ИОНДЫ ЕМЕС БАЗ ТВИН-20 ЖӘНЕ ТВИН-80-НІҢ ДЕЭМУЛЬСИЯЛАУ ӘСЕРІ

Аннотация. Мұнайды өңдеуге дайындауда мұнай эмульсияларын бұзу маңызды болғандықтан Қазақстан Республикасы үшін жаңа деэмульсиялаушы композицияларды жасау өзекті мәселе болып табылады. Жоғары гидрофильді-липофильді баланс (ГЛБ) мәніне ие ионды емес БАЗ Твин-20 және Твин-80-нің деэмульсиялау әсері зерттелді. Термохимиялық өңдеуді зерттеу үшін сулы фаза концентрациялары 30%, 40%, 50%, 60 % (көл.) болатын моделді мұнай эмульсиялары қолданылды. Мұнай эмульсиясының сусыздану дәрежесі Твин-20 қатысында 60°C-да 63%-дан аспады. Твин-20, Твин-80 және анионды БАЗ сульфанола 1:1 (көл.) қатынастағы қоспалардың қатысындағы термохимиялық тұндырудың оптималды шарттары анықталды. Твин-20 мен анионды БАЗ сульфанола 1:1 (көл.) қатынастағы композициясы максималды деэмульсиялауды көрсетеді және 30-50% суы бар мұнай эмульсияларында 60°C 100 минут тұндырудан кейін 97,01%-ға тең екені табылды. Деэмульгирлеуші реагенттер ретінде Твиндердің анионды БАЗ сульфаноламен қоспаларын қолдануға болатын мүмкіндігі көрсетілді.

Тірек сөздер: термохимиялық деэмульсиялау, ионды емес беттік-активті заттар, Твин-20, Твин-80, сульфанола, су-мұнайлы эмульсиялар, мұнай эмульсияларын бұзу.

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А.О.Адилбекова, Қ.И.Омарова, Ш.Абдрахманова

Казахский национальный университет имени аль-Фараби

ДЕЭМУЛЬГИРУЮЩЕЕ ДЕЙСТВИЕ НЕИОННЫХ ПАВ ТВИН-20 И ТВИН-80 НА МОДЕЛЬНЫЕ НЕФТЯНЫЕ ЭМУЛЬСИИ

Аннотация. Разрушение нефтяных эмульсий является важной частью подготовки нефти к переработке, поэтому разработка новых деэмульгирующих композиций является актуальной проблемой для Республики Казахстан. В работе рассмотрено деэмульгирующее действие неионных ПАВ Твин-20, Твин-80, обладающих высоким значением гидрофильно-липофильным балансом (ГЛБ). Для исследования термохимической обработки водонефтяной эмульсии были использованы модельные нефтяные эмульсии на основе нефти месторождения *Северо-Западный Коныс* с концентрацией водной фазы 30%, 40%, 50%, 60 % (объемн.). Степень обезвоживания нефтяной эмульсии в присутствии Твин-20 не превысила 63% при температуре 60°C. Определены оптимальные условия термохимического отстаивания в присутствии смесей неионных ПАВ Твин-20, Твин-80 и анионного ПАВ сульфанола в соотношении 1:1 (объемн.). Максимальная деэмульсация была обнаружена для композиции Твин 20 – сульфанола в соотношении 1:1 (объемн.) при 60°C и равна 97,01% после 100 минут отстаивания для водонефтяных эмульсий с содержанием воды в нефти 30-50%. Результаты подтверждают возможность использования смесей Твинов с анионным ПАВ сульфанола в качестве деэмульгирующих реагентов для обезвоживания нефти.

Ключевые слова: термохимическое деэмульгирование, неионные поверхностно-активные вещества, Твин-20, Твин-80, сульфанола, водонефтяные эмульсии, разрушение нефтяных эмульсий.

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A.Bayeshov¹, A.K.Bayeshova², U.A.Abduvaliyeva²¹Institute of Fuel, Catalysis and Electrochemistry named after D.V.Sokolsky, Almaty, Kazakhstan²Kazakh national university named after Al-Farabi, Almaty, Kazakhstan

E-mail: bayeshov@mail.ru, azhar_b@bk.ru, abdumida14@gmail.com

**INFLUENCE OF CUPROIONS ON COPPER POWDERS
FORMATION IN ELECTROREFINING OF COPPER**

Abstract. The purpose of this work was to determine the ways of copper powders forming penetrating into the sludge when copper is produced by electro-refining. Our studies were carried out by electrolysis in galvanostatic conditions and by potential measurements using Autolab PGSTAT 302 potentiostat. The temperature varied between 25 and 75° C. Copper ions concentration in solutions after electrolysis was determined by potentiometric titration.

It is shown that copper ions (II) in sulfuric acid solutions in the presence of titanium (III) ions are reduced to form elemental copper in powder, forms and sizes of particles in copper powders are determined by the electron microscopic method.

Results of the study showed assumptions about the possibility of forming powders due to mechanical shedding during anodic copper dissolution are not confirmed.

Our studies results allow us to conclude that the anode potential rises, then decreases, therefore, it constantly fluctuates and leads to copper powders formation at this time. Cuproions's concentration depends on copper electrode potential and its oscillation can promote a shift in the equilibrium of $\text{Cu}^0 \leftrightarrow \text{Cu}^+ + e$ reaction to the right or to the left. In industrial conditions, the value of the current in the circuit and the temperature of the electrolyte cannot be kept constant. For this reason, there is a periodic anode potential oscillation with different frequency amplitude. When anode potential is shifted to negative region, it is possible to form a copper powder according to an above reaction.

However, the formed copper atoms cannot penetrate into the crystal lattice of the anode. As a result, finely dispersed copper powders are formed on the electrode surface; they gradually pass into the solution and then penetrate into sludge.

For the first time, on the basis of study and analysis results, a mechanism is established for copper powders formation penetrating into the sludge composition during the electro-refining of copper. It is shown that the formation of copper powders, their penetration into the sludge composition, is mainly directly related to the oscillation of anode potential in electrolysis process and formation of various potential values at various sites of the electrode surface.

Key words: copper, powder, cuproion, sludge, refining, potential, electrolysis, anode, cathode, electrolyte, reduction.

Introduction. Following the traditionally developed technologies using pyrometallurgical method, the metal is extracted with a purity of 99.9% with purification by electro-refining processes of more than 90% copper. At electrolytic refining of copper rare and precious metals not getting in a solution, collect on the bottom of an electrolyzer in the form of a sludge; in this precipitate fall and disperse copper powders, their quantity is about 60%.

From one ton of cathode copper, 1-1.5 kg of sludge is extracted. The composition of the sludge depends on an anode composition. The amount of metals and compounds contained in the sludge, which is formed by the method of electro-refining around the world (on average),%:

Cu – 10 – 66 As – 0.1 – 4.0 Ni – 0.05 – 0.5

Ag – 3 – 55 Bi – 0.001 – 0.5 SiO₂ – 0.3 – 7.0

Au – 0.05 – 4.0 Se – 2 – 28 SO₄²⁻ – 6 – 15

Pb – 0.9 – 12.0 Te – 0.01 – 6.0

Sb – 0.04 – 30.0 Fe – 0.04 – 1.5

Dispersed copper powders, which are part of the sludge composition, make it difficult to separate the extraction of valuable elements such as gold, silver, selenium, tellurium. In short, the fact that copper powders enter the sludge during electro-refining is unnecessary, and many studies are devoted to research related to this phenomenon. However, scientists could not explain the loss of copper powders to the mud for more than 100 years.

In short, some authors [13-15] explain the formation of copper powders during electrolysis by the presence of metals with negative potentials in the form of impurities.

In the opinion of these authors, if there are metals in the composition corresponding to negative potentials (Ni, Fe, Zn and others), then as a result of foundry anodic polarization rapidly dissolves, there is a positive potential of copper, not soluble, then rubbed in the form of a powder.

In fact, the conducted studies have shown that, due to the presence of a large number of negative metals in the composition of copper, when they dissolve, the growth of copper powders.

There is also an opinion that the insolubility of the copper anode can also be one of the reasons for copper powders formation. During electrolysis, it can also be observed that the copper anode dissolves not evenly.

The results of a special study showed that a fine powder precipitated in the sludge is very fine. For this reason, some scientists suggest that these powders are formed chemically as a result of the disproportionation reaction [16,17]:



But the results of the study Makarov G.V. and other authors [10, 13] show that during electro-refining the concentration of monovalent ion in the electrolyte volume does not reach the equilibrium state. Therefore, it is unambiguous to conclude that copper powder cannot be formed as a result of the above chemical reaction. Another proof of this hypothesis is: copper powder formation is observed even when a pure copper anode is dissolved.

If copper powders are formed mechanically, then the size of their particles should be large. But how is this possible from the chemical side? Before us was the task of answering such questions. In connection with this, the purpose of our work is to study copper ions reduction process in various cases.

Methods. The studies were carried out during electrolysis in the galvanostatic regime and using the method of potential measurement by Autolab PGSTAT 302 potentiostat. The temperature was changed between 25-75° C. The concentration of copper ions in solutions after electrolysis was determined by potentiometric titration. Copper (II) ions were oxidized in the presence of titanium (III) ions in sulfur solutions. In this case, copper is recovered by the following reaction and is formed in the form of a powder:



We investigated copper powder components shape and size by electron microscopy.

Results and discussion. Copper powders formation in accordance with reaction (2) is analogous to the result of the following reaction $\text{Cu}^{2+} + e \rightarrow \text{Cu}^0$, because here metal powders are realized by electronic exchange. Forms of copper powders formed during carburization are shown in Figure 1. Photographing was carried out in reflected light with the help of a polished section. The particles of copper powder are different: inaccurate, isometric and some in different forms, oval. The edges of the particles are not smooth. The particle size ranges from 0.001 to 0.10 mm. It was noted that the number of particles in the horizontal direction with a size of 0.01-0.10 mm is dominant. At high temperatures ($t = 90^\circ \text{C}$), copper particles size decreases (the particle size is 0.001-0.005 mm horizontally). That is, the size of the particles depends on the conditions of their formation. Therefore, as previously reported in [13-15], the various shapes and sizes of metallic particles cannot be established as a result of the formation of copper powders by anodic-mechanical weathering.

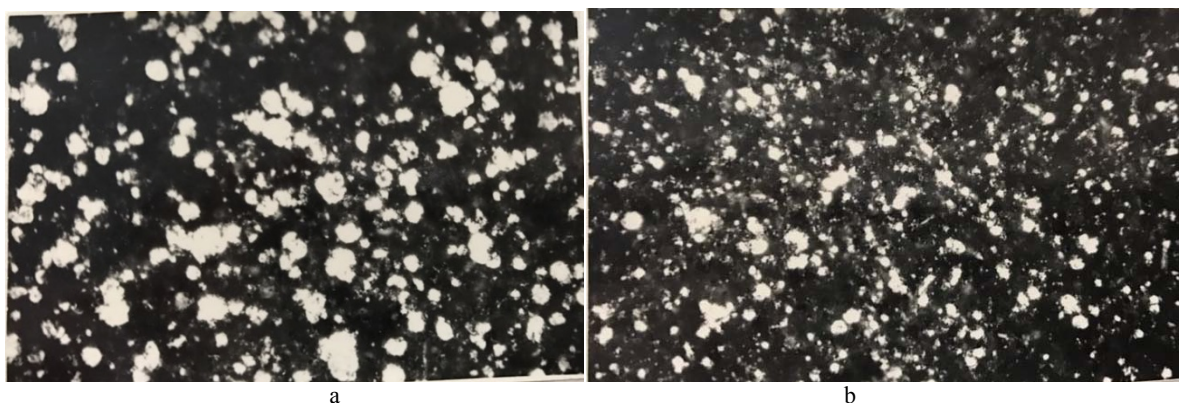


Figure 1 - The microphoto of a polished section of the bricked powder of copper received at cementation of ions of copper (II) by ions of the titan (III)
a) 25°C; b) 90°C; zoom in 1200 times

Copper powders can also be formed on the surface of the cathode. As a rule, the process of electrorefining occurs when the concentration of copper ions is 40 g / L, and the current density in the cathode does not exceed 250 A / m². With such a high concentration on the surface of the cathode, the current density cannot be higher than the limiting current. For comparison, a photomicrograph of the formed copper powder was obtained from a solution containing 1.2 g / L of copper ions (II), 50 g / L sulfuric acid at a cathode current density of 3000 A / m² (Figure 2). From this figure, the formation of a copper powder from homogeneous particles of 1 μm in size is seen.

The results of our preliminary studies allow us to conclude that the anodic potential increases and decreases, which means that its oscillations can lead to the formation of copper powders at this time. As we found, the concentration of cuproion depends on the potential of the copper electrode, and its oscillations can be shifted to the right or left of the $\text{Cu}^0 \leftrightarrow \text{Cu}^+ + e$ reaction. In the case of production it is impossible to maintain a constant current and the temperature of the electrolyte in the circuit, respectively, the anode potential instantaneously drops to a certain value at a certain moment. When the anode potential is shifted to the negative side, the copper powder can be formed by the above reaction. But structured copper atoms cannot enter and settle into the crystal lattice of the anode. As a result, a fine-dispersed copper powder is formed which adheres poorly to the surface of the electrode, which gradually passes into solution, and then to the sludge.

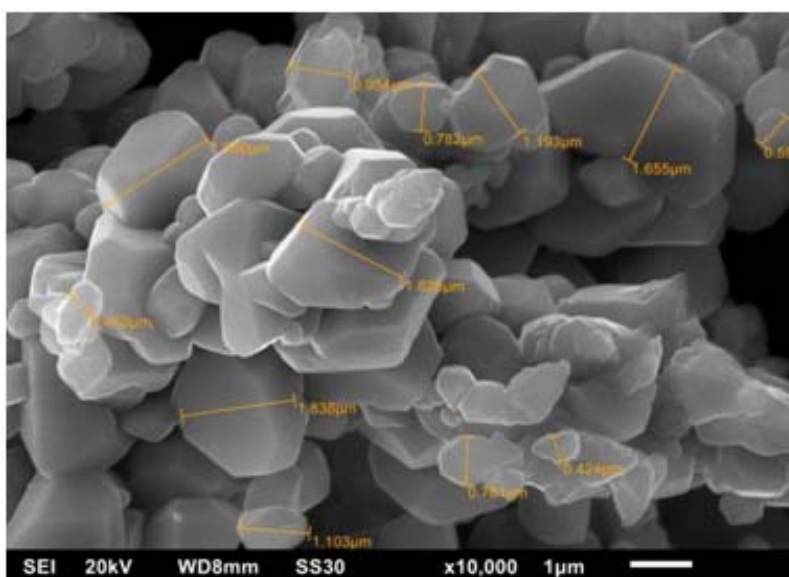


Figure 2—A microphotograph of copper powders formed during the polarization by a cathode current

In other words, copper atom penetration into electrode crystal lattice becomes difficult. The reason for this is that, regardless of small potential shift to negative region, the electrode remains an anode. If we assume that during the electro-refining in the production situation we shift the anode potential with an amplitude of 0.5 mV and an average oscillation frequency by 1 Hz, then by the reaction $\text{Cu}^+ + e \rightarrow \text{Cu}^0$, the forming amount of copper powder can be calculated. According to the literature data [13], in the case of industrial electrolysis (in the air atmosphere) in electrolyte solution's volume, the presence of monovalent copper ions. During the electrolysis in the diffusion layer, there will always be an equilibrium amount of cuproions. They shift toward the formation of copper atoms when the equilibrium is shifted toward the negative potential. Our studies have shown that the concentration of monovalent copper ions in the solution depends on the potential of the copper electrode. (Figure 3).

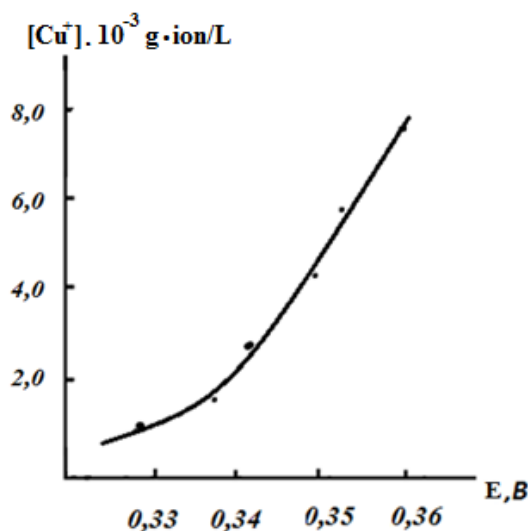


Figure 3 -Dependence of cuproions concentration on electrode potential

If this is so, when the potential of a copper electrode changes by one volt, an approximate value of the change in the concentration of cuproions:

$$\lg (\Delta[\text{Cu}^+])/\Delta E = 0,0064/0,035 = 0,182 \text{ g-ion/L} = 11,6 \text{ g/L} \quad (3)$$

Calculations were made on the basis of data obtained from the copper refining manufactory.

When the anode potential is displaced in the negative direction to 0.001 V by reaction $\text{Cu}^+ + e \rightarrow \text{Cu}^0$ 0.0116 g/L copper powder is formed.

You can calculate the deviation for 20 days at a frequency of 1 Hz:

$$20 \cdot 60 \cdot 60 \cdot 24 = 1728000 \text{ times (number of potential's deviations)} \quad (4)$$

Calculation of copper powder concentration formed from one liter of electrolyte:

$$1728000 \cdot 0.0116 = 20.189 \text{ kg.} \quad (5)$$

And because of the presence of a solution of cuproion in the diffusion layer, it is necessary to calculate the volume of the diffusion layer of one series. The number of serial anodes in the electrolysis workshop is 740, their total area is 1480 m², and the thickness of the diffusion layer is $\delta = 10^{-3} \text{ cm}$ [17].

Using these values, it is possible to calculate the diffusion layer's total volume: $V = S_1 \cdot \delta = 148000 \text{ dm}^2 \cdot 0.0001 \text{ dm} = 14.8 \text{ L}$. The total amount of copper in each series, formed by the reverse ionization reaction, for 20 days:

$$P = 14.8 \cdot 20.189 = 299.597 \text{ kg} \quad (6)$$

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According to the literature, in this case, approximately 100 kg of a copper deposit close to the sludge is obtained [4].

If you pay attention to this, you can see that the amount of copper powder formed in production conditions corresponds to the amount obtained in the production of copper by electro-refining.

Calculations results show that the oscillation of the anode potential can actually be a source of copper powder. Thus, during the deflection of the anode potential in the negative direction, and the electrode surface, the following reaction occurs:



As a result of the above reaction (7), studies were conducted to determine the cause of metallic powders formation. The copper electrode was built into an acid solution of copper sulfate in an inert medium and for a long time was in this state. In which case the following reaction occurs:



During this reaction, the monovalent copper ions were formed in a state of equilibrium, after which the copper electrode was removed. Subsequently, when the electrolyte is cooled to ambient temperature, copper powders are not formed as a result of the reaction (1). The formation of copper powders is observed only when the copper electrode is repeatedly immersed in the electrolyte. Consequently, the formation of a copper powder occurs only when a copper electrode is present in the electrolyte.

It is impossible to exclude the precipitation of copper into the sludge (macroparticles) by means of mechanical precipitation, but this process can be random. Experiments with an anode pulse current were carried out to prove that the anode potential fluctuations are a source of finely dispersed copper powder, i.e. conditions are created for creating the greatest amount of anode energy. The chain transfer of anode pulse current is mechanically realized, and its frequency change is regulated by the engine rotation speed. Experimental results show that the amount of metal powder formed during the copper electrolysis of the pulsed current increases at the current frequencies of the anode pulse (Table 1). In this case, the particle size of the copper powder on the surface of the anode is from 0.001 to 0.10 mmK.

Table 1 – Influence of frequency of anode pulse current on amount of powder of copper: in solution: 40 g/L Cu^{2+} and 150 g/L H_2SO_4 , $t = 60^\circ\text{C}$, current density = 240 A/m², electrode surface area = 6 cm², duration of experiment = 4 hours, (1 pendant corresponds to 0.658 mg of copper)

Anode pulse current frequency, min	The size of the formed copper powder	
	per pendant, 10 ⁻³ mg	in terms of dissolved copper, %
0	0.079	0.012
30	0.201	0.030
60	0.798	0.120
100	0.824	0.121

In the absence of current oscillations, copper powders formation can be explained as follows. As is known from the literature [18], on the electrode surface the current density on each of its parts cannot be the same, resulting in different potential regions. In addition, there is the difference between the intrinsic masses on the surface of anode and mixing of the electrolyte itself by the circulation. According to this information on the electrode surface, the rate of natural convective interactions of the electrolyte is 4 mm/sec and this is 20 times greater than the rate of forced stirring of this electrolyte [19]. At the same time, cuproions can move from the positive part of the anode surface to the negative part can be oxidized to metallic copper. And copper in the form of powder passes into the sludge. The surface roughness of the electrode (anode) increases this effect, since the potentials of the anode peaks are different. If we assume that the step and metal powder electrode processes are formed by the disproportionation reaction, its size should increase as the current density increases, since the amount of univalent copper ions in the intermediate link accordingly increases. The literature on this issue contradicts each other. For example, E. Haertt [20] and E.S. Letskih [21] say that an increase in the current density leads to an increase in the amount of elemental copper in the anode sludge. However, an increase in the current density in the work

of the authors E. Volvill [22] and A. Allmand [23] showed that the amount of elementary copper powder of the anode sludge decreases. According to G.V. Makarov [13], the amount of copper powder does not depend on current density. Such various contradictory opinions can be explained as follows. The amount of copper powder in all cases does not depend on the current density; it depends on the oscillation of anode potential and because of the creation of different potentials in different regions on the electrode surface. This conclusion is justified by the results of our research. According to [24], monovalent copper ions are stable in an inert medium in acidic solutions (in the absence of a copper electrode). The detailed studies that we carry out supplement this idea.

Copper powders are formed when the potential is oscillated under laboratory conditions, and in production conditions copper powder amount formed during the electro-refining of copper is about 0.04%. As is known from the practice of electrostatic copper, the sludge content consists of 0.1% of the dissolved copper anode. In short, for the first time, on the basis of research and analysis results, a mechanism was found for the formation of a copper powder falling into the sludge during copper refining. It was shown the formation of copper powders precipitating in sludge, mainly during electrolysis in the form of a periodic anodic potential with oscillations and the formation of different potentials at each electrode surface area.

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А.Баешов¹, А.К.Баешова², У.А.Абдувалиева²

¹Д.В.Сокольский атындағы Жанармай, катализ және электрохимия институты, Алматы, Қазақстан

²Әл-Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан

ЭЛЕКТРОРАФИНАЦИЯЛАУ КЕЗІНДЕ МЫС ҰНТАҚТАРЫНЫҢ ТҮЗІЛУІНЕ КУПРОИНДАРДЫҢ ӘСЕРІ

Аннотация. Бұл жұмыстың мақсаты мысты электрорафинация әдісімен алу кезінде шлам құрамына өтетін мыс ұнтағының түзілу жолдарын анықтау болып табылады. Зерттеулер гальваностатикалық жағдайда электролиз жүргізу арқылы және Autolab PGSTAT 302 потенциостаты көмегімен потенциалдар өлшеу әдісімен жүргізілді. Температура 25-75⁰С аралығында өзгертілді. Электролизден кейінгі ерітінділердегі мыс иондарының концентрациясы потенциометриялық титрлеу әдісімен анықталды. Мыс (II) иондарының күкіртқышқылды ерітінділерде титан (III) иондарының қатысында тотықсызданып, элементті мыс - ұнтақ күйінде түзілетіні көрсетілді. Түзілген мыс ұнтақтарының бөлшектерінің формасы, өлшемдері электрондық микроскопия әдісімен анықталды. Зерттеу нәтижелері ұнтақтардың анодтың еруі кезінде механикалық үгілу салдарынан түзілуі туралы болжам расталмады.

Біздің тәжірибелеріміздің нәтижелері анод потенциалының жоғарылап, төмендеуі демек, оның ауытқуы мыс ұнтақтарының сол сәтте түзілуіне әкелетіндігі жайында қорытынды жасауға мүмкіндік береді. Купроиондардың концентрациясы мыс электродының потенциалына тәуелді және оның ауытқуы $\text{Cu}^0 \leftrightarrow \text{Cu}^+ + e$ реакциясының тепе-теңдігін оңға немесе солға ығыстыруы мүмкін. Өндірістік жағдайда тізбектегі токтың мөлшерін және электролит температурасын тұрақты түрде ұстап тұру мүмкін емес. Сол себептен анодтағы потенциал әр сәтте периодты түрде әртүрлі амплитудамен белгілі мәнге ауытқып тұрады. Анодтың потенциалы теріс жаққа қарай ығысқан сәтте жоғарыда көрсетілген реакция бойынша мыс ұнтағының түзілу мүмкіндігі туындайды. Бірақ түзілген мыс атомдары анодтың кристалдық торына кіріп, орналаса алмайды. Осының салдарынан электрод бетіне нашар жабысқан майда дисперсті мыс ұнтағы түзіледі, содан кейін олар біртіндеп ерітіндіге көшеді де, соңында шлам құрамына өтеді.

Алғаш рет зерттеу және талдау нәтижелері негізінде мысты рафинациялау кезінде шлам құрамына өтетін мыс ұнтағының түзілу механизмі анықталды. Мыс ұнтақтарының пайда болып, тұнбаға түсіп, шлам құрамына өтуі – негізінен, электролиз кезіндегі анод потенциалының ауытқып тұруымен және электрод бетіндегі әр аумақта әртүрлі потенциалдардың қалыптасуымен тікелей байланысты екені көрсетілді.

Кілт сөздер: мыс, ұнтақ, купроион, шлам, рафинация, потенциал, электролиз, анод, катод, электролит, тотықсыздану

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А.Баешов¹, А.К.Баешова², У.А.Абдувалиева²

¹Институт топлива, катализа и электрохимии имени Д.В. Сокольского, Алматы, Казахстан

²Казахский национальный университет имени аль-фараби, Алматы, Казахстан

ВЛИЯНИЕ КУПРОИОНОВ НА ОБРАЗОВАНИЕ МЕДНЫХ ПОРОШКОВ ПРИ ЭЛЕКТРОРАФИНИРОВАНИИ МЕДИ

Аннотация. Целью данной работы явилось определение путей формирования порошков меди, проникающих в состав шлама при получении меди электрорафинированием. Исследования проводились методом электролиза в гальваностатических условиях и методом измерения потенциалов с помощью потенциостата Autolab PGSTAT 302. Температура изменялась в интервале 25-75⁰С. Концентрацию ионов меди в растворах после электролиза определяли методом потенциометрического титрования. Показано, что ионы меди (II) в сернокислых растворах в присутствии ионов титана (III) восстанавливаются с образованием

элементарной меди в виде порошка. Определены формы и размеры частиц образовавшихся порошков меди электронно-микроскопическим методом. Результаты исследования показали, что предположения о возможности формирования порошков вследствие механического осыпания при анодном растворении меди не подтверждаются.

Результаты наших исследований позволяют сделать заключение о том, что потенциал анода повышается, затем понижается, следовательно, постоянно колеблется и приводит к образованию порошков меди в этот момент. Концентрация купроионов зависит от потенциала медного электрода и его колебание может способствовать сдвигу равновесия реакции $\text{Cu}^0 \leftrightarrow \text{Cu}^+ + e$ вправо или влево. В промышленных условиях величину тока в цепи и температуру электролита невозможно поддерживать постоянными. По этой причине происходит периодическое колебание потенциала анода с различной амплитудой частотой. При смещении потенциала анода в отрицательную область возможно образование порошка меди по указанной выше реакции. Однако образовавшиеся атомы меди не могут внедриться в кристаллическую решетку анода. Вследствие этого на поверхности электрода образуются мелкодисперсные порошки меди, они постепенно переходят в раствор и после проникают в состав шлама.

Впервые на основании результатов исследования и анализа установлен механизм образования порошков меди, проникающих в состав шлама при электрорафинировании меди. Показано, что образование порошков меди, проникновение их в состав шлама, в основном, напрямую связано с колебаниями потенциала анода в процессе электролиза и формированием различных значений потенциала на различных участках поверхности электрода.

Ключевые слова: медь, порошок, купроион, шлам, рафинация, потенциал, электролиз, анод, катод, электролит, восстановление

Information about authors:

Bayeshov A. - Institute of Fuel, Catalysis and Electrochemistry named after D.V. Sokolsky, Almaty, Kazakhstan, head of the laboratory, Doctor of Chemistry, academician of National Academy of Sciences of the Republic of Kazakhstan, bayeshov@mail.ru;

Bayeshova A.K. - Kazakh national university named after Al-Faraby, Almaty, Kazakhstan, Doctor of Engineering, professor, azhar_b@bk.ru;

Abduvaliyeva U.A. - Institute of Fuel, Catalysis and Electrochemistry named after D.V. Sokolsky, Almaty, Kazakhstan, senior research associate, Candidate of Chemistry, abdumida14@gmail.com.

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Sh.K. Amerkhanova¹, M.Zh. Zhurinov², R. M. Shlyapov¹, A.S. Uali¹

L.N.Gumilyov Eurasian National University, Astana, Kazakhstan

D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan

amerkhanovashk@gmail.com**ANALYSIS OF EFFICIENCY OF COLLECTIVE-SELECTIVE
COPPER-LEAD ORE ENRICHMENT BY SODIUM OLEATE
IN THE MAIN FLOTATION**

Abstract: The problem of the polymetallic ores enrichment containing of copper, lead, zinc and other non-ferrous metals minerals' consists in the disclosure of splices, the separation of small-grained particles of one mineral from another mineral or waste rock. The purpose of this paper is studying the flotation reagents behavior in the suspension composition while ore enrichment according to the collectively selective scheme.

The elemental analysis of copper-lead ore samples is carried out. The flotation tests on the FML-1 flotation machine were carried out, the volume of the working chamber was 0.25 L, and the T-92 was used as the foaming agent. The decomposition with concentrated nitric and hydrochloric acids mixture's was applied to carry the ore samples and enrichment products to the solute state. The results of copper-lead ore enrichment the use of sodium oleate in the main flotation are presented. The material balance of copper-lead ore flotation process both for the main and control flotation and for the clean-up operations according to the collectively selective scheme (for the solid component) was calculated. It is shown that the addition of two clean-up operations to the scheme, with sodium dibutyl dithiophosphate as the main reagent, makes it possible to increase the lead and copper concentration in selective concentrates by 3 times. Based on the results of the material balance, the separation potentials and separation capacities of the main, reference and two clean-up flotations were calculated. The negative dynamics of the change in the separation potential from the initial stage of enrichment to the final one indicates the increase in the minerals separation complexity. The presence of the separation potential extremes relative to the metal concentration in the ore indicates a difference in the oxygen-containing and phosphorus-containing collectors reactivity. It has been established that the value of separating power serves as a quantitative measure of the applied flotation agents selectivity. Thus, the efficiency of the proposed enrichment scheme was evaluated based on separation criteria.

Key words: collectively-selective scheme, sodium oleate, sodium dibutyldithiophosphate, material balance, separation potential, separation power.

In contrast to past years, when some ores with a high content of lead, copper or zinc were sent after enrichment with potassium butyanthate in a collective or collectively selective scheme for metallurgical smelting, processing of ores of non-ferrous and rare metals mined in recent years is economically unprofitable without prior complex enrichment [1-5]. The problem of enrichment of sulfide copper-lead ores has not yet been fully resolved, since, on the one hand, ores are difficult to enrich in terms of dispersity and in terms of the identity of the flotation properties of the minerals that make up the ore. Therefore, finding more selectively active collectors [6-10] and more advanced modifiers will lead to further improvement of the flotation process [11-16]. In connection with this, the goal of the work is to evaluate the efficiency of copper-lead ore enrichment in a collectively selective scheme using sodium oleate in the main flotation.

Methods

Foam flotation was carried out on a laboratory flotation machine FML-1 with a chamber volume of 0.5 l by the following procedure: a sample of ore (75% of a fraction of 0.074 mm) with a mass of 10 g was

loaded into the flotation chamber and mixed with water. Lime was added to maintain the desired pH. Then, a solution of the collector of a given concentration, a foaming agent, was added to the chamber, and stirring was continued for 9 minutes. As the flotation agent, collectors, sodium oleate and sodium dibutyl dithiophosphate (basic substance w 60%) were used. Foaming agent was T-92, consumption was 15 g/t. Decomposition of the samples of the initial ore and the resulting concentrates (0.1 g) was carried out with a mixture of concentrated hydrochloric and nitric acids (3: 1) [17]. Determination of the concentration of metal ions Cu^{2+} , Pb^{2+} was carried out using the Varian AA140 atomic absorption spectrometer. Elemental analysis was performed on an X-ray fluorescent analyzer of the Olympus Delta XRF brand (Table 1).

Table 1 - Element composition of copper-lead ore

Element	Mass fraction, %	σ	$Z_{n/2} + \sigma/\sqrt{n}$	Element	Mass fraction, %	σ	$Z_{n/2} + \sigma/\sqrt{n}$
O	50.12	$2.14 \cdot 10^{-7}$	$2.96 \cdot 10^{-7}$	Mn	0.20	$2.50 \cdot 10^{-11}$	$3.46 \cdot 10^{-11}$
Na	2.91	$3.91 \cdot 10^{-9}$	$5.41 \cdot 10^{-9}$	Fe	8.83	$2.38 \cdot 10^{-7}$	$3.29 \cdot 10^{-7}$
Mg	5.64	$2.25 \cdot 10^{-8}$	$3.12 \cdot 10^{-8}$	Ni	0.04	$3.06 \cdot 10^{-10}$	$4.24 \cdot 10^{-10}$
Al	9.18	$5.63 \cdot 10^{-9}$	$7.80 \cdot 10^{-9}$	Cu	0.99	$2.40 \cdot 10^{-8}$	$3.33 \cdot 10^{-8}$
S	3.01	$3.18 \cdot 10^{-9}$	$5.38 \cdot 10^{-9}$	Zn	0.08	$1.41 \cdot 10^{-9}$	$1.95 \cdot 10^{-9}$
Si	17.00	$2.86 \cdot 10^{-7}$	$3.97 \cdot 10^{-7}$	Mo	0.39	$1.23 \cdot 10^{-9}$	$1.70 \cdot 10^{-9}$
K	0.02	$9.00 \cdot 10^{-10}$	$1.25 \cdot 10^{-9}$	Cd	0.01	$6.25 \cdot 10^{-12}$	$8.66 \cdot 10^{-12}$
Ca	1.03	$2.25 \cdot 10^{-10}$	$3.12 \cdot 10^{-10}$	Pb	0.05	$6.25 \cdot 10^{-10}$	$8.66 \cdot 10^{-10}$
Ti	0.48	$5.26 \cdot 10^{-9}$	$7.28 \cdot 10^{-9}$				

The results of elemental analysis show that the useful part of sulfide copper-lead ore (Table 1) is represented by metals Fe, Pb, Cu, Zn and nonmetals S, difficult to enrich the minerals Mn, Ti, the empty rock is composed of elements Ca, C, Si, Al, Mg, which allows to judge the presence of iron sulfides, iron oxides, lead sulfides, copper, zinc, and also silicates, carbonates, calcium and magnesium aluminates in the samples, the most common are quartz, calcite, orthoclase ($\text{K}[(\text{Si}, \text{Al})_4\text{O}_8]$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), olivine MgFeSiO_4 , kaolinite ($\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$).

Technological parameters of enrichment were calculated by formulas

$$\gamma_k = 100(\alpha - \theta)/(\beta - \theta) \quad \gamma_k = 100(\alpha - \theta)/(\beta - \theta) \quad (1)$$

$$E_k = \gamma_k \cdot \beta / \alpha \quad E_k = \gamma_k \cdot \beta / \alpha \quad (2)$$

where γ_k -concentrate yield, %, E_k -metal recovery in concentrate, %, β -metal content in concentrate, % [18].

The separation potential $\Phi(\beta)$ was calculated from the formula

$$\Phi(\beta) = (2x - 1) \cdot \ln \frac{x}{1-x} \quad (3)$$

The separation power was calculated from the formula

$$\Delta U = P \cdot \Phi(\alpha, \beta) \quad (4)$$

where: P is the amount of product obtained, g/h, $\Phi(\alpha, \beta)$ is the separation potential, reckoned from the concentration of the initial product with the content of α .

The formula for calculating $\Phi(\alpha, \beta)$ is given below

$$\Phi(\alpha, \beta) = (2\beta - 1) \cdot \ln \frac{\beta(1-\alpha)}{\alpha(1-\beta)} + \frac{(\beta-\alpha) \cdot (1-2\alpha)}{\alpha(1-\alpha)} \quad (5)$$

Results and Discussion

Based on the modified scheme of collectively-selective flotation of Cu-Pb ore using sodium oleate in the main flotation, a schematic diagram was drawn up (Fig. 1) and calculations of purification operations of enrichment were carried out (Tables 2, 3) [19].

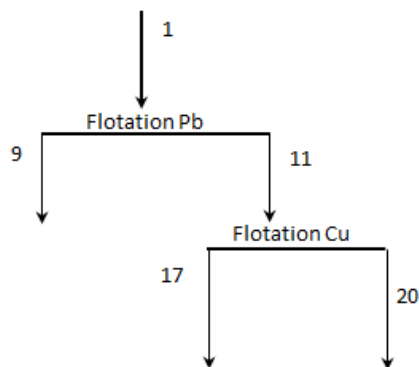


Figure 1 - Schematic diagram of flotation of copper-lead ore

Table 2 - Balance for final products of flotation

Product Number	Product Name	Yield, %	Assay, %		Recovery, %	
			Pb	Cu	Pb	Cu
9	Concentrate Pb	13.79	0.25	0.01	68.95	0.14
17	Concentrate Cu	1.60	0.07	39.46	2.24	63.78
20	Tailings	84.61	0.02	0.42	28.81	36.08
1	Ore	100.00	0.05	0.99	100.00	100.00

Table 3 - Balance of Cu-Pb ore products enrichment

Product Number	Products and operations name	Q , g/h	γ , %	β , %	ε , %
I	Basic lead flotation				
	Come in:				
1	Classifier drain	375	100	0.05	100
12	Combined industrial product	146.57	39.09	0.02	14.95
2	Total:	521.57	139.09	0.04	114.95
	Go out:				
3	Concentrate of basic flotation	197.86	52.76	0.08	83.02
4	Main flotation tailings	323.71	86.32	0.02	31.93
	Total:	521.57	139.09	0.04	114.95
II	First cleansing flotation				
	Come in:				
3	Concentrate of basic flotation	197.86	52.76	0.08	83.02
8	Second cleansing flotation tailings	37.16	9.91	0.03	5.63
5	Total:	235.03	62.67	0.07	88.65
	Go out:				
6	Concentrate of first cleansing	88.88	23.70	0.16	74.58
7	First cleansing flotation tailings	146.15	38.97	0.02	14.07
	Total:	235.03	62.67	0.07	88.65
III	Second cleansing flotation				
	Come in:				
6	Concentrate of first cleansing	88.88	23.70	0.16	74.58
	Total:	88.88	23.70	0.16	74.58
	Go out:				
9	Concentrate	51.71	13.79	0.25	68.95
8	First cleansing flotation tailings	37.16	9.91	0.03	5.63
	Total:	88.88	23.70	0.16	74.58
IV	Control flotation				
	Come in:				
4	Basic flotation tailings	323.71	86.32	0.02	31.93
	Total:	323.71	86.32	0.02	31.93
	Go out:				
10	Foam product control flotation	0.42	0.11	0.39	0.88
11	Tails of the control flotation	323.29	86.21	0.02	31.05
	Total:	323.71	86.32	0.02	31.93

Calculation of the lead flotation cycle. The calculation of the first flotation cycle is carried out according to the following scheme (Figure 2) with the previously identified products. Calculation of the material balance of lead flotation was carried out using the Solver Excel software package. The results of calculating the qualitative-quantitative scheme of the lead flotation cycle are given in Table 2. Calculations were carried out according to the cycle of copper flotation (Figure 3).

Thus, to calculate the cycle of copper flotation, the initial indicators are: a) two indicators relating to the source data (Q_1 and α^{Cu}); b) four indicators of copper recovery in flotation products; (c) Four indicators of copper content in concentrate operations. The number of initial indicators is 4, the number of stages 4. The results are given in Table 4.

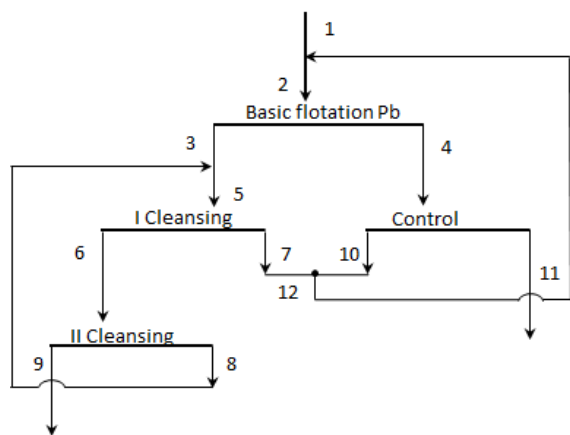


Figure 2 - The lead flotation cycle

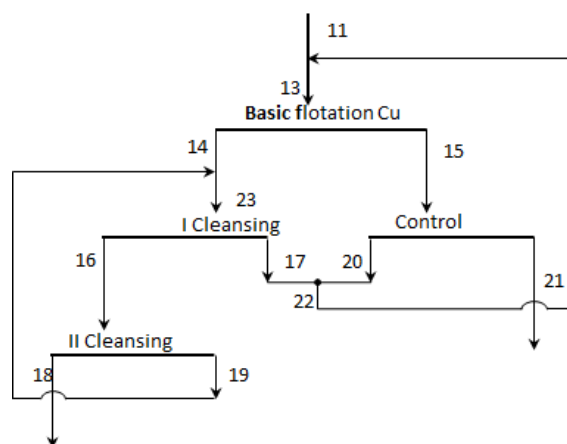


Figure 3 - The cycle of copper flotation

Table 4 - The balance of copper enrichment products

Stage No	Name of operations and products	Q , g/h	γ , %	β , %	ε , %
I	Basic copper flotation				
	Come in:				
11	Basic flotation tailings	323.29	86.21	1.15	99.86
22	Combined industrial product	36.54	9.74	4.00	33.96
13	Total:	359.83	95.95	1.60	133.82
	Go out:				
14	Concentrate of basic flotation	30.71	8.19	9.51	78.65
15	Basic flotation tailings	329.12	87.76	0.72	55.18
	Total:	359.83	95.95	1.60	133.82
II	First cleansing flotation				
	Come in:				
14	Concentrate of basic flotation	30.71	8.19	9.51	78.65
19	Second cleansing flotation tailings	7.34	1.96	2.67	4.56
23	Total:	38.06	10.15	9.40	83.21
	Go out:				
16	Concentrate of the first cleansing flotation	13.34	3.56	19.01	68.34
17	First clearing tailings	24.71	6.59	2.59	14.87
	Total:	38.06	10.15	9.40	83.21
III	Second cleansing flotation				
	Come in:				
16	Concentrate of the first cleansing flotation	13.34	3.56	19.01	68.34
	Total:	13.34	3.56	19.01	68.34
	Go out:				
18	Concentrate	6.00	1.60	39.46	63.78
19	Second cleansing flotation tailings	7.34	1.96	2.67	4.56
	Total:	13.34	3.56	19.01	68.34
IV	Control flotation				
	Come in:				
15	Basic flotation tailings	329.12	87.76	0.72	55.18
	Total:	329.12	87.76	0.72	55.18
	Go out:				
20	Foam product of control flotation	11.83	3.15	5.99	19.10
21	Basic flotation tailings	317.29	84.61	0.42	36.08
	Total:	329.12	87.76	0.72	55.18

The results of the circuit experiments confirm that the following concentrates can be obtained according to the developed technological scheme and the reagent regime: in the intercrack flotation lead concentrate with a lead content of 0.25%, extraction of 68.95%; in the copper flotation cycle, concentrate with a copper content of 39.46%, extraction of 63.78%; the use of purge operations makes it possible to increase the content of the valuable component of β_{Pb} from 0.08 to 0.25%, β_{Cu} from 9.51 to 39.46%. However, in both cases, the extraction of metal and the amount of concentrate are reduced.

The introduction to the circuit of a cycle for a combined industrial product in lead and copper flotations is caused by the need to reduce metal losses with tails. Thus, it has been shown that the use of sodium oleate as the main flotation agent in the lead flotation cycle and at the copper flotation stage of sodium dibutyldithiophosphate allows the development of selective and circuit regimes. Further, the efficiency of flotation enrichment was assessed (Table 5) [20].

Table 5 - Results of separation potentials and separation power calculation for a collectively selective scheme for copper-lead ore enrichment

Stage No	Name of the separation stage	$\Phi(\beta)$		$\Phi(\alpha, \beta)$		$\Delta U, \text{g/h}$	
		Pb	Cu	Pb	Cu	Pb	Cu
I	Basic flotation	7.12	1.82	0.13	6.62	25.75	203.15
II	First cleansing flotation	6.42	0.90	1.04	16.06	92.29	214.29
III	Second cleansing flotation	5.96	0.09	2.39	37.59	123.83	225.54
IV	Control flotation	5.50	2.42	4.76	3.37	1.99	39.87

Analysis of the data in Table 5 showed that more purification operations are needed to obtain cleaner products, namely lead concentrate with a high content of the useful component, than for copper concentrate. On the other hand, the maximum values of the separation potential $\Phi(\alpha, \beta)$ for the second flocculation flotation for copper and lead control flotation serve as an indicator of the completeness of the ore minerals from the separation gangue, but which, according to the minima $\Phi(\beta)$, is complicated by the proximity of the flotation properties of the components of the mixture. The high value of the separation power for the second purification flotation, in both lead and copper, confirms the selectivity of the proposed reagents to the lead and copper minerals and indicates a sufficiently high efficiency of flotation enrichment in the proposed collective selective scheme.

Thus, as a result of the conducted studies, a qualitative-quantitative scheme for flotation of Cu-Pb ore was calculated using sodium oleate as the main reagent. It is shown that the scheme should include two clean-up operations at the Pb flotation stage, one control operation, at the copper flotation stage, two clean-ups of selective concentrate and closed-loop control flotation are also envisaged. An increase in the content of Cu and Pb in similar concentrates was established using the use of β_{Pb} purge operations from 0.08 to 0.25%, β_{Cu} from 9.51 to 39.46%. The results of calculations of the change in separation potentials and separation power indicate a rather high efficiency of the collectively-selective scheme for the enrichment of copper-lead ore.

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Ш.К. Амерханова¹, М.Ж. Жұрынов², Р.М. Шляпов¹, А.С. Уәли¹

¹Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Астана, Қазақстан;

³Д.В. Сокольский атындағы отын, катализ және электрохимия институты, Алматы, Қазақстан

НЕГІЗГІ ФЛОТАЦИЯДА МЫС-ҚОРҒАСЫНДЫ КЕНДІ НАТРИЙ ОЛЕАТЫМЕН ҰЖЫМДЫ-ТАҢДАМАЛЫ БАЙЫТУ ТИІМДІЛІГІНІҢ АНАЛИЗІ

Аннотация: Мыс, қорғасын, мырыш және басқа түсті металдардың минералдарынан тұратын полиметалды кендерді байыту мәселесі жабысқан өсінділерді ашудан, бір минералдың майда сеппе бөлшектерін басқа минералдан немесе бос жыныс бөлуден тұрады. Жұмыстың мақсаты байытудың ұжымды-таңдамалы сұлбасы бойынша суспензияның құрамындағы флотореагентті зерттеу болып табылады. Мыс-қорғасынды кен үлгісінің элементтік талдауы жүргізілді. Флотациялық зерттеулер ФМЛ-1 флотомашинасында жүргізілді, жұмыс камерасының көлемі 0,25 л, көбіктендіргіш агент ретінде Т-92 қолданылды. Кенінің үлгілері және байытудың өнімдері еріген күйге қоспаны концентрленген азот және тұз қышқылдарында еріту арқылы ауыстырылды. Жұмыста негізгі флотацияда натрий олеатын қолдануымен жүретін мыс-қорғасынды кенді байыту нәтижелері келтірілген. Ұжымды-таңдамалы сұлба бойынша (қатты компонент бойынша) негізгі және бақылау флотациясы, қайта тазалау операциялары үшін материалдық баланс есептелген. Сұлбаға натрийдің дибутилдитиофосфатымен жүретін екі қайта тазалау операцияларын қосу селективті концентраттардағы қорғасын және мыс мөлшерін 3 есе арттыратынын көрсетеді. Материалдық баланс нәтижелері бойынша негізгі, бақылау және екі қайта тазалау флотацияларының бөлу потенциалдары және бөлу уақыты есептелді. Байытудың бастапқы стадиясынан соңғы стадиясына дейін бөлу потенциалының теріс динамикасы минералдарды бөлу процесінің күрделілігінің артуы туралы мәліметтейді. Бөлу потенциалдарының кендегі металл мөлшеріне қатысты экстремумдары оттек- және фосфорқұрамды

жинағыштардың реакциялық қабілеттіліктерінің айырмашылығын көрсетеді. Бөлу қуатының шамасы қолданылған флотореагенттердің селективтілік көрсеткіші болып табылады. Осылайша, бөлу критерийлерінің негізінде ұсынылған байыту сұлбасының тиімділігін бағалау жүргізілді.

Кілт сөздер: ұжымды-таңдамалы сұлба, натрий олеаты, натрий дибутилдитиофосфаты, материалдық баланс, бөлу потенциал, бөлу қуаты

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Ш.К. Амерханова¹, М.Ж. Журинов², Р. М. Шляпов¹, А.С. Уали¹

¹Евразийский национальный университет им. Л.Н. Гумилева, Астана, Казахстан;

²Институт топлива, катализа и электрохимии им. Д.В. Сокольского, Алматы, Казахстан

АНАЛИЗ ЭФФЕКТИВНОСТИ КОЛЛЕКТИВНО-СЕЛЕКТИВНОГО ОБОГАЩЕНИЯ МЕДНО-СВИНЦОВОЙ РУДЫ ОЛЕАТОМ НАТРИЯ В ОСНОВНОЙ ФЛОТАЦИИ

Аннотация: Проблема обогащения полиметаллических руд, содержащих минералы меди, свинца, цинка и других цветных металлов состоит в раскрытии сростков, отделении мелкокрапленных частиц одного минерала от другого минерала или пустой породы. Целью работы является изучение поведения флотореагентов в составе суспензии при обогащении по коллективно-селективной схеме. Проведен элементный анализ образцов медно-свинцовой руды. Флотационные испытания выполнены на флотомашине ФМЛ-1, объем рабочей камеры 0,25 л, в качестве пенообразователя использован Т-92. Образцы руды и продукты обогащения переводились в растворенное состояние путем разложения смесью концентрированных азотной и соляной кислот. В работе приведены результаты обогащения медно-свинцовой руды с использованием олеата натрия в основной флотации. Рассчитан материальный баланс процесса флотации медно-свинцовой руды по коллективно-селективной схеме (по твердому компоненту), как для основной и контрольной флотации, так и для перечистных операций. Показано, что добавление в схему двух перечистных операций, с основным реагентом дибутилдитиофосфатом натрия, позволяет повысить содержание свинца и меди в селективных концентратах в 3 раза. По результатам материального баланса рассчитаны разделительные потенциалы и разделительная мощность основной, контрольной и двух перечистных флотаций. Отрицательная динамика изменения разделительного потенциала от начальной стадии обогащения к завершающей свидетельствует о возрастании сложности разделения минералов, наличие экстремумов разделительного потенциала относительно содержания металла в руде указывает на различие в реакционной способности кислородсодержащего и фосфорсодержащего собирателей. Установлено, что величина разделительной мощности служит количественной мерой селективности используемых флотореагентов. Таким образом, на основании критериев разделения проведена оценка эффективности предложенной схемы обогащения.

Ключевые слова: коллективно-селективная схема, олеат натрия, дибутилдитиофосфат натрия, материальный баланс, разделительный потенциал, разделительная мощность

Information about authors:

Amerkhanova Shamshiya Kenzhegazinovna – Professor of the Department of Chemistry, L.N. Gumilyov Eurasian National University, Doctor of Chemistry, Professor

Zhurinov Murat Zhurinovich - Director of the Institute of fuel, catalysis and electrochemistry, Doctor of Chemistry, professor, academician of the National Academy of Sciences of Kazakhstan, President of NAS of RK

Shlyapov Rustam Maratovich – candidate of chemical sciences, Associate Professor of the Department of Chemistry, L.N. Gumilyov Eurasian National University, Ph.D., associate professor

Uali Aitolkyn Saylaubekkyzy – candidate of chemical sciences, Associate Professor of the Department of Chemistry, L.N. Gumilyov Eurasian National University, Ph.D., associate professor

Author for correspondence:

Prof. Amerkhanova Shamshiya Kenzhegazinovna

off.tel. +7(7172)709-500 (33-116), mob. + 77772477197, amerkhanovashk@gmail.com

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Sh.K. Amerkhanova¹, M.Zh. Zhurinov², R. M. Shlyapov¹, A.S. Uali¹

L.N.Gumilyov Eurasian National University, Astana, Kazakhstan

D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan

amerkhanovashk@gmail.com

EVALUATION OF THE SODIUM SELENITE AND TELLURATE TO THE THERMODYNAMICS OF HEAT ACCUMULATION BY COMPOSITES BASED ON SODIUM THIOSULPHATE

Abstract: The main category of materials wear in the process of transport, residential premises operation is a temperature difference between external and internal, a high gradient and cyclic changes in the temperature regime lead to changes in the materials structure and an increase in energy consumption.

Therefore, an urgent problem along with the development of heat-storage materials which make it possible to reduce significantly the heat loss to the environment is the matrix modification through the introduction of various additives. The aim of this investigation is the establishing of adding sodium tellurate and sodium selenate to sodium thiosulfate pentahydrate influence on the heat-storage properties of the obtained mixtures. The behavior of sodium selenate and sodium tellurate in the composition of the mixture with sodium thiosulfate crystalline hydrate was studied by the conductivity method. The changes in the activity coefficients of sodium selenate, the contribution of sodium selenate to the heat content of the mixture with sodium thiosulfate pentahydrate were calculated. Also, the changes in the activity coefficients and association degrees of sodium tellurate - sodium thiosulphate pentahydrate mixtures (1:50) were calculated, according to which the complex formation process is exothermic, heat storage process is electrostatic in nature. Consequently, the stability of the associates is decreased with increasing temperature. It was also found that the mixture cooling to $T=298$ K releases into the environment up to 100 kJ/kg of heat. The temperature of transition to the active state is 353 K. As a result of the studies, optimal warming temperature $T=348$ K, stabilizing effect of tellurate ion on sodium thiosulfate with water molecules associates were found, which together allows the energy coming to the system accumulation, its release during cooling with subsequent.

Key words: sodium thiosulfate pentahydrate, sodium selenate, sodium tellurate, activity coefficients, heat content, crystalline hydrate melt, electrical conductivity.

Introduction

The increase in energy consumption stimulates the demand for materials possessing not only high heat of combustion, but also capable of accumulating heat as a result of various processes. In this regard, the development of heat-storage materials on the basis of various chemical compounds involves the preservation of thermal energy through thermochemical reactions, the accumulation of open and latent heat [1] and their use in construction [2]. Widely distributed materials that convert incoming heat as a result of phase transition [3-4], are based on crystal hydrates [5-7], organic compounds [8-10]. However, efficient operation and operation and selection of heat storage accumulations is possible only if there is information about physical and chemical processes occurring in phase-transition materials. The final stage, in this case, is the creation of a model for changing the properties of materials in the process of heat accumulation [11], with changes in the physicochemical properties of the material being the basis of any model when the heat capacity and composition are varied [7]. Therefore, the control of the change in properties is actual in the creation of models of heat accumulation [12]. In connection with this, the goal of the work is to establish the behavioral features of sodium selenate and tellurate when used as additives in the development of heat-storage materials.

Methods

Materials: Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), sodium selenate (Na_2SeO_4) (pure for analysis), sodium tellurate (Na_2TeO_4), chem.pure, were used as starting materials for the preparation of heat-storage materials.

Preparation of mixtures with heat-accumulating properties. Inorganic mixtures were prepared by mixing sodium thiosulfate pentahydrate and sodium selenate (sodium tellurate) in various proportions by weight (50: 1), the mass of sodium thiosulfate 5 g, from which the mass of additives of sodium selenate (tellurate) was calculated. After mixing, the mixtures were heated to a temperature at which dissolution of the solid phase in the crystallization water was observed.

Determination of the electrical conductivity of melts. Conductometric studies were carried out in a 50 ml thermostated vessel. The electrical conductivity was measured on OK-102 conductivity meter.

The working electrode was made from a pair of platinum plates with an area of 1 cm². To calculate the electrical conductivity from Sim/cm to Om/cm, the instrument constant was determined by measuring the value of χ in 0.001 M KCl at standard temperature [13].

Calculation of the kinetic characteristics of electrical conductivity. To calculate the kinetic characteristics, the Arrhenius equation was used, in which the rate constant was replaced by the specific electrical conductivity.

The activation energy of electrical conductivity was calculated graphically according to the equation:

$$\lg \chi = \lg A_0 - E_a / 2,303RT \quad (1)$$

Calculation of kinetic characteristics was carried out according to the formulas [14].

$$\Delta H^\# = E_a - 2RT \quad (2)$$

Then the value of $\Delta S^\#$ was found from the equation:

$$\Delta S^\# = R [2,303 \lg A_0 - 2,303 \lg(\frac{kT}{h}) - 1] \quad (3)$$

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \quad (4)$$

Results and Discussion

Earlier, the electrical conductivity of mixtures of sodium thiosulfate pentahydrate with sodium selenate [15-16] and sodium tellurate [17] of different composition (1:10, 1:25, 1:50) was determined. The energy characteristics of electrical conductivity are calculated. It is shown that the main criterion for the choice of heat-accumulating compositions is the thermodynamic stability of the mixture or formed complexes during the interaction of the components of the mixture, which is characterized by the chemical potential, the activity of the substances and the activity coefficients. The results are given for a 1:50 mixture (Table 1).

Table 1 - The contribution of sodium selenate to the thermodynamic characteristics of the heat storage process

T, K	298	338	343	348	353
$\ln a_i$	-2.13	-2.14	-2.15	-2.16	-2.17
$\bar{L}_2,^* \text{ kJ} \cdot \text{mole}^{-1}$	$2.27 \cdot 10^{-1}$	$1.36 \cdot 10^{-1}$	$4.53 \cdot 10^{-2}$	$-4.54 \cdot 10^{-2}$	$-1.36 \cdot 10^{-1}$
$\Delta \mu_i, \text{ kJ} \cdot \text{mole}^{-1}$	5.24	6.02	6.14	6.25	6.32
$\Delta S, \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$	-15.60	-16.72	-17.53	-18.32	-18.96

Note: * - The heat content and other thermodynamic values are given to the value of $\text{kJ} \cdot \text{kg}^{-1}$ of the mixture

Table 2 - Thermodynamic characteristics of the heat storage process with a mixture of sodium thiosulfate pentahydrate - sodium selenate

T, K	298	338	343	348	353
$\ln a_i$	-5.23	-4.89	-4.90	-4.90	-4.87
$\bar{L}_2,^* \text{ kJ} \cdot \text{mole}^{-1}$	4.13	$9.77 \cdot 10^{-1}$	$5.84 \cdot 10^{-1}$	$1.90 \cdot 10^{-1}$	$-2.04 \cdot 10^{-1}$
$\Delta \mu_i, \text{ kJ} \cdot \text{mole}^{-1}$	12.97	13.74	13.97	14.181	14.38
$\Delta S, \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$	-5.35	-32.70	-36.06	-39.25	-42.34

Note: * - The heat content and other thermodynamic values are given to the value of $\text{kJ} \cdot \text{kg}^{-1}$ of the mixture

According to the data given in Table 1, it can be assumed that the low contribution to the heat content of the mixture is due to the ionic nature of the bonds formed, i.e. the complexes formed between thiosulfate ions, water molecules and selenate ions have high solubility, the bonds have an electrostatic nature. This is reflected in the general physico-chemical characteristics of the mixture (Table 2).

It is shown that the heat content of the mixture decreases with increasing temperature, and the process of heat accumulation is intensified only when the mixture is heated to a temperature of 353 K. The rise in temperature leads to an increase in the number of interactions between water molecules and a decrease in the proportion of tetrahedrally ordered solvent molecules. Heating promotes the process of ion association in systems [18]. It is also known that in equilibrium high-water crystalline hydrates, the first sphere of metal and anion ions is completely filled with water molecules. Therefore, sharp differences in the electrical conductivity of the mixture with infinite dilution and experimental data are associated with the formation of complex ion-aqueous rather than ionic groupings.

According to the ion-plasma interaction model, the activity coefficients should increase with increasing temperature, however, the experimental indices indicate a reverse process of lowering the activity coefficient when the melt is heated up to 12 ° C above the melting point, which confirms the hypothesis of an increase in inter-ion interaction, which prevails over the thermal motion of the ions and molecules. Therefore, in order to take into account the interionic interaction in concentrated solutions with the addition of sodium tellurate, the formula stated earlier was modified, i.e. the reference frame from the solvent to the melt (matrix) has been changed [19]. Table 3 gives data on the temperature dependence of the association value and the activity coefficients of the mixture and the addition of sodium tellurate.

Table 3 - Temperature dependence of the association value and the activity coefficients of the mixture and the addition of sodium tellurate

T, K	Na ₂ TeO ₄		Na ₂ S ₂ O ₃ ·5H ₂ O – Na ₂ TeO ₄ (50:1)	
	b·10 ³	lnγ _±	b·10 ³	lnγ _±
298	5.753	-0.774	5.753	-4.395
338	-2.673	-0.797	-2.673	-7.519
343	-2.631	-0.805	-2.631	-7.558
348	-2.489	-0.814	-2.489	-7.565
353	-2.113	-0.822	-2.113	-7.484

It is shown that at a ratio of 1:50, the ratio of the practical coefficient of activity of the solution to the theoretical activity coefficient (calculated according to the third Debye-Hückel approximation) decreases with increasing temperature, this indicates the process of heat release. So, according to the Debye-Hückel theory for electrolyte solutions, the increment in the change in the coefficient of activity with temperature is the heat content of the electrolyte solution. It is shown that the more the activity coefficient or degree of association or the chemical potential of the electrolyte changes with increasing temperature, the higher the amount of accumulated heat due to associative formation is. From the kinetic point of view, the process of heat release will be limited by the diffusion of ions (charge carriers) in the volume of the solution from the heated region to the vessel wall, and with the thermodynamic activity of the second component (additive), the activity value being the most informative characteristic of the solution, the chemical potential of the system as a whole, when the external conditions change. Thus, the process of heat accumulation in crystalline hydrate melts is directly proportional to the activity coefficient of the additive component and is of an electrochemical nature. Table 4 shows the results of calculating the contribution of sodium tellurate to the thermodynamic characteristics of the heat accumulation process.

Table 4 - The contribution of sodium tellurate to the thermodynamic characteristics of the heat storage process

T, K	298	338	343	348	353
$\ln a_i$	-2.26	-2.28	-2.29	-2.30	-2.31
$\bar{L}_2, \text{kJ} \cdot \text{mole}^{-1}$	0.09	0.02	-0.05	-0.12	-0.19
$\Delta\mu_i, \text{kJ} \cdot \text{mole}^{-1}$	5.60	6.42	6.54	6.66	6.73
$\Delta S, \text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$	-17.91	-18.81	-19.46	-20.11	-20.59

Note: * - The heat content and other thermodynamic values are given to the value of $\text{kJ} \cdot \text{kg}^{-1}$ of the mixture

It can be seen from the data in Table 4 that at high temperatures the contribution to the change in the amount of heat is negative, i.e. sodium tellurate, in the course of reaction with solvent molecules and thiosulfate ions, releases heat into the system, therefore, when sodium tellurate is added to the solution, sodium molecules bind the solvent molecules [20] and thiosulfate ions to stronger complexes, which requires energy, so at low temperatures there is an endothermic process, further, when the influx of heat increases, the associative ability of tellurate increases, as evidenced by negative values of entropy. Those regions with a higher density of matter and, correspondingly, regions whose density approximates the density of the solvent appear in the system. Therefore, the thermodynamic characteristics of the interaction of the components in the mixture were determined (Table 5).

Table 5 - Thermodynamic characteristics of the heat storage process with a mixture of sodium thiosulfate pentahydrate - sodium tellurate

T, K	298	338	343	348	353
$\ln a_i$	-2.00	-5.13	-5.17	-5.18	-5.09
$\bar{L}_2, \text{ kJ} \cdot \text{mole}^{-1}$	-40.72	-5.62	-1.24	3.14	7.53
$\Delta\mu_i, \text{ kJ} \cdot \text{mole}^{-1}$	4.97	14.41	14.74	14.97	15.17
$\Delta S, \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$	-390.49	-88.17	-52.85	-18.28	15.42
Note: * - The heat content and other thermodynamic values are given to the value of $\text{kJ} \cdot \text{kg}^{-1}$ of the mixture					

In this case, when sodium tellurate is added in an amount of 1:50 to the base salt, the heat content and heat capacity of the mixture increase. It is shown that during the heating to the melting point (51-55 °C) the system still releases heat into the environment due to the decomposition of the salt associates and the additive with the solvent. However, when the temperature reaches 348 K, the system passes to the heat storage regime, i.e. the heat content changes sign from negative to positive, and with increasing temperature the endothermic effect increases. According to the calculations, this mixture is characterized by a high heat capacity (2400 J / mol · K), therefore, when the temperature reaches 353 K, the system accumulates the maximum amount of heat that is released into the environment with subsequent cooling. Calculations showed that cooled from 353 K to 298 K the mixture emits into the environment 88 kJ / kg, which is more than the value determined by the thermocouple measurements. Probably, there is an error and the loss of heat or changes in the thermal conductivity of glass and air is not taken into account. Also, the contribution of tellurate ion to the heat content of the mixture is calculated, it is shown that the presence of a 50-fold excess of the basic salt contributes to the formation of the most thermodynamically advantageous structure in which tellurate ions are the binding centers of the solvent molecules (so-called associate nodes). On the other hand, when it is heated, the chemical potential increases (assumes positive values). Also, the increase in entropy increases during heating.

Thus, the optimal conditions for achieving the maximum heat-accumulating effect of mixtures containing sodium selenate from the thermodynamic position is the high activity of the components of the additive forming the complexes due to hydration energy, ion-dipole interaction with solvent molecules. The temperature of transition to the active state is 353 K. As a result of the studies, optimal conditions have been found: heating to $T = 348 \text{ K}$, stabilizing the effect of tellurate ion on the associates of sodium thiosulfate with water molecules, which together allows to accumulate the energy coming to the system, followed by its release during cooling.

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Ш.К. Амерханова¹, М.Ж. Жұрынов², Р.М. Шляпов¹, А.С. Уәли¹

¹Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Астана, Қазақстан;

³Д.В. Сокольский атындағы отын, катализ және электрохимия институты, Алматы, Қазақстан

НАТРИЙ ТИОСУЛЬФАТЫ НЕГІЗІНДЕГІ КОМПОЗИТТЕРДІҢ ЖЫЛУДЫ ШОҒЫРЛАНДЫРУ ТЕРМОДИНАМИКАСЫНА НАТРИЙ СЕЛЕНАТЫ МЕН ТЕЛЛУРАТЫНЫҢ ӘСЕРІН БАҒАЛАУ

Аннотация: Көлікті, тұрғын үйлерді пайдалану процесінде материалдардың тозуының негізгі себебі сыртқы және ішкі температуралардың айырмасы, дәлірек температуралық режимнің жоғары градиенті мен циклді өзгерістер материалдар құрылымының өзгеруіне, энергияны тұтынудың артуына әкеледі. Сондықтан қоршаған ортаға қатысты жылушығындарды төмендетуге мүмкіндік беретін жылужинақтаушы материалдарды жасау мәселесімен қатар, әртүрлі қоспаларды қосу арқылы матрицаларды түрлендіру болып табылады.

Жұмыстың мақсаты натрий теллурааты және натрий селенаты қоспаларының натрий тиосульфатының пентагидратына, алынған қоспалардың жылужинағыш қасиеттеріне әсерін анықтауда жатыр. Натрий тиосульфаты кристаллогидратымен қоспа құрамындағы натрий селенаты мен натрий теллураатының әсер ету сипатын зерттеу кондуктометриялық әдіспен жүргізілді.

Натрий селенатының белсенділік коэффициентінің өзгеруін, натрий тиосульфаты пентагидратымен қоспасының жылуұстағыштығына натрий селенатының үлесі есептелді. Сонымен қатар, натрий теллурааты – натрийдің тиосульфатының пентагидраты (1:50) қоспасындағы белсенділік коэффициенттер мен ассоциациялану дәрежесінің өзгеруі есептелді, оларға сәйкес күрделі комплекстердің түзілу процесі экзотермиялық, ал жылуды жинау (ұстау) процесінің табиғаты электростатикалық анықталады. Демек, ассоциаттардың беріктігі температураның артуымен төмендейді. Сондай-ақ, қоспа 298 К температураға дейін

салқындауы кезінде қоршаған ортаға 100 кДж/кг дейін бөлінеді. Белсенді күйге өту температурасы 353 К құрайды. Жүргізілген зерттеулер нәтижесінде тиімді шарттар: $T=348$ К дейін қызу, натрий тиосульфатының су молекулаларымен ассоциаттарына теллурад-ионның тұрақтандырушы эффектісі анықталды, ал олардың жиынтығы жүйеге келетін энергияны жинауға (суу барысында жылу бөлінеді) мүмкіндік береді.

Түйін сөздер: натрий тиосульфатының пентагидраты, натрийдің селенаты, натрийдің теллураты, белсенділік коэффициенттері, жылуұстағыштық, кристаллогидрат балқымасы, электрөткізгіштік.

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Ш.К. Амерханова¹, М.Ж. Журинов², Р. М. Шляпов¹, А.С. Уали¹

¹Евразийский национальный университет им. Л.Н. Гумилева, Астана, Казахстан;

²Институт топлива, катализа и электрохимии им. Д.В. Сокольского, Алматы, Казахстан

ОЦЕНКА ВЛИЯНИЯ СЕЛЕНАТА И ТЕЛЛУРАТА НАТРИЯ НА ТЕРМОДИНАМИКУ АККУМУЛИРОВАНИЯ ТЕПЛА КОМПОЗИТАМИ НА ОСНОВЕ ТИОСУЛЬФАТА НАТРИЯ

Аннотация: в процессе эксплуатации транспорта, жилых помещений основной категорией износа материалов является перепад температур внешних и внутренних, именно высокий градиент и циклические изменения температурного режима приводят к изменениям в структуре материалов, к росту потребления энергии. Поэтому актуальной проблемой наряду с разработкой теплоаккумулирующих материалов позволяющих существенно снизить теплотери в окружающую среду, является модификация матрицы посредством введения различных добавок. Цель работы заключается в установлении влияния добавки теллурата натрия и селената натрия к пентагидрату тиосульфата натрия на теплоаккумулирующие свойства полученных смесей. Изучение поведения селената натрия и теллурата натрия в составе смеси с кристаллогидратом тиосульфата натрия проводилось кондуктометрическим методом. Рассчитаны изменения коэффициентов активности селената натрия, вклада селената натрия в теплосодержание смеси с пентагидратом тиосульфата натрия. Также рассчитаны изменения коэффициентов активности и степени ассоциации смеси теллурад натрия – пентагидрат тиосульфата натрия (1:50), согласно которым процесс образования сложных комплексов является экзотермическим, процесс аккумуляирования тепла имеет электростатическую природу. Следовательно, прочность ассоциатов снижается при повышении температуры. Также выявлено что смесь охлаждаясь до $T=298$ К выделяет в окружающую среду до 100 кДж/кг, Температурой перехода в активное состояние является 353 К. В результате проведенных исследований найдены оптимальные условия: нагрев до $T=348$ К, стабилизирующий эффект теллурад-иона на ассоциаты тиосульфата натрия с молекулами воды, что в совокупности позволяет накапливать энергию поступающую к системе, с последующим ее выделением в ходе охлаждения.

Ключевые слова: пентагидрат тиосульфата натрия, селенат натрия, теллурад натрия, коэффициенты активности, теплосодержание, расплав кристаллогидрата, электропроводность

Information about authors:

Amerkhanova Shamshiya Kenzhegazinovna – Professor of the Department of Chemistry, L.N. Gumilyov Eurasian National University, Doctor of Chemistry, Professor;

Zhurinov Murat Zhurinovich - Director of the Institute of fuel, catalysis and electrochemistry, Doctor of Chemistry, professor, academician of the National Academy of Sciences of Kazakhstan, President of NAS of RK;

Shlyapov Rustam Maratovich – candidate of chemical sciences, Associate Professor of the Department of Chemistry, L.N. Gumilyov Eurasian National University, Ph.D., associate professor;

Uali Aitolkyn Saylaubekkyzy – candidate of chemical sciences, Associate Professor of the Department of Chemistry, L.N. Gumilyov Eurasian National University, Ph.D., associate professor.

Author for correspondence:

Prof. Amerkhanova Shamshiya Kenzhegazinovna

off.tel. +7(7172)709-500 (33-116), mob. + 77772477197, amerkhanovashk@gmail.com

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N.A. Zakarina, O. Dolekhanuly, N.A. Kornaukhova.

JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty

nelly_zakarina@rambler.ru

INFLUENCE OF SPACE VELOCITY AND TEMPERATURE ON THE ISOMERIZING ACTIVITY OF ZEOLITE-CONTAINING Pd- CATALYSTS DEPOSITED ON THE PILLARED TAGAN MONTMORILLONITE

Abstract. The paper presents data on the isomerization of n-hexane on the zeolite-free and mordenite-containing Pd -catalysts supported on activated and Al-Zr pillared montmorillonite in Ca-form. Elemental analysis of composites is shown that the content of alkali metals in montmorillonite decreases in the processes of activation and pillaring compared with initial clay sample. For example, the sodium content in Pd /AlZr CaHMM + HM- catalyst does not exceed 0.08%. After pillaring the average Zr content in this catalyst is equal to 9,34mas.%.

It was shown that the introduction of mordenite promotes an increase in the conversion of n-hexane for the 1.5-3.5 times and a significant increase in the amount of disubstituted isohexanes formed. The optimal space velocity of n-hexane feeding (0.64 h^{-1}) was determined, at which the studied Pd- catalyst shows maximum isomerizing activity to form 44.7% of mono- and disubstituted isohexanes and 4,4% isoheptanes. The optimal temperature of n-hexane isomerization over Pd- catalyst was 350°C . The increase of octane number on this catalyst at $350\text{-}400^{\circ}\text{C}$ is 45.4-45.6 units.

The correlation between isomerization activity and the number of medium and strong acid sites was revealed.

Key words: n-hexane, isomerization, space velocity, temperature, selectivity, disubstituted isohexanes, octane number.

Introduction

One of the most environmentally friendly ways to improve the anti-detonation properties of straight-run gasolines is to use the process of catalytic isomerization of n-alkanes to produce high-octane isomers [1-4]. Therefore, the creation of highly effective catalysts for this process operating under mild conditions is an actual task. Previously, we found that the isomerizing activity of Pt and Pd catalysts on Zr pillared CaHMM is significantly reduced during long-term tests [5,6]. When n-hexane was isomerized for 20 hours, there was a strong decrease in the isomerizing activity of the Pt catalyst. This determines the choice of the Al-Zr composition as a pillaring agent, since it is known that the introduction of the second pillaring component significantly increases the thermal stability of the contacts, their specific surface area and acidity [7,8].

It is known that depending on the activity of the catalyst used, the composition of the hydrocarbon feedstock and other process parameters, the magnitude of the space velocity in the refining processes determines the achievement of equilibrium in the system, the direction of the reaction and the yield of the reaction products [9, 10]. The space velocity of the feed determines the specific loading of the reaction volume by the feedstock and characterizes the duration of contact of the reacting intermediates with the catalyst. The influence of contact time or space velocity of supply with feed is the same for many catalytic processes. As the contact time increases, the yield of the product for the reversible catalytic reaction increases, and the more active the catalyst, the shorter the contact time required to achieve a given yield of the product. Temperature, space velocity of raw materials feed and pressure affect the speed and depth of oil hydrocarbons conversion [11,12]. For each type of feedstock and catalyst, there is an optimum range of temperatures, pressures and space velocities of feedstocks.

The purpose of this work is to study the isomerizing properties of Pd- catalysts deposited on the Al-Zr- bimetallic composition pillared activated montmorillonite (CaHMM) using isomerization of n-hexane as the temperature and the space velocity of supply with the raw material are varied.

Experimental

For the preparation of Pd catalysts deposited on the Al-Zr pillared Tagan montmorillonite, preliminarily clay was activated by treatment with a solution of H_2SO_4 and then pillared with a solution of aluminum hydroxocomplex $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. Al-Zr montmorillonite with a ratio Al: Zr = 1 was prepared by sequential addition of Al and then Zr into activated montmorillonite using early known procedure [13,14], followed by washing, drying and calcinations. Pd deposited on AlZr (2.5) CaHMM using PdCl_2 solution. The values in parentheses indicate the initial concentration of aluminum in the hydroxocomplexes in mmol of Al^{3+} and Zr^{4+} per 1 g of montmorillonite in Na- or Ca-forms. The activity of the catalyst was determined by the yield of isohexanes, isoheptanes, the total yield of isomers and the increase in octane numbers (o.n.).

The acid characteristics of the contacts were obtained from the data of TPD ammonia.

Analysis of the hydrocarbon composition and octane number of gasolines was carried out on a chromatograph "Chromatek-1000" with a flame ionization detector and a capillary column 50 m long; temperature of 250°C ; carrier gas is helium. Registration and processing of the chromatograms were carried out with the application of the program "NetChrom-win" (products of the Meta Chrom LLC).

Elemental analysis of composites was carried out with the help of energy dispersive - X-ray fluorescent spectroscopy on the energy dispersive microanalysis system INCA-Energy 450, mounted on a scanning electron microscope JSM6610LV, JOEL, Japan.

Results and its discussion

Elemental analysis of composites is shown that the sodium content in montmorillonite decreases from 1,5% in the initial sample to 0.28% in pillared Al (5.0) NaHMM. Similar regularity was observed for the pillared by AlZr montmorillonite. The sodium content in Pd /AlZr CaHMM + HM- catalyst do not exceed 0.08%. After pillaring the average Zr content in this catalyst is equal to 9,34mas.% (table 1).

Table 1 - Data of elemental analysis of 0,35%Pd Al:Zr(1:1)/CaHMM+15%HM, $[\text{Al}]=[\text{Zr}]=2.5$ mmol/g clay,mas. %

Spectrum	O	Na	Mg	Al	Si	S	Cl	Ti	Fe	Zr	Pd	Total
Spectrum1	49,55	0,09	0,87	15,32	23,72	0,06	0,14	0,09	0,69	9,36	0,14	100,00
Spectrum2	49,46	0,07	0,82	14,34	24,78	0,06	0,10	0,14	0,74	9,34	0,14	100,00
Spectrum3	49,79	0,09	0,84	13,92	24,67	0,05	0,11	0,11	0,79	9,43	0,22	100,00
Average	49,60	0,08	0,84	14,53	24,39	0,06	0,12	0,11	0,74	9,38	0,17	100,00

Earlier, we observed [15] that the incorporation of mordenite into the composition of the Pt catalyst deposited on the pillared Al montmorillonite results in a change in the composition of the products formed from n-hexane, without significantly affecting the conversion. On this catalyst, a large number of disubstituted isohexanes - 2,2 and 2,3-dimethylbutanes, as well as isobutanes, isopentanes and isoheptanes, the number of which increases with temperature. The optimum space velocities of n-hexane feeding are determined at which the studied catalysts exhibit maximum isomerizing activity and maximum increase of octane numbers [16].

A study of the isomerizing properties of Pt / mordenite + Al_2O_3 catalysts and Pt catalysts on granular mordenite without binders showed that the incorporation of mordenite into the catalyst promotes an increase in the conversion of n-alkanes due to optimization of the acid properties of the catalysts [17,18]. Using the example of the isomerization reaction of n-heptane, it was shown that with an increase in the proportion of mordenite from 10 to 50% by weight, a gradual increase in n-heptane conversion occurs. In this case, the zeolite module has little effect on the activity of catalysts with the same zeolite content. The selectivity of isomerization depends only on conversion and does not change with an increase in the proportion of zeolite in the catalyst [19]. In connection with the foregoing, the best samples of Pd catalysts supported on aluminium-zirconium pillared montmorillonite modified with mordenite (HM) were tested in the isomerization reaction of n-hexane at various temperatures with a space velocity of 0.64 h^{-1} . (Table 2).

It can be seen from Table 2 that the conversion of n-hexane on 0.35% Pd /AlZr CaHMM + HM- catalyst increases 4.2 times with increasing temperature from 250 to 400°C (from 12.8% to 53.5 %).

Table 2 - Isomerization of n-hexane on 0.35% Pd /AlZr CaHMM + HM-composite catalyst (space velocity 0.64 h⁻¹)

Catalyst	T, °C	α , %	S _{C6} , %	S _{C6+} , %	Yields of reaction products, %					
					{C ₁ -C ₄ }	i-B	2MB	2,2D MB	2MP	Σ C7
0,35% Pd	250	12,8	60,2	100		1,3	0,1	4,5	3,2	3,7
	300	46,4	87,7	99,3	0,3	1,2	0,8	20,7	20,0	3,4
	350	53,4	83,7	98,6	0,7	1,0	2,6	23,3	21,4	4,4
	400	53,5	80,9	99,0	0,5	1,1	2,8	22,4	20,9	5,8

* Σ C7 = 2,2- dimethylpentane(DMP), 2,4-DMP, 2,2,3-threemethylbutane(TMB), 3,3DMP, 2-methylhexane(MH), 3-MH, 3-ethylpentane(EP).

The selectivity to all the isomers is reduced from 100 to 99.0% with an increase in temperature from 250 to 400°C, but remains very high (98.6-100%) in the entire range of studied temperatures. The selectivity to isohexanes is slightly lower, but if it take into account that the resulting di- and three substituted isoheptanes have high octane numbers, it can be assumed that the resulting mixtures of isomeric hydrocarbons also have high octane numbers.

Analysis of the reaction products showed that the isomerization of n-hexane on the mordenite-containing palladium catalyst proceeds to form C₄-, C₅-, C₆- and C₇- isomers. It should be noted that the amount of isohexanes on this catalyst reaches 44.7% at 350°C, with more than half of this amount being 2,2-dimethylbutane. Quantities of isopentanes and isoheptanes increases with increasing temperature. Thus, the content of isopentanes and isoheptanes increases from 0.1% and 3.3% at a temperature of 250°C to 2.8 and 5.8%, respectively, at 400°C.

Comparison of the obtained results with the data on the catalyst without mordenite shows that the isomer selectivity remains high on this catalyst (Table 3), although the introduction of mordenite promotes an increase in the conversion of n-hexane by 1.5-3.5 times, and at 300°C conversion n-hexane increased more than 8 times (Tables 2 and 3). The selectivity to all isomers at temperatures of 350, 400°C is 96.0-92.9%. The selectivity to isohexanes at 250, 300°C is significantly lower on the mordenite-containing catalyst due to a higher conversion of n-hexane. It should be noted in the same way that the introduction of mordenite promotes a significant increase in the amount of disubstituted dimethylbutanes formed. At the optimum temperature, the amount of 2,2-DMB reaches 23,3%, in addition, there are significant amounts of isopentanes and isoheptanes, especially at temperatures of 350, 400°C, which may be due to the change in the number and strength of acid sites.

Table 3 - Isomerization of n-hexane on Pd / AlZrCaHMM- catalyst at different temperatures (space velocity 0.64h⁻¹)

Ratio Al:Zr, Zr=2,5 mmol/g MM	T, °C	α , %	S _{C4+}	S _{C6}	Yields of products, % by weight						
					Σ C ₁ -C ₄	i-BUT	Σ Pen+ i-Pen	2,2-DMB	2,3-DMB	3-M Pen	i-Hep
1:1	250	5,4	100	100	-	-	-	-	-	5,4	-
	300	5,3	100	100	-	-	-	-	3,5	1,8	-
	350	15,4	96	86,2	-	1,5	0,6	0,8	8,9	3,6	-
	400	39,5	92,9	70,6	0,9	5,6	4,4	2,8	14,7	10,4	0,8

It was shown that with an increase in the amount of palladium from 0.1 to 0.35% in the case of mordenite-free catalysts, an increase in the relative total amount of acid sites from 220.3 to 249.3% is observed, mainly due to an increase in the content of medium and strong acid sites, while the number of weak acid sites decreases. Such a distribution of acid sites should promote the growth of the isomerizing activity of Pd-catalysts, which we observed experimentally[20].

When modifying the catalysts with mordenite, a slight decrease in the total number of acid sites of different strengths is observed, and when mordenite is introduced, as in the case of an increase in the Pd

content, the number of weak acid sites(a.s.) decreases, and the content of medium and strong (a.s.) increases.

Based on the results obtained, it can be concluded that a decrease in the amount of palladium to 0.1% and modification of Pd-catalysts by mordenite lead to an increase in isomerizing properties with the formation of significant amounts of mono- and disubstituted isohexanes, which is due to an increase in the number of medium and strong acid sites[20].

To select the optimal n-hexane feeding space velocities to the Pd / AlZrCaHMM+HM the composite catalyst was tested at a space velocity of 1.28 h⁻¹ (Table 4). An increase of n-hexane feed rate from 0.64 to 1.28 h⁻¹ reduces the overall conversion from 53.4 to 51.4% at 350°C, due to a reduction in the contact time with the catalyst surface. In addition, a comparison with the results obtained at a space velocity of 0.64 h⁻¹ (Table 2) shows that with an increase in the space velocity up to 1.28 h⁻¹, together with a decrease in the conversion of n-hexane, the selectivity to all isomers decreased from 98,6 to 95,5%. A slight decrease in the yield of isohexanes and 2,2-dimethylbutane is observed with an increase in the space velocity of n-hexane. Thus, the amount of isohexanes under these conditions is 41.6% compared to 44.7% at the space velocity of n-hexane of 0.64 h⁻¹.

Table 4 - Isomerization of n-hexane on Pd / AlZrCaHMM + HM composite catalyst (space velocity 1.28 h⁻¹)

Cat.	T, °C	α , %	S _{C6} , %	S _{C6+} , %	Yields of reaction products, %					
					{C ₁ -C ₄ }	i-B	2MB	2,2 DMB	2MP	Σ C7
0,35% Pd	250	7,7	68,8	92,2		0,5	0,1	3,1	2,2	1,8
	300	40,1	78,3	98,8	0,1	0,1	0,3	17,0	14,4	8,2
	350	51,4	80,9	95,5	0,5	0,3	1,5	21,1	20,5	7,5

Reduction of the space velocity of n-hexane to 0.43 h⁻¹ slightly increases the isomerization activity and selectivity of this catalyst (Table 5) compared to the results at a feed space velocity of 1.28 h⁻¹. The yield of isohexanes at this space velocity of n-hexane at 350°C is 44.1%, which is close to the results obtained at a space velocity of 0.64 h⁻¹. Comparison of the results presented in Fig. 1 shows that the optimum space velocity for a Pd / AlZrCaHMM + HM catalyst can be considered to be 0.64 h⁻¹.

Table 5- Isomerization of n-hexane on 0.35% Pd / AlZrCaHMM + HM composite catalyst (space velocity 0.43 h⁻¹)

Cat.	T, °C	α , %	S _{C6} , %	S _{C6+} , %	Yields of reaction products, %					
					{C ₁ -C ₄ }	i-B	2MB	2,2DMB	2MP	Σ C7
0,35% Pd	250	21,8	67,9	100	-	-	-	7,8	7,0	7,0
	300	46,2	86,8	98,7	-	0,1	0,5	20,3	19,8	5,5
	350	53,7	82,1	94,0	0,7	0,4	2,1	23,5	20,6	6,4
	400	56,1	76,3	90,9	1,1	0,7	3,3	22,8	20,0	8,2

The dependence of the yield of isohexanes and isoheptanes on 0.35% Pd / AlZrCaHMM + HM on the temperature at a various space velocity of n-hexane is shown in Fig. 1, from which it can be seen that the yields of all isomers increase with increasing temperature and reach a maximum at 350°C. At all space velocities, the catalyst exhibits a sufficiently high isomerization activity with the formation of 41.6-44.7% isohexanes and 4.4-8.2% isoheptanes. The highest yields of isomers on this catalyst were observed at a space velocity equal to 0.64 h⁻¹.

To estimate the octane-raising properties of isomerizates obtained on a Pd / AlZrCaHMM + HM-catalyst, calculations of the increase of octane numbers (o.n.) based on an analysis of the products obtained by isomerization of n-hexane on this catalyst (figure 2). It can be seen from Fig. 2 that on all the catalysts studied, regardless of the space velocities of n-hexane, there is an increase in o.n. with an increase in temperature, which is associated with an increase in the yield of isomers under these conditions, especially disubstituted with high o.n. For a 0.35% Pd/AlZrCaHMM+HM-catalyst, a constant value of the o.n. increase is characteristic at 350-400°C. The data presented in Fig. 2, allow to draw a conclusion about the optimal space velocity of n-hexane, providing the maximum increase of o.n. on this catalyst. It is shown that for the 0.35% Pd / AlZr CaHMM + HM catalyst, the optimum space velocity is 0.64 h⁻¹. Increase o.n. on this catalyst at 350-400°C is 45.4-45.6 units.

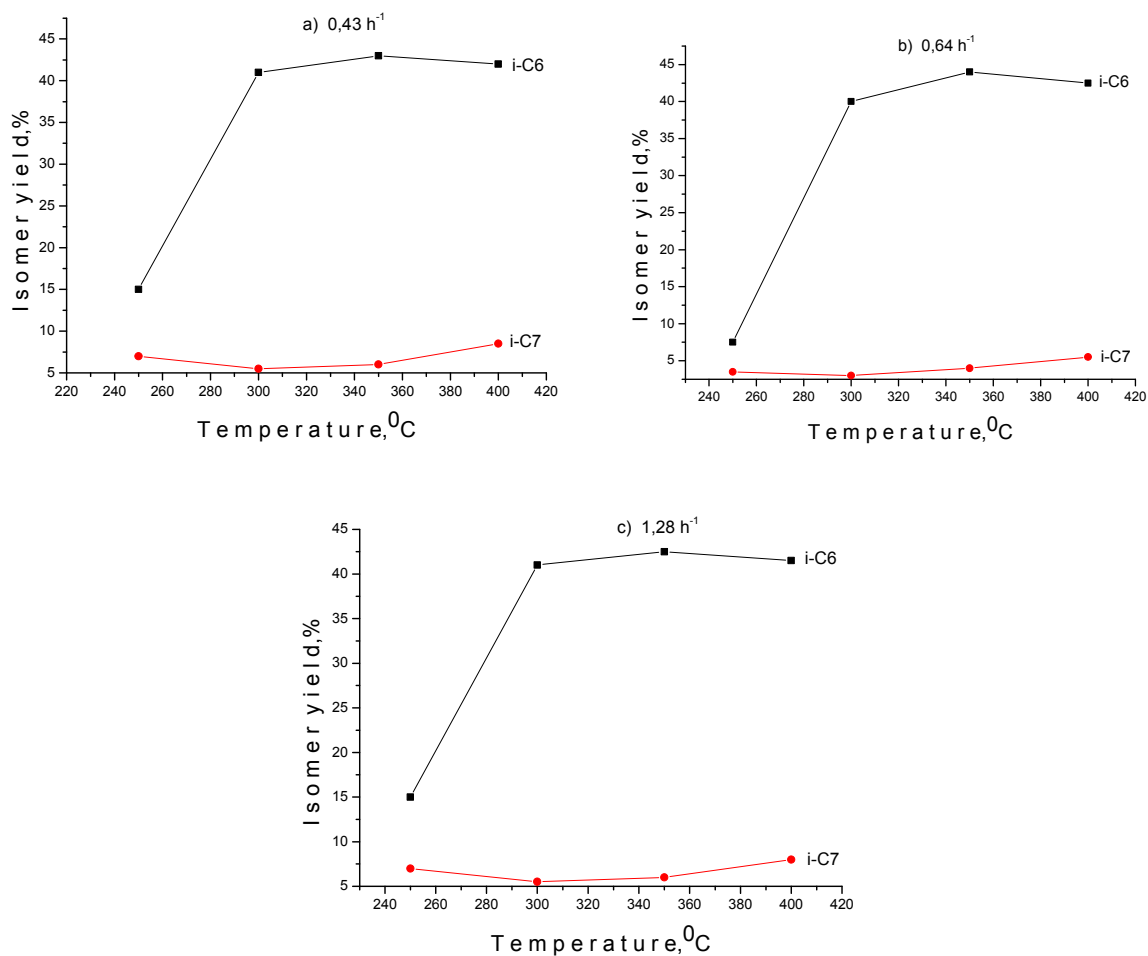


Figure 1 - The yields of isohexanes and isoheptanes on 0.35% Pd / AlZrCaHMM + HM catalyst as a functions of temperature at different space velocities: a) 0.43 h⁻¹, b) 0.64 h⁻¹, c) 1.28 h⁻¹

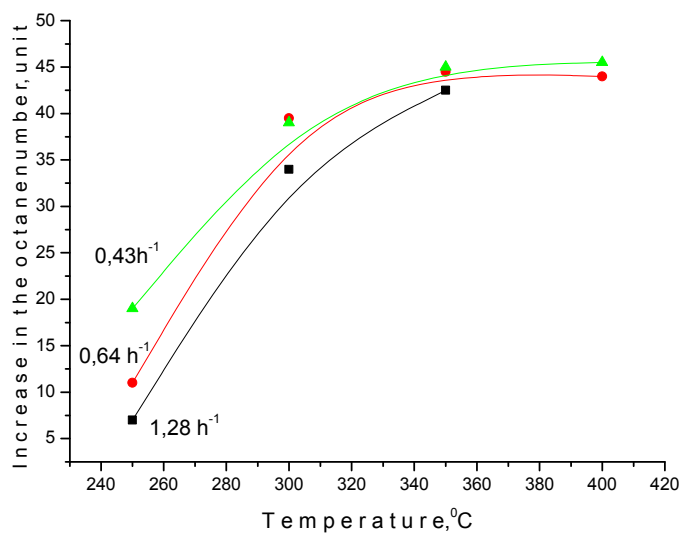


Figure 2 - Dependence of the increase in the octane number of the products obtained by isomerization of n-hexane over 0.35% Pd / AlZrCaHMM + HM on the temperature at different space velocities (1.28h⁻¹, 0.64 h⁻¹, 0.43 h⁻¹)

Conclusion

Thus, based on the analysis of the results obtained, it can be concluded that a sufficiently high level of n-hexane conversion, equal to 53.4-53.7%, with a high isomerizing activity of the mordenite-containing Pd catalyst to form 44.7% of mono- and disubstituted isohexanes and 4.4% isoheptanes is reached at a temperature of 350°C. The optimal space velocity of n-hexane (0.64 h⁻¹) were determined, at which the studied catalyst shows maximum isomerizing activity and maximum increase of octane numbers. Comparison with the data obtained on a 0.5% Pt-catalyst deposited on mordenite in H-form without a binder and on a Pt / SO₄ / ZrO₂ / Al₂O₃ catalyst [18,21] showed that these catalysts are significantly inferior to those developed by the selectivity the formation of isohexanes (83.0-86.0%) and the yields of disubstituted isohexanes. The correlation between isomerization activity and the number of medium and strong acid sites was revealed.

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Н.А. Закарина, О. Дәлелханұлы, Н.А. Корнаухова

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

**ТҮРЛЕНДІРІЛГЕН ТАҒАНДЫҚ МОНТМОРИЛЛОНИТКЕ ҚОНДЫРЫЛҒАН ЦЕОЛИТҚҰРАМДЫ
Pt-КАТАЛИЗАТОРЛАРДЫҢ ИЗОМЕРЛЕУШІ БЕЛСЕНДІЛІГІНЕ КӨЛЕМДІК
ЖЫЛДАМДЫҚ ПЕН ТЕМПЕРАТУРАНЫҢ ӘСЕРІ**

Аннотация. Мақалада Al және Zr-мен пилларирлеген және белсендірілген Ca формалы монтморилло-нитке қондырылған цеолитсіз және цеолитқұрамды Pt-катализаторлардың қ-гексан изомеризациясы бойынша алынған мәліметтері келтірілген. Композиттерге жасалған элементтік анализ белсендіру мен пилларирлеу процестерінде монтмориллониттегі сілтілік металдардың мөлшері азаятынын көрсетті. Мысалы, Pd / AlZr CaНММ + НМ-катализаторындағы натрий үлесі 0,08%-дан аспайды. Пилларирлеген соң бұл катализатордағы Zr мас.үлесі 9,34%.

Морденит енгізу қ-гексанның конверсиясын 1,5-3,5 есе арттыратыны және пайда болатын қосорынбасарлы диметилбутанның мөлшерін айтарлықтай көбейтетіні көрсетілді. Зерттелген катализаторлар максималды изомерлеуші белсенділік танытып 44,7% моно- және қосорынбасарлы изогександар мен 4,4% изогептан түзілетін қ-гексанның тиімді көлемдік жылдамдығы (0,64 сағ-1) анықталды. Pd-катализаторындағы қ-гексан изомерленуінің тиімді температурасы 350⁰С болды. Осы катализаторда 350-400⁰С кезінде октан санының өсуі 45,4 - 45,6 бірлікке тең.

Изомерлеуші белсенділігі мен орта және күшті қышқылды орталықтар санының арасындағы байланыстар анықталды.

Түйін сөздер: қ-гексан, изомерлеу, көлемдік жылдамдық, температура, селективтілік, қосорынбасарлы изомерлер, октан саны

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Н.А. Закарина, О Дәлелханұлы, Н.А. Корнаухова

АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», г. Алматы, Казахстан

**ВЛИЯНИЕ ОБЪЕМНОЙ СКОРОСТИ И ТЕМПЕРАТУРЫ НА ИЗОМЕРИЗУЮЩУЮ
АКТИВНОСТЬ ЦЕОЛИТСОДЕРЖАЩИХ Pd-КАТАЛИЗАТОРОВ, НАНЕСЕННЫХ
НА МОДИФИЦИРОВАННЫЙ ТАГАНСКИЙ МОНТМОРИЛЛОНИТ**

Аннотация. В статье представлены данные об изомеризации n-гексана на бещеолитных и морденитсодержащих Pd-катализаторах, нанесенных на активированный и пилларированный Al-Zr монтмориллонит в Ca-форме. Элементарный анализ композитов показал, что содержание щелочных металлов в монтмориллонитах уменьшается в процессе активации и пилларирования по сравнению с исходным образцом глины. Например, содержание натрия в Pd / AlZr CaНММ + НМ-катализаторе не превышает 0,08%. После пилларирования среднее содержание Zr на этом катализаторе составляет 9,34 мас.%.

Было показано, что введение морденита способствует увеличению конверсии n-гексана в 1,5-3,5 раза и значительному увеличению количества дизамещенных изогексанов. Определена оптимальная объемная скорость подачи n-гексана (0,64 ч-1), при которой изученный Pd-катализатор показывает максимальную изомеризующую активность с образованием 44,7% моно- и дизамещенных изогексанов и 4,4% изогептанов. Оптимальная температура изомеризации n-гексана на Pd-катализаторе составляет 350⁰С. Увеличение октанового числа на этом катализаторе при 350-400⁰С составляет 45,4 - 45,6 единиц.

Выявлена корреляция между изомеризующей активностью и числом средних и сильных кислотных центров.

Ключевые слова: n-гексан, изомеризация, объемная скорость, температура, селективность, дизамещенные изомеры, октановое число.

Information about authors:

N.A. Zakarina - Doctor of Chemical Sciences, Professor, Head of the laboratory of oil processing technology of JSC «D.V. Sokolsky Institute of fuel, catalysis and electrochemistry», Almaty, Kazakhstan. Tel. +77014018953, e-mail: nelly_zakarina@rambler.ru;

O. Dolelkhanuly – master of chemical sciences, researcher of the laboratory of oil processing technology, JSC «D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry», Almaty, Kazakhstan. Tel. +77071983714, e-mail: orken_kz777@mail.ru;

N.A. Kornaukhova - Candidate of chemical sciences, the leading researcher of laboratory of oil processing technology, JSC «D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry», Almaty, Kazakhstan. Tel. +77772673778, e-mail: n_korn77@mail.ru.

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N.N. Mofa, B.S. Sadykov, A.E. Bakkara,
N.G. Prikhodko, B.T. Lesbayev, Z.A. Mansurov

Institute of Combustion Problems, Almaty, Kazakhstan
al-Farabi Kazakh National University, Almaty, Kazakhstan
bakkara_ayagoz@mail.ru

MODIFICATION OF THE SURFACE OF ALUMINUM AND MAGNESIUM PARTICLES UNDER THE CONDITIONS OF MECHANOCHEMICAL TREATMENT AS A METHOD OF OBTAINING ENERGY-INTENSIVE COMPOSITIONS

Abstract. The paper presents the results of a mechanical treatment of metal powders (aluminum brand PA-4 and magnesium brand MPF-3) in a dynamic action mill using graphite as a surfactant additive in order to improve the dispersion of powders and modify the surface layer of particles. The mechanical treatment of metals, with graphite, contributes to the change in the structure, the composition of the surface of metal particles, an increase in the proportion of the active metal, and the formation of an organic coating of dispersible particles. The obtained metal particles with graphite were studied by physicochemical analysis methods, a granulometric method for estimating the particle size distribution carried out on the instrument Malvern 3600E. The effect of mechanochemical treatment of metal powders on the process of technological combustion of thermite mixtures is investigated. The results of the study showed that after the machining, the particle size of the metal powders decreases and, as a consequence, the specific surface area of the metal particles increases with the accumulation of defects in the crystal lattice. In the process of mechanochemical treatment, the size of the crystallites depending on the mass of the fraction of graphite used in the composition of the Me/C composite. When using aluminum and magnesium as a fuel component after mechanochemical treatment in the presence of graphite, the thermal kinetic characteristics of the combustion process increase.

Key words: mechanochemical treatment, aluminum, magnesium, modification, technological combustion.

Introduction. Metal powders are one of the most important components of fuels of various compositions and purpose. Their use is primarily due to the high thermal effect of oxidation of the metal, as well as the decrease in the average molecular weight of the gaseous combustion products as a result of deoxidation of H_2O and CO_2 during their interaction with the metal [1]. This is especially important for hydro-reacting fuel systems, in which the metal contains up to 80% and it is the main fuel [2-4]. The most common and quite energy-intensive metal fuel for fuel systems for various purposes is aluminum. In some fuels, especially ballistite, aluminum particles, because of the low oxidative activity of oxygen-containing combustion products, ignite with a large delay in time. In such cases, magnesium or its alloys with aluminum are used, the particles of which ignite faster than aluminum and burn completely [1, 3]. The most important characteristic of metallic powders, when used in combustible mixtures, is the content of the active (non-oxidized) metal, as well as the size and shape of the particles. In most cases, ultrafine powders with a particle size of less than 1 μm are used. And in recent years, more attention has been paid to nanodispersed powders, since they are characterized by increased chemical activity, this allowing to increase the burning rate of fuel [5-7].

To ensure the stability of the properties of metallic powders and to maintain the active metal content, they are passivated and hydrophobized [8]. In the first case, a solid and strong oxide-hydroxide film is formed on the surface of the particles preventing interaction of the metal with the oxidizing medium. And in the second, the surface of particles is covered with a layer of a fatty acid salt, in particular, sodium

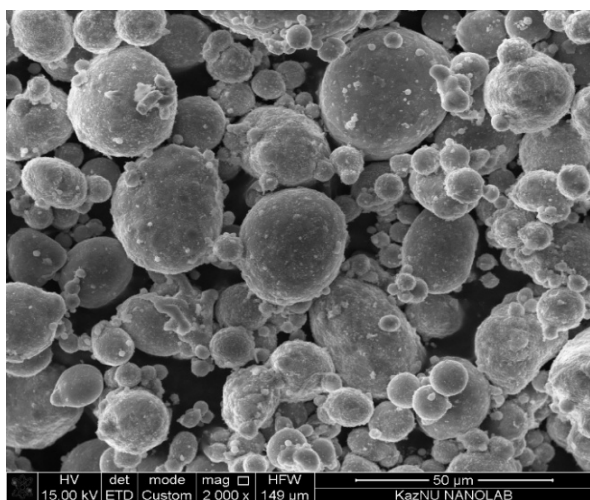
stearate. However, the presence of an oxide-hydroxide film on the surface of particles firstly reduces the proportion of the active metal, and secondly, the ignition begins only from the moment of contact of the fuel with the oxidizer as a result of the cracking of the oxide film by the volumetric expansion of the molten metal inside the oxide capsule.

To a large extent, the state of metal particles, in particular aluminum and magnesium, is primarily modified in terms of increasing the proportion of the active metal and provides resistance to the external oxidizing medium, as well as to increase the activity of combustion in the composition of combustible mixtures, using mechanochemical treatment (MCT) of the powder in planetary centrifugal mills. In the mechanochemical treatment with various organic modifiers, the fraction of the oxide film of the particles can be reduced to a considerable extent in the process of grinding the powder, replacing it with an organic one. As was shown in [9, 10], as a result of MCT of aluminum with graphite in an inert atmosphere, the reactivity of aluminum increases substantially, and in the first stages of processing a homogeneous composite product Al/C is formed, in which fine-dispersed aluminum particles are stabilized in highly dispersed graphite. With prolonged mechanical treatment, there takes place chemical interaction of aluminum with carbon with the formation of the crystal phase of Al_4C_3 [10]. Much attention is also paid to the possibility of mechanical activation of magnesium [11].

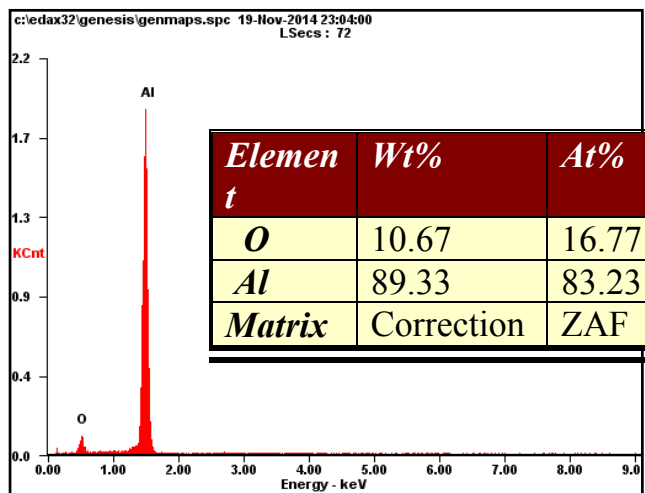
To obtain highly dispersed metal particles of aluminum and magnesium with a modified particle surface, it is important to select the optimum MCT conditions for a particular modifying additive. In this paper, we present the results and a comparative analysis of the MCT studies of aluminum and magnesium in the presence of graphite.

Results and discussion. For the experiments we used aluminum PA-4 and magnesium powder of the brand MPF-3. The microstructure of the initial particles of powdered aluminum and magnesium was investigated. According to the results of microstructural analysis, PA-4 aluminum particles have a spherical shape with a size of 20 to 63 microns (figure 1 a, b). The specific surface of such samples, according to the results of the BET analysis, is $3.692 \text{ m}^2/\text{g}$. The energy dispersive spectrum showed that in the composition of the initial aluminum grade PA-4, the mass fraction of oxygen is more than 10%. The presence of oxygen atoms indicates the presence of a sufficiently dense layer of oxide film on the surface of particles.

The results of the microstructural analysis of the original MPF-3 magnesium powder showed (figure 1 c, d) that magnesium particles have a scaly form and the average particle size of the sample exceeds $200 \mu\text{m}$, with a flake thickness of about $20 \mu\text{m}$. The specific surface of such samples, according to the results of the BET method, is $0.181 \text{ m}^2/\text{g}$. The results of EDX analysis show the presence of 2.26% oxygen in magnesium, i.e. the presence of oxide film on the surface of particles. However, the X-ray phase analysis of initial magnesium of MPF-3 brand showed that it contains 9.6% $\text{Mg}(\text{OH})_2$, i.e. the surface of the particles is covered with a hydroxide film.



a



b

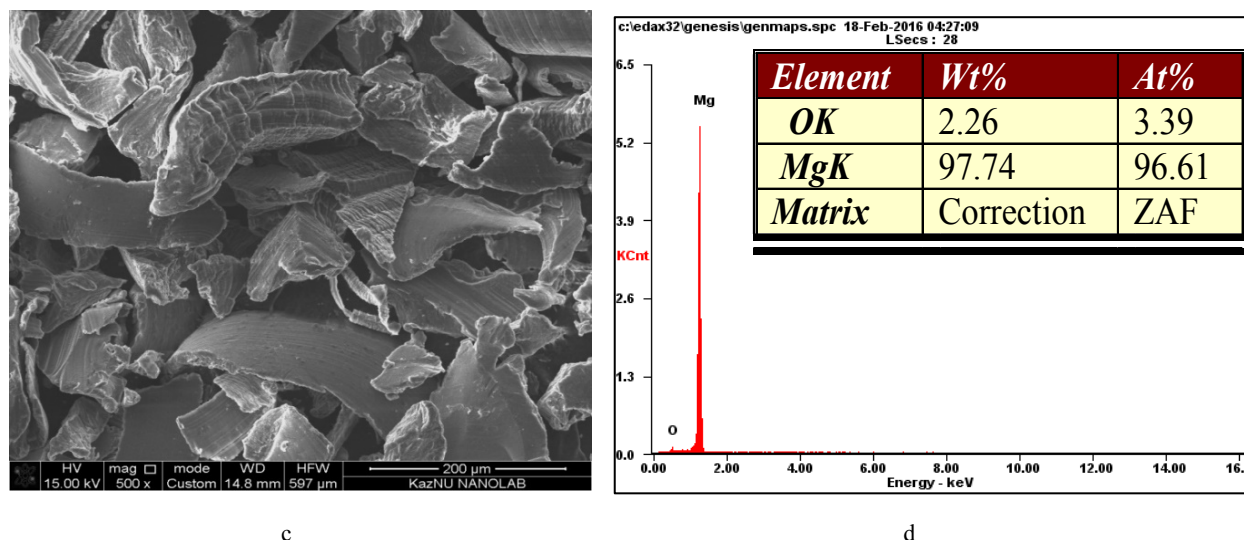


Figure1 - Electron-microscopic images (a, c), the energy-dispersive spectrum and the mass fraction of the elements (b, d) of the original aluminum powder PA-4 (a, b) and magnesium MPF-3 (c, d)

Mechanical grinding of Al and Mg particles is difficult due to their plasticity. To facilitate the dispersion process, surfactants, for example, stearic acid, graphite and other organic compounds, are added. Thus, when processing aluminum with graphite additives, the dispersing process is facilitated, and the presence of graphite in a mixture with the metal is a positive factor for subsequent targeted use, for example, in the composition of energy condensed systems [12-17]. Thus, modification of the surface of metallic nanoparticles by graphite during MCT is carried out not only to protect the metal from oxidation, but also to increase the energy content of the obtained composite mixture.

Mechanochemical treatment of powders was carried out in the centrifugal planetary mill Pulverizette 5 (manufactured by FRITSCH) with the volume of each working chamber of 500 mm³, the rotation speed of the platform is 400 rpm, the acceleration of the movement of grinding balls 40 g, the energy consumption 1.5 kW/h. Mechanochemical treatment was carried out in an air atmosphere at a powder/ball ratio (M_p/M_B) = 1/4. When grinding, the amount of the modifying additive varied (5-20%). The processing time was not more than 20 minutes to exclude self-ignition. The choice of the optimal time for the MCT was due to the results of previous studies [18,19]. To prevent oxidation of aluminum particles by air oxygen after MCT and to assess the changes actually associated with mechanical action, samples of the dispersed mixture were passivated with hexane (C₆H₁₄).

After MCT of aluminum with graphite, the particles have a plate (scaly) shape of different thickness, i.e. in the process of grinding, the shape of the particles changes and the formation of the layer structure of the Al/C composite occurs (figure 2 a).

The specific surface area of the powders, which was determined by the BET method, increases substantially after the MCT. Thus, the specific surface area of the treated mixture (Al 80% + C 20%) increases to 9.554 m²/g according to BET analysis. The state of the surface layer also changes. Elemental analysis of the composite (Al 80% + C 20%) after MCT showed that the mass fraction of aluminum in the composite is 80.69%, that of carbon 13.57% of the total mass of the sample, and the amount of oxygen is 5.75% (figure 2 b). Consequently, in the aluminum-graphite MCT process, aluminum is partially reduced in the surface oxide layer of the particles and the oxygen content in the composite decreases.

As a result, MCT of magnesium with graphite, the particles retain a plate-like shape (figure 2 c). The specific surface for the composite particles (Mg 80% + C 20%) increases to 16.383 m²/g. The EDX analysis of the elemental composition of the Mg/C composites showed that the mass fraction of oxygen atoms increases after MCT, so for Mg 80% + C 20% it is more than 6% (figure 2d).

Consequently, on the surface of magnesium particles after MCT, the thickness of the oxide layer increases. However, based on the results of X-ray phase analysis, neither oxides nor hydroxides are formed on the surface of the particles, the amount of which can reach 15% (figure 3).

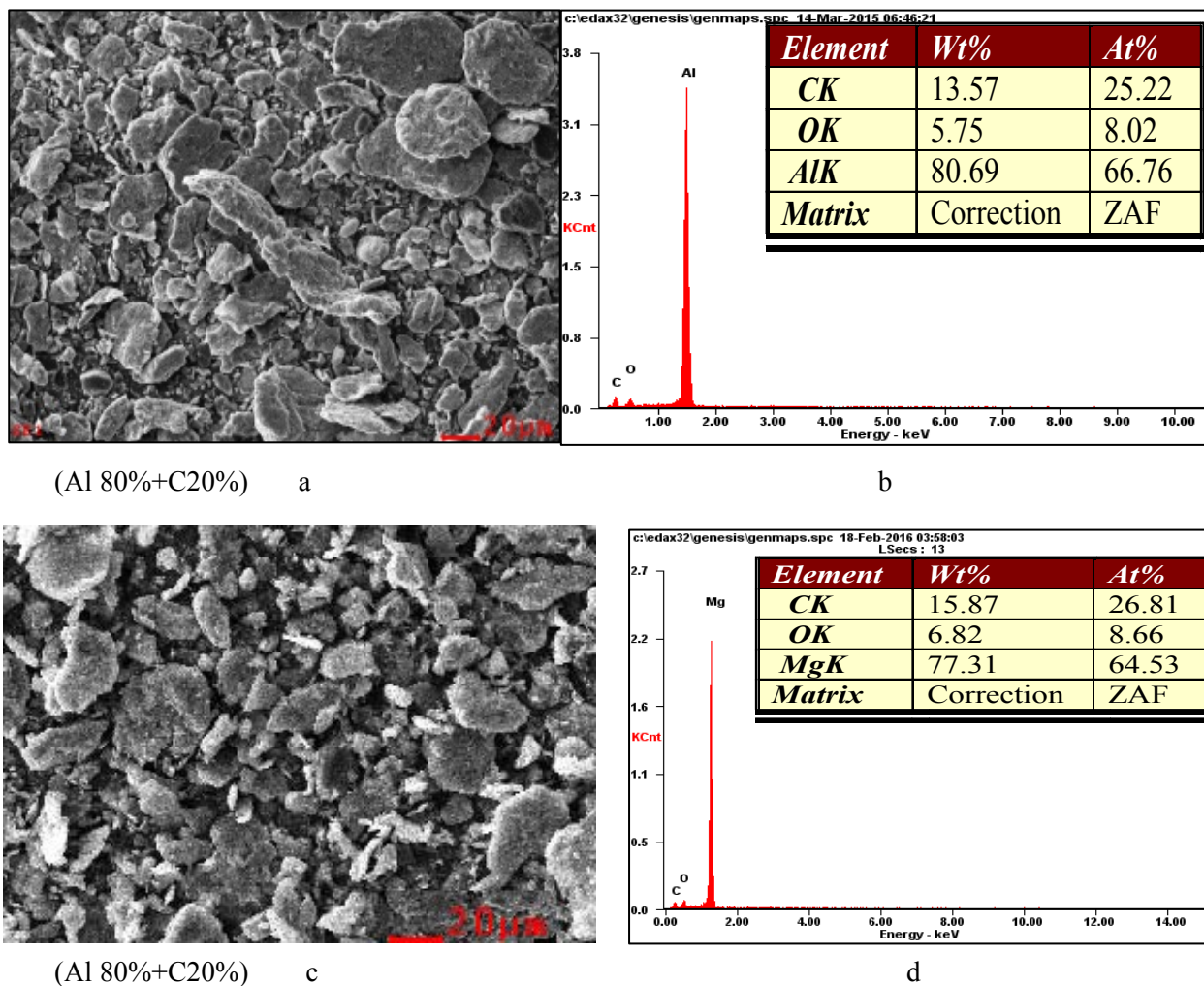


Figure 2 - Electron-microscopic images (a, c), the energy-dispersive spectrum and the mass fraction of elements (b, d) in the composite (Al 80% + C 20%) and (Mg 80% + C 20%) after 20 minutes of MCT

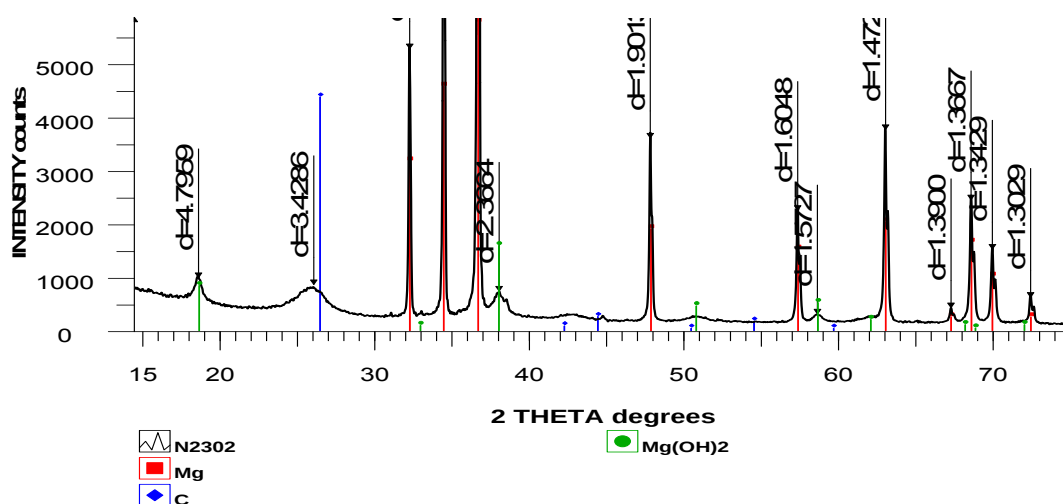


Figure 3- Diffraction of the sample (Mg 80% + C 20%), after 20 minutes of MCT

Evaluation of the particle size distribution carried out on the Malvern 3600E showed that when the graphite content in the aluminum system increases to 15-20% after grinding, the bulk of the powder has a

particle size of less than 5 μm . Almost half of them have a size of less than 2 μm (figure 4 a) resulting in the increase in the specific surface area of the aluminum particles of grade PA-4 from 3.7 to 9.5 m^2/g .

After grinding magnesium in a mixture with graphite, the bulk of the powder of the Mg/C mixture has a particle size of less than 5 μm , which are practically agglomerates of nanosized particles (figure 4 b).

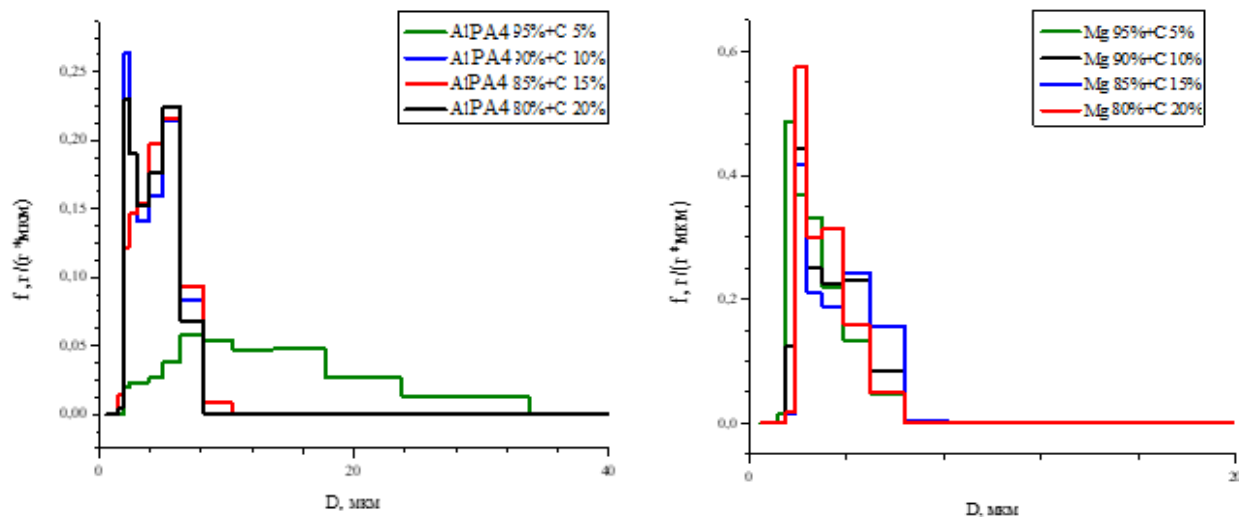


Figure 4 - The mass distribution of the Al/C (a) composite particle and the Mg/C (b) composite after 20 minutes of MCT

To evaluate the substructure features of aluminum particles after MCT, crystallite sizes were measured by the XRD method in the obtained Al/C, Mg/C composites. According to the results of the analysis, in the process of mechanochemical treatment, the size of the crystallites varies from the amount of the modifier used (table 1).

Table 1 - The size of aluminum and magnesium crystallites after 20 minutes of MCT with graphite

The content of graphite in composites	The size of crystallites L , $\text{\AA}$	
	Al	Mg
-	690	580
5 % C	560	600
10 % C	490	770
15% C	440	590
20 % C	410	520

With mechanical action, both accumulation and redistribution of defects over the volume of the particle takes place. As a result of MCT aluminum with graphite, the size of crystallites decreases and the content of carbon increases in the Al/C composite. During MCT of magnesium with graphite, at first there proceeds growth of crystallites and at a carbon content of 15-20%, the size of the crystallites, decrease i.e. there takes place more intensive accumulation of defects in the volume of grains. This may be due to the fact that during MCT carbon atoms penetrate into the grain of the aluminum particle and together with the defects diffuse by its volume under the action of mechanical stresses. In some cases, this process is likely to contribute to stabilization of defects, in other cases, it transfers them to the particle grain boundary and, as a consequence, the size of crystallites grows[20]. The surface film of particles of both aluminum and magnesium is destroyed (loosened) and saturated with highly disperse carbon particles (figure 5).

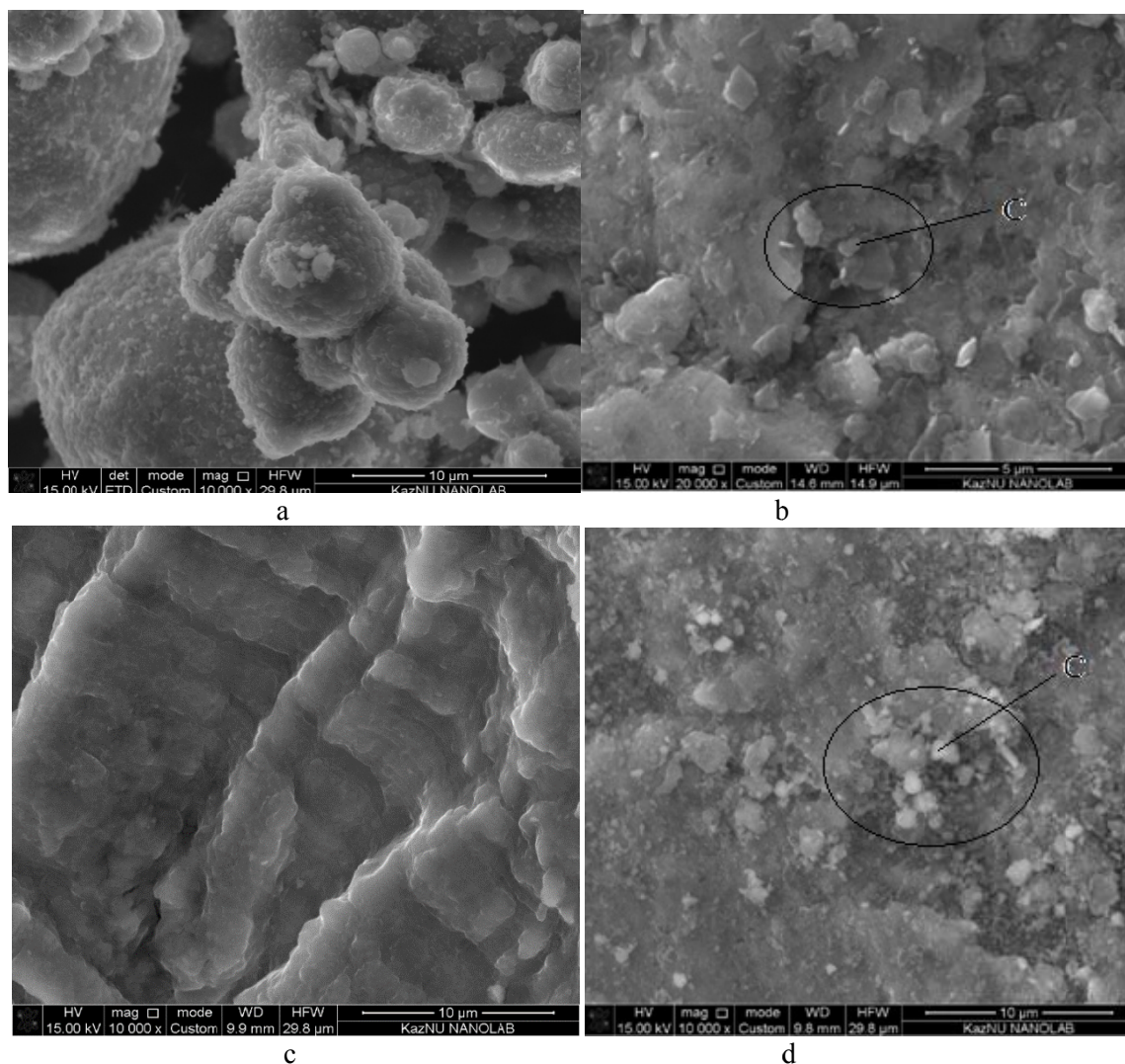


Figure 5 - Electron-microscopic images of aluminum and magnesium particles in the initial state (a, c) and in the composite (Al 80% + C 20%) and (Mg 80% + C 20%) after 20 minutes of MCT (b, d)

Thus, the use of graphite during MCT of aluminum and magnesium, according to all the characteristics analyzed, contributes to a change in the morphology and structure of the particles of the formed metal/carbon composites (Me/C). The observed changes in the size of aluminum and magnesium particles modified by the organic additive (graphite) during MCT is a consequence of the fact that in the formation of the surface layer of particles in all the considered cases, an important role is played by carbon, also dispersed in the MCT process.

Structural changes during MCT of the investigated Me/C composites lead to a change in their chemical activity, which is clearly manifested in the solid-phase combustion (ie self-propagating high-temperature synthesis - SHS) of the mixture of aluminum or magnesium powder, as a fuel, with silicon dioxide, used as an oxidizing agent. Silicon dioxide, in this case, is used in an unactivated state. Mixtures were prepared at the stoichiometric ratio of the components: (Al 37.5% + SiO₂ 62.5%) and (Mg 44% + SiO₂ 56%). After MCT of aluminum with graphite and introduction of the resulting powder, respectively, in an amount of 37.5% and 44% into the charge with quartz, a considerable reduction in the induction period of ignition is observed as well as an increase in the rate and temperature at all stages of the combustion process as compared to a non-activated fuel (figure 6 a). For a mixture of quartz with a composite (Mg/C) after MCT, the induction period of ignition also decreases and the temperature and burning time of mixtures with SiO₂ increase, but this is less expressed than in the case with aluminum (figure 6 b).

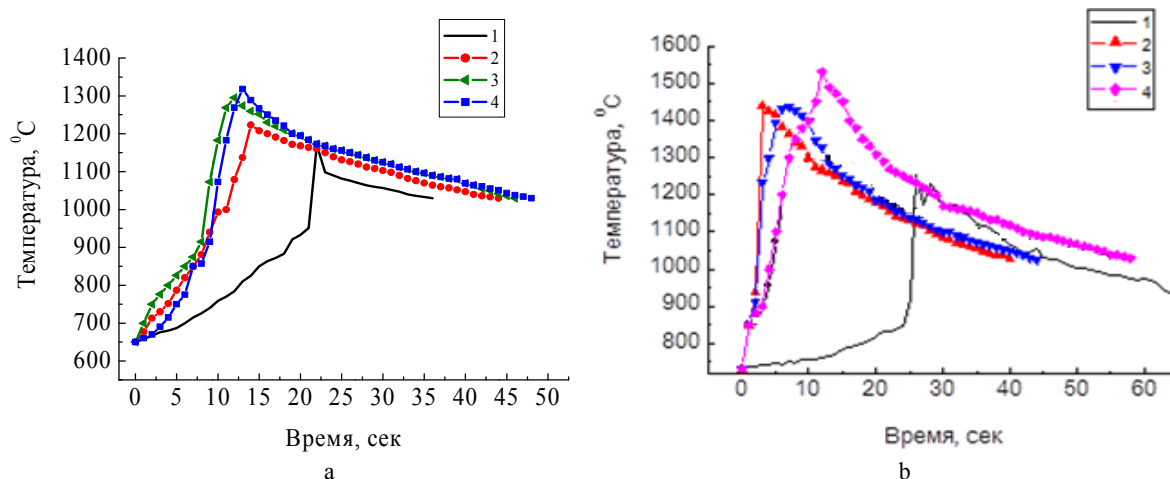


Figure 6 - Thermograms of combustion of the system ($\text{SiO}_2 + \text{Me}$) with aluminum and magnesium in the initial state and after 20 minutes of MCT with different amounts of graphite: a- $\text{SiO}_2 + (\text{Al/C})$, b- $\text{SiO}_2 + (\text{Mg/C})$; 1 - Me initial; 2 - 5%; 3 - 10%; 4 - 20% C

Table 2 shows the parameters of the main characteristics of the combustion process and the strength of the synthesized samples. It is seen in Table 2 that composition $[(\text{Al} + \text{C } 20\%)_{\text{MCT}} 37.5\% + \text{SiO}_2]$ has the maximum combustion temperature, but its strength is significantly reduced compared to the sample without carbon. This is due to the release of gaseous products, the amount of which increases with the increase in carbon content in the mixture, thus leading to formation of the porous structure of the sample (figure 7 a). The maximum burning rate (118.2 deg/sec) during SH-synthesis was stated for the system $[(\text{Al} + \text{C } 5\%)_{\text{MCT}} + \text{SiO}_2]$. This is possibly related to the optimum ratio of the particle size of the constituent components of the mixture, and correspondingly to the increase in the packing density, which provides a close contact between the oxidant and the fuel.

Table 2 - The indices of the maximum temperature, the burning rate of mixtures of SiO_2 with modified aluminum and magnesium, and the strength characteristics of the synthesized samples

Composition of modified fuel based on aluminum	$T_{\text{max}}, ^\circ\text{C}$	Burning rate, deg/sec	σ , MPa
Al initial + (SiO_2)	1319	19.16	37.6
(Al + 5 % C) _{MCT} + (SiO_2)	1441	118.2	8.36
(Al + 10 % C) _{MCT} + (SiO_2)	1436	83.7	12.54
(Al + 20 % C) _{MCT} + (SiO_2)	1532	56.8	2.11
Mg initial + (SiO_2)	1170	23.6	50
(Mg+5%C) _{MCT} + (SiO_2)	1295	40.9	5.8
(Mg+10%C) _{MCT} + (SiO_2)	1318	58.6	1
(Mg+20%C) _{MCT} + (SiO_2)	1223	51.4	1

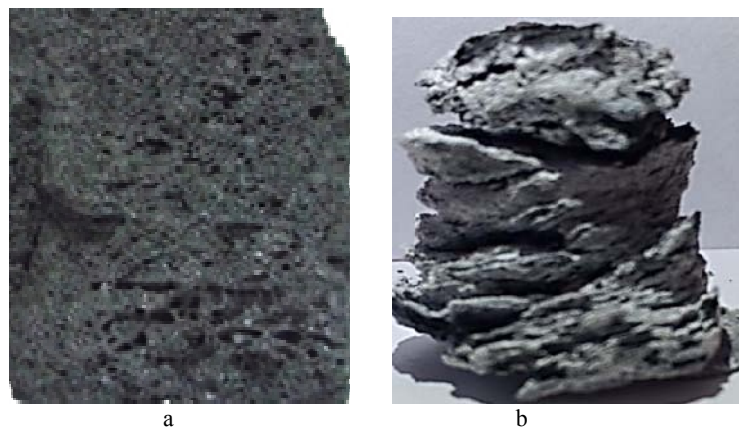


Figure 7 - The break and appearance of SHS samples obtained with aluminum (a) and magnesium (b) modified during MCT with the content of graphite equal to 20%

In the samples obtained with a fuel in the form of carbon-modified aluminum, a fine-porous structure with dense partitions is formed. This fact testifies to the prospects of using such materials for obtaining heat-insulating systems. Products of technological combustion of samples, the combustible component of which is the composite (Mg/C), have a low index of strength characteristics due to the porous, loose structure of the samples (figure 7 b). This is due to the fact that combustion proceeds layer-by-layer and a large amount of gaseous synthesis products are formed.

Conclusion. Thus, MCT of aluminum and magnesium with graphite contributes to a change in the morphology and structure of the particles during formation of composites (Me/C), the change in the size of aluminum and magnesium particles, and the surface modification with an organic additive (graphite). The use of mechanical treatment leads to a decrease in the particle size of metal powders and, as a consequence, an increase in the specific surface area of metal particles with an accumulation of defects in the crystal lattice. In the grinding process, the particle surface is constantly in an excited highly active state, and the presence of organic additives in the course of MCT provides the formation of an organic coating on the surface of the particles.

The combustion results of mixtures in which aluminum and magnesium were used as a fuel component after MCT in the presence of graphite showed the efficiency of this method in increasing the thermo-kinetic characteristics of the combustion process, as well as the conditions for the preparation of the combustible material and procedure the combustion process due to which formation of a large volume of gaseous synthesis products. The latter fact is important when using the obtained nanostructured Me/C composites in the composition of combustible systems intended, for example, for gas generators or for swelling and production of porous systems of a certain purpose. Such compositions are generally heterogeneous condensed systems.

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Н.Н. Мофа, Б.С. Садыков, А.Е. Баккара, Н.Г. Приходько, Б.Т. Лесбаев, З.А. Мансуров

Жану проблемалар институты, Алматы, Қазақстан
әл-Фараби атындағы ҚазҰУ, Алматы, Қазақстан

АЛЮМИНИЙ ЖӘНЕ МАГНИЙ БӨЛШЕКТЕРІНІҢ БЕТТЕРІН МЕХАНОХИМИЯЛЫҚ ӨНДЕУ РЕЖИМІНДЕ МОДИФИЦИРЛЕУ – ЖЫЛУСЫЙЫМДЫ КОМПОЗИТТЕР АЛУ ТӘСІЛІ

Аннотация. Мақалада металл ұнтақтарын (алюминий ПА-4 маркасы және магний MPF-3 маркасы) беттік белсенді зат ретінде графит көмегімен, ұнтақ дисперстілігін арттыру және бөлшек беттік қабатын модифицирлеу мақсатында динамикалық диірменде механохимиялық өңдеу жұмыстарының нәтижелері келтірілген. Металдарды графитпен механохимиялық өңдеу металл бөлшектерінің құрылымы және қасиеттерінің өзгеруіне, белсенді металл мөлшерінің жоғарылауына және дисперстелінетін бөлшектер бетінде органикалық жабындылардың пайда болуына әкеледі. Алынған металл және графит бөлшектері физика-химиялық талдау әдістері, «Малверн 3600Е» құрылғысы көмегімен жүргізілетін, бөлшек өлшемдерінің таралуын гранулометриялық әдіс көмегімен зеттеулер жүргізілді. Термитті жүйелердің технологиялық жану үдерісіне металл ұнтақтарын механохимиялық өңдеудің әсері зерттелінді. Зерттеу нәтижелері механохимиялық өңдеуден кейін металл ұнтақтарының бөлшектерінің өлшемдері төмендеп, сәйкесінше кристаллитті торда ақаулар жиналып, меншікті беттік көлемі жоғарылайтындығын көрсетті. Механохимиялық өңдеу үдерістері кезінде Ме/С композит құрамында графиттің массалық үлесіне байланысты кристаллиттер өлшемі өзгеретіндігі анықталды. Алюминий және магний бөлшектерін графитпен механохимиялық өңдеуден кейін жанғыш зат ретінде қолдану жану үдерістерінің термо-кинетикалық сипаттамаларының жоғарылауына алып келетіндігі көрсетілді.

Түйін сөздер: механохимиялық өңдеу, алюминий, магний, модифицирлеу, қаттыфазалы жану

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Н.Н. Мофа, Б.С. Садыков, А.Е. Баккара, Н.Г. Приходько, Б.Т. Лесбаев, З.А. Мансуров

Институт проблем горения, Алматы, Казахстан;
Казахский национальный университет имени аль-Фараби, Алматы, Казахстан

МОДИФИЦИРОВАНИЕ ПОВЕРХНОСТИ ЧАСТИЦ АЛЮМИНИЯ И МАГНИЯ В РЕЖИМЕ МЕХАНОХИМИЧЕСКОЙ ОБРАБОТКИ – СПОСОБ ПОЛУЧЕНИЯ ЭНЕРГОЕМКИХ КОМПОЗИЦИЙ

Аннотация. В работе представлены результаты механохимической обработки порошков металлов (алюминия марки ПА-4 и магния марки MPF-3) в мельнице динамического действия с использованием графита в качестве поверхностно активной добавки с целью повышения дисперсности порошков и модифицирования поверхностного слоя частиц. Механическая обработка металлов с графитом способствует изменению структуры и состава поверхности металлических частиц, повышению доли активного металла и формированию органического покрытия диспергируемых частиц. Полученные частицы металлов с графитом были исследованы физико-химическими методами анализа, гранулометрическим методом для оценки распределения частиц по размерам, проводимая на приборе «Малверн 3600Е». Исследовано влияние механохимической обработки порошков металлов на процесс технологического горения термитных смесей. Результаты исследования показали, что после механической обработки размеры частиц порошков металлов уменьшается и как следствие увеличивается удельная поверхность частиц металлов с накоплением дефектов в кристаллической решетке. В процессе механохимической обработки, размер кристаллитов изменяется от массовой доли используемого графита в составе композита Ме/С. При использовании в качестве горючего компонента алюминия и магния после механохимической обработки в присутствии графита повышаются термо-кинетические характеристики процесса горения.

Ключевые слова: механохимическая обработка, алюминий, магний, модифицирование, твердофазное горение.

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**A.S. Bukanova, F.B.Kairlieva, L.B.Sakipova,
O.Y.Panchenko, N.A.Karabasova, R.N. Nasirov**

Atyrau University named after Kh.Dosmukhamedov

E-mail: rnasirov.48@mail.ru

BINDING D-ELEMENTS OF GROUP VIII OF THE 4TH PERIOD OF THE PERIODIC SYSTEM

Abstract. This article briefly reviews the connecting d-elements of the fourth period I-VIII groups of the periodic system. Also compares the main elements of the group VIIIA and VIIIB transition group, their properties and electronic formulas.

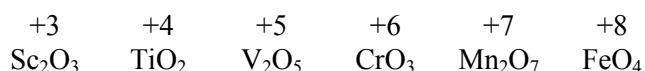
If we collate the VIIIB subgroup of iron elements with the valence states of argon, krypton VIIIA of the main subgroup, then argon in oxidation rates of 0, +2, +6 is an analog of krypton, and in the oxidation +8 Ar will not be a krypton's analog. On the contrary, in low oxidation rates, iron differs from argon, and in the oxidation of +8, iron is an incomplete analog of argon. Iron is a binder between subgroup VIIIA and subgroup VIIIB by electron configurations with a valence corresponding to the group number of the periodic table.

Gas XeO_4 under ordinary conditions, has not been studied sufficiently, but electron diffraction data and IR spectroscopy indicate that its molecule is tetrahedral. Its structure, based on isomorphism, is similar to the tetrahedral structure of FeO_4 , OsO_4 , RuO_4 .

Key words: transition metals, degree of oxidation, binding element, the terms Klechkovskii, characteristic elements, isomorphism.

In the study of d-elements of the periodic table, it is necessary to focus on their relationship with cp- and s- elements. They are called transient and are located in large periods between p- and s- elements, and the ions of which are characterized by one of the $nd^x (0 \leq x \leq 10)$ states (for example, $\text{Sc}^{3+} - d^0$, $\text{Zn}^{2+} - d^{10}$)

The highest oxidation state of most d-elements corresponds to the group number of the periodic system in which they are located, for example, manifested in oxides:



Scandium and its analogues in the corresponding periods are the first d-elements. They begin to fill the pre-surface layer. Unlike other d-elements, scandium and its analogues are characterized by the oxidation state +3. In its chemical behavior scandium is similar to aluminum at the same time. The formula of higher scandium oxide- Sc_2O_3 shows the basic properties- $\text{Sc}(\text{OH})_3$. Electronic structure of the outer energy layer of scandium is fully consistent with the second rule Kleczkowska. Consequently, its valence electrons are at 4s - and 3d- sublevels. Therefore, the highest degree of oxidation is equal to +3, which corresponds to the group number. And the electronic structure of the atom ends with s-electrons, so this element exhibits metallic properties. The remaining 9 d-elements from IV period are a continuation of the electronic layer. These d-elements in their period are the first d-elements, that is, they begin to fill the d-orbitals, ends at the atom Zn.

The so-called long version of the periodic system proposed by B. V. Nekrasov is often used [1]. In this version, the periods are not divided into parts, but written completely in one line. Similar elements are connected by straight lines. Here it is necessary to compare the oxidation state of the elements

corresponding to the group number of the periodic system. The main achievement of B. V. Nekrasov is that he established Sc, Ti, V, Cr, Mn, Cu, Zn at maximum valence by characteristic elements, but it remains uncertain which elements of the triad are analogs for inert gases at their maximum oxidation state.

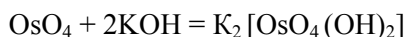
However, this cannot be considered a mistake, as the experimental facts at the time was not enough.

In the periodic system, a number of elements are combined into triads (triads of iron, ruthenium and osmium). Inside the triad, the properties of the elements are close. This group includes three of the triad of metals (nine d-elements)

Period 4 5 6
Elements Fe, Co, Ni Ru, Ph, Pd Os, Ir, Pt

and the noble gases that complete each age. As in any other group, the members of the VIII group can be divided into the main VIIIA - and the side VIIIB – subgroups.

The subgroup of iron includes ruthenium and osmium-each in its period are d-elements, which begins filling the d-orbitals of the previous layer by electron. The maximum oxidation state (+8) is equal to the group number of the periodic table. For iron, the most characteristic oxidation States are +2 and +3, iron derivatives are also known, in which the oxidation state is +4, +6 and +8. There is information about the preparation of iron oxide- $\text{FeO}_4(+8)$. This is not a stable volatile compound of pink color[2]. Tetraoxide osmium and ruthenium toxic. Thanks to the acid properties OsO_4 during the interaction with basic compounds:



complexes are formed.

Elements	Fe	Ru	Os
Oxidation	2, 3, 4,	2, 3, 4,	2, 3, 4,
Degree	6, 8	5, 6, 7, 8	6, 8

Vertically, the first d–element of the VIIIB group is iron (IV–th period), followed by ruthenium (V–th period) and osmium (VI–th period). Their electronic configurations of the outer shell of Fe $[\text{Ar}]3d^64s^2$, Ru $[\text{Kr}] 4d^75s^1$ and Os $[\text{Xe}] 4f^{14}5d^66s^2$ atoms.

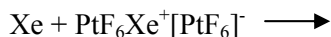
Between elements in the vertical columns show some of the features and a closer resemblance. For example, members of the Fe, Ru and Os series are particularly active catalysts in the synthesis of ammonia from hydrogen and nitrogen elements.

If we compare the VIIIB subgroup of iron elements with the valent States of argon, krypton VIIIA of the main subgroup, then argon in the oxidation States 0, +2, +6 is an analogue of krypton, and in the oxidation state +8 Ar will not be an analogue of krypton. In contrast, in the low oxidation States of the iron differs from that of argon, and in the oxidation state +8 iron is incomplete analogue of ar (see tab.1). Electronic configurations of Fe, Ar and Kr in atomic state and oxidation States +2, +6 and +8 (tab.1). Iron is a connecting element between the subgroup VIIIA and the subgroup VIIIB by electronic configurations with valence, corresponding to the group number of the periodic system.

Table 1 - Comparison of electronic configurations of iron, argon and krypton as VIII–group elements

Oxidation degree	Fe (VIIIB)	Ar (VIIIA)	Kr (VIIIA)
0	$[1s^22s^22p^63s^23p^6] 3d^64s^2$	$[1s^22s^22p^6] 3s^23p^6$	$[1s^22s^22p^63s^23p^6] 3d^{10}4s^24p^6$
+2	$[1s^22s^22p^63s^23p^6] 3d^6$	$[1s^22s^22p^6] 3s^23p^4$	$[1s^22s^22p^63s^23p^6] 3d^{10}4s^24p^4$
+6	$[1s^22s^22p^63s^23p^6] 3d^2$	$[1s^22s^22p^6] 3s^2$	$[1s^22s^22p^63s^23p^6] 3d^{10}4s^2$
+8	$1s^22s^22p^63s^23p^6$	$1s^22s^22p^6$	$[1s^22s^22p^63s^23p^6] 3d^{10}$

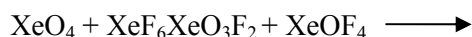
Until recently, it was believed that noble gases were not at all capable of entering into chemical reactions, and placed them in the "zero" group of the periodic table of D.I. Mendeleev, where the elements with "zero" valency were supposed to be. In 1962 the Canadian chemist N. Bertlett succeeded in obtaining compounds of inert gases with fluorine [3]:



Here, PtF₆ takes one electron away from xenon. Investigating the chemical properties of the PtF₆ compounds of the VIIIB group, N. Bertlett observed that with prolonged exposure to air it changes color, resulting in the formation of O₂ + [PtF₆]⁻. The reason for this is that the first ionization energy of xenon is comparable in magnitude to the ionization energy of molecular oxygen (1175 kJ / mol for O₂ → O₂⁺⁺ + e⁻). Therefore, in this case, xenon hexafluoroplatinate is formed similarly to oxohexafluoroplatinate.

A few months later, XeF₄ and XeF₂ were synthesized in other laboratories [4].

As is known, the degree of oxidation of xenon is (+8) [5].



xenon belongs to the VIIIA group.

Tetraoxide is obtained by the action of anhydrous H₂SO₄ on barox oxoxenate (+8) at room temperature:

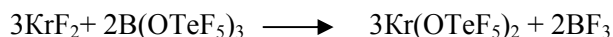


HeO₄ under ordinary gas conditions, has not been studied sufficiently, but the data of electron diffraction and IR spectroscopy indicate that its molecule is tetrahedral. Its structure is similar on the basis of isomorphism, the tetrahedral structure of OsO₄, RuO₄. The derivatives of xenon (+6) are strong oxidants. However, when even more powerful oxidants are applied to them, compounds with a degree of oxidation (+8) can be obtained. Of these compounds, xenon-x-fluoride XeF₈, xenonetetraoxide XeO₄, and xenonodifluoride XeO₃F₂ are known. These compounds are similar to the acidic compounds OsO₄ and RuO₄.

The elements of the krypton subgroup-kryptonKr, xenon Xe, radon Rn, are characterized by a lower ionization energy of atoms than the typical elements of neon and argon VIIIB of the group. Therefore, the elements of the krypton subgroup give compounds of the usual type. And in this direction, the elements of the krypton subgroup differ from other noble gases by the large dimensions of the atoms (molecules) and the high polarizability in the series of He-Ne-Ar-Kr-Xe atoms. Due to the high stability of the electronic structure of the atom (ionization energy 15.76 eV), the valence-type compounds for argon have not been obtained.

For He, Ne and Ar, stable compounds are not known [6]. And the next noble gas - krypton has chemical compounds, but their

less than xenon. In addition to KrF₂, KrF₄, the formation of the first compounds containing Kr-O bonds was detected [7] by NMR spectroscopy (19F, 17O) to monitor the synthesis of the stable compound [Kr (OTeF₅)₂]:



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Figure 1 - Addition to the long version of the periodic system proposed by B.V. Nekrasov

Having a relatively larger atomic size, argon is more inclined to form intermolecular bonds than helium and neon. Therefore, the most common clathrates formed by Ar, Kr and Xe with hydroquinone 1,4-C₆H₄ (OH)₂ and water. Clathrates can serve to store noble gas reserves.

It can be assumed that iron is a link between subgroup VIIIB and subgroup VIIIA at maximum valence (+8). Fe and Ar at maximum valence (+8) are connected by a small dotted line (Fig. 1). For the remaining III, IV, V, VI, VII, I and II groups of the fourth period, the connecting elements are Sc, Ti, V, Cr, Mn, Cu, Zn [1, 8, 9].

Substances formed by elements of the main and secondary subgroups, in some cases, differ in their properties. However, in the highest degree of oxidation, their properties are close. For example, VIIA-subgroup-halogen-oxidizers, VIIB-subgroup-reduction metals, where they exhibit low valence (Cl₂O-acidic oxide, MnO-base), the differences were sharply expressed. However, in their highest degree of oxidation, these elements in the composition of the corresponding compounds are similar in properties [9]. Thus, halogens and metals of the VII group oxidize strongly with strong acids: tetraoxochlorate (+7) hydrogen HClO₄ and tetraoxomanganate (+7) hydrogen HMnO₄, which are also the strongest oxidants.

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**А.С. Буканова, Ф.Б.Қайрлиева, Л.Б.Сакипова,
О.Ю.Панченко, Н.А.Қарабасова, Р.Н. Насиров**

Х.Досмұхамедов атындағы Атырау мемлекеттік университеті

Д.И.МЕНДЕЛЕЕВТИҢ ПЕРИОДТЫҚ ЖҮЙЕСІНДЕГІV ПЕРИОДЫНЫҢ БАЙЛАНЫСТЫРУШЫ d -ЭЛЕМЕНТТЕРІ

Аннотация. Мақалада Д.И. Менделеевтің периодтық жүйесінің IV-периодындағы I–VIII топтардың негізгі және қосымша топтарындағы элементтер қарастырылды. Мұнда VIII A негізгі және VIII B қосымша топша элементтерінің электрондық құрылымы және қасиеттері салыстырылды.

Ал, егер VIIIA негізгі тобы элементтері аргонды, криптонды VIIIB тобының элементі темірмен салыстырсак, онда олардың электрондық құрылымын салыстыру нәтижесінде 0, +2, +6 тотығу дәрежелері үшін криптон аргонның аналогы, ал +8 тотығу дәрежесі үшін олар аналог еместігі белгілі. Оған керісінде бұл максимал валенттілікте темір аргонның аналогы. Міне, бұл бізге темір металы VIII A және VIIIB топтарын байланыстырушы элемент екендігіне күмән келтірмейді (+8 тотығу дәрежесінде).

ХеО₄ толығымен зерттелген жоқ, бірақ электронография және ИҚ-спектроскопиялық зерттеулер оның молекуласы изоморфизм негізінде FeO₄, OsO₄, RuO₄ сияқты тетраэдрлік құрылымға ие болатындығын көрсетті.

Түйін сөздер: ауыспалы металдар, тотығу дәрежесі, байланыстырушы элемент, Клечковскийдің ережелері, сипаттамалық элементтер, изоморфизм.

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**А.С. Буканова, Ф.Б.Қайрлиева, Л.Б.Сакипова,
О.Ю.Панченко, Н.А.Қарабасова, Р.Н. Насиров**

Атырауский государственный университет им.Х.Досмұхамедова

СВЯЗЫВАЮЩИЕ d-ЭЛЕМЕНТЫ I-VIII ГРУППЫ 4-ГО ПЕРИОДА ПЕРИОДИЧЕСКОЙ СИСТЕМЫ Д.И.МЕНДЕЛЕЕВА

Аннотация. В статье вкратце рассматриваются связывающие d-элементы четвертого периода I-VIII группы периодической системы Д.И. Менделеева. Сравниваются элементы VIIIA главной группы и VIIIB побочной группы, их электронные формулы и свойства.

Если сопоставить VIIIB подгруппу элементов железа с валентными состояниями аргона, криптона VIIIA главной подгруппы, то аргон в степенях окисления 0, +2, +6 является аналогом криптона, а в степени окисления +8 Ar не будет аналогом криптона. Напротив, в низких степенях окисления железо отличается от аргона, а в степени окисления +8 железо является неполным аналогом аргона. Железо является как бы связующим элементом между подгруппой VIIIA и подгруппой VIIIB по электронным конфигурациям при валентности, отвечающей номеру группы периодической системы.

ХеО₄ в обычных условиях газ, изучен пока недостаточно, но данные электронографии и ИК-спектроскопии указывают на то, что его молекула тетраэдрическая. Его строение аналогично на основе изоморфизма, тетраэдрическому строению FeO₄, OsO₄, RuO₄.

Ключевые слова: переходные металлы, степень окисления, связывающий элемент, правила Клечковского, характеристические элементы, изоморфизм.

Сведения об авторах:

Буканова Айгуль Сокеевна – к.т.н., доцент, зав.кафедрой «Химия и химическая технология»;

Қайрлиева Фазилат Басаровна – к.т.н., ст. преподаватель кафедры «Химия и химическая технология»;

Сакипова Лидия Бағитжановна – магистр, ст. преподаватель кафедры «Химия и химическая технология»;

Панченко Ольга Юрьевна - магистр, ст. преподаватель кафедры «Химия и химическая технология»;

Қарабасова Нағима Асылбековна - магистр, ст. преподаватель кафедры «Химия и химическая технология»;

Насиров Рахметулла – д.х.н., профессор кафедры «Химия и химическая технология».

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O.A. Nurkenov^{1,2}, M.K. Ibrayev², S.D. Fazylov¹,
A.T. Takibayeva², I.V. Kulakov³, A.E. Tuktybayeva²

¹Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan;²Karaganda State Technical University, Karaganda, Kazakhstan;³Dostoevsky Omsk State University, Omsk, RussiaE-mail: nurkenov_oral@mail.ru, altynarai81@mail.ru

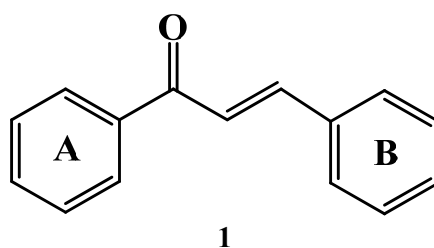
CHALCONES-SYNTHONS IN SYNTHESIZING BIOLOGICALLY ACTIVE MATTERS

Abstract. The review paper summarizes and systematizes the literature data of recent years, as well as the results of the authors' research in the field of functionally substituted chalcones. The most common natural chalcones, methods of production, reactivity and biological properties of synthetic chalcones are given.

Keywords: substituted aromatic aldehyde, chalcone, pyrazoline, flavonone, cytokine, NF- κ B transcription factor.

Important representatives of organic compounds having a preparative value are α , β -unsaturated carbonyl compounds, among which benzylideneacetophenones (chalcones) occupy a notable place. Since the discovery in 1896 of chalcones [1], the interest in the chemistry of its substituted and heterocyclic analogs has not faded. The name "chalkone" was proposed by the Polish chemist Stanislaw Kostanecki. It comes from the Greek word "*chalcos*" ($\chi α λ κ \acute{o} s$) that means "copper".

Chalcones 1,3-diphenyl-2-propen-1-ones (1) belong to the compounds in which two aromatic nuclei are bound by three carbon atoms of the α , β -unsaturated carbonyl system [2]. Chalcones can have *cis*- and *trans*-forms, but the *trans*-form is thermodynamically more stable.



1. Widespread natural chalcones

Chalcones are quite widespread in nature: they are found in flowers, fruits, seeds, and wood. They are closely related to a number of substances that belong to the class of flavonoids: flavones, flavonones, flavonols. Most of the representatives of the chalcones are found in all plant organs in the form of aglycones and glycosides and differ in the number of substituents in the A ring. So, for example, butein chalcone that is often found in the family of comatose chalcones, is in the form of *Coreopsis giganiea* 4-glycoside; chalconoraine is in the form of 2-glycoside isosalipurposide in *Salix purpurea* [3, 4]. By now more than 200 different aglicones of the chalconic nature are known. Quite often dihydrochalcones are found in plants, in which the three-carbon fragment has a reduced double bond. They are known exclusively in glycosidized form, as well as methoxy- and pyrano-derivatives. So, some species of apple

tree contain glycoside phloridzin (2'-glucoside, 4', 2', 4,6-tetraoxydihydrochalcone) that causes intensive release of glucose from the body in a person (phloridzin diabetes), sibilin (3-hydroxyflavone-4'-glucoside), azepogenin in the form of azobothin 2'-glycoside [4]. It is believed that chalcones are precursors of various groups of flavonoid compounds in biosynthesis.

Many bright colors of the plant world of our planet in spring, summer and autumn are caused by compounds of one flavonoid class, i.e. chalcones. They are called "antichlorophylls", they are yellow pigments of flowers that turn orange in pairs of ammonia. In particular, discoloration of the contained chalcones of the preparative forms is used in the field of pharmaceuticals, for example as a color-changing oral care component that can be phenyl-3-methoxy-4-hydroxystyryl ketone and 3-(4'-hydroxy-3'-methoxy)1-phenylprop-2-en-1-on [5]. Chalcones are relatively often found in one family: *Compositae*, especially in *Coreopsis* and *Dahlia*. They are also found in some *Leguminosae* (*Butia*, *Cylicodiscus*, *Glycyrrhiza*, *Plathymenia*, *Ulex*) and in *Dihymocarpus* (*Gesneriaceae*). Table 1 lists some chalcones and their derivatives isolated from natural raw materials.

Table 1- Chalcones and their derivatives isolated from natural sources

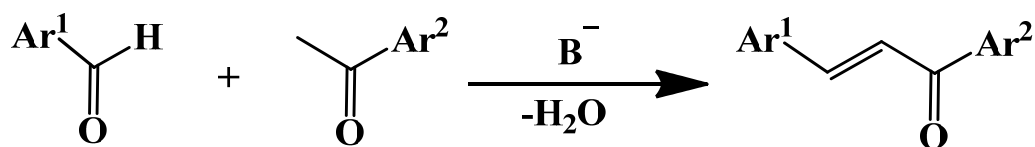
No	Chalcones and their derivatives	Natural sources	Reference
1	2'-hydroxy-2,4,6-trimethoxychalcone	<i>Andrographis lincate</i> (<i>Acanthaceae</i>)	[6]
2	2', 4'-dihydroxy-4-methoxydihydrochalcone (davidigenin)	<i>Artemisia dracunculifolia</i> L. (<i>Asteraceae</i>)	[7]
3	2', 4', 4'-trihydroxy-3'-[6-hydroxy-3,7-dimethyl-2 (E) -7-octadienyl] chalcone	<i>Artocarpus nobilis</i>	[8; 9]
4	2', 4', 6', 4-tetrahydroxychalcone (isosalipurpol);	<i>Arabidopsis thaliana</i> (<i>Angiosperm</i>)	[10; 11; 12; 13]
5	2' & 4' & 6' & 4'-trihydroxychalcone (iso-liquitytigenin)	<i>Asarum canadense</i> (<i>Aristolochiaceae</i>)	[14]
6	chalcononanerenine 2'-O-β-D-glucoside-4'-O-β-gentobiose; 2', 4'-di-O-β-D-glucoside	<i>Boesenbergia pandurata</i> (<i>Rub.</i>)	[15]
7	2', 6'-dihydroxy-4'-methoxychalcone;	<i>Brassica alba</i> (<i>Cruciferae</i>)	[16]
8	2'-hydroxy-4,4'-trimethoxychalcone	<i>Caesalpinia pulcherrima</i> L.	[17]
9	4-hydroxy-2', 4'-dimethoxy dihydrochalcone; isocyclitis	<i>Crinum bulbispermum</i> bulbs.	[18]
10	4,4'-bis-a-O-glucosyl-4,2', 4'-trihydroxy-6', -methoxychalcone (aglycone)	<i>Derodendron phlomidis</i> (<i>Vcrbenaceae</i>)	[19]
11	3'- (3'-methyl-3'-hydroxybutyl) -2', 4,4'-trihydroxy-6'-methoxychalcone; 4'-O-glucuronyl-2,4-dihydroxy-6'-methoxy-3'-prenylalkalcone; 1 - [(2', 4'-dihydroxy-3'-isoprenyl-6'-methoxy) -phenyl] - [3- (4-hydroxyphenyl)] - 2,3-epoxypropan-1-one; 4-acetoxy-2', 4'-dihydroxy-6'-methoxy-3'-prenylalkalcone; 1 - [(2', 4'-dihydroxy-3'-isoprenyl-6'-methoxy) -phenyl] - [3- (4-hydroxyphenyl)] - 2,3-epoxypropan-1-one; 4-acetoxy-2', 4'-dihydroxy-6'-methoxy-3'-prenylalkalcone	<i>Humulus lupulus</i> L. (<i>Cannabaceae</i>)	[20; 21]
12	4', 6', 4-trihydroxy-5-methoxychalcone; 4', 6'-dihydroxy-4, 5-dimethoxychalcone	<i>Iryanthra polyneura</i> (<i>Myristicaceae</i>)	[22]
13	2', 4', 6'-trihydroxy-4-methoxydihydrochalcone;	<i>Iryanthra virola</i> (<i>Myristicaceae</i>)	[22]
14	2'-methoxy-4', 6', 4-trihydroxydihydrochalcone;	<i>Iryanthera sagotiana</i> (<i>Myristicaceae</i>)	[22]
15	2', 4-dimethoxy-4', 6'-dihydroxydihydrochalcone;	<i>Marchantia paleacea</i>	[10]
16	2'-glucoside-4', 6'-dihydroxy-4-methoxy-dihydro-chalcone; 4', 6', 4-trihydroxy-5-methoxydihydro-chalcone; 2', 4, 5-trimethoxy-4', 6'-dihydroxydihydrochalcone; 4', 6'-dimethoxy-6'-α-dihydroxydihydrochalcone	<i>Medicago sativa</i> L.	[10; 12]
17	Bi-2', 4', 6'-trihydroxy-4-methoxydihydrochalcone	<i>Melletia ferruginea</i> (<i>Fabaceae</i>)	[23]
18	2', 4', 6', 4-tetrahydroxychalcone (naringenin)	<i>Vitis vinifera</i> (<i>Angiosperm</i>)	[12; 24]

2. Methods of obtaining synthetic chalcones

Synthetic chalcones are of considerable interest for chemists and pharmacists, which is due to several factors: the comparative simplicity of the chemical structure that allows synthesizing on their base a large

variety of molecules with high pharmacological activity, as well as the possibility of using them as valuable synthetic intermediates, for example, in the synthesis of various heterocyclic compounds. It should be noted that α , β -unsaturated ketone groups are probably responsible for most of the observed biological properties of chalcones, since these groups are present in all biologically active molecules, and their removal is associated with losing activity [25]. Many authors attribute the presence of this fragment to the different biological activity of the substituted chalcones: anti-inflammatory [26], antitubercular [27], antioxidant, antiviral, antimicrobial, antifungal and many other activities [28, 29]. Substituted chalcones are promising antitumor preparations [30, 31]. They also attract attention as preparations that have selective activity against dermatophytes [32]. Substituted chalcones are of interest as components for solar cells [33], ion-selective electrodes, molecular devices and photofunctional materials [34-38].

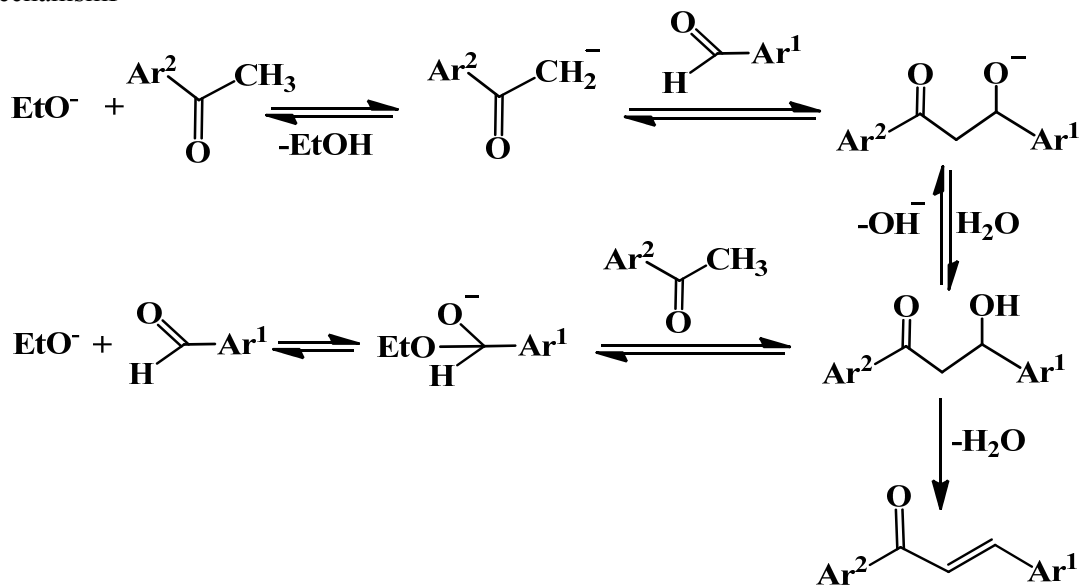
The most significant method of synthesizing chalcones is known [39] the croton condensation involving formyl- and acetyl-containing compounds. According to the Claisen-Schmidt reaction, from 32 substituted acetophenones and 40 aromatic benzaldehydes there were obtained 1280 substituted chalcones by combinatorial synthesis methods. The use of these chalcones in 9 condensation and cyclization reactions led to producing 74,000 five- and six-membered cyclic compounds [40].



$\text{Ar}^1, \text{Ar}^2 = \text{Ph, substituted phenyls, heterocycles}$

When studying the Claisen-Schmidt reaction using the UV spectroscopy method, it was found that the interaction of substituted benzaldehydes with acetophenone is described by the second-order velocity equation. In this connection the authors of [41] proposed two reaction mechanisms. The first one is through removing acetophenone by the proton base from the methyl group (mechanism I), the second one is through attacking the ethylate anion on the carbon of the carbonyl group of the aldehyde (mechanism II). Using the thermodynamic parameters in the discussion of each stage of the proposed mechanisms, the authors concluded that the mechanism II should be more profitable [41]:

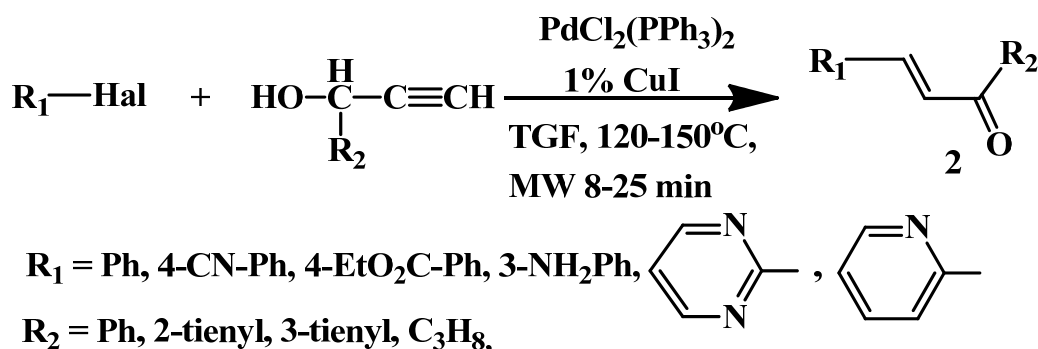
Mechanism I



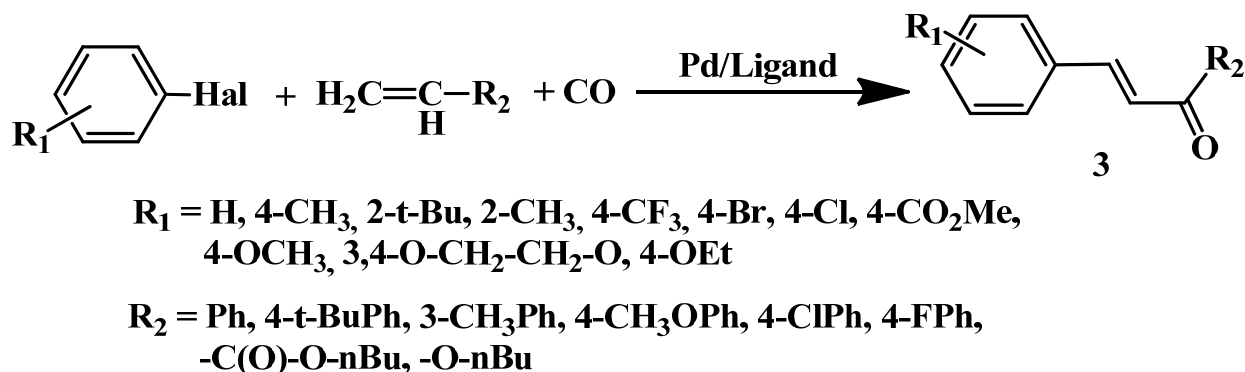
$\text{Ar}^1, \text{Ar}^2 = \text{Ph, substituted phenyls, heterocycles}$

But in some cases, with the use of substituted chalcones, this method is accompanied by side oxidation-reduction processes leading to reducing the yield of the desired product. In literature a large number of methods for synthesizing chalcones using homogeneous and heterogeneous catalysis techniques have been described [42, 43], among which the catalysis with activated barium hydroxide [44], hydrochloric acid formed in situ by interaction of SOCl_2 in absolute EtOH [45], $\text{BF}_3\text{-Et}_2\text{O}$ [46], potassium hydroxide deposited on $\text{KF-Al}_2\text{O}_3$ in combination with ultrasonic irradiation, ionic liquids [47, 48]. There are known works using microwave irradiation, using metal oxides, $\text{I}_2\text{-Al}_2\text{O}_3$ without using solvents, which reduced the reaction time from 3 hours to 80 seconds [49, 50]. These conditions allow getting rid of unwanted reaction products [51], increasing the yield and shortening the reaction time to several minutes.

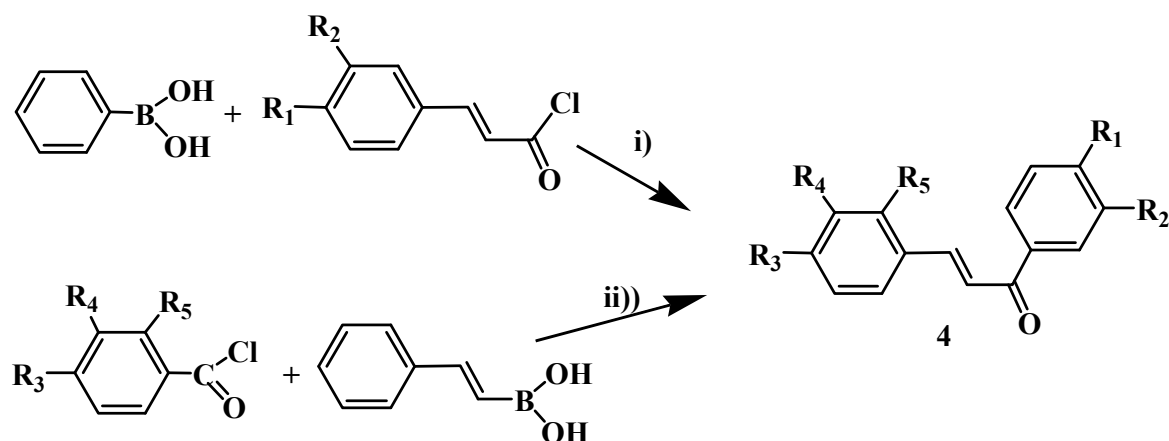
In addition to the Claisen-Schmidt reaction, alternative ways of synthesizing substituted chalcones are described in literature, which make it possible to obtain them with high yields under mild conditions. In some cases the methods allow avoiding undesirable redox processes or obtaining compounds not available in the classical Claisen-Schmidt reaction. However, in this case, as a rule, expensive reagents are required, the use of microwave or ultrasound exposure and inert atmosphere. Thus, for synthesizing chalcones 2, there was used the Sonogashira coupling reaction under microwave conditions between the aryl halide and substituted propargyl alcohol, which allowed producing the target products with high yields in a short time [26]. It was shown that the reaction proceeded only in the presence of an electron-withdrawing group as a substituent in the aromatic nucleus R_1 .



In [52] there are presented the data of the Heck coupling-carbonylation reaction involving aryl halide and styrene or substituted vinyl in the presence of carbon monoxide using a palladium catalyst leading to formation of chalcones 3. It is shown that the yields of the product 3 make 41-90%, depending on using the ligand and a substituent in the aromatic ring of the chalcone.



The authors of Ref. [53] obtained chalcones 4 under mild conditions using several variants of the Suzuki reaction: the first one using cinnamoyl chloride and phenylboronic acid, and the other with benzoyl chloride and phenyl vinyl boric acid. Both reactions led to the desired product 4.

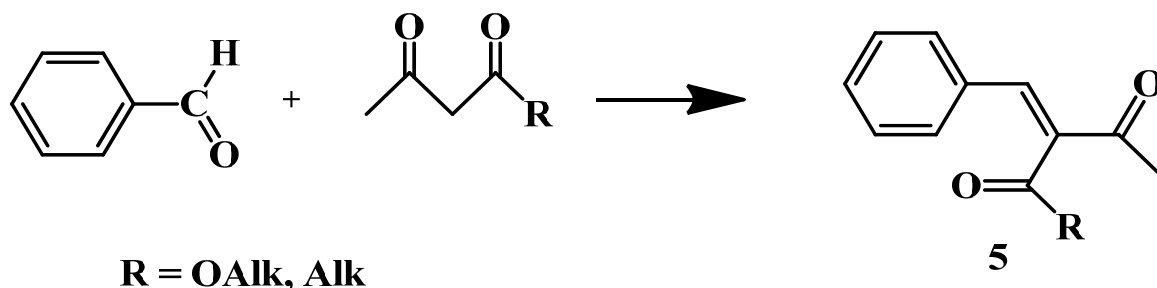


$\text{R}_1 = \text{H}, \text{OCH}_3$; $\text{R}_2 = \text{H}, \text{NO}_2, \text{OCH}_3$;
 $\text{R}_3 = \text{H}, \text{OCH}_3$; $\text{R}_4 = \text{H}, \text{CF}_3, \text{NO}_2, \text{OCH}_3$; $\text{R}_5 = \text{H}, \text{CF}_3$

i): $(\text{PPh}_3)_4\text{Pd}(\text{o})$, Cs_2CO_3 , toluol. Yield 40-50%

ii): $(\text{PPh}_3)_4\text{Pd}(\text{o})$, Cs_2CO_3 , toluol. Yield 70-95%

Chalcones can also be obtained by the Knoevenagel condensing, i.e. interaction of aldehydes or ketones with compounds having an active methylene component, for example, acetoacetic ether under conditions of the basic catalysis [39]. This reaction with interaction of benzaldehyde with AAE leads to the formation of chalcone 5.

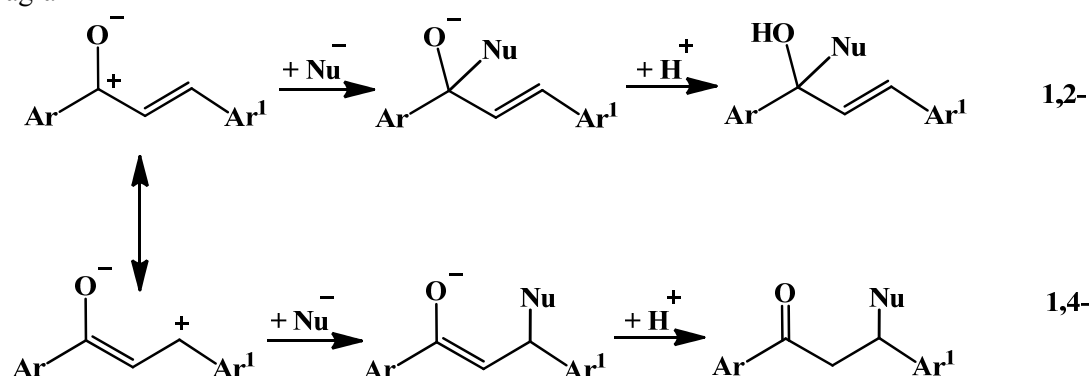


Despite a large amount of literature dealing with optimization of methods for synthesizing chalcones, a lot of authors use an exclusively traditional method of synthesis, i.e. Claisen-Schmidt condensation (mixing under basic conditions in ethanol within 3-48 hours) [31, 34-37, 54].

3. Reactivity of chalcones

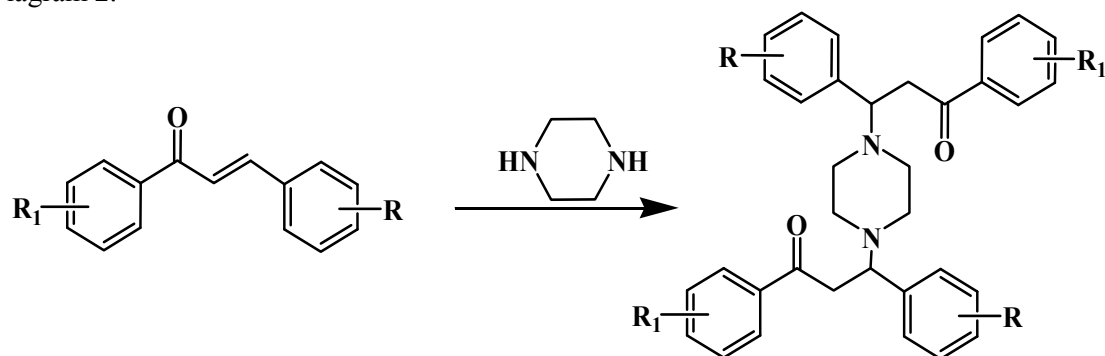
Chalcones possess high reactivity. This is connected with the presence in their molecule of two electrophilic centers: a carbonyl group and a β -carbon atom of the conjugated double bond [1]. Chalcones can react as ambiguous electrophiles as a result of delocalization of the electron density in the conjugate system $\text{C}=\text{C}-\text{C}=\text{O}$. When interacting with the chalcone, the nucleophile attacks either the carbon atom of the carbonyl group (1,2-addition) or the β -carbon atom (1,4-addition); the mechanism of the reactions is shown in Diagram 1. The nature of these two electrophilic centers in chalcones is different, which is reflected in the high regioselectivity of reactions with mono- and binucleophiles.

Diagram 1



The interaction of chalcones with piperazine usually leads to the formation of Michael bis-aza-adducts. These reactions performed under various conditions, have been repeatedly described in literature as an example of forming a carbon-nitrogen bond [55-57]. Thus, chalcones, both unsubstituted and substituted, react with anhydrous piperazine in toluene giving the corresponding Michael bis-aza-adducts [55]. Similarly there takes place a reaction in the mixture of cyclohexane ether (1:2) in the presence of calcined potassium carbonate [56]. Under ultrasonic irradiation chalcones interact with piperazine in water, also forming Michael bis-aza-adduct with a high yield [57].

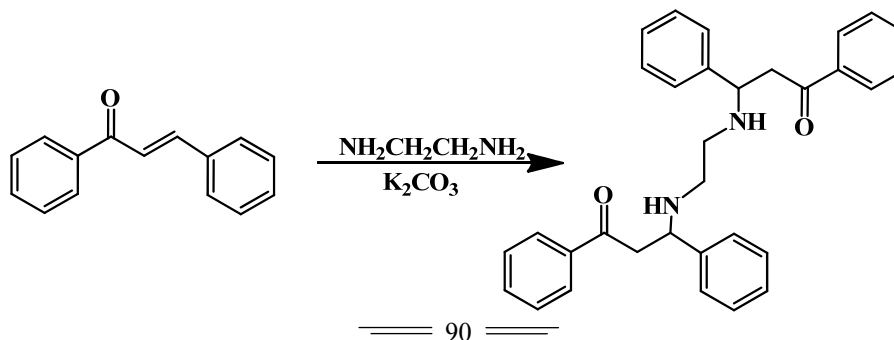
Diagram 2.



$\text{R}_1=\text{R}=\text{H}$; $\text{R}_1=\text{H}$, $\text{R}=3\text{-NO}_2$; $\text{R}_1=\text{H}$, $\text{R}=2\text{-Cl}$; $\text{R}_1=4\text{-Cl}$, $\text{R}=\text{H}$; $\text{R}_1=\text{H}$, $\text{R}=4\text{-Cl}$; $\text{R}_1=\text{R}=4\text{-Cl}$;
 $\text{R}_1=4\text{-Br}$, $\text{R}=\text{H}$; $\text{R}_1=\text{H}$, $\text{R}=4\text{-Me}$; $\text{R}_1=4\text{-Me}$, $\text{R}=\text{H}$; $\text{R}_1=\text{H}$, $\text{R}=4\text{-OMe}$; $\text{R}_1=\text{R}=4\text{-Me}$;
 $\text{R}_1=4\text{-Me}$, $\text{R}=4\text{-OMe}$; $\text{C}_6\text{H}_5\text{CH}_3$.

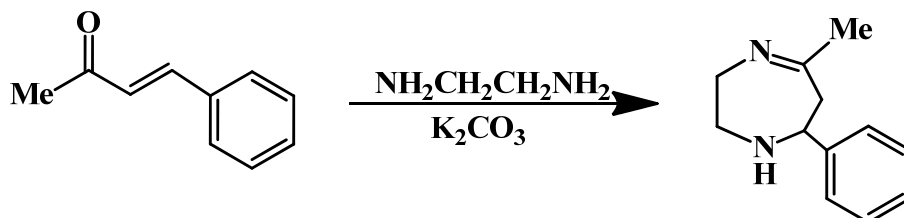
The reactions of chalcones with ethylenediamine can proceed with forming Michael bis-aza-adducts [56] or diazepines [58, 59]. Thus, the interaction of unsubstituted chalcones with ethylenediamine in low-polar solvents occurs along the path of attaching to the β -atom of carbon and leads to Michael bis-aza-adduct [56].

Diagram 3



However, the formation of Michael bis-aza-adducts is not the only way of the reaction proceeding. In [58] the reaction of chalcone with ethylenediamine there was obtained tetrahydrodiazepine with the 59% yield.

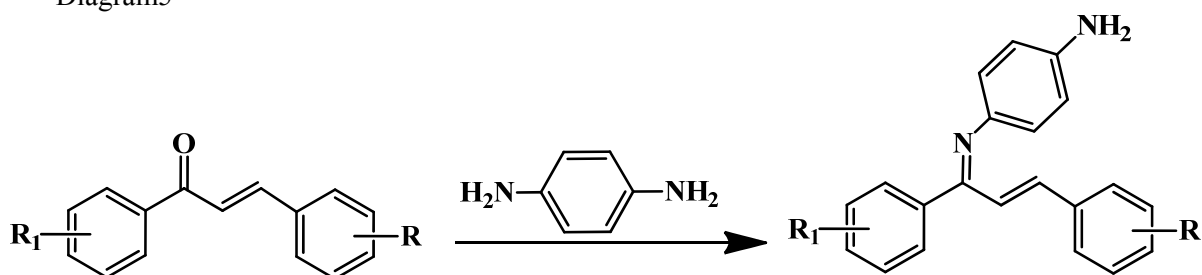
Diagram 4



The mechanism of this reaction is not described in literature, but it can be assumed that it proceeds in two stages: at first there is formed the Michael aza adduct, then there takes place its cyclization by attacking the second amino-group on the carbon atom of the carbonyl group.

The interaction of chalcones with *n*-phenylenediamine leads to the formation of Schiff bases that can then be used in synthesizing flavones. Synthesizing flavones and their derivatives attracts considerable attention due to their high antioxidant [60–63], anxiolytic [64], antitumor [65] and anti-inflammatory [66, 67] activity. In [68] the synthesis of iminoflavones is reported by the oxidative cyclization of chalconeimines. One of the stages of this synthesis is interaction of chalcones with substituted anilines, in particular, *n*-phenylenediamine, and forming the corresponding imine with a high yield. The Schiff bases that possess antibacterial activity were also obtained in [69] by the reaction of chalcones with *n*-phenylenediamine in water-alcohol alkali.

Diagram 5



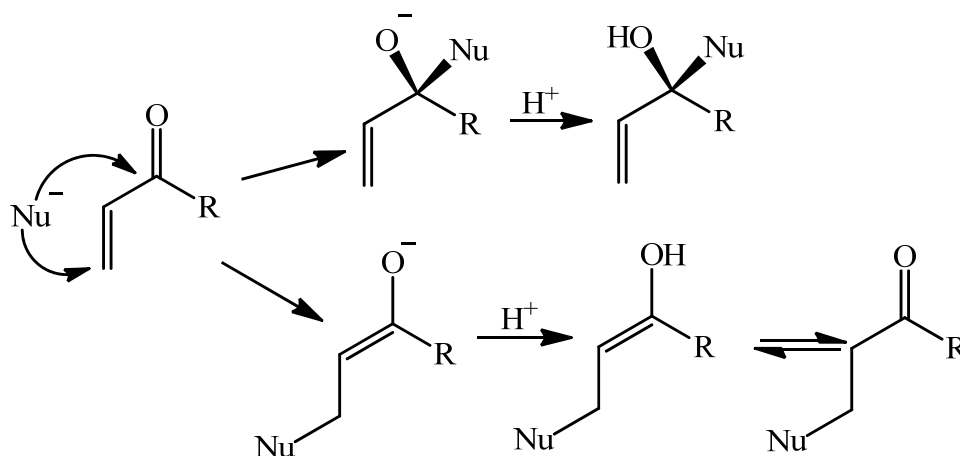
R₁=2-OH, 5-Br, R=4-OMe.

R₁=R=H, R₁=H, R=4-OMe; R₁=2-OH, R=4-NMe₂; R₁=H, R=4-NMe₂; R₁=2-OH, 5-Cl, R=4-OMe; R₁=2-OH, 5-Cl, R=H; R₁=2-OH, 5-Cl, R=4-NMe₂; R₁=2-OH, 5-Me, R=4-NMe₂.

It is known that α,β -unsaturated carbonyl compounds make it possible to synthesize practically any three-, four-, five-, six-, seven-membered carbo- and heterocycles with various substituents [1]. Therefore, chalcones are extremely popular as key intermediates in combinatorial chemistry [70]. The presence of two electrophilic centers in chalcones upon interaction with binucleophiles leads to the formation of heterocycles including annelated ones [1].

Among numerous reactions in which chalcones can participate, the interaction with binucleophilic reagents that leads to a variety of carbo- and heterocyclic compounds, in particular to substituted cyclohexanones and pyrimidines that also possess a wide spectrum of biological activity, is of particular interest.

The interaction of α,β -unsaturated carbonyl compounds (aldehydes, ketones (chalcones), acids, ethers) with nucleophiles leads to the formation of a new C-C or C-N bond. A new bond is formed between the donor and the second or fourth carbon atom of the acceptor. The first type of reaction is a simple addition via the carbonyl group, in the second case when the nucleophile is attached, the electron pair moves from the donor carbon to the acceptor oxygen.



The factors determining this process direction are charge interacting and orbital matching that are closely related to the concepts of hardness and softness of acids and bases. The interaction of a hard acid with hard bases is determined by the interaction of charges, while the reaction of a soft acid with a soft base proceeds under orbital control [71]. The relative reactivity of carbanions in the reactions of 1,2- and 1,4-addition has been considered from the standpoint of perturbation theory of molecular orbitals. Within the framework of this theory, taking into account the electronic structure of the fragment, the maximum positive effective charge on carbonyl carbon, the maximum localization of HOMO is at the β -carbon atom. The addition on the carbonyl group goes under the charge control, and 1,4-addition under the orbital control. As a consequence, all other conditions being equal, the process of nucleophile addition via the carbonyl group is favored by the charge localization at the nucleophilic center, the lowering of the HOMO energy. On the contrary, increasing the degree of the charge delocalization, increasing the HOMO level of the nucleophile promotes the flow of orbitally controlled 1,4-addition [1].

The balance between the two directions of reactions is so sensitive to various actions (solvent, catalyst, temperature) that relatively small changes are sufficient to make one of the processes dominant.

Therefore, both the advantage and the disadvantage of this reaction is the different reactivity of the nucleophilic centers, since the conditions depend not only on the structure of the reaction products, but also on their yield and purity. The development of approaches to the production of various products depending on the reaction conditions has attracted the attention of synthetics in recent years. Such processes are called "selective switch reactions". They have become widespread recently, especially for synthesizing biologically active compounds. The "switching" methods, in addition to the above-mentioned ones (solvent, catalyst, temperature), can be microwave or ultrasonic effects [72, 73].

4. Biological activity of chalcone derivatives

Compounds with the chalconic fragment show different types of biological activity. For example, they show significant activity against a variety of tumors and have chemoprotective properties. This can be attributed to their antioxidant activity [74-77]. Other important properties of chalcones are the ability to inhibit bacterial growth [78], as well as manifestation of antifungal and antiviral activity [79]. In addition, they have the ability to strengthen capillaries and can be used as anti-inflammatory agents [80]. In addition to these types of activity, they possess antimalarial [81-85], anti-cancer [86-88], larvicide [89], immunomodulating [90], antihyperglycaemic, antituberculous [91], antiprotozoal and antimitotic activity [92] and can be used as antibacterial [93, 94] and antifungal [95, 96] preparations. The inhibitory effect on enzymes, especially on the α -amylase of mammals [97], cyclooxygenase (COG) [98], monoamine oxidase (MAO) [99], leukotriene B [100], tyrosinase [101], aldose reductase [102], etc.

High biological activity manifested by the chalcones, promoted the development of studying the interaction of these compounds with various biological targets. There are numerous experimental data of the chalcone functions in plants, which make it possible to assert that many chalcones play an active physiological role in the plant organism. They can be relatively easily oxidized or reduced and their oxidation-reduction potential indicates that they take part in the metabolism. Some compounds of the

chalcone structure perform a protective function [95], the functions of respiratory catalysts and are involved in oxidation-reduction processes during respiration of plant cells.

The compounds with electron-donor substituents, for example, methoxy-, hydroxyl groups, show the greatest antimicrobial activity [103]. Chalcones containing one or two chlorine or fluorine atoms exhibit high antifungal and antimicrobial activity. Among the chalcones containing the oxathiolone fragment [104] there have been found compounds showing cytotoxicity against human cancer cells, as well as against *Micrococcus luteus*, *Staphylococcus aureus*, *Micobacterium tuberculosis* H Rv.

Interesting properties of chalcones also include initiation of apoptosis of cancer cells [105], inhibition of their mitochondrial respiration. The authors of [106] noted that chalcones with a smaller number of hydroxyl groups in rings A and B are more effective in this respect compared to chalcones containing more hydroxyl groups. This difference in activity is explained by the acidity of the phenolic OH groups. One of the widely known mechanisms according to which chalcones show cytotoxic activity is the interaction of chalcones in the mitosis phase. N.H. Nam with co-authors [106] studied the activity of the derivatives of 2', 5'-dihydroxychalcones and found that most chalcones exhibit cytotoxic activity against various lines of tumor cells.

Dehydroxyderivatives of chalcones show antioxidant activity that depends on the compound structure [107]. The mechanism of antioxidant activity of chalcones is discussed in [108]. When a chalcone molecule interacts with a radical, a phenoxide radical is formed with the *ortho*- and *para*-dihydroxylated systems of the benzene ring are systems with delocalized electrons, therefore the phenoxide radicals formed in them are readily converted into stable seven-quinone radicals that are further converted into quinones. *Meta*-dihydroxylated benzene ring system is less effective for electron delocalization, as a result of which phenoxide radicals are unable to enter further transformations. It has been established that chalcones with *ortho*- (i.e. 2', 3'- and 3', 4'-) and *para*- (i.e. 2', 5'-) substituents exhibit a very high antioxidant activity (80-90 % in comparison with the control at the concentration of 50 μ M), which is comparable with the activity of ascorbic acid and α -tocopherol. On the other hand, chalcones with *meta*- (i.e. 2', 4'- and 3', 5'-) substituents show rather sharp decrease in activity (25% vs. control) at the concentration of 200 μ M ($IC_{50} > 200 \mu$ M). These data show that the position of the two hydroxyl groups in the B nucleus is an important structural factor of their antiradical activity, while *para*-substituted compounds show a higher activity than the *ortho*-substituted ones. The variation of the substituents in the *para*-position in the A ring does not strongly affect the antiradical activity. This indicates that the electronic effects of the *para*-substituent of the benzene ring do not affect the antiradical activity.

The potential antioxidant activity of some hydroxychalcones was evaluated owing to their ability to inhibit 1,1-diphenyl-2-picrylhydrazyl radicals and free hydroxyl radicals [108]. For naringenin and phloretin, antiproliferative activity against the breast cancer cell line (MCF-7) has not been detected. But other chalcones (including 2'-hydroxychalcon) have shown antiproliferative activity at high concentrations (10.50 μ M), and at low concentrations (0.01-1 μ M) they accelerated the cell growth.

For manifesting anti-inflammatory activity of chalcones α,β -unsaturated carbonyl functional group is responsible. H.L. Yadav and co-workers [109] synthesized a series of five derivatives of chalcones and investigated their anti-inflammatory activity in rats that modeled carrageenan hind paw edema. The chalconic derivatives in the dose of 25 mg/kg fedorally, significantly inhibited the development of edema. The results of studying the anti-inflammatory activity of chalcones are also given in Ref. [50]. Activated macrophages play the key role in anti-inflammatory responses and releasing a variety of mediators, including nitric oxide (NO) that is a potential vasodilator that facilitates leukocytes migration and edema forming, as well as leukocyte activity and cytokine formation. The chalcones with substituents that increase the electron density of the Bring, for example, MeO-, BuO-, Me N-groups, do not show significant activity in inhibiting the NO production process [110].

S.J. Won et al. [111] showed that 2', 4'-dihydroxychalcone, 2'-hydroxy-2-thienylchalcone, 2'-hydroxy-3-thienylchalcone and 2', 5'-dihydroxyindol-3-yl-chalcone are potential anti-inflammatory agents.

Hyperglycemic activity of chalcones was studied in [112]. Non-insulin-dependent diabetes (Type II diabetes) is a chronic metabolic disease characterized by insulin resistance, hyperglycemia and hyperinsulinemia. From *Broussonetia papyrifera* there have been isolated substituted chalcones that selectively inhibit enzymes of protein tyrosine phosphatase (PTP1B) and aldose reductase. Their

antioxidant properties allow considering them as hyperglycemic agents, because oxidative stress also plays an important role in diabetics. 3,4-dimethoxy derivatives show a significant anti-hyperglycemic effect, while monomethoxy derivatives show reduced activity.

Chlorine-containing chalcones show significant antiparasmodial activity, and chalcones with triazole, pyrrole and benzotriazole rings possess antiparasitic activity. It has been found that the chlorine-derived chalcones with the morpholino ring possess the lowest activity. Compounds containing a triazole ring and chlorine have the greatest antiparasmodial activity, confirming the fact that small lipophilic groups containing one or more nitrogen atoms can increase antimalarial activity *in vitro*.

In vitro studies of the antiparasmodial activity of substituted [(4-Cl, 4-MeO, 3,4,5-(MeO)₃] have shown that small and medium-sized lipophilic groups containing nitrogen atoms or amine in the acetophenone fragment are potential antimalarial agents. Such compounds can provide additional hydrogen bonding to the histidine residue present in the active site of the cysteine proteinase enzyme. Antileishmanial activity [113, 114] is characteristic of chalcones with a more hydrophilic character, that is, for HO-derivatives of chalcones, as well as for chalcones with naphthalene and pyridine fragments in the A nucleus. The inhibiting activity of tyrosinase of a number of chalcones with respect to melanin formation reactions and their antioxidant potentials has been studied [115]. The position of OH groups in aromatic A and B nuclei is very important, since hydroxylation over the B ring leads to a much higher ability to inhibit tyrosinase than hydroxylation over the A ring.

5. Conclusion

Valuable pharmacological properties of natural chalcones possessing a wide spectrum of biological action allow predicting and expanding the possibilities of developing new approaches to solving the problem of increasing biological activity of this class. By changing the structure of the chalcone molecules it is possible to increase the absolute indices of their activity in biological tests. Chalcones as α,β -unsaturated ketones are of interest as starting materials for the production of unavailable derivatives of other classes of compounds, which is due to the presence of two electrophilic centers: the carbon atom of the carbonyl group and the β -carbon atom.

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О.А. Нуркенов^{1,2}, М.К. Ибраев², С.Д. Фазылов¹, А.Т. Такибаева², И.В. Кулаков³, А.Е. Туктыбаева²

¹Қазақстан Республикасының органикалық синтез және көмірхимия институты, Қарағанды, Қазақстан;

²Қарағанды мемлекеттік техникалық университеті, Қарағанды, Қазақстан;

³Ф.М.Достоевский атындағы Омск мемлекеттік университеті, Омск, Ресей

ХАЛКОНДАР–БИОЛОГИЯЛЫҚ БЕЛСЕНДІ ЗАТТАР СИНТЕЗІНДЕГІ СИНТОНДАР

Аннотация: бұл шолу мақаласында соңғы жылдардағы әдеби мәліметтер, сондай-ақ функционалды орынбасқан халкондар облысындағы авторлардың зерттеулер нәтижелері жинақталып, жүйеленген. Кең таралған табиғи халкондар, синтетикалық халкондардың алу әдістері, реакциялық қабілеті мен биологиялық қасиеттері келтірілген.

Түйін сөздер: орынбасқан ароматты альдегид, халкон, пиразолин, флавонон, цитокин, транскрипционды фактор NF-κB

О.А. Нуркенов^{1,2}, М.К. Ибраев², С.Д. Фазылов¹, И.В. Кулаков³, А.Т. Такибаева², А.Е. Туктыбаева²

¹Институт органического синтеза и углехимии Республики Казахстан, Караганда, Казахстан;

²Карагандинский государственный технический университет, Караганда, Казахстан;

³Омский государственный университет им. Ф.М. Достоевского, Омск, Россия

ХАЛКОНЫ - СИНТОНЫ В СИНТЕЗЕ БИОЛОГИЧЕСКИ АКТИВНЫХ ВЕЩЕСТВ

Аннотация: в обзорной статье обобщены и систематизированы литературные данные последних годов, а также результаты исследований авторов в области функционально замещенных халконов. Приведены наиболее распространенные природные халконы, методы получения, реакционная способность и биологические свойства синтетических халконов.

Ключевые слова: замещенный ароматический альдегид, халкон, пиразолин, флавонон, цитокин, транскрипционный фактор NF-κB.

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P.Zh. Zhanymkhanova, E.M. Gabdullin, A.Zh. Turmukhambetov, S.M. Adekenov

JSC International Research and Production Holding "Phytochemistry",
4 M. Gazaliev str., 100009, Karaganda, Kazakhstan,
tel./fax: +7(7212) 433127, e-mail: phyto_pio@mail.ru

ALKALOID-BEARING SPECIES OF THE GENUS *ACONITUM* L.

Abstract. Analytical review of alkaloid-bearing plants of the genus *Aconitum* L. has been carried out. The obtained data will serve as a basis for scientific research of some plant species in the genus *Aconitum* L., isolation of alkaloids including high purity aconitine to create a new drug substance.

By identifying specific habitats of species of this genus in the flora of Kazakhstan, it is established that most herbarium materials have been collected in mountainous floristic regions of the flora of Kazakhstan, which justifies the need to study samples of the genus *Aconitum* L. from the indicated floristic areas. The herbarium fund of the International Research and Production Holding "Phytochemistry" JSC (KG) includes herbarium materials of 9 species of the genus *Aconitum* L., of which the most common species are *Aconitum leucostomum* Worosch. and *Aconitum monticola* Steinb. forming large thickets in the nature.

Keywords: *Aconitum* L., alkaloids, chemical study, herbarium materials, cameral treatment.

Representatives of the genus *Aconitum* L. belong to one of the most valuable alkaloid-bearing plants of the family *Ranunculaceae*, and are a rich source of polyfunctional heterocyclic compounds - diterpene alkaloids. Plants of the genus *Aconitum* L. are accessible and widely spread in Kazakhstan, CIS countries, China and Central Asia; however, they differ in qualitative composition and content depending on the area of their growth. The increased attention of researchers to diterpene alkaloids is due to the known complexity of their structure resulting in a broad spectrum of pharmacological activity. Diterpene alkaloids have a wide range of biological activities: anti-inflammatory, local anesthetic, antiarrhythmic, antispasmodic, antitumor, and muscle relaxant, which allows them to be considered as a source of promising pharmacological compounds.

The pharmacological study of plants of the genus *Aconitum* L. revealed that during the flowering stage all the aerial parts - stalks, leaves, and flowers are very poisonous. Moreover, the most deadly are rhizomes and tubers of the plant when the accumulation of alkaloids occurs. It has been determined that in parts of this plant species the amount of alkaloids gradually increases during the whole vegetative period and reaches its maximum in the autumn.

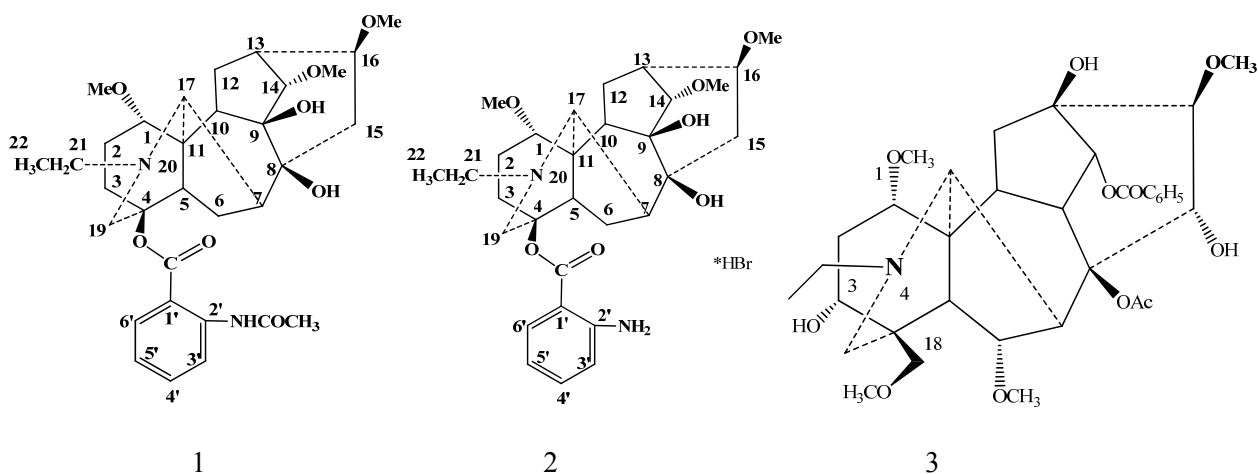
Aconitum species are of interest as medicinal plants because they have numerous isoprenoid compounds as major secondary metabolites, i.e. tetracyclic diterpenoid alkaloids. The structure of isoprenoids of the genus *Aconitum* is unusual since the lowest terpenoids (mono-C-10 and C-15 sesquiterpenes) are present only in small amounts in these plants, mainly in flowers, whereas all other parts accumulate diterpenoid compounds of peculiar structural types.

Over 70% of modern homeopathic remedies are produced from medicinal plant materials. Plants of the genus *Aconitum* L. are one of the most popular in homeopathy. Homeopathic Pharmacopoeias of the leading countries of the world (Germany, France, the USA, and others) include aconite preparations obtained from the following plant species: *Aconitum napellus* L., *Aconitum ferox* Wall., *Aconitum lycoctonum* L.

According to the Flora of the USSR, there are over 300 *Aconitum* species all over the world, 70 of which are in the territory of the former USSR. In turn, 14 species are found in the flora of Kazakhstan.

They grow in the mountains on forest and subalpine meadows, among bushes [1-2]. N.G. Gemedzhiyeva in her research [3-4] noted that all 14 species belong to alkaloid-bearing plants.

Scientists of a number of countries are conducting rigorous studies of plants of the genus *Aconitum* L. A great contribution to the study of plant species of the genus *Aconitum* has been made by Uzbek researchers S.Yu. Yunusov, M.S. Yunusov, V.A. Telnov, E.F. Akhmetova, I.A. Bessonova, as well as foreign scientists H. Takayama, W.S. Pelletier, and others who determined the main composition of alkaloids. They developed cost-effective and environmentally-friendly production technologies of the *Allapinin* on the basis of lappaconitine **1** from the roots and rhizomes of *Aconitum leucostomum* Worosch. and *Aconitum septentrionale* Koelle.; *Antiaritm* drug **2** from the by-products of allapinin production, cumulative antiarrhythmic drugs *Aklezin* from the aerial parts of *Aconitum leucostomum* Worosch., and *Aksaritim* from the rhizomes of *Aconitum septentrionale* Koelle.. The production technology of the *Aconitine* bioreactant substance **3** has been developed from the tubers of *Aconitum soongaricum* Stapf. [5-12].



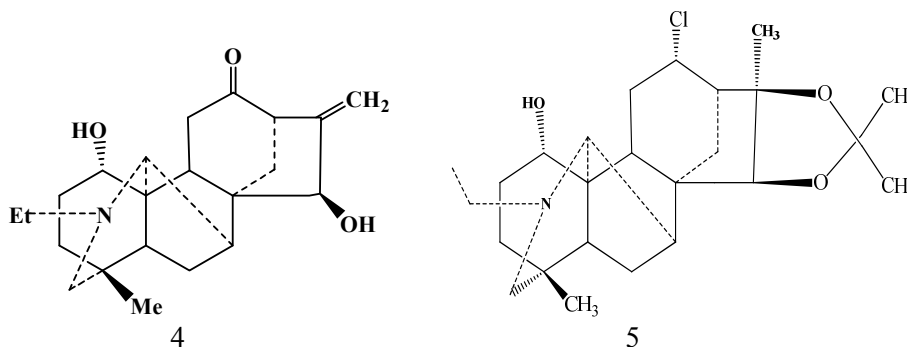
Thanks to the research of academicians-chemists S.Yu. Yunusov and M.S. Yunusov and academician-cardiologist E.I. Chazov alkaloid lappaconitine has firmly taken its place in a series of antiarrhythmic agents in the form of *Allapinin* drug. It is indicated for supraventricular and ventricular extrasystoles, paroxysmal forms of flicker and atrial flutter, tachycardia. Lappaconitine is worth mentioning because it happened to be susceptible to the synthetic transformations resulting in substances with the preserved pharmacological activity but without major harmful side effects. It should be noted that the introduction of a bromine atom into lappaconitine molecule leads to a compound with a 5 times lower toxicity and 10 times higher activity as an antiarrhythmic drug. Lappaconitine is produced by two species *Aconitum lycoctonum* L. and *Aconitum septentrionale* Koelle. According to the research of a prominent botanist N.I. Fedorov, only in the territory of Bashkiria the available stock of the roots of *Aconitum lycoctonum* L. is sufficient to meet the demands of the health care system of Russia.

Several *Aconitum* species, of which the most promising producer is *Aconitum soongaricum* Stapf, contain aconitine. Due to the highest toxicity this alkaloid has not been applied in medicine. However, experimental pharmacology could not have been conceived without it. Unlike other antiarrhythmics which influence only the calcium channels and cover both the calcium and sodium channels of arrhythmia, aconitine is a selective sodium channel blocker. The studies of antiarrhythmic drugs without aconitine are unreliable.

In 1820, Peschier was the first who pointed out that aconitine is present in the leaves of *Aconitum*. Geiger and Hesse isolated aconitine from the parts of *Aconitum* in 1838, and Morzon in 1839; while Plaita in 1850 proposed a chemical formula for amorphous aconitine [13]. Aconitine is one of the major alkaloids related to some of the extremely toxic ones, which are contained in some *Aconitum* species [14].

Alkaloid songorine **4** has a more balanced structure in terms of functionalization; it exhibits an effect on the central nervous system. It is produced by *Aconitum barbatum* Pers. spread in Altai, which can be cultivated.

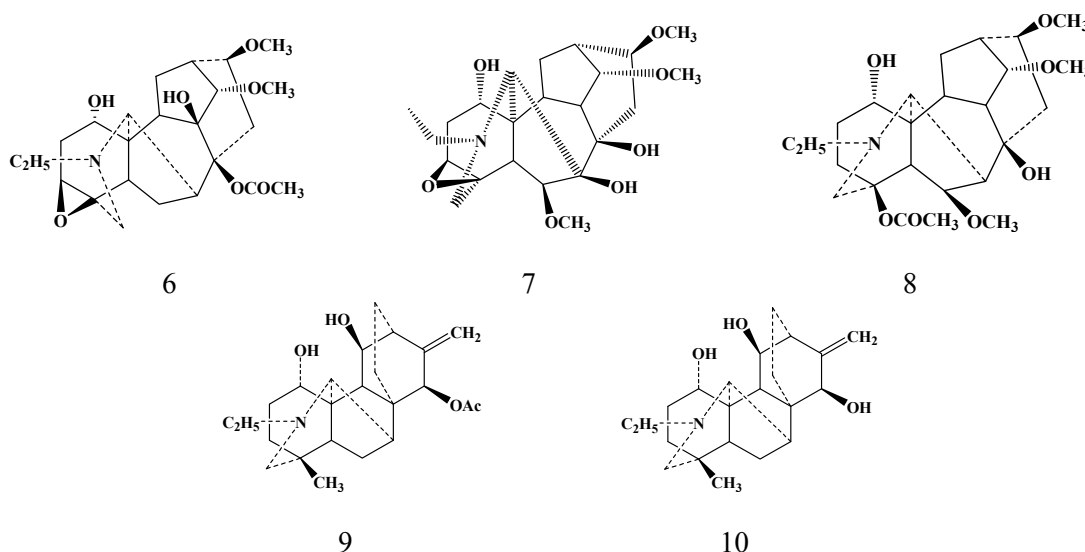
Alkaloids aconitine, mesaconitine, napelline, aconifine, 8-acetylcelsine have been isolated during the chemical studies of *Aconitum karakolicum* Rapaics., *Aconitum altaicum* Steinb., and *Aconitum kirinense* Nakai. Aconitine and a novel alkaloid aconifine **5** have been isolated for the first time from *Aconitum karakolicum* Rapaics. and *Aconitum altaicum* Steinb.. *Aconitum soongaricum* Stapf. and *Aconitum karakolicum* Rapaics. species are closely related to each other morphologically [15-20].



Researchers isolated alkaloids talassamine, talatizamine, 14-*O*-acetyltalatizamine, isotalatizidine, isoboldine, talatizidine, crystalline hydrochloride from *Aconitum talassicum* M. Pop. Extraction of *Aconitum talassicum* M. Pop. was carried out with chloroform, with the raw material preliminarily alkalinized with bicarbonatum natrium, then the extract was acidified with sulfuric acid and the alkaloids separated with chloroform. The sum of alkaloids was eluted with a chloroform-methanol (100:1) mixture on a silica gel column followed by recrystallization with methanol [21-23].

Researchers of the Institute of Organic Chemistry of the UrB RAS (Ufa) isolated 6 previously known alkaloids hypaconitine, mesaconitine, neoline and three aporphine alkaloids glaucine, N-methylaurotetanine, and isoboldine from *Aconitum neosachalinense* H. Lev.. The extraction was performed with water in the presence of acetone followed by separation on a column [24].

The Russian scientists [25] developed an isolation method for the diterpene alkaloids from *Aconitum kirinense* Nakai. growing on the territory of Primorsky Krai. The alkaloids were separated by gas and high performance liquid chromatography (GC and HPLC) methods with mass spectrometric detection of separated peaks and fragmentation in atmospheric-pressure chemical ionization (APCI), atmospheric-pressure ionization - electrospray (API-ES), and electron impact modes. Using liquid chromatography – mass spectroscopy (LC-MS) with fragmentation in APCI and API-ES modes, the following 6 diterpene alkaloids were identified in *Aconitum kirinense* Nakai.: 8-acetylcelsine **6**, tugiaconitine **7**, akiramine **8**, kirinine **9**, lepenine **10**.



During the study of callus formation of *Aconitum barbatum* Pers., the optimal conditions for the cell

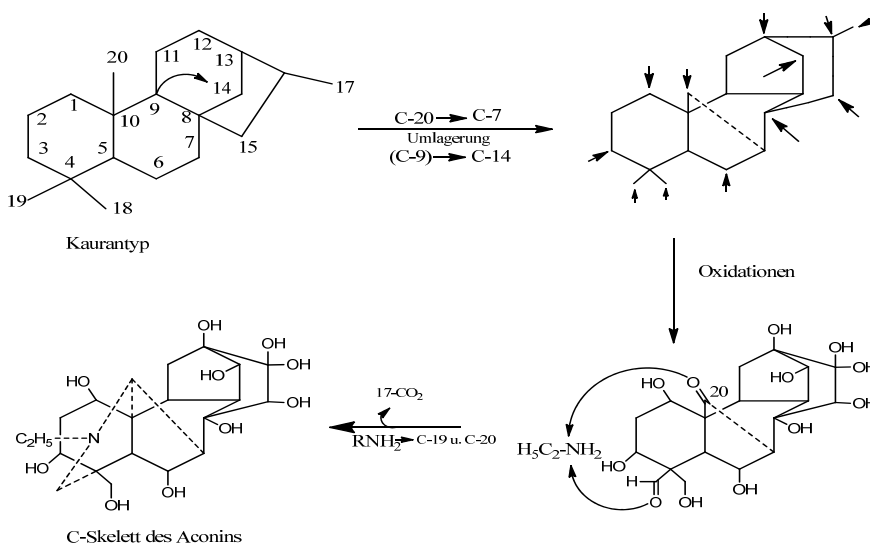
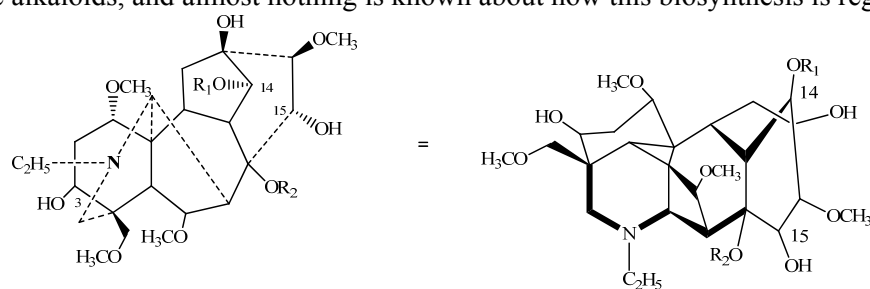
culture of this plant were selected, callus culture viability was determined, the sum of alkaloids was obtained from the callus mass of intact plant raw materials, individual diterpene alkaloids were isolated and purified using a liquid column chromatography. It has been found that the tissue culture contains the following alkaloids: songorine, songoramine, napelline, 12-*epi*-napelline N-oxide, and mesaconitine [26].

The Chinese scientists were the first to isolate C19-diterpene alkaloids habaenine C, vilmorrianine C, classicauline C from *Aconitum habaense* W.T.Wang. [27].

Scientists from Georgia conducted a chemical study of underground organs of *Aconitum orientale* Mill. and *Aconitum nasutum* Fisch. ex Reichenb. It was determined that both species *Aconitum* L. of the flora of Georgia have alkaloids aconitine, lappaconitine, and karakoline. In *Aconitum orientale* Mill., there are bases of ranaconitine, gigactonine, licoctonine, and in *Aconitum nasutum* Fisch. ex Reichenb. talitizamine, cammaconine, aconisine [28-29].

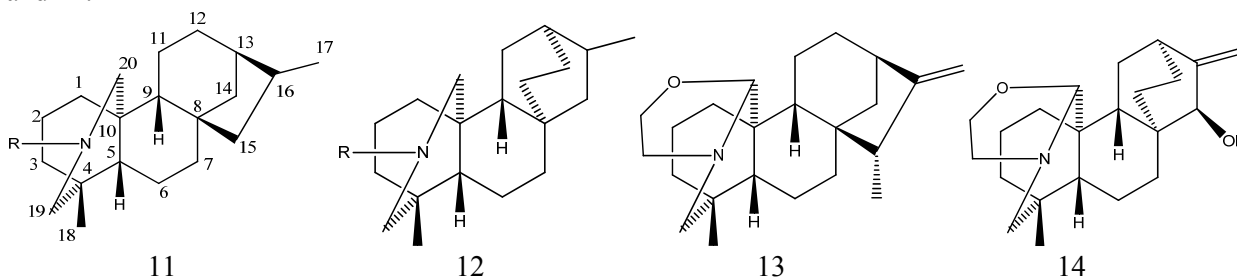
All *Aconitum* diterpene alkaloids are characterized by a high density of oxygen-containing functional groups, but aconitine molecule is an unconditional record holder. It is likely that the highest saturation by these groups is the reason of an extreme toxicity of aconitine.

Biosynthesis, pharmacological activity, and also the dynamics of accumulation of diterpene alkaloids of some plant species of the genus *Aconitum* have not been studied in full. Biogenetically, the aconine bases are most likely derived from tetracyclic or pentacyclic diterpenes in which the nitrogen atom of methylamine, ethylamine, or β -aminoethanol binds to C17 and C19 in the C19 diterpenoid skeleton, and to C19 and C20 in the C20 diterpenoid skeleton to form a substituted piperidine ring. That is why the aconitine-type compounds are considered as alkaloids *sui generis*, because their nitrogen is not derived from an amino acidic metabolism. They are defined as pseudo-alkaloids. Little is known about how plants synthesize these alkaloids, and almost nothing is known about how this biosynthesis is regulated.



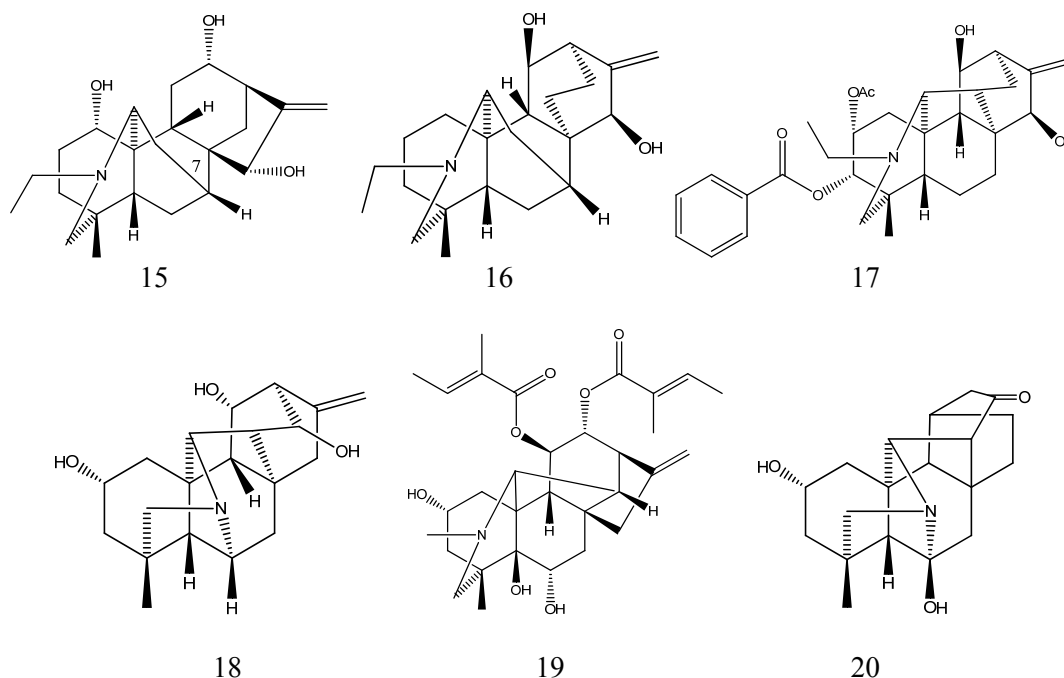
Their biogenetic precursors are the diterpenoids of the ent-kauran and atisiran series. In both cases,

during the biosynthesis an additional nitrogen-containing cycle is formed in such a way that the heteroatom becomes a bridge between the C19 and C20 atoms. In this case, two structural subtypes, C20 and C19, which are designated by the number of carbon atoms of the cyclic skeleton, are distinguished. In contrast, C20 alkaloids are derived from two carbon frameworks **11** and **12**. In specific substances, these carbon skeletons are usually framed by oxygen-containing substituents, as in veathine **13** and atizine **14**, giving the names to the corresponding subgroups of the C20 series. In both cases, there are frequent cases of the formation of additional hetero- or carbocycles in addition to those already present in structures **13** and **14**.



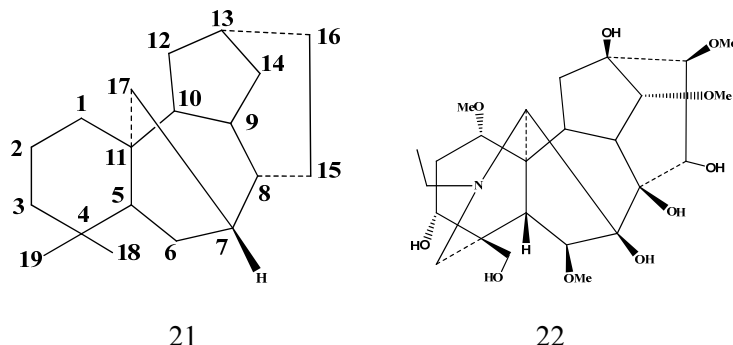
R = H, Me, Et

Additional cycles can arise by creating bonds between C20 and C7 atoms, as well as C20 and C14 atoms. In the first case, a cyclic system is constructed like in the alkaloids napelline **15** and denudatine **16**. The second variant is realized in the hedagine molecule **17**. In the structures of the latter type, it is possible to form another cycle by binding the nitrogen atom to the C6 carbon as in getisine **18**. All compounds with the carbon-nitrogen skeleton are classified as the getisine group. In a small family of anopterin **19**, C20 and C14 atoms are bound by carbon-carbon bond to the ent-kauran-type skeleton. Alkaloid delnudine **20** also belongs to the C20 series. Its molecule is a result of the getisine precursor rearrangement.



The base of the structure of the diterpenoid alkaloids of the C19 series is the rearranged carbon skeleton of kauran **21**, also called daconane. Like in C20 compounds, a nitrogen bridge is formed between the C17 and C19 atoms. By the name of the alkaloid lycoctonine **22**, a carbon-nitrogen skeleton in its base is also called lycoctonane. Within the C19 alkaloid family, two main subgroups are distinguished. Having the same carbon-nitrogen skeleton, they differ from each other by the substitution pattern at C6 and C7

atoms. To the lycotoxinesubgroup are referred bases with a hydroxyl substituent at the C7 position and a β -methoxy one at the C6 atom. The presence of an α -glycol moiety is also characteristic for this subgroup of substances. Aconitine is a representative of the other subgroup of C19 alkaloids bearing its name. There are no substituents at the C7 atom, and a methoxy group at the C6 atom has an α -orientation.

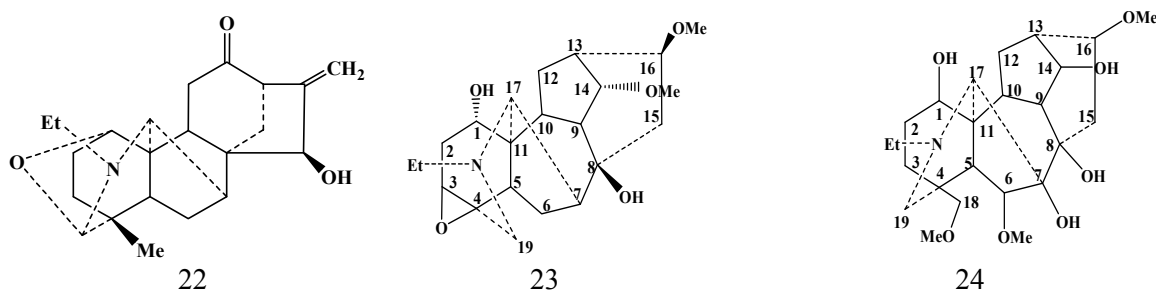


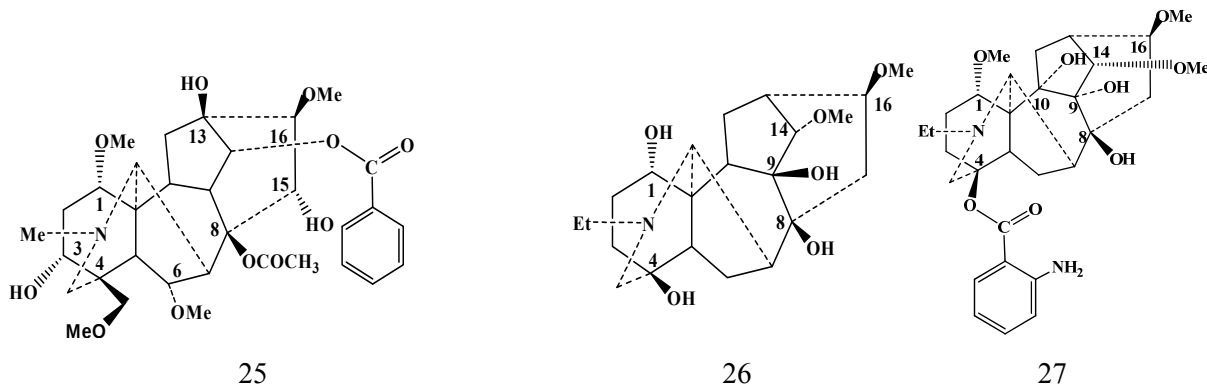
The group of C19 diterpenoid alkaloids is quite numerous. By 1987, 175 natural representatives of this group had been known. Over 150 of them were isolated from plants of the genera *Aconitum* L. and *Delphinium* L.

C19 and C20 diterpenoid bases in their majority are highly poisonous substances. Thus, LD 50 of aconitine is only 0.22 mg/kg. Due to this fact, *Aconitums* and *Delphiniums* are among the deadliest plants of the middle latitudes. The toxic effect of their nitrogen metabolites is realized in a disruption of the nervous system activity and a heart function. In small doses, many of these substances exhibit anti-inflammatory, analgesic, antiarrhythmic, anti-epileptic properties. Moreover, different alkaloids have their own spectrum of physiological effects. For instance, aconitine is a strong analgesic agent, while lycotoxine is completely deprived of this action. The practical application of diterpenoid alkaloids as drugs is restricted due to the poisoning hazard in case of an overdose. Despite this fact, *Allapinin* (lappaconitine hydrobromide) is produced in Russia and is known as one of the best antiarrhythmic drugs.

For a number of years, JSC International Research and Production Holding "Phytochemistry" have been working on isolation and study of alkaloids from plant species of the genus *Aconitum* L. A general production technology of alkaloids from plant raw material has been developed using conventional extraction techniques and a column chromatography. The isolation methods are specific for each alkaloid and have their own peculiarities, which makes it possible to obtain alkaloids with 95-99.9% purity according to the HPLC analysis results [30, 31].

During the chemical study of roots of *Aconitum monticola* Steinb. we have isolated and identified alkaloids songorine **4** (yield 0.1%), the accompanying alkaloid songoramine **22**, monticamine **23**, delcosine **24**. Delcosine has been isolated from *Aconitum monticola for the first time. The chemical composition of *Aconitum leucostomum* Worosch. has been studied and four main compounds have been isolated, they are as follows: mesaconitine **25**, lappaconidine **26**, sepaconitine **27**, lappaconitine **1**. X-ray diffraction analysis has been carried out for the first time to determine the spatial structure of a lappaconitine molecule [32-34].*





The optimal conditions for separation and analysis of alkaloids songorine, lappaconitine, and associated components have been determined by HPLC. The method of quantitative analysis of the investigated compounds has been developed for the plants of *Aconitum soongaricum* Stapf., *Aconitum anthoroideum* DC., and *Aconitum villosum* Reichenb., growing on the territory of Kazakhstan. The content of alkaloids in plants under study varies according to HPLC data, i.e. songorine from 0.01% to 0.23%, lappaconitine from 0.01% to 0.04% of the air-dry raw materials [35].

Phytochemical screening of the harvested wild samples from the genus *Aconitum* L., allowed us to establish the pronounced antibacterial activity of the cumulative extract from *Aconitum anthoroideum* DC., an analgesic activity of the cumulative extract from *Aconitum leucostomum* Worosch. and *Aconitum villosum* Reichenb., and a cytotoxic activity of extracts from *Aconitum monticola* Steinb., *Aconitum anthoroideum* DC., *Aconitum leucostomum* Worosch., and *Aconitum villosum* Reichenb. Fl. Alt. The expressed antiviral activity of lappaconitine and the sum of alkaloids from *Aconitum monticola* Steinb. and *Aconitum anthora* have been determined for the first time against the carnivore plague virus and infectious rhinotracheitis, which makes them promising ingredients for the development of a new drug [36].

It has been revealed that the main components of *Aconitum monticola* Steinb. are songorine and songoramine **22**; *Aconitum soongaricum* Stapf. - aconitine **3** and delcosine **24**; *Aconitum leucostomum* Worosch. - lappaconitine **1**.

In the herbarium fund of JSC International Research and Production Holding "Phytochemistry", there are collections of 9 species from the genus *Aconitum*, the most common of which are *Aconitum leucostomum* Worosch. and *Aconitum monticola* Steinb. forming large thickets in the wild.

We have conducted a camera treatment of herbarium materials of *Aconitum* species in the herbarium fund of JSC IRPH «Phytochemistry» (KG) to identify the specific habitats of plants from this genus in the flora of Kazakhstan.

***Aconitum monticola* Steinb.** in Fl. URSS. 7 (1937) 730, 209. - Gamajun. in Fl. Kazakh. 4 (1961) 52, tab. 6, fig. 1. - Vorosch. in Bull. Main bot. garden, 72 (1969) 37. - *A. pallidum* auct. non Rchb.: Kar. et Kir. in Bull. Soc. Nat. Mosc. 15 (1842) 138. - *A. lycoctonum* auct. non L.: O. et B. Fedtsch. in Tr. Society nat. Kazan. Univ. 33, 3 (1899) 79, quoad var. *pallidum*. - O. et B. Fedtsch. Conspect. Fl. Turk. 1 (1906) 22, quoad var. *pallidum*. Type in Leningrad.

Herbarium collections: East Kazakhstan region, the Koksur ridge, a forest meadow. 14.VIII.2014; Almaty region, Zhungarsky Alatau, in the vicinity of Lepsinsk village, the lower part of the ravine Rusachka. 10. VII.2000.

***Aconitum leucostomum* Worosch.** Bull. Main. bot. garden, 11 (1952) 62. - *A. excelsum* p. p. non Rchb. Fl. USSR, VII (1937) 201; Kryl. Fl. West. Sib. V (1931) 1151. - *A. vulparia* C.A. Mey. ex Ldb. Fl. Alt. II (1830) 287, non Rchb. Type in Vienna.

Herbarium collections: Karaganda region, the Karkaraly mountains, in the vicinity of Lake Pashennoe, in the floodplain by the stream. 16.VI.1976 (KG); East Kazakhstan region, in the

neighborhood of Leninogorsk, Ivanovsky ridge, larch planting site. 21.VII.1976 (KG); Karaganda region, Karkaralinsk district, the surroundings of Shaitan-kul lake, the shore by the stream. 7.VII. 1984 (KG); East Kazakhstan region, in the vicinity of Leninogorsk, the linear albumen of the field pit, the sole of the mountain 23.VIII. 1985 (KG); East Kazakhstan region, the road Ust-Kamen - Leninogorsk, in the vicinity of Bystruha village, the slopes of the mountains. 23.VIII.1985 (KG); Semipalatinsk region, near the village Alekseevka, the Tarbagatai mountains. 10.VII.1994 (KG); Almaty region, Aksai gorge of Zailiysky Alatau 2200 m, along the Aksay river, 12.VII.2000 (KG); East Kazakhstan region, Listvyaga ridge, the Upper Katun district, herb meadows at foothills, 2100 m above sea level. 26.VII.2004 (KG); East Kazakhstan area, Western Altai, Ivanovsky ridge, thinned larch-cedar forest. H=1800 m. 11. VIII.1997 (KUZ); Kazakhstan, East Kazakhstan region, Western Altai, Ivanovskiy range. Fir-birch forest. H=1700 m. 08.VII.1997 (KUZ); East Kazakhstan region, Western Altai, Ivanovsky range, a temporary watercourse side. A high-grass alpine meadow. H=1900 m. 11.VIII.1997 (KUZ); East Kazakhstan region, Western Altai, Ivanovsky range, 4 km north-east. peak of Vysheyvanovsky Belok. Alpine meadow. H=1900 m. 08.VII.1997 (KUZ); East Kazakhstan region, Western Altai, Ivanovsky range, a temporary watercourse side. A high-grass alpine meadow. H=1900 m. 27.VII.1997 (KUZ).

***Aconitum septentrionale* Koelle.** 1786, Spicil. Observ. Acon. : 22; Friesen, 1993, Fl. Sib. 6.: 138.

Herbarium collections: Kazakhstan, Pavlodar region, Bayanaul mountains, glades at the foothills. 08.VIII.2006. (KUZ).

***Aconitum anthoroideum* DC.** in Syst. nat. 1 (1818) 366. - Gamagun. in Fl. Kazakh. 4 (1961) 53, tab. 7, fig. 3. - Vorosch. in Bull. Main Bot. garden of the Academy of Sciences of the USSR. 72 (1969) 37. A. Anthora var. anthoroideum Rgl. in Ind. Sem. Hort. Petropol. (1861) 41. - Kryl. Fl. Sib. Occid. 5 (1931) 1147. - A. anthora auct. non L. : O. et B. Fedtsch. in Tr. Society Nat. Kazan. Univ. 33, 3 (1899) 79. - O. et B. Fedtsch. Consp. Fl. Turk. 1 (1906) 22. - Steinb. in Fl. URSS. 7 (1937) 190, quoad pl. ex Dshung. et Tarb. Type in London.

Herbarium collections: East Kazakhstan region, in the vicinity of Leninogorsk down the road to Bogdanicha. 06. VIII.1963 (KG); East Kazakhstan region, Alpine meadows near the Topolovka river (near Katun village) 28. VII.2004 (KG); East Kazakhstan region, in the vicinity of Zavodinka village. 01.VIII.2012 (KG); East Kazakhstan region, Western Altai, Ivanovsky ridge, eastern foothills of the peaks Vysheyvanovsky Belok. Moraine. H=2000 m. 26.VII.1997. VII (KUZ); East Kazakhstan region, Western Altai, Ivanovsky ridge, northern spurs of Vysheyvanovsky Belok peak, tundra. H=2100 m. 22.VII.1997 (KUZ).

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Herbarium collections: East Kazakhstan region, Listvyagaridge, 15 km down the village Kegi, a shrubby herbal forest edge. 02.08.2004.

***Aconitum altaicum* Steinb.** Fl. USSR, VII (1937) 731, 222. - *A. napellus* var. *alpinum* Rgl. Ind. Sem. Hort. Bot. Petropol. (1861) 45 p.p.; Kryl. Fl. West. Sib. V (1931) 1149. Type in Leningrad.

Herbarium collections: East Kazakhstan region, Narymsky ridge, in the neighborhood of village Novoberezovka, vally of the river Terekty. 1120 m. above sea level. 26.VIII.1976 (KG); East Kazakhstan region, in the vicinity of Leninogorsk. 09.IX.1982 (KG).

***Aconitum volubile* Pall.** ex Koelle, Spicil. Acon. (1788) 21; Fl. USSR, VII (1937) 213; Kryl. Fl. West. Sib. V (1931) 1150. Type in London. - *A. tortuosum* Willd. Enum. Hort. Berol. (1809) 576.

Herbarium collections: East Kazakhstan region, branch of the state farm Ulanovskiy, natural boundary Katre. 27.VIII.1985 (KG); East Kazakhstan region, Ridder, in the neighborhood of the village Kedrovka. 05.VIII.2012 (KG); East Kazakhstan region, Western Altai, northern foothills of Ivanovsky ridge, stow Gray Meadow, floodplain of the river White Uba. H=1200 m. 14.VIII.1997 (KUZ).

***Aconitum barbatum* Pers.** Syn. Pl. II (1807) 83; Fl. USSR, VII (1937) 204; Kryl. Fl. West. Sib. V (1931) 1153 - *A. sibiricum* Poir. Encycl. meth. Suppl. I (1810) 113. - *A. hispidum* DC. Syst. Nat. I (1818) 367. - *A. Gmelini* Rchb. Uebers. Gatt. Aconitum (1819) 63. - *A. ochranthum* C. A. M. in Ldb. Fl. Alt. II (1830) 285. - *A. lycoctonum* var. *barbatum* Rgl. Bull. Soc. Nat. Mosc. XXXVI, 3 (1861) 77. Type in London.

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Thus, based on the results of cameral treatment of herbarium materials in the herbarium fund of JSC IRPH "Phytochemistry" (KG), it has been established that most herbarium collections were harvested in mountainous floristic regions of the flora of Kazakhstan, which highlights the need to study samples from the genus *Aconitum* in these floristic areas. The herbarium fund contains herbarium materials of 9 species of the genus *Aconitum*, of which the most common are *Aconitum leucostomum* Worosch. and *Aconitum monticola* Steinb. forming large thickets in the nature.

The conducted analytical review will serve as a ground for phytochemical studies of plants of the genus *Aconitum*. In the course of future research, we plan to extract alkaloids from some plants of the genus *Aconitum* and carry out chemical transformations of these alkaloids to obtain new substances with the improved physico-chemical properties, a more pronounced biological activity, a lower toxicity, and a prolonged action as compared to the original natural analogues. The promising sources for production of biologically active alkaloids, including aconitine, are *Aconitum soongaricum* Stapf., *Aconitum monticola* Steinb., and *Aconitum leucostomum* Worosch., growing in the territory of Kazakhstan.

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П.Ж. Жанымханова, Е.М. Габдуллин, А.Ж. Тұрмұхамбетов, С.М. Әдекенев

«Фитохимия» халықаралық ғылыми-өндірістік холдингі» АҚ, Қарағанды қ., 100009, М. Ғазалиев көш., 4,
тел./факс: 8(7212)433127, e-mail: phyto_pio@mail.ru

***ACONITUM* L. ТУЫСТАС ӨСІМДІКТЕРДІҢ АЛКАЛОИДТЫ ТҮРЛЕРІ**

Аннотация. *Aconitum* L. туыстас өсімдіктердің алкалоидты түрлеріне талдамалы шолу жүргізілді. Алынған деректер *Aconitum* L. туыстас өсімдіктердің бірқатар түрлерін ғылыми зерттеу, сондай-ақ жаңа дәрілік зат жасауға арналған алкалоидтарды, соның ішінде тазалығы жоғары аконитинді бөліп алу үшін негіз болады.

Аталған өсімдік түрлерінің Қазақстан флорасындағы нақты өсу орындарын анықтау бойынша кеппешөп материалдарының басым бөлігі Қазақстан флорасының таулы флоралық аудандарында жиналғаны белгілі болды. Бұл аталған флоралық аудандардағы *Aconitum* L. туыстас өсімдіктердің үлгілерін зерттеу қажеттілігін көрсетеді. «Фитохимия» халықаралық ғылыми-өндірістік холдингі» АҚ-да (KG) *Aconitum* L. туыстас 9 өсімдік түрінің кеппешөп материалдары бар, олардың ішінде табиғатта үлкен тоғайларды құрайтын *Aconitum leucostomum* Worosch. және *Aconitum monticola* Steinb. өсімдік түрлері неғұрлым жиі кездеседі.

Түйін сөздер: *Aconitum* L., алкалоидтар, химиялық зерттеу, кеппешөп материалдары, камералық өңдеу.

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П.Ж. Жанымханова, Е.М. Габдуллин, А.Ж. Турмухамбетов, С.М. Адекенов

АО «Международный научно-производственный холдинг «Фитохимия», г. Караганда, 100009,
ул. М. Газалиева, 4, тел./факс: 8(7212)433127, e-mail: phyto_pio@mail.ru

АЛКАЛОИДОНОСНЫЕ ВИДЫ РОДА *ACONITUM* L.

Аннотация. Проведен аналитический обзор алкалоидоносных растений рода *Aconitum* L. Полученные данные послужат основой для научных исследований некоторых видов растений рода *Aconitum* L., выделению алкалоидов, в том числе аконитина высокой чистоты для создания нового лекарственного вещества.

По выявлению конкретных мест произрастания видов данного рода во флоре Казахстана, установлено, что большинство гербарных материалов собраны в горных флористических районах флоры Казахстана, что свидетельствует о необходимости изучения образцов рода *Aconitum* L. из указанных флористических районах. В гербарном фонде АО «Международный научно-производственный холдинг «Фитохимия» (KG) имеется гербарные материалы 9 видов рода *Aconitum* L., из них наиболее часто встречаются виды рода *Aconitum leucostomum* Worosch. и *Aconitum monticola* Steinb., образующие большие заросли в природе.

Ключевые слова: *Aconitum* L., алкалоиды, химическое изучение, гербарные материалы, камеральная обработка.

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D.Zh. Kalimanova, A.D. Kalimukasheva, N.Zh. Galimova

Atyrau State University named by Kh. Dosmukhamedov, Atyrau, Kazakhstan

E-mail: dana80_04@mail.ru, aral1959@mail.ru, gnazymzh@gmail.com

**RESULTS OF GEOCHEMICAL INVESTIGATIONS
OF THE NORTH-EASTERN PART OF CASPIAN (OIL PRODUCTS
IN THE DONAL DEPOSITS IN THE URAL RIVER)**

Abstract. This article examines the results of geochemical studies of the north-eastern part of the Caspian Sea and the determination of petroleum products in bottom sediments in the Ural rivers. The analysis of the concentrations of oil products, organ chlorine pesticides, polychlorinated biphenyls, synthetic surfactants and phenols in the landfill is given. The region of the Northern Caspian adjacent to the Kazakhstan coast was chosen as the study area. The area under investigation is characterized by a gentle slope of the bottom and a slow increase in depth. The soils here are mostly muddy and silt or sandy.

Seasonal fluctuations in the level of the Caspian Sea do not exceed a few dm. Northeast coast of the Caspian Sea is characterized by high surges.

The site of the research is unique both in geochemical and hydro-chemical regimes, and in hydrobiological characteristics. Complex studies of the main geochemical, hydrological and hydro-chemical characteristics at stations located at the surface and bottom of the sea were carried out. Observation of bottom sediments of the Eastern part of the Northern Caspian was carried out in the autumn and spring period, and it was revealed that the concentration of oil products in the bottom sediments in the fall period decreases compared to the summer period. In general, based on the results of the conducted studies, a preliminary conclusion can be drawn that the natural self-cleaning potential of the North Caspian is in a state of some kind of dynamic equilibrium with modern anthropogenic loads.

Key words: oil products, organ chlorine pesticides, polychlorinated biphenyls, phenol, concentration.

Introduction. Granulometric composition of bottom sediments. Bottom sediments in the study area are sufficiently monotonous and are represented by shells, sands, aleurites, rarely aleuropelites and their combinations. The formation of bottom sediments is dominated by processes of biogenic accumulation, terrigenous demolition and chemogenic precipitation. [1]

The biogenic component of the sediments under study, is mainly included in fractions > 0.25 mm. Fraction > 1 mm is represented mainly by whole shells of lamellar branch and gastropod mollusks and their fragments. Fraction 1.0 - 0.1 mm is composed of fragments of shells of mollusks and foraminifera. Shells of mollusks consist mainly of calcite with the presence of aragonite and dolomite. Biogenic formations have a predominant development. Shell and sand are different in their composition. Under the influence of waves, the shell often forms on the bottom of linear and patchy-banded clusters a few meters wide.

The sands are represented by coarse, medium and fine-grained differences (fractions 1-0.25, 0.25-0.1 mm predominate). In composition, these are mainly detrital formations with a small admixture of terrigenous minerals. Sands are usually present as a filler and do not form isolated fields.

Methods of research. Three well-known elements of the triangle of knowledge - education, scientific research, innovation - are often underestimated for the development of a successful economy. In addition, the combination and synchronization of these three different industries form the basis for economic success.

The discussion of the results. The terrigenous component of precipitation is concentrated mainly in silts (fraction 0.1-0.05 mm). It is represented by quartz, feldspar, fragments of rocks, secondary, accessory and ore minerals. Terrigenous deposits have a significant development within the Kashagan range. The most common mineral is quartz. [2]

Aleuro-pelitic fraction (<0.05 mm) is present as an impurity and does not form independent differences. The maximum values are confined to the north-eastern and north-western parts of the polygon. The third constituent of bottom sediments are chemogenic oolites, which are extremely rare at the landfill stations. [3]

Considering the lithological composition of the bottom sediments, it should be noted that representatives of all the listed genetic types have been found almost everywhere. This is also evidenced by the basic statistical characteristics (Table 1).

Table 1 - The main statistical characteristics of the content of granulometric fractions (%) of bottom sediments

Fractions	Amount	Maximum	Medium	Minimum
	25	31,14	7,98	0,46
Fractions 10-5 mm	25	38,27	6,87	0,40
Fractions 5-2 mm	25	43,79	17,20	1,62
Fractions 2-1 mm	25	35,02	7,45	0,37
Fractions 1-0.5 mm	25	33,90	10,48	0,61
Fractions 0,5-0,25 mm	25	28,11	5,90	0,62
Fractions 0,25-0,1 mm	25	85,49	28,46	1,28
Fractions 0,1-0,05 mm	25	43,71	8,72	0,41
Fractions <0.05 mm	25	25,06	6,94	0,01

Petroleum products in bottom sediments

Studies have shown that the ability of bottom sediments to adsorb oil within each of the granulometric types, in turn, is also due to their dispersity in the density and cohesion of the particles. Thus, according to the data obtained (Table 2), a noticeable

the relationship between the granulometric composition of bottom sediments and the content of hydrocarbons sorbed on them. [4]

The content of oil in bottom sediments decreases from clayey silts to loamy and sandy loam and from dusty sands to large silt. At the same time, an increase in the content of hydrocarbons in bottom sediments is combined with a decrease in their relative density and an increase in dispersion, despite the considerable porosity and looseness that is common to the sediments studied. The reason for the increased concentrations in finely dispersed bottom sediments is undoubtedly the fact that they have a large sorption surface and, consequently, the ability to retain sorbed substances. [5-7]

However, in the case of a disturbed structure of bottom sediments or other effects, the sorption values of each of the granulometric types can vary significantly under the influence of hydrometeorological factors (wave, flow), dredging and hydrotechnical work, which was repeatedly observed in natural conditions.

Table 2 - The content of hydrocarbons in various types of bottom sediments

Type of sediment	Number of definitions	Average hydrocarbon content, mg / g dry ground	The limit of hydrocarbon fluctuations, mg / g dry ground
Il clayey	7	6,6	1,0-17,1
Il loam	4	1,5	0,5-2,0
Il sandy loam	17	0,9	0,3-2,2
The sand is large	2	0,2	0,1-0,2
Sand Medium	2	0,7	0,1-0,7
Sand fine	1	2,2	-
Sand silty	2	6,4	3,8-8,9

Elevated levels of oil products in the bottom sediments of the Kashagan structure are observed in the southeastern part of the test site, which may indicate either anthropogenic contamination of the soil or the inflow from deep horizons. To more accurately determine the nature of the appearance of a high concentration of petroleum products in bottom sediments, additional research is needed at this site. [8]

Phenols in the bottom sediments of the landfill. The content of phenols in the bottom sediments on the Kashagan structure, in most cases does not exceed the detection limit of 0.05 mg / kg. The main statistical characteristics are presented in Table 3.

Table 3 - Basic statistical characteristics of the content of petroleum products and phenols (mg / kg) in bottom sediments

Parameter	Maximum	Medium	Minimum
Petroleum products	10,30	5,20	0,90
Phenols	0,34	<0,05	<0,02

Organochlorine pesticides in sediments

The contents of organochlorine pesticides in April 2003 were in almost all cases below detection limits, except for α -HCH and γ -HCH. The main statistical characteristics are presented in Table 4

Table 4 - Basic statistical characteristics of the content of organochlorine pesticides (μg / g) in bottom sediments

Parametr	Maximum	Medium	Minimum
α - HCH	0,0009	0,0004	0,0002
γ - HCH	0,0040	0,0012	0,0002
Heptachlor	<0,0005	<0,0005	<0,0005
4,4- DDE	<0,0005	<0,0005	<0,0005
4,4- DDD	0,0030	<0,0005	<0,0005
4,4DDT	0,0030	<0,002	<0,002

Polychlorinated biphenyls (PCBs) in bottom sediments

No connection forms independent fields, so a total value was used to characterize the area.

Elevated levels of PCBs in bottom sediments are found in the southeastern and central parts of the landfill. These anomalies can be explained either by technogenic pollution of the soil, or by the inflow of PCBs from deep horizons. [9]

A feature of polychlorinated biphenyls (PCBs) is their high chemical stability. The initial quantities of these substances entering the environment can be retained for a long time, circulating and spreading in the ecosystem.

Synthetic surfactants (SAB) in bottom sediments. Elevated concentrations of synthetic surfactants (SAWS) in bottom sediments on the Kashagan structure are observed in the northern part of the structure. The main statistical characteristics are presented in Table 5. [10-12]

Table 5 - The main statistical characteristics of the content of surfactants and PCBs (mg / g) in bottom sediments

Parametr	Amount	Maximum	Medium	Minimum
SPAC	25	44,00	<11,34	<0,1
PCBs	25	11,170	<2,046	<0,1

Analysis of concentrations of petroleum products, organochlorine pesticides, polychlorinated biphenyls, synthetic surfactants and phenols in the sediments of the landfill shows that soils on the investigated area can be classified as pure.

Conclusions. In general, based on the results of the conducted studies, a preliminary conclusion can be drawn that the natural self-cleaning potential of the North Caspian is in a state of some kind of dynamic equilibrium with modern anthropogenic loads. However, this balance can be violated under the influence of intensive expansion of economic activity both, first of all, on the water area of the Caspian Sea and on its coast.

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Д.Ж.Калиманова, А.Д.Калимукашева, Н.Ж.Галимова

Х.Досмұхамедов атындағы Атырау мемлекеттік университеті, Атырау, Қазақстан

**КАСПИЙДІҢ СОЛТҮСТІК-ШЫҒЫС БӨЛІГІНІҢ ГЕОХИМИЯЛЫҚ ЗЕРТТЕУЛЕРІНІҢ
НӘТИЖЕЛЕРІ (ЖАЙЫҚ ӨЗЕНІ СУ ТҮБІ ШӨГІНДІЛЕРІНДЕГІ МҰНАЙ ӨНІМДЕРІ)**

Аннотация. Бұл мақалада Каспий теңізінің солтүстік – шығыс бөлігінің геохимиялық зерттеулер нәтижесі және Жайық өзеніндегі су түбі шөгінділеріндегі мұнай өнімдерін анықтау қарастырылады. Мұнай өнімдері, хлорорганикалық пестицидтер, полихлорлы бифенилдер, полигон шөгінділеріндегі синтетикалық белсенді заттар мен фенолдар. Зерттеу аймағы ретінде Солтүстік Каспийдің Қазақстанның жағалауына жақын орналасқан шығыс учаскесі алынды. Зерттеу аймағы тегіс төмендеумен және тереңдіктің баяу өсуі арқылы сипатталады. Ол жерде топырақ көбінесе қышқылды немесе құмды болады.

Каспий теңізінің деңгейіндегі маусымдық ауытқулар бірнеше миллиметрден аспайды. Каспий теңізінің солтүстік-шығыс жағалауы жоғары қарқынмен сипатталады.

Зерттеу аймағы геохимиялық және гидрохимиялық режимдерде де, гидробиологиялық сипаттамаларда да қолайлы орналасқан. Теңіз бетінде және түбінде орналасқан станциялардағы негізгі геохимиялық, гидрологиялық және гидрохимиялық сипаттамаларын кешенді зерттеу. Солтүстік Каспийдің шығыс бөлігінің су түбіндегі шөгінділерді байқау күзгі және көктемгі кезеңдерде жүргізілді және күзгі кезеңдегі төменгі шөгінділердегі мұнай өнімдерінің шоғырлануы жазғы кезеңмен салыстырғанда төмендегені анықталды.

Жалпы, жүргізілген зерттеулердің нәтижелері бойынша Солтүстік Каспийдің табиғи өзін-өзі тазарту потенциалы заманауи антропогендік жүктемелермен біршама динамикалық тепе-теңдік жағдайында екендігін алдын-ала тұжырым жасауға болады.

Түйін сөздер: мұнай өнімдері, хлорорганикалық пестицидтер, полихлорильді бифенилдер, фенол, концентрация.

Д.Ж.Калиманова, А.Д.Калимукашева, Н.Ж.Галимова

Атырауский государственный университет им.Х.Досмухамедова, Атырау, Казахстан

РЕЗУЛЬТАТЫ ГЕОХИМИЧЕСКИХ ИССЛЕДОВАНИЙ СЕВЕРО-ВОСТОЧНОЙ ЧАСТИ КАСПИЯ (НЕФТЕПРОДУКТЫ В ДОННЫХ ОТЛОЖЕНИЯХ РЕКИ УРАЛ)

Аннотация. В данной статье рассматриваются результаты геохимических исследований северо-восточной части Каспийского моря и определение нефтепродуктов в донных отложениях реки Урал. Дается анализ концентраций нефтепродуктов, хлорорганических пестицидов, полихлорированных бифенилов, синтетических поверхностно-активных веществ и фенолов на полигоне. Область Северного Каспия, прилегающая к казахстанскому побережью, была выбрана как область исследования. Исследованная область характеризуется наклоном дна и медленным увеличением глубины. Почвы здесь в основном грязевые, иловые или песчаные.

Сезонные колебания уровня Каспийского моря не превышают нескольких метров. Северо-восточное побережье Каспийского моря характеризуется высокими скачками.

Место исследования уникально как в геохимическом, так и в гидрогидрохимическом режимах, а также в гидробиологических характеристиках. Проведены комплексные исследования основных геохимических, гидрологических и гидрохимических характеристик на станциях, расположенных на поверхности и дне моря. Наблюдение донных осадков восточной части Северного Каспия проводилось в осенне-весенний период, и было обнаружено, что концентрация нефтепродуктов в донных отложениях в осеннем периоде уменьшается по сравнению с летним периодом. В целом, исходя из результатов проведенных исследований, можно сделать предварительный вывод о том, что природный самоочищающийся потенциал Северного Каспия находится в состоянии своего рода динамического равновесия с современными антропогенными нагрузками.

Ключевые слова: нефтепродукты, хлорорганические пестициды, полихлорированные бифенилы, фенол, концентрация.

Сведения об авторах:

Калиманова Данагул Жаскайратовна - Кандидат биологических наук, ст. преподаватель кафедры «Химия и химическая технология», Атырауский государственный университет им.Х.Досмухамедова;

Калимукашева Арал Демеуовна - доцент кафедры «Химия и химическая технология», Атырауский государственный университет им.Х.Досмухамедова;

Галимова Назым Жаксикаевна - магистрант кафедры «Химия и химическая технология», Атырауский государственный университет им.Х.Досмухамедова.

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**Zh. K. Dzhanmuldaeva¹, A.A. Kadirbaeva¹,
G.M.Seitmagzimova¹, Zh.M. Altybayev², Sh.K. Shapalov²**

¹M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

²South Kazakhstan Pedagogical University, Shymkent, Kazakhstan

Zanyld@mail.ru, arsenal_575@inbox.ru, shermahan_1984@mail.ru

ON THE METHOD OF MANUFACTURE OF ORGANOMINERAL FERTILIZER BASED ON DOUBLE SUPERPHOSPHATE

Abstract. The paper considers features and advantages of using organomineral fertilizers. Large amount of weakly alkaline lignin-containing solutions being a hard-recyclable waste of cellulose production is formed as a result of the steam-explosive catalysis of herbal agricultural raw materials. The paper considers the possibility of using it as an organic component of organomineral fertilizer. Optimal parameters of the process of double superphosphate production were determined based on laboratory investigation results. The obtained product does not meet requirements of the State standard for double superphosphate, but it is similar to double superphosphate composition. We offer to conduct the process of product granulation in the presence of lignin-containing solution which is a waste of cellulose production to improve the quality, increase the assortment and the agrochemical composition of the fertilizer. Based on the research results we suggest a technological scheme of organomineral fertilizer production on a basis of double superphosphate with the use of lignin-containing solution. The obtained organomineral fertilizer has good physical qualities: it does not clump, does not cake up and does not lose its friability.

Key words: organomineral fertilizers, delignification, lignin-containing solution, double superphosphate, wet-process phosphoric acid (WPA).

Introduction. It is known that organomineral fertilizers combine the advantages of individual organic and mineral fertilizers, strengthen and prolong the action of each of the components and simultaneously remove disadvantages of both fertilizers. The mineral part of organomineral fertilizers dissolve well in the soil solution and ensure fast assimilation by plants. Organic components have a prolonged effect and guarantee the supply of plants with nutrients for a long time. The separate application of organic and mineral fertilizers does not give such an effect. Organic and mineral parts of organomineral fertilizers interact between each other and nutrients (nitrogen, phosphorus and potassium) pass into more accessible compounds for plants. When using organomineral fertilizers, nitrogen mobility reaches 95-98%, phosphorus - 90-95%, potassium - 95%, and they are completely used by plants, while these elements are used in mineral fertilizers only by 30-35%. Therefore, the average doses of granular organomineral fertilizers are about 10 times lower compared to organic fertilizers and 2-3 times lower compared to mineral fertilizers. The ecological component is also very important in the production of organomineral fertilizers, i.e. the amount of both mineral and organic waste on the Earth will decrease. The effectiveness of the use of organomineral fertilizers has been confirmed by numerous tests, while it has been established that the content of organic matter in the soil increased on average by 16-25%. Agrochemical analysis of soil showed a significant increase of the level of macro- and microelements in the soil. The amount of nitrogen in the soil, compared with control sites, increased by an average of 2.2-2.8 times, the content of phosphorus increased by 1.3-2.0 times, potassium by 1.3-2.5 times, calcium by 1.3-1.9 times, magnesium by 1.3-1.6 times [1].

Organomineral fertilizers are characterized by high agrochemical efficiency. There are physiologically active substances in the organomineral fertilizers, which influence the growth of plants, create a loose soil structure, increase the total surface of the finished product volume. Organomineral

fertilizers promote to adsorption and retention of moisture (up to 50%), as well as nutrients such as nitrogen, phosphorus, potassium, calcium, minor-nutrient elements. They have good physical qualities: they do not clump, do not cake up and do not lose their friability even when the moisture content in them is up to 50% (absolute). The use of organomineral fertilizers prevents and eliminates the possibility of elution of nutrient elements and allows to reduce significantly (by 25-50%) the norm of introducing nutrients into the soil. In addition, the use of organomineral fertilizers will allow to reduce soil salinity, provide optimal water and air regime, increase humus content in the soil, reduce the harmful effects of high doses of NPK fertilizers, pesticides, toxic chemicals and radionuclides, to increase soil fertility, crop yield, their quality value and ensure environmental safety [2].

Scientists of M. Auezov South Kazakhstan State University have developed a technology of cellulose production based on the process of steam-explosive autocatalysis of herbal agricultural raw materials, such as wheat straw and rice hulls. The developed cellulose technology is associated with the formation of large amount of weakly alkaline lignin-containing solutions. They have studied the process of explosive autocatalysis of wheat straw and rice hulls in the presence of weak alkaline solutions of cellulose production; paper or corrugated cardboard are produced from the cellulose hereafter. It has been established that the use of steam explosion of straw or rice hulls with subsequent extraction by alkaline solutions allows obtaining cellulose with better strength characteristics than that at acid delignification. Lignin is removed from these solutions; this process is called as delignification. At that, weakly alkaline lignin-containing solutions are formed, which are hard-recyclable wastes of paper production [3,4]. Further processing or recycling of these wastes is an actual production problem and an essential element of the creation of non-waste technology.

In this context, the development of the technology of organomineral fertilizer with the possibility of utilization of delignification extract is topical issue. Its use as an organic component of organomineral fertilizer based on double superphosphate can be one of such methods. To prepare an organomineral fertilizer on the basis of double superphosphate, we suggest adding the delignification extract at the granulation stage.

The proposed technology of organomineral fertilizer based on double superphosphate consists of several stages: 1) decomposition of phosphate raw materials with wet-process phosphoric acid (WPA); 2) drying the pulp; 3) granulation of the product in the presence of the lignin-containing solution; 4) drying and sifting the finished product. To determine optimal parameters of the process of obtaining organomineral fertilizer on the basis of double superphosphate, the influence of WPA norm, concentration and temperature on phosphorite decomposition degree and the additive of lignin-containing solution influence on the process conditions and the quality of the product were studied.

Materials and methods. Laboratory experiments of the decomposition of Karatau phosphorites with wet-process phosphoric acid for obtaining double superphosphate were carried out as follows. The WPA stoichiometric norm was calculated according to a simplified procedure that does not take into account the mineralogical composition of raw materials [5]. The required amount of wet-process phosphoric acid was heated up to a certain temperature and then mixed with phosphorite for 1 hour at stirring. The formed pulp was dried for 1.5 hours in a dryer at 105-110°C (to approach the temperature regime of ageing the double superphosphate in production conditions). The obtained chamber double superphosphate was analyzed for moisture content and all forms of P_2O_5 content by standard methods in accordance with GOST 20851.2-75 and GOST 20851.4-75.

Following raw materials were applied for the laboratory research: Karatau phosphorites of composition (mass %): $P_2O_{5\text{total}}$ - 25,0; CaO - 37.04; MgO - 2.4; Fe_2O_3 - 1.18; Al_2O_3 - 0.8; insoluble residue - 21.62; F - 2.38; moisture - 0.32 and wet-process phosphoric acid produced from these raw materials; its composition (mass %): $P_2O_{5\text{total}}$ - 21.6; CaO - 0.57; MgO - 1.49; Fe_2O_3 - 0.99; Al_2O_3 - 0.86; F - 1.74; SO_4 - 2.22. Wet-process phosphoric acid used for the experiments was produced at the Plant of mineral fertilizers of "Kazphosphate" LLP. A complete analysis of Karatau phosphorites and WPA was conducted in the central laboratory of "Kazphosphate".

Results and discussion. To study the influence of WPA norm on the phosphorite decomposition degree the interaction process was carried out at a temperature of 70°C during 1 hour and a drying process was carried out at a temperature of 105-110°C. The WPA consumption coefficient was varied within 70-110% of the stoichiometry. The results of laboratory studies are presented in Table 1.

As can be seen from Table 1, the phosphorite decomposition degree increases when increasing the WPA consumption rate, the content of $P_2O_{5\text{free}}$ also increases. In the dried samples, the $P_2O_{5\text{total}}$ ranges as 33,3-38,0%, and $P_2O_{5\text{free}}$ is 5.6-7.9%. At the acid norm above 90% of stoichiometry, the phosphorite

decomposition degree does not increase significantly. At the norm of 110% of stoichiometry the decomposition degree is 91.8%, however, the content of free P_2O_5 is also high. Therefore, the optimal WPA norm is 90% of stoichiometry.

Table 1 - Influence of WPA consumption rate on the phosphorite decomposition degree at 70°C

№	WPA consumption rate, % of stoichiometry	Drying temperature, °C	$P_2O_{5\text{ total}}$, %	$P_2O_{5\text{ free}}$, %	Decomposition level, %
1.	70	105-110	33,3	5,6	80,2
2.	80	105-110	34,6	6,2	85,1
3.	90	105-110	35,7	6,9	89,3
4.	100	105-110	36,9	7,2	90,5
5.	110	105-110	38,0	7,9	91,8

Under these conditions, a relatively high phosphorite decomposition degree is attained and a product with good physical properties is obtained, i.e. the prepared product can be processed further. The next step of the product treatment is granulation in the presence of the lignin-containing solution.

To study the effect of temperature on the phosphorite decomposition degree, decomposition temperature was varied within 40-90°C, the WPA consumption rate was 90% of the stoichiometry as an optimal value determined earlier. It is known that the phosphorite decomposition degree decreases with increasing temperature, this is explained by the nature of the change in solubility in $CaO-P_2O_5-H_2O$ system [5]. When temperature increasing the supersaturation degree with calcium hydrophosphate increases. As a result, calcium hydrophosphate film is formed on the surface of the phosphorite grains, which leads to decomposition process deceleration. At temperature below 70°C, the phosphorite decomposition degree is somewhat higher, but the temperature of the superphosphate mass is reduced due to the relatively low ratio of the amount of heat released from the decomposition reaction to the weight of the superphosphate mass. This will increase the moisture content of the product. Evaporation of moisture takes place and the content of phosphoric acid in the liquid phase increases in the process of drying. The calcium hydrophosphate film formed on the surface of the phosphorite grains dissolves, an activity of hydrogen ions in the liquid phase increases, as a result of which the phosphorite further decomposition takes place. The results of studies showed that increasing the temperature above 70°C causes more viscous and dense pulp formation. At a temperature of 70°C, more mobile pulp is obtained, which will easily be transported to the dryer.

Thus, optimal parameters of the process of obtaining double superphosphate were determined: WPA consumption rate is 90% of stoichiometry; the decomposition temperature is 70°C. Under these conditions, the product of the following composition was obtained, (mass %): $P_2O_{5\text{ total}}$ - 35.7; $P_2O_{5\text{ available}}$ - 31.9 and $P_2O_{5\text{ free}}$ - 6.9. This product does not meet the requirements for the double superphosphate GOST, but it is similar to double superphosphate composition.

The lignin-containing solution obtained as a result of a steam explosion of rice hulls is an alkaline water extract containing 26% of lignin with pH = 12-13. After complete evaporation of this extract, the chemical composition of the obtained precipitate, determined from scanning electron microscopy, (mass %) is following: C-34.85; O-35.68; Na-0.62; Si-1.15; S-0.16; K-24.52. As can be seen from the data, the dry residue is mainly represented by carbon, oxygen, and potassium; there are sodium, sulfur and silicon in relatively small amounts.

Studying the fertilizer granulation process in the presence of lignin-containing solution has shown that the use of lignin-containing solution leads to the neutralization of free acidity forming potassium phosphates in the complex of phenylpropyl functional groups and the enrichment of the product additionally with potassium nutrient. As a result of double superphosphate preparation in laboratory conditions with the use of delignification solution at the granulation stage we have obtained the organomineral fertilizer of the composition, mass %: $P_2O_{5\text{ total}}$ – 33,8; $P_2O_{5\text{ available}}$ – 32,11; $P_2O_{5\text{ free}}$ – 0; organic constituent – 5,39.

The results of investigations of lignin-containing solution additive influence on commodity fraction product output from the granulation stage are given in Figure 1.

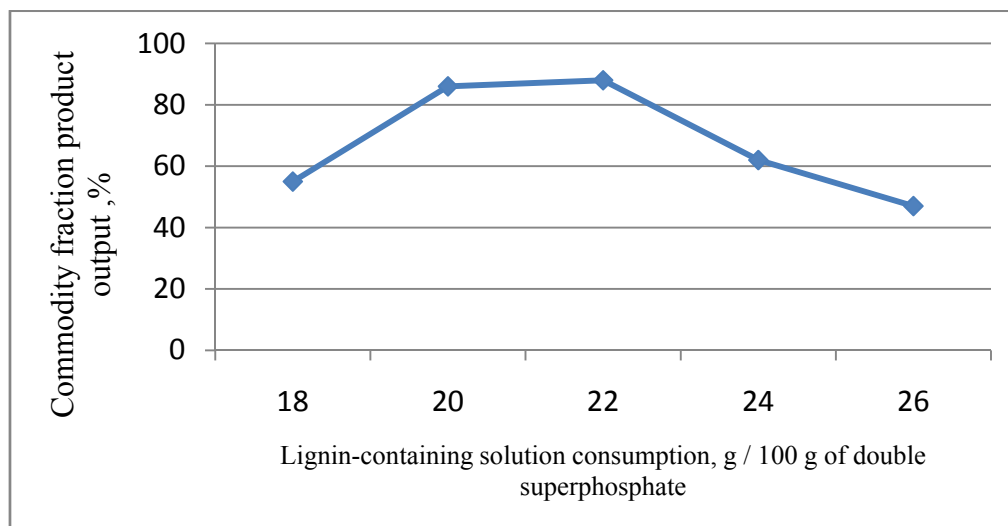


Figure 1 – Dependence of commodity fraction product output on lignin-containing solution consumption

It demonstrates that optimal lignin-containing solution additive, providing maximum of commodity fraction product output, has very narrow range. Outside the range either pelletizing does not take place or spontaneous agglomeration takes place. Insignificant additive increase or decrease leads to sharp reduction of commodity fraction product output. It is explained that the additive decrease is accompanied with moisture input decrease, i.e. there is the lack of moisture for complete wetting fertilizer grain surface; at that pelletizing does not take place. And when the additive increasing the amount of moisture input increases which results in excessive growth of charge moisture content and formation of large lumps and agglomerates.

The results of laboratory testing have shown that optimal lignin-containing solution additive is 20-22 g / 100 g of powdered double superphosphate. The maximal commodity fraction product output – 86-88% is observed at this condition.

The proposed technological scheme for the production of organomineral fertilizer based on double superphosphate consists of several stages: 1) the decomposition of phosphate raw materials with WPA of $P_2O_{5\text{total}}$ 21.6% concentration (by mass), at 90% WPA consumption rate for 1 hour at 70-90°C, while the phosphate raw material decomposing by 55-60%; 2) Drying the pulp at 105-110°C. During the drying process, the decomposition of raw materials continues and the total decomposition degree of raw materials increases to 85-90%; 3) Granulation of the product in the presence of the lignin-containing solution; 4) Drying the prepared granules to the moisture content of 3-4% in warm conditions at the temperature of 60-70°C.

Conclusion. Optimal parameters of the process of double superphosphate production were determined based on laboratory investigation results: decomposition of phosphate raw materials with WPA for 1 hour at 70-90°C with further decomposition during the drying process, then lignin-containing solution addition with the norm of 20-22 g / 100 g of powdered double superphosphate on the granulation stage. When using lignin-containing solution at the granulation stage of double superphosphate production we can prepare the new mineral fertilizer of improved quality. It will promote to increase product output and to increase the assortment and the agrochemical composition of the organomineral fertilizer. Simultaneously the cellulose production waste can be utilized completely. The prepared organomineral fertilizer based on double superphosphate contains P_2O_5 in easily assimilated form for plants and an organic part that is of prolonged action. The use of such a fertilizer extends the term of its effective action in the soil.

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Ж.К. Жанмолдаева¹, А.А. Қадірбаева¹, Г.М. Сейтмагзимова¹, Ж.М. Алтыбаев², Ш.К. Шапалов²

¹М.Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент, Қазақстан;

²Оңтүстік Қазақстан педагогикалық университеті, Шымкент, Қазақстан

ҚОС СУПЕРФОСАТ НЕГІЗІНДЕ ОРГАНОМИНЕРАЛДЫ ТЫҢАЙТҚЫШТЫ ДАЙЫНДАУ ӘДІСІ БОЙЫНША

Аннотация. Мақалада органоминаралды тыңайтқыштардың ерекшеліктері мен артықшылықтары көрсетілген. Шөпті ауылшаруашылық шикізаттарын целлюлоза алу мақсатымен бу-жарылыс катализ арқылы өңдеу нәтижесінде көп мөлшерде әлсіз сілтілі лигнинқұрамдас ерітінділер пайда болады. Мақалада осы ерітіндіні органоминаралды тыңайтқыштың органикалық құрамдас бөлігі ретінде қолдану қарастырылған. Зертханалық зерттеулер нәтижесінде қос суперфосфат алу процесінің тиімді технологиялық параметрлері анықталған. Алынған суперфосфат қос суперфосфатқа қатысты стандарт талаптарына сәйкес келмейді, бірақ құрамы бойынша қос суперфосфатқа жақын. Тыңайтқыштардың сапасын жоғарылату, ассортиментін көбейту және агрохимиялық құрамын жақсарту мақсатымен оны целлюлоза өндірісінің қалдығы – лигнин-құрамдас ерітіндінің қатысында түйіршіктеу ұсынылған. Зерттеу нәтижелері бойынша лигнинқұрамдас ерітінділерді қолдану арқылы қос суперфосфат негізінде органоминаралды тыңайтқыш алудың технологиялық сызба нұсқасы ұсынылған. Алынған органоминаралды тыңайтқыштың физикалық қасиеттері жақсы: жұмырланбайды, нығыздалмайды және үгілгіштігін жоғалтпайды.

Түйін сөздер: органоминаралды тыңайтқыштар, дәнекерлеу, лигнинді ерітінділер, қос суперфосфат, экстракциялық фосфор қышқылы.

Ж.К. Жанмолдаева¹, А.А. Қадірбаева¹, Г.М. Сейтмагзимова¹, Ж.М. Алтыбаев², Ш.К. Шапалов²

¹Южно-Казахстанский государственный университет им. М.Ауэзова, Шымкент, Казахстан;

²Южно-Казахстанский педагогический университет, Шымкент, Казахстан

ПО МЕТОДУ ИЗГОТОВЛЕНИЯ ОРГАНОМИНЕРАЛЬНОГО УДОБРЕНИЯ НА ОСНОВЕ ДВОЙНОГО СУПЕРФОСФАТА

Аннотация. В статье представлены особенности и преимущества использования органоминаральных удобрений. В результате паро-взрывного катализа травянистого сельскохозяйственного сырья с целью получения целлюлозы образуется большое количество слабощелочных лигнинсодержащих растворов, которые являются трудноутилизируемым отходом. В статье рассмотрена возможность применения его в качестве органической составляющей органоминарального удобрения. По результатам лабораторных исследований определены оптимальные параметры процесса получения двойного суперфосфата. Полученный продукт не соответствует требованиям стандарта на двойной суперфосфат, но по своему составу схож с двойным суперфосфатом. С целью улучшения качества, увеличения ассортимента и агрохимического состава удобрения предлагается процесс грануляции продукта проводить в присутствии лигнинсодержащего раствора – отхода производства целлюлозы. По результатам исследований предложена технологическая схема производства органоминарального удобрения на основе двойного суперфосфата с использованием лигнинсодержащего раствора. Полученное органоминаральное удобрение имеет хорошие физические качества: не комкуются, не слеживаются и не теряют своей рассыпчатости.

Ключевые слова: органоминаральные удобрения, делигнификация, лигнинсодержащие растворы, двойной суперфосфат, экстракционная фосфорная кислота (ЭФК).

Information about authors:

Dzhanmuldaeva Zh.K. – candidate of technical Sciences, Professor, Department “Chemical technology of inorganic substances”, M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

Kadirbaeva A.A. - candidate of technical Sciences, Associated Professor, Department “Chemical technology of inorganic substances”, M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

Seitmagzimova G.M. - candidate of technical Sciences, Professor, Department “Chemical technology of inorganic substances”, M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

Altybayev Zh.M. - PhD, Senior teacher, Department of chemistry and biology, M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

Shapalov Sh.K. - PhD, Senior teacher, Department of chemistry and biology, South Kazakhstan Pedagogical University, Shymkent, Kazakhstan.

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**G.Z. Turebekova¹, Sh.K. Shapalov¹, G.B. Alpamysova², G. I. Issayev³,
G.Zh. Bimbetova⁴, K. Kerimbayeva², A.M. Bostanova⁵, A.E. Yessenaliyev⁴**

¹South Kazakhstan pedagogical university, Shymkent, Kazakhstan;

²South Kazakhstan state pedagogical university, Shymkent, Kazakhstan;

³International Kazakh-Turkish University named after H.A. Yassavi, Turkestan, Kazakhstan;

⁴M. Auezov South Kazakhstan state university, Shymkent, Kazakhstan;

⁵Caspian State University of Technologies and Engineering named after Sh.Yessenov, Aktay, Kazakhstan

E-mail: g.ture@mail.ru, shermahan_1984@mail.ru, xap68@mail.ru, gani.isaev@mail.ru, ardak_bostan@mail.ru

THE OPPORTUNITIES OF THE RATIONAL USE OF THE WASTE OF OIL PRODUCTION AND OIL REFINING IN THE MANUFACTURE OF TIRE RUBBER

Abstract. In the process of extraction and processing of oil from the Tengiz field, a lot of elemental sulfur is formed from hydrogen sulphide, which is stored in an open area and is the cause of environmental problems in the region. Many elemental sulfur consumes the rubber industry for the vulcanization of rubbers. Sulfur vulcanizing agents included in the group, ensures the vulcanization, i.e., the transformation of plastic and viscoelastic rubber compounds in highly elastic rubber due to the formation of a uniform spatial with the sulfur atoms linking the individual chemical bonds of the macromolecules rubber. Previously, we have carried out work on the application of purified sulphur in the Tengizbrekina and tread rubber compounds that have shown promise for the future. However, the manufacture of frame rubber compounds using purified Tengiz sulfur is not justified, because rubber was hard. In this work, we have conducted research and presented the results of experiments on the possibility of application of polymeric sulfur, obtained from purified Tengiz sulfur. The use of polymeric sulfur can also adjust the elastic properties of the resulting rubbers. Polymeric sulfur was introduced on a laboratory mill at the end of mixing, in a second stage, in order to prevent premature vulcanization. In the process of cleaning crude oil from hydrogen sulfide produced many elemental sulfur, which is in Tengiz a result of processing of sour oil and gas, indicating the content of hydrogen sulfide. Sulfur vulcanizing agents included in the group, ensures the vulcanization, i.e., the transformation of plastic and viscoelastic rubber compounds in highly elastic rubber due to the formation of a uniform spatial with the sulfur atoms linking the individual chemical bonds of the macromolecules rubber. Particular attention is paid to development of curing agents. Previously, we have carried out work on the application of purified sulphur in the Tengizbrekina and tread rubber compounds that have shown promise for the future. However, the manufacture of frame rubber compounds using purified Tengiz sulfur is not justified, because rubber was hard. Thus, the results of studies have shown that the use of Tengiz sulfur leads to improved physical and mechanical properties and quality of rubbers. A secondary use of sulfur - a waste of oil production can improve the ecology of Kazakhstan.

Key words: sulfur waste; oil sludge; organic part of oil sludge; rubber compounds; curing system; plasticizers.

Introduction. By the size of the established reserves, the geological and thermo-baric conditions in occurrence of oil-bearing horizons and the technical-economic features of the development of Tengiz is unique not only among the deposits of Kazakhstan, but also the world. In 1998, “Tengizchevroil” conducted three-dimensional seismic studies here, after which the explored oil reserves were estimated by the enterprise at 1,3 billion tons. The productive horizons of the Tengiz field lie at a depth of more than 5000 m, this oil-bearing reservoir occupies the land with the width of 19,3 km and the length of 21 km. Features of the field deposit: high intra-layer pressure and high concentration of hydrogen sulphide require the solution of the most complicated technical and technological problems. Especially solving the environmental problems of sulfur utilization [1,2].

Tengiz oil is light; density at 20°C 789,2– 851,4 kg/m³, sulfurous is characterized by the significant content. In the process of cleaning the crude oil from hydrogen sulfide, TCO produces the elemental

sulfur, which is in Tengiz the results of processing “acidic” oil and gas, indicating the content of hydrogen sulphide in them. From year to year, the artificial “mountains” of sulfuric massives are grown, about 69 kg of sulfur per 1 ton of the produced oil. The giant volumes of oil production waste-sulfur (today more than 8 million tons of the products are stored in “sulfur cards”) cause serious concern of ecologists and local population, since under the local climatic conditions sulfur can pass to many sulfur compounds. Moreover, the sulfur arrays are located in the sanitary protection zone of the Tengiz gas processing manufacture, gassed zone, under the influence of flaring off the gases, containing carbon, hydrogen, various metals and much more. One of the main problems arising in oil production in Tengiz is the danger of soil and groundwater contamination, the spread of sulfur dust, and the entry of sulfur sulfide into the atmosphere [3-5].

In the practice of the world oil and gas industry, basically three methods of obtaining solid sulfur are used: flake, granular and lumpy. On Tengiz sulfur is released in the liquid form. A lot of elemental sulfur is consumed by the rubber industry - for the vulcanization of the rubbers. Sulfur, which enters the curing group, provides the curing, it means, the transformation of a plastic and viscoelastic rubber compound into a highly elastic rubber as a result of the formation of a single spatial grid with sulfur atoms, connecting the individual macromolecules of rubber by chemical bonds [3]. During the extraction and processing of oil from the Tengiz field, a lot of sulfur waste is generated, which is stored in open fields. Under the influence of the atmosphere, high temperature (in summer up to 45-50°C), etc., many sulfur compounds are formed that are harmful to human health and the environment. The research shows the possibility of using sulfur as a vulcanizing agent of the rubber compounds.

The rubber industry of Kazakhstan has a very limited assortment of ingredients of the rubber compounds. An important scientific direction of petro-chemistry is the production of plasticizers, softeners, vulcanizing agents, fillers based on the man-made waste. This makes it possible to expand the raw material base, use large reserves of oil refining waste reduce the anthropogenic load on the environment and solve the problem of the production of import-substituting softeners and vulcanizing agents for the rubber industry of Kazakhstan. A feature of Kazakh oils is an increased content of sulfur compounds, as a result of which a lot of sulfur waste is formed [6-10].

It is generally accepted to use in the formulations of rubber mixtures of organic and inorganic low-molecular compounds. By the effectiveness of the action of polymers and products of low-molecular compounds are divided into softeners and plasticizers. Softeners are called low-molecular compounds, which reduce the temperature of fluidity and do not affect the glass transition temperature of rubbers. Plasticizers are low-molecular compounds, which reduce the glass transition temperature and the flow temperature of rubbers. An important requirement for plasticizers and softeners is their low cost. Great importance is also attached to the availability of the raw materials used to produce them. Various other requirements for plasticizers and softeners (no washing out with water, oils, etc.) are determined by the specific conditions in which the finished product containing the plasticizer and softener will work.

Experimental part. As a vulcanizing agent in rubber compounds sulfur is used, therefore in our work it is proposed to use the purified Tengiz sulfur from oil production and refining waste in the vulcanizing system.

Tests of the organic part of oil sludge (OPOS), extracted from oil sludge of the LLP “PetroKazakhstanOilProducts” (PKOP) in the formulations of rubber compounds based on the rubbers of general purpose as softeners, with the replacement of the traditional softeners PN-6SH and softener ASSC, were carried out. Based on the results of the determination of technological properties, it was found that OPOS has a plasticizing effect [10,11].

Sludge collectors save the general character of the structure, i.e. when storing the oil sludge, depending on the difference in the physicochemical parameters of the components, over time; it is divided into three layers. Light liquid hydrocarbons are concentrated in the upper layer, the middle layer is characterized by high water content, and heavy fractions of hydrocarbons, resins, asphaltenes and particles of the mineral phase are collected in the lower bottom layer [12-15].

As a result of the conducted studies of oil sludge LLP “PKOP” found that the indicators of the phase composition and physicochemical properties vary depending on the conditions of their formation, storage and the depth of the layer. The top layer is a watered oil product with a content of up to 2.4% finely dispersed mechanical impurities and belongs to the class of water-in-oil emulsions. The water content does not exceed 5.4%. The content of petroleum products is 25.9%. The middle layer is represented by an oil-in-water emulsion. This layer contains 53.1% water and 5.7% mechanical impurities. The content of petroleum products is 11.2%. The lower layer contains 40.6% water, 35.6% mechanical impurities,

petroleum products 1.3%. Oil sludge as a polydisperse unstable system is characterized by the fact that its physical characteristics are not constant, i.e. when determined for the same oil-slime sample, the results obtained may differ by 50 percent or more. Therefore, for the experiment, an average sample of oil sludge from the settling pit of LLP "PKOP" was selected.

Optimization of compounding the rubber compounds. By sequential study of the effect on the properties of rubber of the contents of each of the components alone (sulfur and oil sludge) with fixed amounts of other ingredients, optimization of the developed rubber compounds for making the filler cord of the bead of car tires was carried out.

In order to identify the optimum quantity of OPOS in the composition of rubber mixtures, rubber mixtures with different contents of OPOS were obtained. Plasticizers and softeners have been replaced with OPOS. Also in the formulations of rubber compounds as a vulcanizing agent, a mixture of polymer and colloidal sulfur from the Tengiz field was used. Recipes of rubber compounds used in the manufacture of the bead tape are given in Tables 1.

The highly disperse mineral fraction of oil sludge (1-5 microns) is used in the rubber compound formulation for the production of the filler cord of the side wing of passenger tires.

Table 1 - The formulation of the optimum rubber compound for the manufacture of the filler cord of the side wing

Title of the ingredients	For 100 mass parts of the rubber					
	Model	Research variant				
1	2	3	4	5	6	7
HSI-3	40,0	40,0	40,0	40,0	40,0	40,0
Fill with rubber	60,0	60,0	60,0	60,0	60,0	60,0
Sulfur technical	2,4	-	-	-	-	-
Sulfur Tengiz	-	1,2	1,6	2,0	2,2	2,4
Sulfenamide "C"	1,2	1,2	1,2	1,2	1,2	1,2
Santogard RU	0,4	0,4	0,4	0,4	0,4	0,4
Zinc White ceruse	5,0	5,0	5,0	5,0	5,0	5,0
Stearic acid technical	2,0	2,0	2,0	2,0	2,0	2,0
Softener ASSC	4,0	4,0	4,0	4,0	4,0	4,0
Organic part of oil sludge	-	4,0	5,0	6,0	6,5	7,0
Oil PN-6SH	4,0	-	-	-	-	-
AcetonilP	2,0	2,0	2,0	2,0	2,0	2,0
DiafenFP	2,0	2,0	2,0	2,0	2,0	2,0
Technical carbon	70,0	60,0	55,0	50,0	45,0	40,0
Mineral part of oil sludge	-	10,0	15,0	20,0	25,0	30,0

Methods . The vulcanization characteristics of the rubber compounds obtained with a "Monsanto" rheo-meter confirmed the fact that various dosages of OPOS and sulfur directly influence the kinetics of vulcanization of rubber compounds. The addition of OPOS into rubber compounds leads to a decrease in the minimum viscosity and rigidity of the elastomeric matrix system. This decrease is directly proportional to the percentage of OPOS. The use of Tengiz sulfur allows preserving the duration of the vulcanization plateau, thereby preventing the re-vulcanization of the rubber of the filler cord.

Results and its discussion. The optimum component ratio, leading to the decrease in the minimum viscosity and an increase in the vulcanization start time, characterizing the best technological properties of rubber compounds, is observed at 7 and 8 parts by the weight for the rubber compounds intended for the filler cord. From the analysis of volcano-metric curves of rubber compounds, it follows that the optimum time to achieve vulcanization of the rubber compound for the rubber compound of the filler cord is 23 minutes.

The physical and mechanical tests of the experimental rubbers led to the conclusion that it is most expedient to use the organic part of the oil sludge in the rubber compound formulations for the filler cord of the wing wings, since when replacing the traditional softeners with the OPOS the properties of rubbers correspond to the control standards. The best results are observed with a dosage of 8-10 parts by weight OPOS for the rubber compounds intended for the filling cord. Dependences of the main physico-mechanical parameters of vulcanization of rubber filler cord from the dosage of OPOS and Tengiz sulfur are given in Table 2.

Table 2 - Properties of vulcanizes based on rubbers of general purpose for a filling cord with additions of organic part of oil sludge and Tengiz sulfur

Title of the indexes	Norms of controlling	1-v	2-v	3-v	4-v	5-v
Conditional tensile strength, kgp / cm ² , not less than	92	107	104	109	111	111
Relative elongation at break, %, not less than	270	270	300	310	310	295
Hardness on A blinders, cond. units	70	75	77	77	78	75

Conclusions: A slight decrease in strength indexes and an increase in the elastic properties of rubbers with increasing dosage of OPOS can be explained by the mechanism of plasticizing effect of low-molecular compounds of the organic part of oil sludge that penetrate between macromolecules, thereby reducing the intermolecular interaction of rubber macromolecules. A slight decrease in strength properties of rubber filler wings is not important, since the main strength of the structure of the wing wings is attached to the side rings of brass wire. The use of the same Tengiz sulfur allowed preserving the kinetics of vulcanization, which could decrease with the use of OPOS. Also, the use of Tengiz sulfur allowed increasing the hardness of rubbers, which is necessary to increase the rigidity of the tire's bead.

Thus, the results of extended tests have shown that it is possible to replace traditional softeners in rubber mixes with organic part of oil sludge and use Tengiz as a vulcanizing agent. Fillers in the formulation of rubber compounds for making a filler cord can be partially replaced with a mineral part of the oil sludge.

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Г.З. Туребекова¹, Ш.К. Шапалов¹, Г.Б. Алпамысова², Г.И. Исаев³,
Г.Ж.Бимбетова⁴, К. Керімбаева², А.М. Бостанова⁵, А.Е. Есеналиев⁴

¹Оңтүстік Қазақстан педагогикалық университеті Шымкент, Қазақстан;

²Оңтүстік Қазақстан мемлекеттік педагогикалық университеті Шымкент, Қазақстан;

³Қ.А. Ясауи атындағы Халықаралық қазақ- түрік университеті, Түркістан, Қазақстан;

⁴М. Әуезов атындағыОңтүстікҚазақстан мемлекеттік университеті Шымкент, Қазақстан;

⁵Ш.Есенов атындағы Каспий мемлекеттік технологиялар мен инжиниринг университеті, Актау, Қазақстан

МҰНАЙ ӨНДІРУ МЕН МҰНАЙ ӨНДЕУ ҚАЛДЫҚТАРЫН ШИНАЛЫҚ РЕЗИНАЛАР ӨНДІРІСІНДЕ ҰТЫМДЫ ПАЙДАЛАНУ МҮМКІНДІГІ

Аннотация. Тенгиз кен орнының мұнайын өндіру және өңдеу кезінде ашық алаңдарда сақталатын күкірттің көп қалдықтары түзіледі. Атмосфераның әсерінен, яғни жоғары температура (жазда 45-50⁰С дейін) мен басқа да факторлардың әсерінен, адам денсаулығы мен қоршаған ортаға зиянды әсерін тигізетін күкірттің көп қоспалары түзіледі. Жұмыста күкіртті резина қоспасын вулкандашушы агент ретінде қолдану мүмкіндігі көрсетілген.

Компонент құрамының әрқайсысына бөлек (күкірт және мұнай шламы) резина қоспасына әсерін жүйелі түрде зерттеу арқылы, жеңіл шина бортының толықтырғыш бауын дайындау кезінде өңделген резина қоспасына, тіркелген басқа да ингредиенттер санына оңтайландыру жүргізілді.

Тенгиз күкіртін қолдану, ОЧН қолдану кезінде кемуге мүмкіндік беретін вулкандашу кинетикасын сақтауға мүмкіндік берді. тенгиз күкіртін қолдану, Сонымен қатар дөңгелектің сыртқы бортының Кермектіктің арттыру үшін қажет резинаның қаттылығын жоғарылатады.

Кеңейтілген сынақтардың нәтижелері, резина қоспасында қолданылатын дәстүрлі жұмсартқыштарды мұнай шламы мен вулкандашушы агент ретінде қолданылатын тенгиз күкіртін не алмастыру мүмкіндігін көрсетті

Толықтырғыш бауды дайындауға арналған резина қоспасының рецептіндегі толықтырғыштар мұнайшламының минералды бөлігіне ішінара ауыстырылуы мүмкін.

Түйін сөздер:күкірт, полимерлі күкірт, өнеркәсібінде алынған заттар, шиналық, резенке, резенке қоспалар, вулканизаттар, вулканизациялау агенті, вулкандашу жүйесі, протекторлық резенке қоспалар, бреккерлық резенке қоспалар.

Г.З. Туребекова¹, Ш.К.Шапалов¹, Г.Б. Алпамысова², Г.И. Исаев³,
Г.Ж. Бимбетова⁴, К. Керимбаева², А.М. Бостанова⁵, А.Е. Есеналиев⁴

¹Южно-Казахстанский педагогический университет, Шымкент, Республика Казахстан;

²Южно-Казахстанский государственный педагогический университет, Шымкент, Республика Казахстан;

³Международный казахско- турецкий университет им. Х.А. Яссави, Туркестан, Республика Казахстан;

⁴Южно-Казахстанский государственный университет им. М. Ауезова, Шымкент, Республика Казахстан;

⁵Каспийский государственный университет технологий и инжиниринга им Ш.Есенова, Республика Казахстан

ВОЗМОЖНОСТИ РАЦИОНАЛЬНОГО ИСПОЛЬЗОВАНИЯ ОТХОДОВ НЕФТЕДОБЫЧИ И НЕФТЕПЕРЕРАБОТКИ В ПРОИЗВОДСТВЕ ШИННЫХ РЕЗИН

Аннотация. При добыче и переработки нефти Тенгизского месторождения образуется много отходов серы, которая хранится на открытых площадках. Под воздействием атмосферы, высокой температуры (летом до 45-50⁰ С) и др. факторов образуется много соединений серы вредных для здоровья человека и окружающей среды. В работе показана возможность использования серы в виде вулканизирующего агента резиновых смесей.

Путем последовательного изучения влияния на свойства резин содержания каждого из компонентов в отдельности (серы и нефтешлама) при фиксированных количествах других ингредиентов была проведена оптимизация разработанных резиновых смесей для изготовления наполнительного шнура борта легковых шин.

Применение тенгизской серы позволило сохранить кинетику вулканизации, которая могла бы снизиться при применении ОЧН. Также применение тенгизской серы позволило повысить твердость резин, которая необходима для повышения жесткости борта автопокрышки.

Результаты расширенных испытаний показали возможность замены традиционно используемых в резиновых смесях мягчителей на органическую часть нефтешлама и использования тенгизской серы в виде вулканизирующего агента. Наполнители в рецептуре резиновых смесей для изготовления наполнительного шнура могут быть частично заменены на минеральную часть нефтешлама.

Ключевые слова: сера, полимерная сера, продукты нефтедобычи, шинные резины, резиновая смесь, вулканизат, вулканизирующий агент, вулканизирующая система, бреккерная резиновая смесь, протекторная резиновая смесь.

Information about authors:

G.Z.Turebrova- candidate of technical sciences, Associated Professor, Department of chemistry and biology, South Kazakhstan pedagogical university, Shymkent, Kazakhstan;

Sh.K.Shapalov – PhD, senior teacher, Department of chemistry and biology, South Kazakhstan pedagogical university, Shymkent, Kazakhstan;

G.B.Alpamysova - candidate of agricultural sciences, Deccan of faculty of natural Sciences, South Kazakhstan state pedagogical university, Shymkent, Kazakhstan;

G. I Issayev - candidate of technical sciences, head of Department of biology;

G.Zh.Bimbetova- candidate of technical sciences, Associated Professor, M. Auezov South Kazakhstan state university, Shymkent, Kazakhstan;

K Kerimbayeva- of technical sciences, Associated Professor, Department of chemistry, South Kazakhstan pedagogical university, Shymkent, Kazakhstan;

A.M Bostanova - candidate of biology, Associated Professor, head of education methodical Department, Caspian State University of Technologies and Engineering named after Sh.Yessenov, Aktay, Kazakhstan;

A.E. Yessenaliyev – candidate of juridical sciences, head of the Department Assembly of Peoples of Kazakhstan, M. Auezov South Kazakhstan state university, Shymkent, Kazakhstan.

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A.O.Adilbekova, K.I.Omarova, Sh.Abdrakhmanova

Al-Farabi Kazakh National University, Almaty, Kazakhstan
Akbota.Adilbekova@kaznu.kz, omar_kainzhamal@mail.ru, sholpan_kz@mail.ru

**DEMULSIFICATION EFFECT OF NON-IONIC SURFACTANTS
TWEEN-20, TWEEN-80 ON MODEL WATER-IN-OIL EMULSIONS**

Abstract. Breaking of water-in-oil emulsions is a necessary part of crude oil preparation for processing and the development of new demulsifying compositions has importance for the Republic of Kazakhstan. In this research the demulsification effect of non-ionic surfactants Tween-20, Tween-80 with high value of hydrophilic-lipophilic balance (HLB) was considered. For thermal treatment of water-in-oil emulsion the model emulsions based on crude oil of North-West Konys with 30%, 40%, 50%, 60 % (vol.) of water phase concentration were studied. *The degree of oil emulsion dewatering in the presence of Tween-20* do not exceed 63% at temperature 60°C. The optimal term of thermal chemical breaking down by means of mixtures of non-ionic surfactants Tween-20, Tween-80 and anionic surfactant sulfanol at a ratio of 1:1 (vol.) was determined. The maximum demulsification equaled to 97.01 % after 100 min for 30-50 % water-in-oil emulsions was found out for Tween-20 – sulfanol mixture at a ratio of 1:1 at 60°C. The results confirm the opportunity of using of mixtures of Tweens with anionic surfactant sulfanol as demulsifying reagents.

Keywords: thermal chemical demulsification, non-ionic surfactants, Tween-20, Tween-80, sulphanol, water-in-oil emulsions, breaking of water-in-oil emulsions.

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А.О.Адилбекова, К.И.Омарова, Ш.Абдрахманова

Казахский национальный университет имени аль-Фараби

**ДЕЭМУЛЬГИРУЮЩЕЕ ДЕЙСТВИЕ НЕИОННЫХ ПАВ ТВИН-20
И ТВИН-80 НА МОДЕЛЬНЫЕ НЕФТЯНЫЕ ЭМУЛЬСИИ**

Аннотация. Разрушение нефтяных эмульсий является важной частью подготовки нефти к переработке, поэтому разработка новых деэмульгирующих композиций является актуальной проблемой для Республики Казахстан. В работе рассмотрено деэмульгирующее действие неионных ПАВ Твин-20, Твин-80, обладающих высоким значением гидрофильно-липофильным балансом (ГЛБ). Для исследования термохимической обработки водонефтяной эмульсии были использованы модельные нефтяные эмульсии на основе нефти месторождения *Северо-Западный Коныс* с концентрацией водной фазы 30%, 40%, 50%, 60 % (объемн.). Степень обезвоживания нефтяной эмульсии в присутствии Твин-20 не превысила 63% при температуре 60°C. Определены оптимальные условия термохимического отстаивания в присутствии смесей неионных ПАВ Твин-20, Твин-80 и анионного ПАВ сульфанола в соотношении 1:1 (объемн.). Максимальная деэмульсация была обнаружена для композиции Твин 20 – сульфанол в соотношении 1:1 (объемн.) при 60°C и равна 97,01% после 100 минут отстаивания для водонефтяных эмульсий с содержанием воды в нефти 30-50%. Результаты подтверждают возможность использования смесей Твинов с анионным ПАВ сульфанолом в качестве деэмульгирующих реагентов для обезвоживания нефти.

Ключевые слова: термохимическое деэмульгирование, неионные поверхностно-активные вещества, Твин-20, Твин-80, сульфанол, водонефтяные эмульсии, разрушение нефтяных эмульсий.

Введение

Водонефтяные эмульсии (микрогетерогенные и ультрадисперсные капли воды, взвешенные в сырой нефти) образуются в результате добычи нефти. Устойчивость водонефтяных эмульсий может варьироваться от нескольких минут до нескольких лет и зависит от месторождения нефти и физико-химических характеристик нефти [1, 2]. Разрушение нефтяных эмульсий является важной частью подготовки нефти к переработке, поэтому разработка новых деэмульгирующих композиций является актуальной проблемой для Республики Казахстан.

Эмульсии сырой нефти должны быть разрушены, так как они из-за наличия воды и растворенных в ней хлоридов, вызывают коррозию трубопроводов, оборудования, используемого для переработки нефти, выкипание нефти при перегонке, что вызывает увеличение стоимости транспортировки и переработки нефти. Кроме того, наличие эмульгированной воды вызывает изменения свойств сырой нефти, таких как вязкость, плотность и др. [3].

Наиболее используемыми деэмульгаторами для разрушения нефтяных эмульсий являются высокомолекулярные неионные поверхностно-активные вещества (НПАВ). Такие ПАВ дают хороший деэмульгирующий эффект и не оставляют никаких противоионов в сырой нефти и нефтепродуктах. Молекулы неионных ПАВ с большим числом гидрофильных групп показывают хорошую деэмульгирующую способность [4].

В настоящей работе для подбора высокоэффективных дестабилизаторов водонефтяных эмульсий с оптимальным составом и природой композиционных компонентов были использованы полисорбаты, или так называемые Твины, которые относятся к полимерным ПАВ. Твины представляют собой вязкие, маслянистые жидкости и являются производными полиэтиленгликолей – сорбитанаэтерифицированного жирными кислотами. Гидрофильные свойства Твинам обеспечивают группы окиси этиленов $-(CH_2CH_2O)-$ и полиэфир карбоновой кислоты, а липофильные свойства – полисорбитан. Данные НПАВ используются на практике в основном для стабилизации эмульсии масло-вода, следовательно, было предположено что такие НПАВ могут быть эффективны для разрушения эмульсии воды в масле, т.е. могут быть использованы для разрушения водонефтяных эмульсий. Полимерные деэмульгаторы с довольно высокими значениями ГЛБ могут адсорбироваться на межфазной границе вода-нефть и разрушить адсорбционный слой эмульгаторов [1, 5]. Присутствие развитой гидрофильной части способствует большему отделению воды из нефти. Твины имеют подходящий гидрофильно-липофильный баланс из-за большого числа окисей этиленов. Оксигетилированные группы взаимодействуют с водной фазой за счет водородных связей и обеспечивают сильную гидрофильную часть молекуле ПАВ.

В работах [6, 7] показано, что высокая молекулярная масса, увеличение числа гидроксильных агентов и процента неионных полимеров в композициях деэмульгаторов улучшает деэмульгирующее действие ПАВ. Исследования показали, что увеличение числа ГЛБ эффективно для деэмульгирования [8]. Так как Твины имеют высокое значение ГЛБ, они, вероятно, могут способствовать разрушению эмульсии воды в сырой нефти.

В настоящее время недостаточно исследований по деэмульгирующему действию Твинов и их композиций для разрушения нефтяных эмульсий местных месторождений, испытывающих недостаток в эффективных деэмульгаторах.

Экспериментальная часть

Для исследования деэмульгирования были использованы НПАВ Твин 20 и Твин 80 и анионное поверхностно-активное вещество (АПАВ) сульфанол.

Твин-20 – полиоксиэтилен (20) сорбитан монолаурат, $C_{58}H_{114}O_{26}$. Твин-80 – полиоксиэтилен (20) сорбитан моноолеат, $C_{64}H_{124}O_{26}$.

Сульфанол, представляет собой смесь изомеров натриевых солей алкилбензолсульфокислот, с общей формулой $R-C_6H_4NaO_3S$, где R радикал соответствующий общей формуле C_nH_{2n+1} , где $n=14-18$.

Для приготовления модельной эмульсии вода-нефть была использована нефть месторождения Северо-Западный Коныс. Были определены ее физико-химические свойства нефти: плотность (833

кг/м³), содержание хлористых солей (1,5 мг/л), механических примесей (0,067 %), содержание серы (0,163 %)[9].

Обратные эмульсии вода-нефть были приготовлены путем смешивания безводной нефти месторождения Северо-Западный Конысс дистиллированной водой с получением эмульсии с концентрацией водной фазы 30%, 40%, 50%, 60 % (объемн.). Водная фаза содержала 20 % хлорида натрия. Эмульгирование было проведено при помощи гомогенизатора IKAT 10 basicUltra-Tiрах(Германия) при скорости 10000 rpm в течение 30 минут. Подготовленную эмульсию оставляли на неделю для стабилизации посредством адсорбции поверхностно-активных компонентов, входящих в состав сырой нефти. Увеличение времени перемешивания и числа оборотов перемешивания не оказало значительного влияние на устойчивость нефтяных эмульсий.

Измерение кинематической вязкости нефтяных эмульсий проводили с помощью стеклянных вискозиметров для нефти и нефтепродуктов по времени истечения нефтяной эмульсии.

Дисперсность водных капель была определена при помощи оптического микроскопа. Каплю нефти помещали на стеклянную пластину и распределяли на ее поверхности. Изображения были получены с помощью микроскопа «Leica DM6000M» в Национальной нанотехнологической лаборатории КазНУ имени аль-Фараби.

Для определения деэмульгирующей способности деэмульгатора 50 мл нефти помещали в градуированную пробирку, добавляли с помощью микродозатора необходимое количество деэмульгатора и перемешивали посредством гомогенизатора в течение 5 мин при 10000 об/мин. Затем пробирку устанавливали в термостат при температуре 40-60°C и определяли через каждые 10 мин объем выделившейся воды. Одновременно визуально оценивали интенсивность окрашивания водного слоя и четкость границы поверхности раздела фаз.

Результаты и их обсуждения

Для изучения разрушения нефтяных эмульсий были получены модельные эмульсии на основе нефти месторождения Северо-Западный Коныс. Модельные эмульсии имели различное содержание дисперсной фазы от 30% до 60% (объемн.). Данным концентрациям водной фазы искусственных эмульсий соответствует обводненность сырой нефти месторождений Казахстана в результате длительной эксплуатации скважин. Увеличение содержания воды также помогает моделировать нефтяные эмульсии с различной вязкостью.

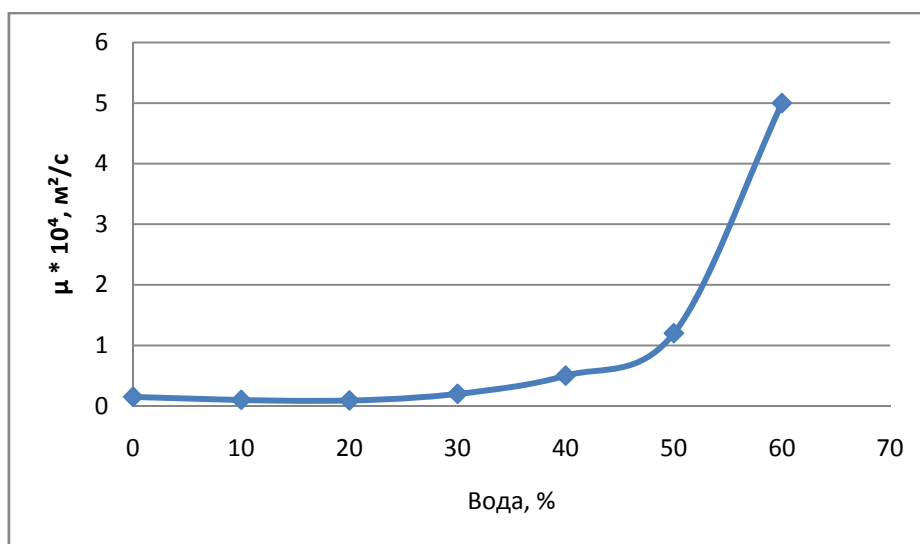
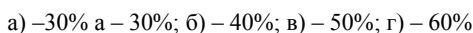


Рисунок 1— Зависимость кинематической вязкости нефтяной эмульсии от содержания воды. T=20°C

Эмульсии с содержанием воды 10% и 20% по вязкости близки к исходной нефти. Увеличение содержания воды в нефти до 50 % - 60 % существенно сказывается на вязкости эмульсии. Для 60 % вязкость возрастает в 50 раз по сравнению с исходной нефтью.



на сорбите (иначе – сорбитол, глюцит – вещество, часто применяемое в качестве заменителя сахара в диетических продуктах, получают его из фруктов, часто из косточек плодов) и жирных кислотах из базовых масел: кокосового – Твин-20, оливкового – Твин-80. Твины обладают свойством легко разлагаться в природных средах, что, вероятно, не будет вызывать ухудшения качества обрабатываемой нефти, как при воздействии другими химическими реагентами[12]. Кроме того, было интересно исследовать деэмульгирующее действие Твинов, так как в их составе содержится достаточно большое количество групп оксидов этиленов, число их в Твинах равно 20. То есть, как было указано выше они обладают развитой гидрофильной частью, способной проникать в межфазный слой вокруг глобулы воды.

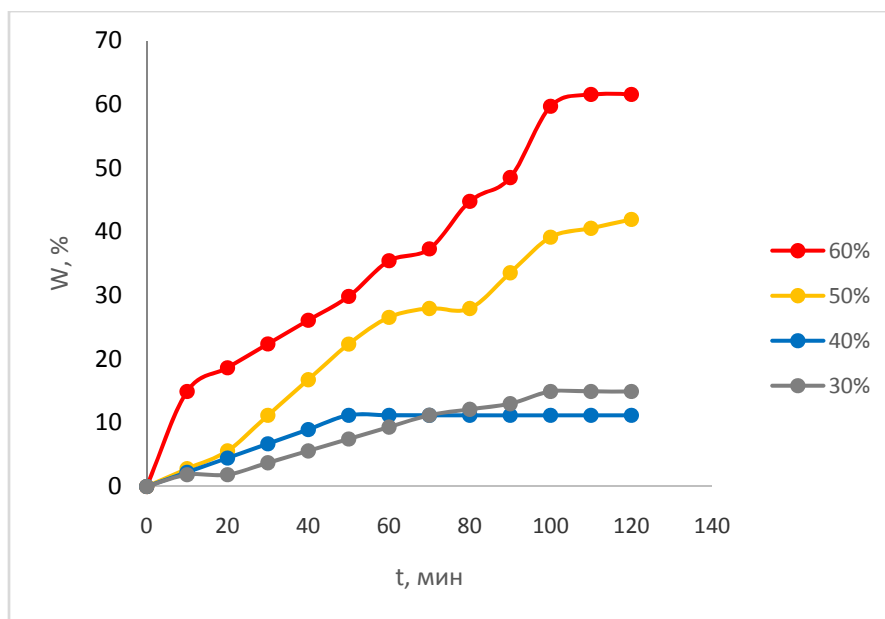


Рисунок 3– Количество отделившейся воды из нефтяных эмульсий различной концентрации при добавлении в качестве деэмульгатора водного раствора Твин-20.
T = 60°C

Увеличение температуры до 60°C приводит к уменьшению вязкости нефтяной среды, а также к увеличению разности плотности дисперсной фазы и дисперсионной среды, что облегчает коалесценцию глобул воды при их столкновении согласно закону Стокса. Однако, дальнейшее увеличение температуры с целью повышения водоотделения не целесообразно, так как это может привести к улетучиванию легких фракций нефти.

Было изучено деэмульгирующее действие композиций Твинов с анионоактивным поверхностно-активным веществом сульфанола. Сульфанол является более гидрофильным ПАВ по сравнению с НПАВ, поэтому для увеличения гидрофильно-липофильного баланса было исследовано деэмульгирующее действие композиции Твин – сульфанол. Кроме того, сульфанол относится к достаточно доступным техническим анионным ПАВ. Композиция Твин 20 – сульфанол была использована в соотношении 1:1 (объемн.).

При комнатной температуре и при повышении температуры до 40°C в присутствии композиции НПАВ-АПВ водоотделения также, как и в случае индивидуальных Твин-20 и Твин-80 не наблюдалось. Начиная с 50°C, уже через 10 минут отстаивания степень обезвоживания была равна 60% и достигла 95,24% для 30-50% водонефтяных эмульсий после 100 минут обработки. При 60°C для 30-50% эмульсий максимальная степень обезвоживания 97,01%, а для 60% эмульсии – 83,96% (рисунок 4).

Для композиции Твин - сульфанол в отличие от индивидуальных НПАВ, видно, что 60% эмульсии имеет более низкую степень дегидратации, чем водонефтяные эмульсии с меньшей концентрацией водной фазы.

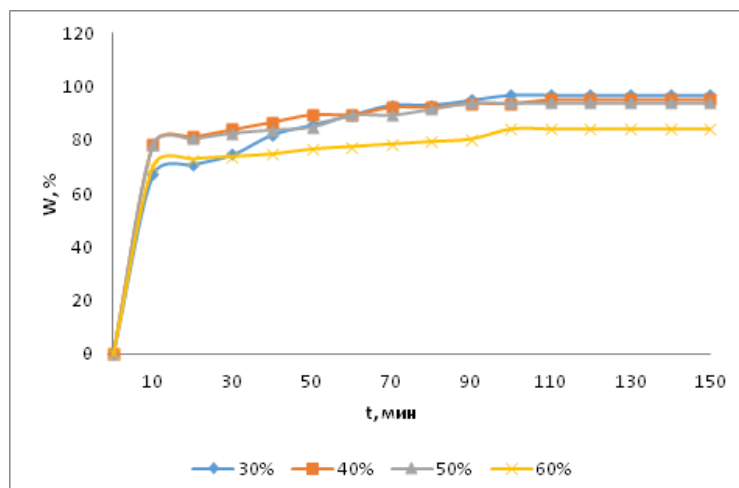


Рисунок 4– Степень обезвоживания нефтяных эмульсий различной концентрации в присутствии композиции Твин-20 – сульфанола. $T = 60^{\circ}\text{C}$

Для водных смесей Твин 80 – сульфанола степень водоотделения при 50°C для 30-40% эмульсий степень разрушения равна 78,43%. А для 60% эмульсии $W = 63,43\%$ при этой же температуре. При увеличении температуры до 60°C для водонефтяных эмульсий 30-40% максимальная степень обезвоживания составила 82,09% и 75,63% соответственно, для 60% эмульсии – 59,7% (рисунок 5).

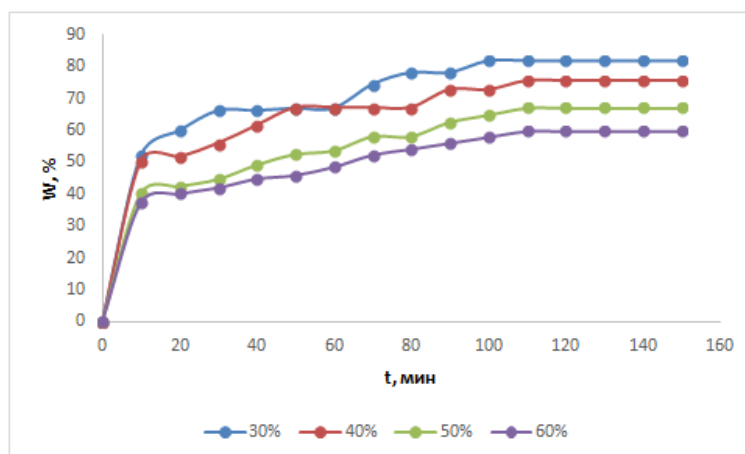


Рисунок 5– Степень обезвоживания нефтяных эмульсий различной концентрации в присутствии композиции Твин-80 – сульфанола. $T = 60^{\circ}\text{C}$

Смесь Твин-20 – сульфанола показывает большее деэмульгирующее действие на водонефтяные эмульсии, как и в случае индивидуальных НПВ. Это может быть связано с большей межфазной активностью Твин-20, по сравнению с Твин-80. Смесь ПАВ Твин-20 – сульфанола оказывает аддитивное деэмульгирующее действие для дестабилизации эмульсий, вследствие вытеснения природных стабилизаторов нефтяных эмульсий с межфазного слоя вода / нефть.

Закключение

Были определены оптимальные условия термохимического отстаивания в присутствии неионных ПАВ (Твин-20, Твин-80) с сравнительно высокими значениями ГЛБ и их смесей с анионным ПАВ сульфанола. Использование Твин-20 для разрушения нефтяных эмульсий не превысило 63% при температуре обработки 60°C . Степень обезвоживания для Твин-80 была ниже, около 12 % для 50% водонефтяной эмульсии.

Было исследовано деэмульгирующее действие смеси 1% водных растворов НПАВ и АПАВ в соотношении 1:1 (объемн.). Максимальная деэмульсация была обнаружена для композиции Твин 20 – сульфанола в соотношении 1:1 (объемн.) при 60°C и равна 97,01% после 100 минут отстаивания для водонефтяных эмульсий с содержанием воды в нефти 30-50%. Показана возможность использования смесей Твинов с анионным ПАВ сульфанола в качестве деэмульгирующих реагентов для обезвоживания нефти.

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А.О.Адильбекова, Қ.И.Омарова, Ш.Абдрахманова

Әл-Фараби атындағы Қазақ ұлттық университеті

МОДЕЛЬДІ МҰНАЙ ЭМУЛЬСИЯЛАРЫНА ИОНДЫ ЕМЕС БАЗ ТВИН-20 ЖӘНЕ ТВИН-80-НІҢ ДЕЭМУЛЬСИЯЛАУ ӘСЕРІ

Аннотация. Мұнайды өңдеуге дайындауда мұнай эмульсияларын бұзу маңызды болғандықтан Қазақстан Республикасы үшін жаңа деэмульсиялаушы композицияларды жасау өзекті мәселе болып табылады. Жоғары ГЛБ мәніне ие ионды емес БАЗ Твин-20 және Твин-80-нің деэмульсиялау әсері зерттелді. Термохимиялық өңдеуді зерттеу үшін сулы фаза концентрациялары 30%, 40%, 50%, 60 % (көл.) болатын моделді мұнай эмульсиялары қолданылды. Мұнай эмульсиясының сусыздану дәрежесі Твин-20 қатысында 60°C-да 63%-дан аспады. Твин-20, Твин-80 және анионды БАЗ сульфанола 1:1 (көл.) қатынастағы қоспалардың қатысындағы термохимиялық тұндырудың оптималды шарттары анықталды. Твин-20 мен анионды БАЗ сульфанола 1:1 (көл.) қатынастағы композициясы максималды деэмульсиялауды көрсетеді және 30-50% суы бар мұнай эмульсияларында 60°C 100 минут тұндырудан кейін 97,01%-ға тең екені табылды. Деэмульгирлеуші реагенттер ретінде Твиндердің анионды БАЗ сульфаноламен қоспаларын қолдануға болатын мүмкіндігі көрсетілді.

Түйін сөздер: термохимиялық деэмульсиялау, ионды емес беттік-активті заттар, Твин-20, Твин-80, сульфанола, су-мұнайлы эмульсиялар, мұнай эмульсияларын бұзу.

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A.Bayeshov¹, A.K.Bayeshova², U.A.Abduvaliyeva²

¹Institute of Fuel, Catalysis and Electrochemistry named after D.V. Sokolsky, Almaty, Kazakhstan;

²Kazakh national university named after Al-Faraby, Almaty, Kazakhstan,

E-mail: bayeshov@mail.ru, azhar_b@bk.ru, abdumida14@gmail.com

INFLUENCE OF CUPROIONS ON COPPER POWDERS FORMATION IN ELECTROREFINING OF COPPER

Abstract. The purpose of this work was to determine the ways of copper powders forming penetrating into the sludge when copper is produced by electro-refining. Our studies were carried out by electrolysis in galvanostatic conditions and by potential measurements using Autolab PGSTAT 302 potentiostat. The temperature varied between 25 and 75° C. Copper ions concentration in solutions after electrolysis was determined by potentiometric titration.

It is shown that copper ions (II) in sulfuric acid solutions in the presence of titanium (III) ions are reduced to form elemental copper in powder, forms and sizes of particles in copper powders are determined by the electron microscopic method.

Results of study showed an assumptions about possibility of forming powders due to mechanical shedding during anodic copper dissolution are not confirmed.

Our studies results allow us to conclude that the anode potential rises, then decreases, therefore, it constantly fluctuates and leads to copper powders formation at this time. Cuproions's concentration depends on copper electrode potential and its oscillation can promote a shift in the equilibrium of $\text{Cu}^0 \leftrightarrow \text{Cu}^+ + e$ reaction to the right or to the left. In industrial conditions, the value of the current in the circuit and the temperature of electrolyte can not be kept constant. For this reason, there is a periodic anode potential oscillation with different frequency amplitude. When anode potential is shifted to negative region, it is possible to form a copper powder according to an above reaction.

However, the formed copper atoms can not penetrate into crystal lattice of the anode. As a result, finely dispersed copper powders are formed on the electrode surface; they gradually pass into the solution and then penetrate into sludge.

For the first time, on the basis of study and analysis results, a mechanism is established for copper powders formation penetrating into the sludge composition during the electro-refining of copper. It is shown that the formation of copper powders, their penetration into the sludge composition, is mainly directly related to the oscillation of anode potential in electrolysis process and formation of various potential values at various sites of the electrode surface.

Key words: copper, powder, cuproion, sludge, refining, potential, electrolysis, anode, cathode, electrolyte, reduction.

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ҒТАМР 31.15.33

А.Баешов¹, А.К.Баешова², У.А.Абдувалиева²

¹Д.В.Сокольский атындағы Жанармай, катализ және электрохимия институты, Алматы, Қазақстан;

²Әл-Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан

ЭЛЕКТРОРАФИНАЦИЯЛАУ КЕЗІНДЕ МЫС ҰНТАҚТАРЫНЫҢ ТҮЗІЛУІНЕ КУПРОИНДАРДЫҢ ӘСЕРІ

Аннотация. Бұл жұмыстың мақсаты мысты электрорафинация әдісімен алу кезінде шлам құрамына өтетін мыс ұнтағының түзілу жолдарын анықтау болып табылады. Зерттеулер гальваностатикалық жағдайда электролиз жүргізу арқылы және Autolab PGSTAT 302 потенциостаты көмегімен потенциалдар өлшеу әдісімен жүргізілді. Температура 25-75⁰C аралығында өзгертілді. Электролизден кейінгі ерітінділердегі мыс иондарының концентрациясы потенциометриялық титрлеу әдісімен анықталды. Мыс (II) иондарының күкіртқышқылды ерітінділерде титан (III) иондарының қатысында тотықсызданып, элементті мыс - ұнтақ күйінде түзілетіні көрсетілді. Түзілген мыс ұнтақтарының бөлшектерінің формасы, өлшемдері электрондық микроскопия әдісімен анықталды. Зерттеу нәтижелері ұнтақтардың анодтың еруі кезінде механикалық үгілу салдарынан түзілуі туралы болжам расталмады.

Біздің тәжірибелеріміздің нәтижелері анод потенциалының жоғарылап, төмендеуі демек, оның ауытқуы мыс ұнтақтарының сол сәтте түзілуіне әкелетіндігі жайында қорытынды жасауға мүмкіндік береді. Купроиондардың концентрациясы мыс электродының потенциалына тәуелді және оның ауытқуы $\text{Cu}^0 \leftrightarrow \text{Cu}^+ + e$ реакциясының тепе-теңдігін оңға немесе солға ығыстыруы мүмкін. Өндірістік жағдайда тізбектегі токтың мөлшерін және электролит температурасын тұрақты түрде ұстап тұру мүмкін емес. Сол себептен анодтағы потенциал әр сәтте периодты түрде әртүрлі амплитудамен белгілі мәнге ауытқып тұрады. Анодтың потенциалы теріс жаққа қарай ығысқан сәтте жоғарыда көрсетілген реакция бойынша мыс ұнтағының түзілу мүмкіндігі туындайды. Бірақ түзілген мыс атомдары анодтың кристалдық торына кіріп, орналаса алмайды. Осының салдарынан электрод бетіне нашар жабысқан майда дисперсті мыс ұнтағы түзіледі, содан кейін олар біртіндеп ерітіндіге көшеді де, соңында шлам құрамына өтеді.

Алғаш рет зерттеу және талдау нәтижелері негізінде мысты рафинациялау кезінде шлам құрамына өтетін мыс ұнтағының түзілу механизмі анықталды. Мыс ұнтақтарының пайда болып, тұнбаға түсіп, шлам құрамына өтуі – негізінен, электролиз кезіндегі анод потенциалының ауытқып тұруымен және электрод бетіндегі әр аумақта әртүрлі потенциалдардың қалыптасуымен тікелей байланысты екені көрсетілді.

Кілт сөздер: мыс, ұнтақ, купроион, шлам, рафинация, потенциал, электролиз, анод, катод, электролит, тотықсыздану.

Кіріспе. Дәстүрлі қалыптасқан технологиялар бойынша пирометаллургиялық әдіспен алынған кара мыстың 90%-тен астамы электрорафинация процестері арқылы тазаланып, нәтижесінде 99,9%-тен жоғары тазалықтағы металл алынады [1-10]. Мысты электролиттік рафинациялау кезінде сирек және бағалы металдар ерітіндіге өтпей, қосылыс түрінде электролизердің түбіне шлам болып шөгіп жинақталады, бұл тұнбаға дисперсті мыс ұнтақтары да түседі, оның мөлшері 60%-тен асады.

Бір тонна катодтық мыс алынғанда, 1-1,5 кг шлам бөлінеді. Шламның құрамы анодтың құрамына тәуелді. Бүкіл әлемдегі электрорафинация әдісі бойынша таза мыс алу кезінде түзілетін шламның құрамындағы металдар мен қосылыстардың мөлшері (орташа есеппен алынған), %:

$\text{Cu} - 10 - 66 \text{ As} - 0,1 - 4,0 \text{ Ni} - 0,05 - 0,5$

$\text{Ag} - 3 - 55 \text{ Bi} - 0,001 - 0,5 \text{ SiO}_2 - 0,3 - 7,0$

$\text{Au} - 0,05 - 4,0 \text{ Se} - 2 - 28 \text{ SO}_4^{2-} - 6 - 15$

$\text{Pb} - 0,9 - 12,0 \text{ Te} - 0,01 - 6,0$

$\text{Sb} - 0,04 - 30,0 \text{ Fe} - 0,04 - 1,5$

Шлам құрамына түсетін дисперсті мыс ұнтақтары, оның құрамындағы алтын, күміс, селен, теллур сияқты құнды элементтерді бөліп алуды қиындатып жібереді. Қысқаша айтқанда, электрорафинация кезінде дисперсті мыс ұнтақтарының шлам құрамына түсуі - қажетсіз құбылыс, осы мәселеге көптеген зерттеулер де арналған. Бірақ ғалымдар мыс ұнтақтарының шламға түсуінің табиғатын 100 жылдан аса уақытта нақты түсіндіре алмай келеді.

Егер қысқаша тоқталар болсақ, электролиз кезінде мыс ұнтақтарының түзілуін кейбір авторлар [13-15], оның құрамындағы теріс потенциалды металдардың қоспа түрінде болуымен түсіндіреді. Бұл авторлардың пікірі бойынша, құрамында теріс потенциалдарға ие металдар (Ni, Fe, Zn және т.б.) бар құйма анодтық поляризация нәтижесінде тез еріп кетеді де, потенциалы оң мыс, ерімей, ұнтақ түрінде үгітіліп түседі. Шынында да, жүргізілген зерттеулер көрсеткендей, мыстың құрамында теріс металдардың мөлшері көп болған сайын, олар еріген кезде мыс ұнтақтарының мөлшерінің өсетіндігі байқалған.

Мыс анодының бір қалыпты ерімеуі де мыс ұнтақтарының түзілу себебінің бірі болуы мүмкін деген көзқарастар да бар. Электролиз кезінде мыс анодының біркелкі ерімейтіндігін көзбен де көруге болады.

Арнайы зерттеулердің нәтижелері шламға түскен мыс ұнтағының өте майда екендігін көрсеткен. Сол себепті кейбір ғалымдар, бұл ұнтақтар химиялық жолмен диспропорциялану реакциясының нәтижесінде түзіледі деген жорамалға келген [16,17]:



Бірақ Г.В. Макаровтың және тағы да басқа авторлардың [10, 13] зерттеу нәтижелері көрсеткендей, электроаффинация кезінде электролит көлеміндегі бір валентті иондардың концентрациясы тепе-теңдік жағдайына дейін жетпейтіні байқалған. Сол себептен мыс ұнтағының жоғарыда көрсетілген химиялық реакцияның жүруі нәтижесінде түзілуі мүмкін емес екендігін біржақты пайымдауға болады. Бұл болжамдардың тағы да бір дәлелі: таза мыс анодты еріген кезде де мыс ұнтағының түзілуі байқалады.

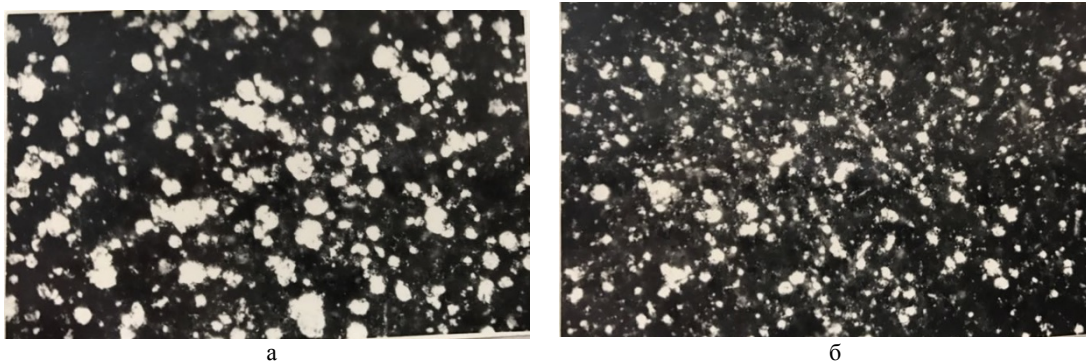
Егер мыс ұнтақтары механикалық жолмен түзілсе, олардың бөлшектерінің өлшемдері ірілеу болуы тиіс. Ал химиялық жағдайда бұл қалай болады? Осындай сұрақтарға жауап беру қажет болды. Осыған орай, біздің жұмысымыздың мақсаты мыс иондарының тотықсыздану процесін әртүрлі жағдайларда зерттеу болып табылады.

Әдістеме. Зерттеулер гальваностатикалық жағдайда электролиз жүргізу арқылы және Autolab PGSTAT 302 потенциостаты көмегімен потенциалдар өлшеу әдісімен жүргізілді. Температура 25-75°C аралығында өзгертілді. Электролизден кейінгі ерітінділердегі мыс иондарының концентрациясы потенциометриялық титрлеу әдісімен анықталды. Мыс (II) иондары күкіртқышқылды ерітінділерде титан (III) иондарының қатысында тотықсыздандырылды. Бұл кезде мыс келесі реакция бойынша тотықсызданады да, ұнтақ күйінде түзіледі:



Түзілген мыс ұнтақтарының бөлшектерінің формасын, өлшемдерін электрондық микроскопия әдісімен зерттедік.

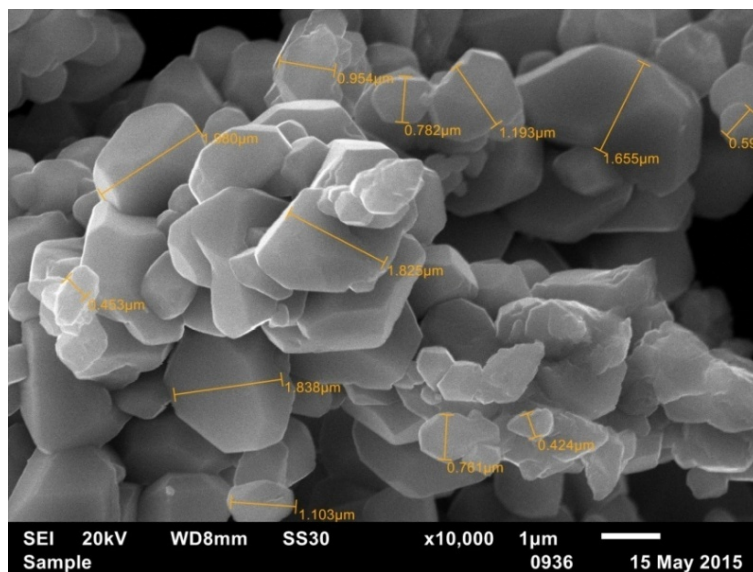
Алынған нәтижелер және оны талқылау. Мыс ұнтақтарының осы реакция (2) бойынша түзілуі мынадай реакцияның $\text{Cu}^+ + e \rightarrow \text{Cu}^0$ нәтижесіне ұқсас, себебі бұл жерде де металл ұнтақтары электрон алмасу арқылы іске асады. Цементация кезінде түзілетін мыс ұнтақтарының формалары 1-суретте көрсетілген. Суретке түсіру шағылысқан жарықта аншлиф арқылы іске асырылды. Мыс ұнтақтарының бөлшектері әртүрлі болады: дұрыс емес, изометрлік, ал кейбіреулері әртүрлі кескінде, сопақшалау. Бөлшектердің шеттері тегіс емес болып келеді. Бөлшектердің өлшемдері 0,001-0,10 мм аралығында ауытқиды. Көлденеңінде өлшемдері 0,01 – 0,10 мм болатын бөлшектердің мөлшері басым екені байқалды. Ал жоғары температураларда ($t = 90^\circ\text{C}$) мыс бөлшектерінің өлшемдері кішірейеді (көлденеңінде 0,001-0,005 мм бөлшектердің мөлшері басым). Яғни, бөлшектердің өлшемі олардың түзілу жағдайына байланысты болады. Сондықтан, бұрын жасалған болжамдағыдай [13-15], металл бөлшектерінің әртүрлі формалары мен өлшемдері мыс ұнтақтарының анодтық-механикалық үгілуі нәтижесінде түзілуінің дәлелі бола алмайды.



1-сурет. Мыс (II) иондарының үш валентті титан (III) иондарымен цементациялануы кезінде алынған брикеттелген мыс ұнтағының аншлифінің суреті: а) 25°C б) 90°C; үлкейту x 1200.

Мыс ұнтақтары катод бетінде де түзілуі мүмкін деп жорамалдауға болады. Әдетте электрорафинация процесі мыс иондарының концентрациясы 40 г/л-ге тең, ал катодтағы ток тығыздығы 250 А/м²-ден жоғары емес болған кезде жүреді. Мұндай үлкен концентрацияда катод бетінде шектелген токтан жоғары ток тығыздығының орнығуы тіптен мүмкін емес. Салыстыру үшін құрамында 1,2 г/л мыс (II) иондары, 50 г/л күкіртқышқылы бар ерітіндіден катодтық ток тығыздығы 3000 А/м²-ге тең болғанда түзілген мыс ұнтақтарының микрофотографиясы алынды (2-сурет). Бұл суреттен бөлшектерінің размерлері 1 мкм шамадағы біркелкі болып келетін мыс ұнтақтарының түзілетіні анықталды. Әдеби деректер бойынша [13,19] шлам құрамындағы мыс ұнтақтарының размерлері 0,007-0,10 мм болатындығы көрсетілген.

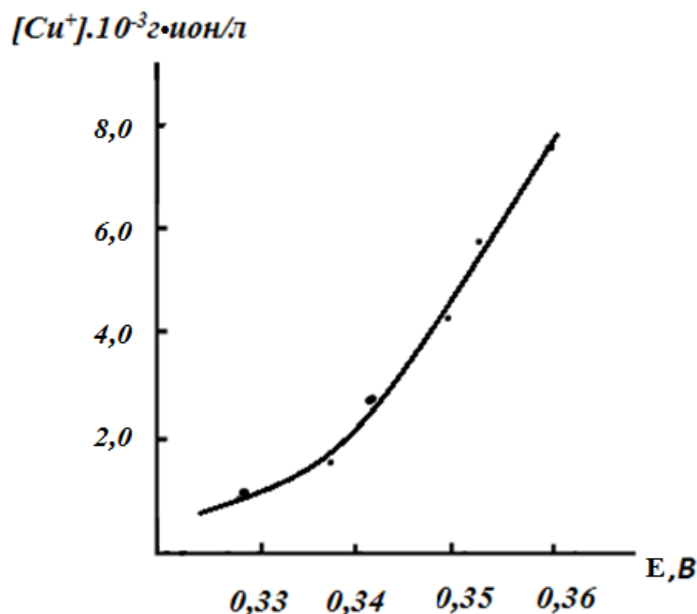
Біздің алдын-ала жан-жақты жүргізген жұмыстарымыздың нәтижелері анод потенциалының жоғарылап, төмендеуі демек, оның ауытқуы мыс ұнтақтарының сол сәтте түзілуіне әкелетіндігі жайында қорытынды жасауға мүмкіндік береді. Біз анықтағандай, купроиондардың концентрациясы мыс электродының потенциалына тәуелді және оның ауытқуы $\text{Cu}^0 \leftrightarrow \text{Cu}^+ + e$ реакциясының тепе-теңдігін оңға немесе солға ығыстыруы мүмкін. Өндірістік жағдайда тізбектегі токтың мөлшерін және электролит температурасын тұрақты түрде ұстап тұру мүмкін емес, сәйкесінше анодтағы потенциал әр сәтте белгілі мәнге ауытқып тұрады. Анодтың потенциалы теріс жаққа қарай ығысқан сәтте жоғарыда көрсетілген реакция бойынша мыс ұнтағының түзілу мүмкіндігі туындайды. Бірақ түзілген мыс атомдары анодтың кристалдық торына кіріп, орналаса алмайды. Осының салдарынан электрод бетінде нашар жабысатын майда дисперсті мыс ұнтағы түзіледі, олар біртіндеп ерітіндіге көшіп, содан кейін шламға түседі.



2-сурет - Катодты токпен поляризациялау кезінде түзілген мыс ұнтақтарының микросуреті

Басқаша түсіндіретін болсақ, электродтың кристалдық торына мыс атомының енуі қиындай түседі. Оның себебі, потенциалдың теріс жаққа қарай аз мәнге ғана ығысуына қарамастан, электрод анод болып қала береді. Егер, біз мысты электрорафинациялау кезінде өндірістік жағдайда анодтың потенциалы 0,5 мВ амплитудамен және 1Гц жиілікте орташа ауытқып отырады деп болжасақ, $\text{Cu}^+ + e \rightarrow \text{Cu}^0$ реакциясы бойынша түзілетін мыс ұнтағының мөлшерін есептеуге болады. Әдеби мәліметтерде [13] өндірістік электролиз жағдайында да (ауа атмосферасында) ерітіндіде бір валентті мыс иондары электролит көлемінде болатыны көрсетілген. Ал электролиз кезінде диффузиялық қабатта әрқашанда купроиондардың тепе-теңдік мөлшері болады. Олар тепе-теңдік теріс потенциал жағына ығысқан сәтте мыс атомдарының түзілу бағытына қарай ығысады.

Біздің зерттеулеріміз бір валентті мыс иондарының ерітіндідегі концентрациясы мыс электродының потенциалына тәуелді екенін көрсетті (3 сурет).



3 сурет - Купроиондар концентрациясының электродтық потенциалдың мәніне тәуелділігі

Олай болса, мыс электродындағы потенциалдың бір вольтке өзгергенде байқалатын купроиондардың концентрациясының өзгеруін жуықтап есептеуге болады:

$$\lg(\Delta[\text{Cu}^+])/\Delta E = 0,0064/0,035 = 0,182 \text{ г-ион/л} = 11,6 \text{ г/л} \quad (3)$$

Мысты электрорафинациялау цехында алынған деректерге сүйеніп, есептеулер жүргіздік. Анодтың потенциалы теріс жаққа қарай 0,001 В –ке ығысқан сәтте $\text{Cu}^+ + e \rightarrow \text{Cu}^0$ реакциясы бойынша 0,0116 г/л мыс ұнтағы түзіледі. 1гц-ке тең жиілікте 20 тәулік ішінде болатын ауытқу санын есептеуге болады:

$$20 \cdot 60 \cdot 60 \cdot 24 = 1728000 \text{ рет (потенциалдың ауытқу саны)} \quad (4)$$

Бір литр электролитте түзілетін мыс ұнтағының мөлшерін есептейік: $1728000 \cdot 0,0116 = 20,189$ кг. Ал реакцияға диффузиялық қабаттағы купроиондар қатысатындықтан, бір сериядағы диффузиялық қабаттың көлемін есептеу қажет. Электролиз цехындағы сериялық анодтар саны 740 дана, олардың жалпы беті 1480 м², ал диффузиялық қабаттың қалыңдығы $\delta = 10^{-3}$ см [17]. Осы мәндерді пайдаланып, диффузиялық қабаттың жалпы көлемін есептеуге болады:

$$V = S_{\text{ж}} \cdot \delta = 148000 \text{ дм}^2 \cdot 0,0001 \text{ дм} = 14,8 \text{ литр}. \quad (5)$$

Әрбір сериядағы кері иондану реакциясы бойынша түзілген мыстың жалпы мөлшері, 20 тәулік ішінде:

$$P = 14,8 \cdot 20,189 = 299,597 \text{ кг} \quad (6)$$

Әдебиеттегі мәліметтер бойынша осындай жағдайда шламға жуық шамамен 100 кг мыс ұнтағы өтеді [4]. Назар аударатын болсақ, түзілген мыс ұнтағының мөлшері өндірістік жағдайда мысты электрорафинациялауда алынған мөлшерімен қанағаттанарлық сәйкестікте екендігін байқауға болады. Есептеулердің нәтижелері анодтық потенциалдың ауытқуы, шын мәнінде, мыс ұнтағының түзілуінің көзі бола алатындығын көрсетеді. Сонымен, анод потенциалының теріс жаққа қарай ауытқуы кезінде электрод бетінде төмендегі реакция орын алады:



Жоғарыда келтірілген реакцияның (7) жүру нәтижесінде металл ұнтақтарының түзілу себептерін анықтау үшін арнайы зерттеулер жүргізілді. Инертті ортада қышқылды мыс сульфаты

ерітіндісіне мыс электроды салынды және ұзақ уақыт осы күйде ұсталды. Сол кезде мынадай реакция орын алады:



Осы реакцияның жүру барысында тепе-теңдік күйде бір валентті мыс иондары түзілді, содан кейін мыс электроды алып тасталды. Осыдан кейін электролитті бөлме температурасына дейін суытқан кезде мыс ұнтақтарының реакция (1) нәтижесінде түзілуі байқалмайды. Мыс ұнтақтарының түзілуі тек мыс электродын қайта электролитке салған кезде ғана байқалады. Демек, мыс ұнтағының түзілуі электролитте мыс электроды бар кезде ғана орын алады.

Механикалық үгілу жолымен мыстың (макробөлшектердің) шламға түсуін жоққа шығаруға болмайды, бірақ бұл процесс кездейсоқ болуы мүмкін. Анодтық потенциалдың ауытқуы майда дисперсті мыс ұнтағының түзілу көзі болатындығын дәлелдеу үшін анодты импульсті токпен арнайы тәжірибелер жүргізілді, яғни анод потенциалының ең көп мөлшерде ауытқуын туғызу үшін жасанды жағдайлар жасалды. Анодты импульсті токты тізбек арқылы жіберу механикалық тәсілмен іске асырылды, ал оның жиілігін өзгерту электромотордың айналу жылдамдығымен реттелді.

Тәжірибе нәтижелері көрсеткендей, импульсті токпен мыстың электролизі кезінде анодты импульсті токтың жиіліктері өсуі кезінде түзілетін металл ұнтағының мөлшері артатыны байқалды (1-кесте). Бұл кезде анод бетінде түзілген мыс ұнтақтарының бөлшектерінің размерлері 0,001 – 0,10 мм аралығында болады.

1-кесте - Мыс ұнтағының мөлшеріне анодты импульсті токтың жиілігінің әсері: ерітіндіде: 40 г/л Cu^{2+} , 150 г/л H_2SO_4 , температура -60°C, ток тығыздығы - 240 А/м², электрод бетінің ауданы - 6 см², тәжірибе ұзақтығы - 4 сағ., (1 кулон 0,658 мг мысқа сәйкес)

Анодты импульсті ток жиілігі, минутта	Түзілген мыс ұнтағының мөлшері	
	1 кулонға есептегенде, 10 ⁻³ мг	%, еріген мыстан есептегенде
0	0,079	0,012
30	0,201	0,030
60	0,798	0,120
100	0,824	0,121

Токтың ауытқуы болмаған кезде мыс ұнтақтарының түзілуін төмендегідей түсіндіруге болады. Белгілі әдебиетте көрсетілгендей [18], электрод бетіндегі ток тығыздығы оның әрбір аумағында бірдей бола алмайды, нәтижесінде әртүрлі потенциалдар аумағы орнығады.

Одан басқа анод бетіндегі меншікті салмақтар айырмашылығының және циркуляция салдарынан электролиттің өздігінен араласып тұратыны белгілі. Бұл мәліметтер бойынша электрод бетінде электролиттің табиғи конвективті араласуының жылдамдығы 4 мм/сек тең және ол электролиттің мәжбүрлі араласу жылдамдығынан 20 есе артық [19].

Осы кезде, купроиондар анод бетінің оң потенциал бөлігінен теріс потенциал бөлігіне қарай ығысып, металдық мысқа дейін тотықсыздана алады. Ал мыс ұнтақ күйінде шламға өтеді. Электрод (анод) бетінің кедір-бұдыр болуы бұл эффектін жоғарылатады, себебі анодтың көтерілім және ойық аймақтарында потенциалдар мәндері әр түрлі. Егер электродты процестер сатылы және металдық ұнтақ диспропорциялану реакциясы бойынша түзіледі деп есептесек, онда оның мөлшері ток тығыздығы артқан сайын өсуі керек, себебі аралық бір валентті мыс иондарының саны, сәйкесінше, өседі. Бұл мәселе бойынша әдебиеттегі мәліметтер бір-біріне қарама-қайшы. Мысалы, Е.Хайнерт [20] және Е.С.Лецих [21], ток тығыздығының артуы анодтық шламдағы элементті мыс мөлшерінің жоғарылауын тудыратынын айтады. Ал, басқа авторлар Е.Вольвилль [22] және А.Аллмандтың [23] жұмыстарында ток тығыздығының артуы анодтық шламдағы элементті мыс ұнтағының мөлшерінің төмендеуіне әкеледі деп көрсетілген. Ал Г.В.Макаровтың [13] мәліметтері бойынша мыс ұнтағының мөлшері ток тығыздығына байланысты емес. Осындай әртүрлі қарама

қайшы пікірлерді былайша түсіндіруге болады. Мыс ұнтағының мөлшері барлық жағдайда тоқ тығыздығына тәуелді емес, ол анод потенциалының ауытқуына және электрод бетінің әртүрлі аумақтарында әртүрлі потенциалдардың орнығуына байланысты. Бұл тұжырымды біз жүргізген зерттеулердің нәтижелері көрсетіп отыр. Сонымен қатар [24] мәліметтер бойынша, мыстың бір валентті иондары инертті ортада қышқылды ерітінділерде тұрақты (мыс электроды болмаған кезде) болатыны байқалған. Біз жүргізген жан-жақты зерттеулер де осы ойды толықтыра түседі.

Зертханалық жағдайда потенциалдың ауытқуы кезінде және өндірістік жағдайда мысты электрорафинациялау кезінде түзілген мыс ұнтақтарының мөлшері шамамен 0,04% құрайды. Мысты электрорафинациялау практикасынан белгілі болғандай, шламның мөлшері еріген мыс анодының мөлшерінің 0,1 % - ін құрайды.

Қорыта айтқанда, алғаш рет зерттеу және талдау нәтижелері негізінде мысты рафинациялау кезінде шламға түсетін мыс ұнтағының түзілу механизмі анықталды. Мыс ұнтақтарының пайда болып, тұнбаға түсіп, шлам құрамына кіруі негізінен электролиз кезіндегі анод потенциалының периодты түрде ауытқып тұруымен және электрод бетіндегі әр аумақта әртүрлі потенциалдардың қалыптасуымен тікелей байланысты екені көрсетілді.

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А. Башов¹, А.К. Башова², У.А. Абдувалиева²

¹Институт топлива, катализа и электрохимии имени Д.В. Сокольского, Алматы, Казахстан;

²Казахский национальный университет имени аль-Фараби, Алматы, Казахстан

ВЛИЯНИЕ КУПРОИОНОВ НА ОБРАЗОВАНИЕ МЕДНЫХ ПОРОШКОВ ПРИ ЭЛЕКТРОРАФИНИРОВАНИИ МЕДИ

Аннотация. Целью данной работы явилось определение путей формирования порошков меди, проникающих в состав шлама при получении меди электрорафинированием. Исследования проводились методом электролиза в гальваностатических условиях и методом измерения потенциалов с помощью потенциостата Autolab PGSTAT 302. Температура изменялась в интервале 25-75⁰С. Концентрацию ионов меди в растворах после электролиза определяли методом потенциометрического титрования. Показано, что ионы меди (II) в сернокислых растворах в присутствии ионов титана (III) восстанавливаются с образованием элементной меди в виде порошка. Определены формы и размеры частиц образовавшихся порошков меди электронно-микроскопическим методом. Результаты исследования показали, что предположения о возможности формирования порошков вследствие механического осыпания при анодном растворении меди не подтверждаются.

Результаты наших исследований позволяют сделать заключение о том, что потенциал анода повышается, затем понижается, следовательно, постоянно колеблется и приводит к образованию порошков меди в этот момент. Концентрация купроионов зависит от потенциала медного электрода и его колебание может способствовать сдвигу равновесия реакции $\text{Cu}^0 \leftrightarrow \text{Cu}^+ + e$ вправо или влево. В промышленных условиях величину тока в цепи и температуру электролита невозможно поддерживать постоянными. По этой причине происходит периодическое колебание потенциала анода с различной амплитудой частотой. При смещении потенциала анода в отрицательную область возможно образование порошка меди по указанной выше реакции. Однако образовавшиеся атомы меди не могут внедриться в кристаллическую решетку анода. Вследствие этого на поверхности электрода образуются мелкодисперсные порошки меди, они постепенно переходят в раствор и после проникают в состав шлама.

Впервые на основании результатов исследования и анализа установлен механизм образования порошков меди, проникающих в состав шлама при электрорафинировании меди. Показано, что образование порошков меди, проникновение их в состав шлама, в основном, напрямую связано с колебаниями потенциала анода в процессе электролиза и формированием различных значений потенциала на различных участках поверхности электрода.

Ключевые слова: медь, порошок, купроион, шлам, рафинация, потенциал, электролиз, анод, катод, электролит, восстановление.

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**N.N. Mofa, B.S. Sadykov, A.E. Bakkara,
N.G. Prikhodko, B.T. Lesbayev, Z.A. Mansurov**

Institute of Combustion Problems, Almaty, Kazakhstan
al-Farabi Kazakh National University, Almaty, Kazakhstan
bakkara_ayagoz@mail.ru

**MODIFICATION OF THE SURFACE OF ALUMINUM AND
MAGNESIUM PARTICLES UNDER THE CONDITIONS OF
MECHANOCHEMICAL TREATMENT AS A METHOD
OF OBTAINING ENERGY-INTENSIVE COMPOSITIONS**

Abstract. The paper presents the results of a mechanical treatment of metal powders (aluminum brand PA-4 and magnesium brand MPF-3) in a dynamic action mill using graphite as a surfactant additive in order to improve the dispersion of powders and modify the surface layer of particles. The mechanical treatment of metals, with graphite, contributes to the change in the structure, the composition of the surface of metal particles, an increase in the proportion of the active metal, and the formation of an organic coating of dispersible particles. The obtained metal particles with graphite were studied by physicochemical analysis methods, a granulometric method for estimating the particle size distribution carried out on the instrument Malvern 3600E. The effect of mechanochemical treatment of metal powders on the process of technological combustion of thermite mixtures is investigated. The results of the study showed that after the machining, the particle size of the metal powders decreases and, as a consequence, the specific surface area of the metal particles increases with the accumulation of defects in the crystal lattice. In the process of mechanochemical treatment, the size of the crystallites depending on the mass of the fraction of graphite used in the composition of the Me/C composite. When using aluminum and magnesium as a fuel component after mechanochemical treatment in the presence of graphite, the thermal kinetic characteristics of the combustion process increase.

Key words: mechanochemical treatment, aluminum, magnesium, modification, technological combustion.

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**Н.Н. Мофа, Б.С. Садыков, А.Е. Баккара,
Н.Г. Приходько, Б.Т. Лесбаев, З.А. Мансуров**

Институт проблем горения, Алматы, Казахстан;
Казахский национальный университет имени аль-Фараби, Алматы, Казахстан

**МОДИФИЦИРОВАНИЕ ПОВЕРХНОСТИ ЧАСТИЦ АЛЮМИНИЯ
И МАГНИЯ В РЕЖИМЕ МЕХАНОХИМИЧЕСКОЙ ОБРАБОТКИ –
СПОСОБ ПОЛУЧЕНИЯ ЭНЕРГОЕМКИХ КОМПОЗИЦИЙ**

В работе представлены результаты механохимической обработки порошков металлов (алюминия марки ПА-4 и магния марки МРФ-3) в мельнице динамического действия с использованием графита в качестве поверхностно активной добавки с целью повышения дисперсности порошков и модифицирования

поверхностного слоя частиц. Механическая обработка металлов с графитом способствует изменению структуры и состава поверхности металлических частиц, повышению доли активного металла и формированию органического покрытия диспергируемых частиц. Полученные частицы металлов с графитом были исследованы физико-химическими методами анализа, гранулометрическим методом для оценки распределения частиц по размерам, проводимая на приборе «Малверн 3600Е». Исследовано влияние механохимической обработки порошков металлов на процесс технологического горения термитных смесей. Результаты исследования показали, что после механической обработки размеры частиц порошков металлов уменьшается и как следствие увеличивается удельная поверхность частиц металлов с накоплением дефектов в кристаллической решетке. В процессе механохимической обработки, размер кристаллитов изменяется от массовой доли используемого графита в составе композита Me/C . При использовании в качестве горючего компонента алюминия и магния после механохимической обработки в присутствии графита повышаются термо-кинетические характеристики процесса горения.

Ключевые слова: механохимическая обработка, алюминий, магний, модифицирование, твердофазное горение.

Введение. Металлические порошки являются одной из важнейших компонент горючих композиций различного состава и назначения. Использование их, прежде всего, обусловлено высоким тепловым эффектом окисления металла, а также уменьшением средней молекулярной массы газообразных продуктов сгорания в результате раскисления H_2O и CO_2 при взаимодействии их с металлом [1]. Особенно важное значение это имеет для гидрореагирующих топливных систем, в которых металла содержится до 80%, и он является основным горючим [2-4]. Наиболее распространенным и достаточно энергоемким металлическим горючим для топливных систем различного назначения является алюминий. В некоторых топливах, прежде всего баллистических, частицы алюминия из-за низкой окислительной активности кислородсодержащих продуктов горения воспламеняются с большой задержкой по времени. В таких случаях используют магний или его сплавы с алюминием, частицы которых воспламеняются быстрее, чем алюминий и сгорают полностью [1, 3]. Важнейшей характеристикой металлических порошков при использовании их в составе горючих смесей является содержание активного (неокисленного) металла, а также размер и форма частиц. В большинстве случаев используются ультрадисперсные порошка с размером частиц менее 1 мкм. В последние годы все больше внимания уделяется нанодисперсным порошкам, поскольку они отличаются повышенной химической активностью, что позволяет увеличить скорость горения топлива [5-7].

Чтобы обеспечить стабильность свойств металлических порошков и сохранить содержание активного металла их пассивируют и гидрофобизируют [8]. В первом случае на поверхности частиц создается сплошная и прочная оксидно-гидроксидная пленка, препятствующая взаимодействию металла с окислительной средой. А во-втором, поверхность частиц покрывается слоем соли жирной кислоты, в частности стеаратом натрия. Однако наличие оксидно-гидроксидной пленки на поверхности частиц, во-первых, снижает долю активного металла, а во-вторых воспламенение начинается только с момента контакта горючего с окислителем в результате растрескивания оксидной пленки под воздействием объемного расширения расплавленного металла внутри оксидной капсулы.

В значительной степени изменить состояние металлических частиц, в частности алюминия и магния, прежде всего в плане повышения доли активного металла и обеспечить устойчивость к внешней окислительной среде, а также повысить активность при горении в составе горючих смесей можно используя механохимическую обработку (МХО) порошка в планетарно-центробежных мельницах. При механохимической обработке с различными органическими модификаторами в процессе измельчения порошка можно в значительной степени снизить долю оксидной пленки частиц заменив ее органической. Как было показано работами [9,10] в результате МХО алюминия с графитом в инертной атмосфере реакционная способность алюминия существенно возрастает, причем на первых стадиях обработки образуется однородный композиционный продукт Al/C , в котором частицы высокодисперсного алюминия стабилизированы в среде высокодисперсного графита. При длительной механической обработке происходит химическое взаимодействие алюминия с углеродом с образованием кристаллической фазы Al_4C_3 [10]. Большое внимание уделяется и возможности механической активации магния [11].

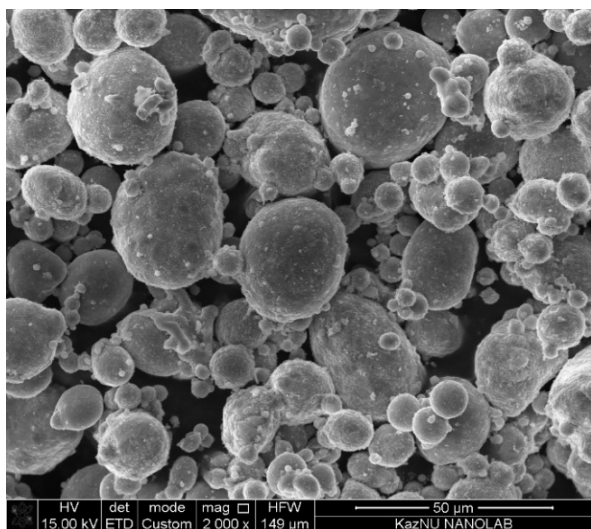
Для получения высокодисперсных металлических частиц алюминия и магния с модифицированной поверхностью частиц важно выбрать оптимальные условия МХО для конкретной модифицирующей добавки. В настоящей статье представлены результаты и сравнительный анализ проведенных исследований по МХО алюминия и магния в присутствии графита.

Результаты и обсуждение. Для экспериментов использовался алюминий марки ПА-4 и порошок магния марки МРФ-3. Была исследована микроструктура исходных частиц порошкообразного алюминия и магния. Согласно результатам микроструктурного анализа, частицы алюминия марки ПА-4 имеют сферическую форму с размером от 20 до 63 мкм (рисунок 1а,б). Удельная поверхность таких образцов, согласно результатам БЭТ анализа, составляет 3,692 м²/г. Энергодисперсионный спектр показал, что в составе исходного алюминия марки ПА-4 массовая доля кислорода составляет более 10%. Присутствие атомов кислорода свидетельствует о наличии достаточно плотного слоя оксидной пленки на поверхности частиц.

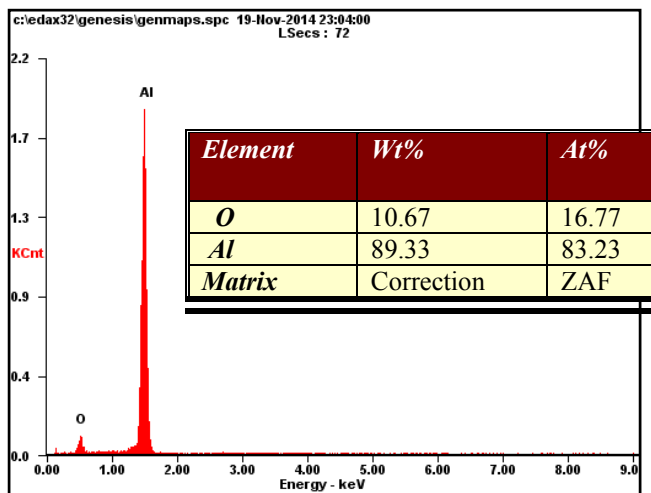
Результаты микроструктурного анализа исходного порошка магния марки МРФ-3 показали (рисунок 1в,г), что частицы магния имеют чешуйчатую форму, а средний размер частиц образца превышает 200 мкм, при этом толщина чешуек около 20 мкм. Удельная поверхность таких образцов, согласно результатам метода БЭТ, составляет 0,181 м²/г. Результаты EDX анализа показывают присутствие в магнии 2,26% кислорода, т.е. наличие на поверхности частиц оксидной пленки. Однако, рентгенофазовый анализ исходного магния марки МРФ-3 показал, что в его составе присутствует 9,6% Mg(OH)₂, т.е. поверхность частиц покрыта гидроксидной пленкой.

Механическое измельчение металлических частиц Al и Mg затруднено из-за их пластичности. Для облегчения процесса диспергирования добавляют поверхностные активные вещества, например, стеариновую кислоту, графит и другие органические соединения. Так, при обработке алюминия с добавками графита облегчается процесс диспергирования, а также присутствие графита в смеси с металлом является положительным фактором при последующем целевом использовании, например, в составе энергетических конденсированных систем [12-17]. Таким образом, модификация поверхности металлических наночастиц графитом при МХО, осуществляется не только с целью защиты металла от окисления, но и для повышения энергоёмкости полученной композиционной смеси.

Механохимическую обработку (МХО) порошков проводили в центробежно-планетарной мельнице ЦПМ «Пульверизетте 5» (производитель – FRITSCH) с объемом каждой рабочей камеры 500 мм³, скорость вращения платформы 400 оборот./мин, ускорение движения размольных шаров 40g, потребляемая мощность энергии 1,5 кВт/ч. МХО проводили в атмосфере воздуха при соотношении порошок/шар (M_П/M_Ш) = 1/4. При измельчении варьировалось количество вводимой модифицирующей добавки (5-20%).



а



б

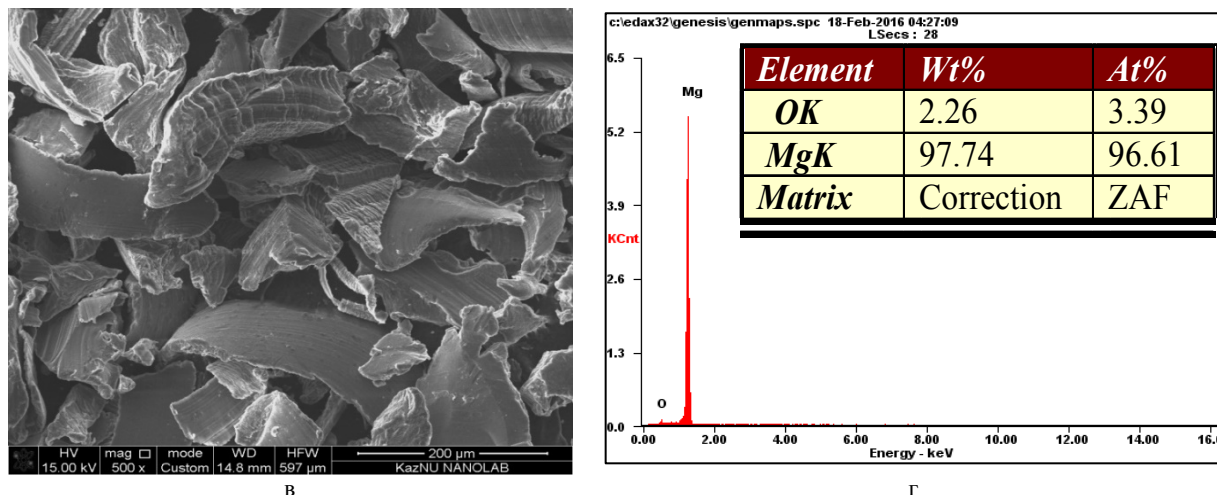


Рисунок 1 - Электронно-микроскопические снимки (а, в), энергодисперсионный спектр и массовая доля элементов (б, г) исходного порошка алюминия марки ПА-4 (а, б) и магния марки МРФ-3 (в, г)

Время обработки составляло не более 20 минут, чтобы исключить самовоспламенение. Выбор оптимального времени МХО был обусловлен результатами ранее проводимых исследований [18, 19]. Чтобы предотвратить окисление частиц алюминия кислородом воздуха после МХО и оценить изменения, действительно связанные с механическим воздействием, образцы диспергированной смеси пассивировались гексаном (C_6H_{14}).

После МХО алюминия с графитом частицы имеют пластинчатую (чешуйчатую) форму различной толщины, т.е. в процессе измельчения происходит изменение формы частиц и образование слоистой структуры композита Al/C (рисунок 2а).

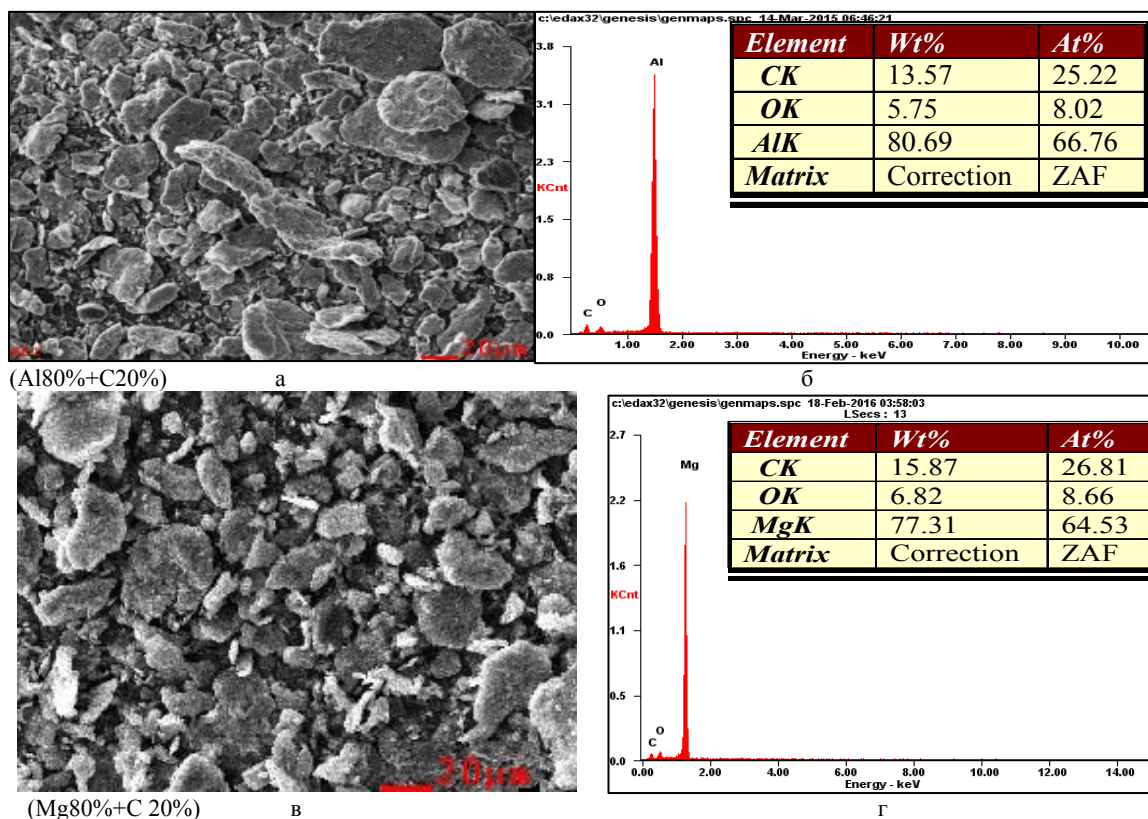


Рисунок 2 - Электронно-микроскопические снимки (а, в), энергодисперсионный спектр и массовая доля элементов (б, г) в композите (Al80%+C 20%) и (Mg 80%+C20%) после 20 минут МХО

Удельная поверхность порошков, которая определялась методом БЭТ, после МХО существенно возрастает. Так, удельная поверхность обработанной смеси (Al 80%+C 20%) по результатам БЭТ анализа повышается до $9,554 \text{ м}^2/\text{г}$. Изменяется и состояние поверхностного слоя. Элементный анализ композита (Al 80%+C 20%) после МХО показал, что массовая доля алюминия в композите составляет 80,69%, углерода содержится 13,57% от общей массы образца, а количество кислорода - 5,75% (рисунок 2б). Следовательно, в процессе МХО алюминия с графитом частично происходит восстановление алюминия в поверхностном оксидном слое частиц и уменьшение содержания кислорода в композите.

В результате МХО магния с графитом частицы сохраняют пластинчатую форму (рисунок 2 в). Удельная поверхность для частиц композита (Mg 80%+C 20%) повышается до $16,383 \text{ м}^2/\text{г}$. Результаты EDX анализа элементного состава частиц композитов Mg-С показали, что после МХО массовая доля атомов кислорода повышается, так для (Mg 80%+C 20%) она составляет более 6% (рисунок 2г).

Следовательно, на поверхности частиц магния после МХО толщина оксидного слоя растёт. Однако по результатам рентгенофазового анализа на поверхности частиц образуются не оксиды, а гидроксиды, количество которых может достигать 15% (рисунок 3).

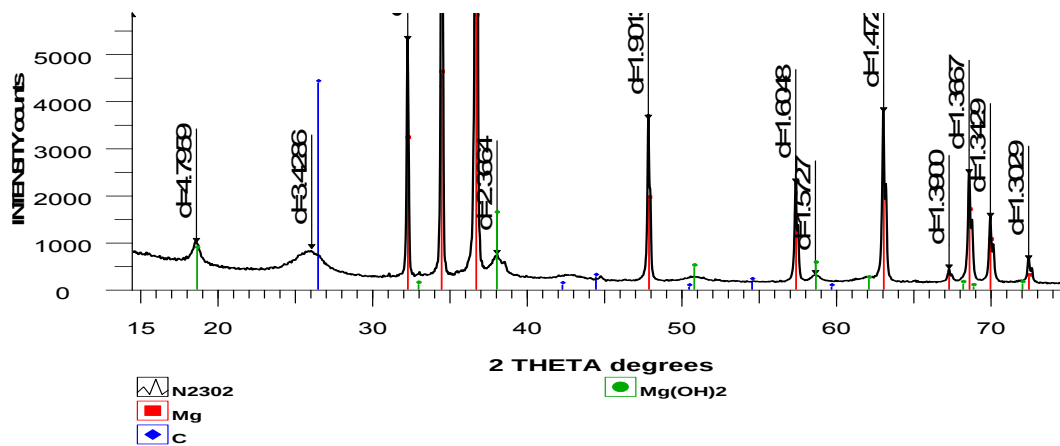


Рисунок 3 - Дифрактограмма образца (Mg80% + C 20%), после 20 минут МХО

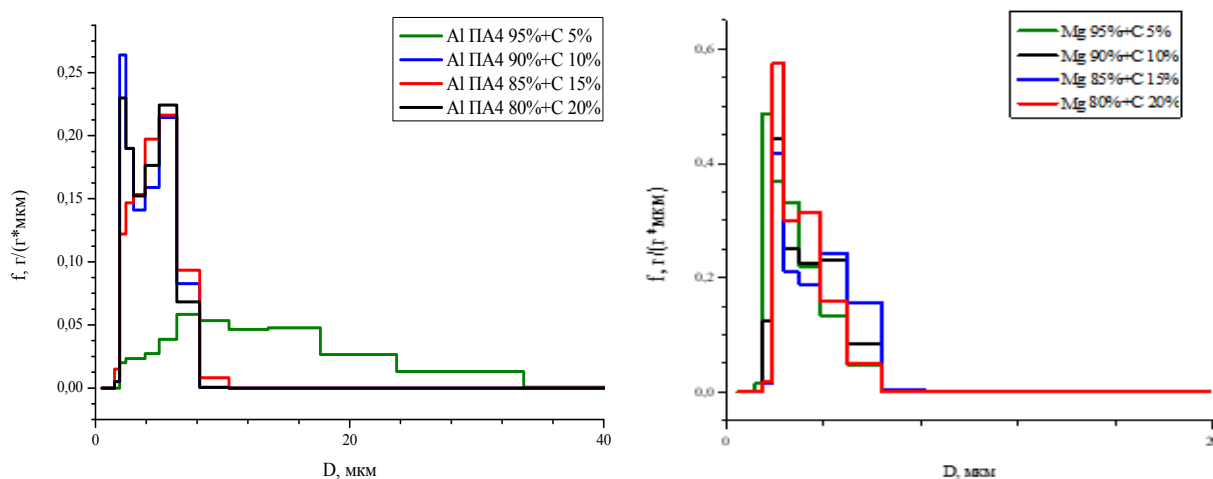


Рисунок 4 - Массовое распределение частиц композита Al/C (а) и композита Mg/C (б) после МХО, время 20 минут

Оценка распределения частиц по размерам, проводимая на приборе «Малверн 3600Е», показала, что при увеличении содержания графита в системе с алюминием до 15-20% после

измельчения основная масса порошка имеет размер частиц меньше 5 мкм. Практически половина из них имеет размер менее 2 мкм (рисунок 4а), что и отразилось в увеличении удельной площади поверхности частиц порошка алюминия марки ПА-4 от 3,7 до 9,5 м²/г.

После измельчения магния в смеси с графитом основная масса порошка смеси Mg/С имеет размер частиц меньше 5 мкм, которые практически представляют собой агломераты наноразмерных частиц (рисунок 4б).

Для оценки субструктурных особенностей частиц алюминия после МХО были исследованы размеры кристаллитов методом РФА в полученных композитах Al/С, Mg/С. Согласно результатам анализа, в процессе механохимической обработки, размер кристаллитов изменяется от количества используемого модификатора (таблица 1).

Таблица 1 - Размер кристаллитов алюминия и магния после 20 минут МХО с графитом

Содержание графита в композитах	Размер кристаллитов L, Å	
	Al	Mg
-	690	580
5 % C	560	600
10 % C	490	770
15%С	440	590
20 % C	410	520

При механическом воздействии происходит как накопление, так и перераспределение дефектов по объему частицы. В результате МХО алюминия с графитом наблюдается уменьшение размера кристаллитов с увеличением содержания углерода в композите Al/С. При МХО магния с графитом происходит сначала рост кристаллитов, а при содержании углерода 15-20% уменьшение размера кристаллитов, т.е. более интенсивное накопление дефектов в объеме зерен. Это может быть связано с тем, что вовремя МХО атомы углерода проникают в зерно алюминиевой частицы и вместе с дефектами диффундируют по ее объему под действием механических напряжений. В одних случаях вероятно, это процесс способствует стабилизации дефектов, в других выносу их на границу зерна частицы и как следствие того, росту размера кристаллитов [20]. Поверхностная пленка частиц как алюминия, так и магния разрушается (разрыхляется) и насыщается высокодисперсными частицами углерода (рисунок 5).

Таким образом, использование графита при МХО алюминия и магния согласно всем анализируемым характеристикам, способствует изменению морфологии и структуры частиц при формировании композитов металл/углерод (Me/С). Наблюдаемые изменения размера частиц алюминия и магния, модифицированные органической добавкой (графит) при МХО, является следствием того, что в формировании поверхностного слоя частиц во всех рассмотренных случаях значительную роль играет углерод, также диспергируемый в процессе МХО.

Структурные изменения при МХО исследуемых композитов Me/С приводят и к изменению их химической активности, что наглядно проявляется в процессе твердофазного горения (т.е. в режиме самораспространяющегося высокотемпературного синтеза - СВС) смеси алюминиевого или магниевого порошка, как горючего, с диоксидом кремния, используемого в качестве окислителя.

Диоксид кремния в данном случае используется в неактивированном состоянии. Смеси готовились при стехиометрическом соотношении компонентов: (Al 37,5% + SiO₂ 62,5%) и (Mg 44% + SiO₂ 56%). После МХО алюминия с графитом и введении полученного порошка соответственно в количестве 37,5% и 44% в шихту с кварцем наблюдается значительное снижение индукционного периода зажигания, повышение скорости и температуры на всех стадиях процесса горения по сравнению с неактивированным горючим (рисунок 6 а). Для смеси кварца с композитом (Mg/С) после МХО также снижается индукционный период зажигания и повышается температура и продолжительность горения смесей с SiO₂, но проявляется это менее эффективно, чем с алюминием (рисунок 6 б).

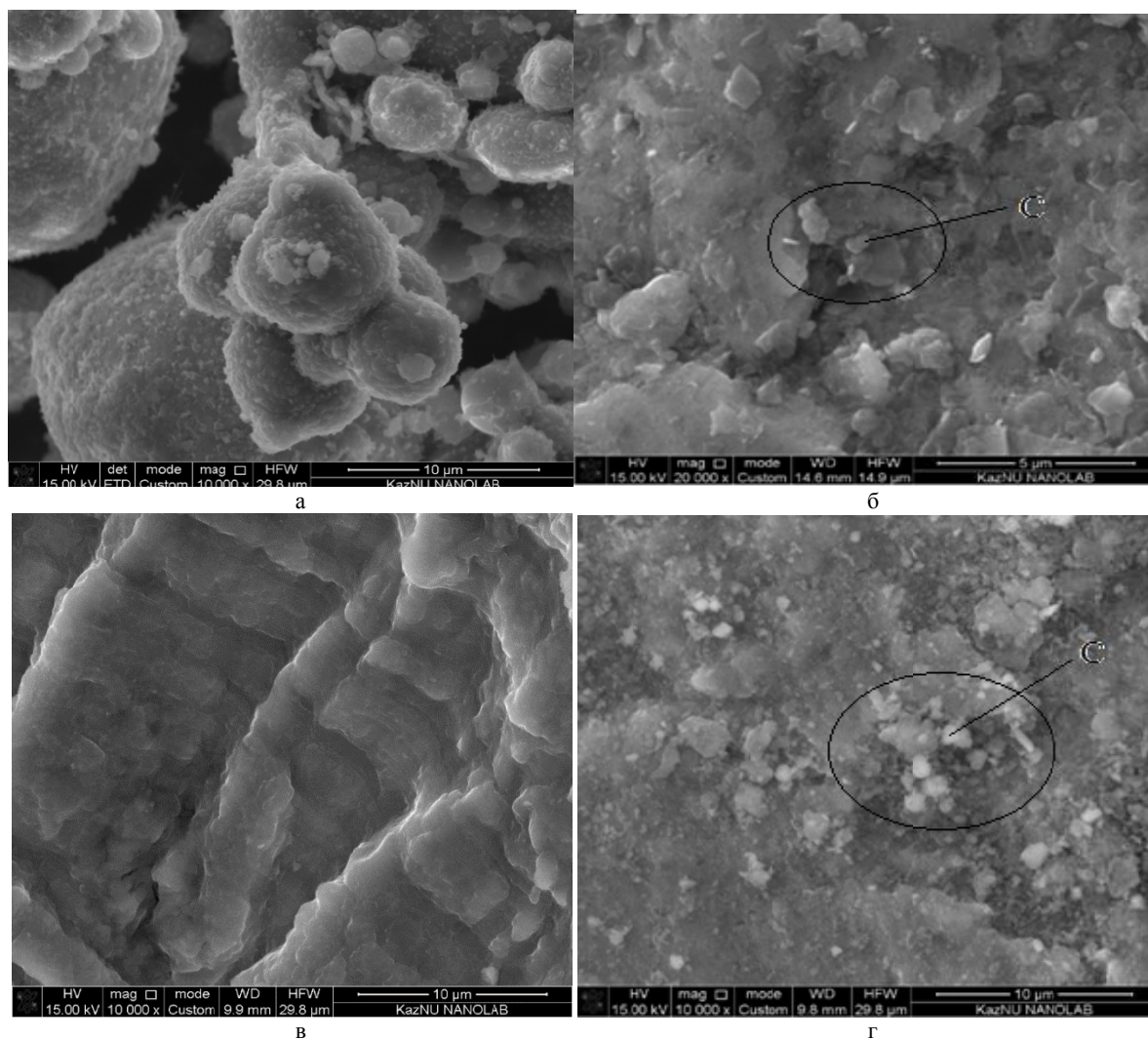


Рисунок 5 - Электронно-микроскопические снимки частиц алюминия и магния в исходном состоянии (а, в) и в композите (Al80%+C 20 %) и (Mg 80%+C20%) после 20 минут МХО (б, г)

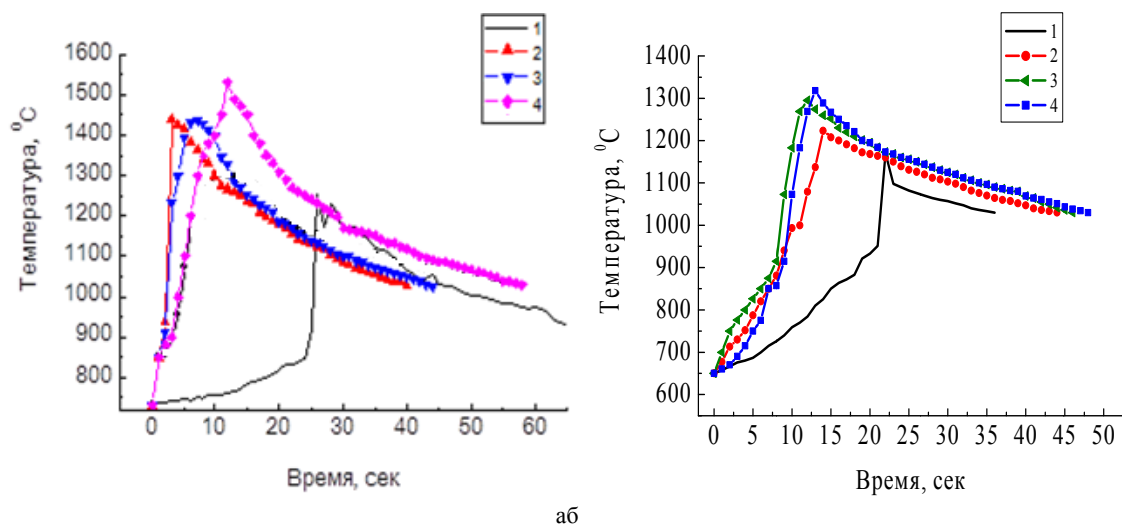


Рисунок 6 - Термограммы горения систем $(\text{SiO}_2 + \text{Me})$ с алюминием и магнием в исходном состоянии и после 20 минут МХО с разным количеством графита: а - $\text{SiO}_2 + (\text{Al}/\text{C})$, б - $\text{SiO}_2 + (\text{Mg}/\text{C})$; 1 - Меисх; 2 - 5 %; 3 - 10 %; 4 - 20 % C

В таблице 2 приведены показатели основных характеристики процесса горения и прочность синтезированных образцов. Из таблицы 2 следует, что максимальную температуру горения имеет состав

$[(Al+C 20\%)_{MXO} 37,5\% + SiO_2]$, но прочность его существенно снижается по сравнению с образцом без углерода. С введением углерода в состав и с увеличением его количества при МХО алюминия прочность синтезированного СВС-образца снижается. Это связано с выделением газообразных продуктов, количество которых повышается с увеличением содержания углерода в составе смеси, что приводит к формированию пористой структуры образца (рисунок 7а). Максимальная скорость горения (118,2 град/сек) при СВ-синтезе была установлена для системы $[(Al+C 5\%)_{MXO} + SiO_2]$.

Таблица 2 - Показатели максимальной температуры, скорости горения смесей SiO_2 модифицированным алюминием и магнием и прочностные характеристики синтезированных образцов

Состав модифицированного горючего на основе алюминия	Tmax, 0C	Скорость горения, град/сек	σ, МПа
Al исх + (SiO ₂)	1319	19,16	37,6
Al + 5 % C	1441	118,2	8,36
Al + 10 % C	1436	83,7	12,54
Al + 20 % C	1532	56,8	2,11
Mg исх + (SiO ₂)	1170	23,6	50
Mg+5%С	1295	40,9	5,8
Mg+10%С	1318	58,6	1
Mg+20%С	1223	51,4	1

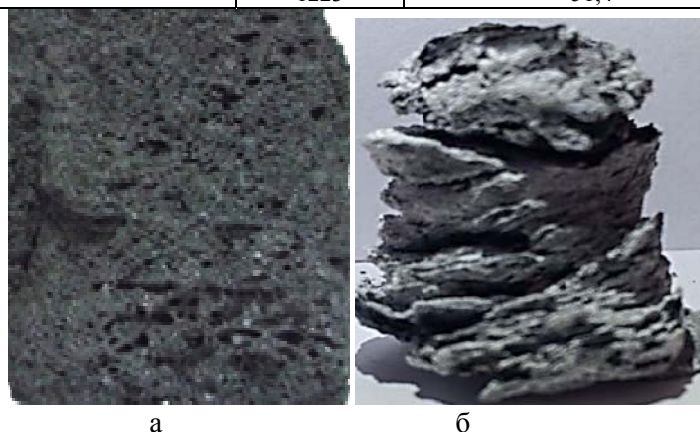


Рисунок 7 - Излом и внешний вид СВС-образцов, полученных смодифицированным при МХО алюминием (а) и магнием (б) при содержании 20% С

Это возможно связано с оптимальным соотношением размера частиц составляющих компонентов смеси, и соответственно с повышением плотности упаковки, которая обеспечивает плотность контакта между окислителем и горючим.

В образцах, полученных сгорючим, в виде алюминия, модифицированного углеродом, формируется мелкопористая структура с плотными перегородками. Этот факт свидетельствует о перспективности использования таких материалов для получения теплоизоляционных систем.

Продукты технологического горения образцов, горючим компонентом которых является композит (Mg/C), имеют низкий показатель прочностных характеристик из-за пористой, рыхлой структуры образцов (рисунок 7б). Это обусловлено тем, что горение протекает послойно и в большом количестве образуются газообразные продукты синтеза.

Заключение. Таким образом, МХО алюминия и магния с графитом способствует изменению морфологии и структуры частиц при формировании композитов (Me/C), изменению размера частиц алюминия и магния и модифицированию поверхности органической добавкой (графит). Применение механической обработки приводит к уменьшению размеров частиц порошков металлов и как следствие увеличению удельной поверхности частиц металлов с накоплением дефектов в кристаллической решетке. В процессе измельчения поверхность частиц постоянно

находится в возбужденном высокоактивном состоянии, а присутствие при МХО металлических частиц органических добавок обеспечивает формирование органического покрытия на поверхности частиц.

Результатами горения смесей, в которых в качестве горючего компонента использовался алюминий и магний после МХО в присутствии графита, показана эффективность этого метода для повышения термо-кинетических характеристик процесса горения, а также определены условия подготовки горючего материала и проведения процесса горения, при которых возможно образование в большом объеме газообразных продуктов синтеза. Последний факт имеет важное значение при использовании полученных наноструктурированных композитов Me/C в составе горючих систем, предназначенных, например, для газогенераторов или для вспучивания и получения пористых систем определенного назначения. Такие композиции, как правило, представляют собой гетерогенные конденсированные системы.

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**Н.Н. Мофа, Б.С. Садыков, А.Е. Баккара,
Н.Г. Приходько, Б.Т. Лесбаев, З.А. Мансуров**

Жану проблемалар институты, Алматы, Қазақстан
эл-Фараби атындағы ҚазҰУ, Алматы, Қазақстан

АЛЮМИНИЙ ЖӘНЕ МАГНИЙ БӨЛШЕКТЕРІНІҢ БЕТТЕРІН МЕХАНОХИМИЯЛЫҚ ӨНДЕУ РЕЖИМІНДЕ МОДИФИЦИРЛЕУ – ЖЫЛУСЫЙЫМДЫ КОМПОЗИТТЕР АЛУ ТӘСІЛІ

Аннотация. Мақалада металл ұнтақтарын (алюминий РА-4 маркасы және магний МРФ-3 маркасы) беттік белсенді зат ретінде графит көмегімен, ұнтақ дисперстілігін арттыру және бөлшек беттік қабатын модифицирлеу мақсатында динамикалық диірменде механохимиялық өңдеу жұмыстарының нәтижелері келтірілген. Металдарды графитпен механохимиялық өңдеу металл бөлшектерінің құрылымы және қасиеттерінің өзгеруіне, белсенді металл мөлшерінің жоғарылауына және дисперстелінетін бөлшектер бетінде органикалық жабындылардың пайда болуына әкеледі. Алынған металл және графит бөлшектері физика-химиялық талдау әдістері, «Малверн 3600Е» құрылғысы көмегімен жүргізілетін, бөлшек өлшемдерінің таралуын гранулометриялық әдіс көмегімен зеттеулер жүргізілді. Термитті жүйелердің технологиялық жану үдерісіне металл ұнтақтарын механохимиялық өңдеудің әсері зерттелінді. Зерттеу нәтижелері механохимиялық өңдеуден кейін металл ұнтақтарының бөлшектерінің өлшемдері төмендеп, сәйкесінше кристаллитті торда ақаулар жиналып, меншікті беттік көлемі жоғарылайтындығын көрсетті. Механохимиялық өңдеу үдерістері кезінде Ме/С композит құрамында графиттің массалық үлесіне байланысты кристаллиттер өлшемі өзгеретіндігі анықталды. Алюминий және магний бөлшектерін графитпен механохимиялық өңдеуден кейін жанғыш зат ретінде қолдану жану үдерістерінің термо-кинетикалық сипаттамаларының жоғарылауына алып келетіндігі көрсетілді.

Түйін сөздер: механохимиялық өңдеу, алюминий, магний, модифицирлеу, қаттыфазалы жану.

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**A.S. Bukanova, F.B.Kairlieva, L.B.Sakipova,
O.Y.Panchenko, N.A.Karabasova, R.N. Nasirov**

Atyrau University named after Kh.Dosmukhamedov
E-mail: rnasirov.48@mail.ru

BINDING D-ELEMENTS OF GROUP VIII OF THE 4th PERIOD OF THE PERIODIC SYSTEM

Abstract. This article briefly reviews the connecting d-elements of the fourth period I-VIII groups of the periodic system. Also compares the main elements of the group VIIIA and VIIIB transition group, their properties and electronic formulas.

If we collate the VIIIB subgroup of iron elements with the valence states of argon, krypton VIIIA of the main subgroup, then argon in oxidation rates of 0, +2, +6 is an analog of krypton, and in the oxidation +8 Ar will not be a krypton's analog. On the contrary, in low oxidation rates, iron differs from argon, and in the oxidation of +8, iron is an incomplete analog of argon. Iron is a binder between subgroup VIIIA and subgroup VIIIB by electron configurations with a valence corresponding to the group number of the periodic table.

Gas XeO₄ under ordinary conditions, has not been studied sufficiently, but electron diffraction data and IR spectroscopy indicate that its molecule is tetrahedral. Its structure, based on isomorphism, is similar to the tetrahedral structure of FeO₄, OsO₄, RuO₄.

Key words: transition metals, degree of oxidation, binding element, the terms Klechkovskii, characteristic elements, isomorphism.

УДК 546.6.

**А.С. Буканова, Ф.Б.Кайрлиева, Л.Б.Сакипова,
О.Ю.Панченко, Н.А.Карабасова, Р.Н. Насиров**

Атырауский государственный университет им.Х.Досмухамедова

СВЯЗЫВАЮЩИЕ d-ЭЛЕМЕНТЫ I-VIII ГРУППЫ 4-ГО ПЕРИОДА ПЕРИОДИЧЕСКОЙ СИСТЕМЫ Д.И.МЕНДЕЛЕЕВА

Аннотация. В статье вкратце рассматриваются связывающие d-элементы четвертого периода I-VIII группы периодической системы Д.И. Менделеева. Сравниваются элементы VIIIA главной группы и VIIIB побочной группы, их электронные формулы и свойства.

Если сопоставить VIIIB подгруппу элементов железа с валентными состояниями аргона, криптона VIIIA главной подгруппы, то аргон в степенях окисления 0, +2, +6 является аналогом криптона, а в степени окисления +8 Ar не будет аналогом криптона. Напротив, в низких степенях окисления железо отличается от аргона, а в степени окисления +8 железо является неполным аналогом аргона. Железо является как бы связующим элементом между подгруппой VIIIA и подгруппой VIIIB по электронным конфигурациям при валентности, отвечающей номеру группы периодической системы.

XeO₄ в обычных условиях газ, изучен пока недостаточно, но данные электронографии и ИК-спектроскопии указывают на то, что его молекула тетраэдрическая. Его строение аналогично на основе изоморфизма, тетраэдрическому строению FeO₄, OsO₄, RuO₄.

Ключевые слова: переходные металлы, степень окисления, связывающий элемент, правила Клечковского, характеристические элементы, изоморфизм.

При изучении d-элементов периодической системы Д.И. Менделеева, необходимо остановиться на их связи с p- и s- элементами. Они называются переходными и расположены в больших периодах между p- и s- элементами, и ионы которых характеризуются одним из состояний nd^x ($0 \leq x \leq 10$) (например $Sc^{3+} - d^0$, $Zn^{2+} - d^{10}$).

Высшая степень окисления большинства d- элементов отвечает номеру группы периодической системы, в которой они находятся, например проявляется в оксидах:

+3	+4	+5	+6	+7	+8
Sc ₂ O ₃	TiO ₂	V ₂ O ₅	CrO ₃	Mn ₂ O ₇	FeO ₄

Скандий и его аналоги в соответствующих периодах являются первыми d-элементами. У них начинает заполняться предвнешний слой. В отличие от других d-элементов, для скандия и его аналогов характерна степень окисления +3. По своему химическому поведению скандий похож одновременно и на алюминий. Формула высшего оксида скандия- Sc₂O₃ проявляет основные свойства – Sc(OH)₃. По электронному строению внешнего энергетического слоя скандий полностью соответствует второму правилу Клечковского. Следовательно, его валентные электроны находятся на 4s – и 3d- подуровнях. Поэтому высшая степень окисления равна +3, что соответствует номеру группы. Причем электронное строение атома заканчивается s-электронами, поэтому этот элемент проявляет металлические свойства. Остальные 9 d-элементов IV периода являются продолжением этого электронного слоя. Эти d-элементы в своем периоде являются первыми d-элементами, то есть у них начинают заполняться d - орбитали, завершается у атома Zn.

Часто используется так называемый длинный вариант периодической системы, предложенный Б.В. Некрасовым [1]. В этом варианте периоды не делят на части, а записывают полностью в одну строчку. Сходные элементы соединяют прямыми линиями. Здесь необходимо сравнить степень окисления элементов, отвечающей номеру группы периодической системы. Основным достижением Б.В. Некрасова является то, что он установил Sc, Ti, V, Cr, Mn, Cu, Zn при максимальной валентности характеристическими элементами, но осталось неопределенным, какие элементы триады являются аналогами для инертных газов при их максимальной степени окисления.

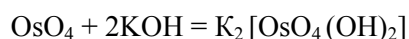
Однако это ошибочным считать нельзя, так как экспериментальных фактов в то время было недостаточно.

В периодической системе ряд элементов объединяются в триады (триады железа, рутения и осмия). Внутри триады свойства элементов близки. В эту группу входит три триады металлов (девять d-элементов)

Период	4	5	6
Элементы	Fe, Co, Ni	Ru, Rh, Pd	Os, Ir, Pt

и благородные газы, завершающие каждый период. Так же как в любой другой, члены VIII группы могут быть разделены на главную VIIIA - и побочную VIIIB – подгруппы.

В подгруппу железа входит рутений и осмий- каждый в своем периоде являются d-элементами, у которых начинается заполнение d-орбиталей предвнешнего слоя электроном. Максимальная степень окисления (+8) равна номеру группы периодической системы. Для железа наиболее характерны степени окисления +2 и +3, известны также производные железа, в которых степень окисления равна +4, +6 и +8. Имеются сведения о получении оксида железа - FeO₄ (+8). Это очень не устойчивое летучее соединение розового цвета[2]. Тетраоксиды осмия и рутения ядовиты. Благодаря кислотным свойствам OsO₄ при взаимодействии с основными соединениями:



образуются комплексы.

Элементы	Fe	Ru	Os
Степень окисления	2, 3, 4, 6, 8	2, 3, 4, 5, 6, 7, 8	2, 3, 4, 6, 8

По вертикалям первый d-элемент VIIIВ группы – это железо (IV-й период), затем следует рутений (V-й период) и осмий (VI-й период). Их электронные конфигурации внешней оболочки у атомов Fe [Ar]3d⁶4s², Ru[Kr] 4d⁷5s¹ и Os[Xe] 4f¹⁴5d⁶6s².

Между элементами вертикальных столбцов проявляются отдельные черты и более близкого сходства. Например, члены ряда Fe, Ru и Os являются особенно активными катализаторами при синтезе аммиака из элементов водорода и азота.

Таблица 1 - Сравнение электронных конфигураций элементов железа, аргона и криптона VIII – группы

Степень окисления	Fe (VIIIВ)	Ar (VIIIА)	Kr (VIIIА)
0	[1s ² 2s ² 2p ⁶ 3s ² 3p ⁶] 3d ⁶ 4s ²	[1s ² 2s ² 2p ⁶] 3s ² 3p ⁶	[1s ² 2s ² 2p ⁶ 3s ² 3p ⁶] 3d ¹⁰ 4s ² 4p ⁶
+2	[1s ² 2s ² 2p ⁶ 3s ² 3p ⁶] 3d ⁶	[1s ² 2s ² 2p ⁶] 3s ² 3p ⁴	[1s ² 2s ² 2p ⁶ 3s ² 3p ⁶] 3d ¹⁰ 4s ² 4p ⁴
+6	[1s ² 2s ² 2p ⁶ 3s ² 3p ⁶] 3d ²	[1s ² 2s ² 2p ⁶] 3s ²	[1s ² 2s ² 2p ⁶ 3s ² 3p ⁶] 3d ¹⁰ 4s ²
+8	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶	1s ² 2s ² 2p ⁶	[1s ² 2s ² 2p ⁶ 3s ² 3p ⁶] 3d ¹⁰

Если сопоставить VIIIВ подгруппу элементов железа с валентными состояниями аргона, криптона VIIIА главной подгруппы, то аргон в степенях окисления 0, +2, +6 является аналогом криптона, а в степени окисления +8 Ar не будет аналогом криптона. Напротив, в низких степенях окисления железо отличается от аргона, а в степени окисления +8 железо является неполным аналогом аргона (см. таб.1). Приводятся электронные конфигурации Fe, Ar и Kr в атомарном состоянии и степенях окисления +2, +6 и +8 (таб.1). Железо является как бы связующим элементом между подгруппой VIIIА и подгруппой VIIIВ по электронным конфигурациям при валентности, отвечающей номеру группы периодической системы.

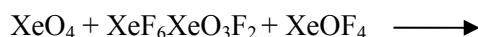
До недавнего времени считали, что благородные газы вообще не способны вступать в химические реакции, и помещали их в «нулевую» группу периодической системы Д.И. Менделеева, где и должны были находиться элементы с «нулевой» валентностью. В 1962 году Канадскому химику Н. Бертлетту удалось получить соединения инертных газов с фтором [3]:



Здесь PtF₆ отнимает один электрон от ксенона. Исследуя химические свойства PtF₆ соединений VIIIВ группы Н.Бертлетт заметил, что при длительном выдерживании на воздухе он меняет цвет, в результате образуется O₂⁺[PtF₆]⁻. Причина этого первая энергия ионизации ксенона сравнима по величине с энергией ионизации молекулярного кислорода (1175 кДж/моль для O₂ O₂⁺+e⁻). Поэтому в данном случае подобно к оксогексафторплатинату образуется ксенонгексафторплатинат.

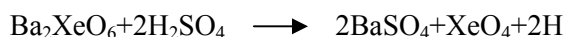
Через несколько месяцев в других лабораториях были синтезированы XeF₄ и XeF₂ [4].

Как известно, степень окисления ксенона равна (+8) [5].



ксенон относится к VIIIА группе.

Тетраоксид получают действием безводной H₂SO₄ на оксоксенат (+8) бария при комнатной температуре:



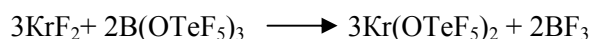
XeO₄ в обычных условиях газ, изучен пока недостаточно, но данные электронографии и ИК-спектроскопии указывают на то, что его молекула тетраэдрическая. Его строение аналогично на основе изоморфизма, тетраэдрическому строению OsO₄, RuO₄. Производные ксенона (+6) –

сильные окислители. Однако при действии на них еще более сильных окислителей можно получить соединения со степенью окисленности (+8). Из подобных соединений известны ксеноноктафторид XeF_8 , ксенонтетраоксид XeO_4 и ксеноноксодифторид XeO_3F_2 . Эти соединения подобны кислотным соединениям OsO_4 и RuO_4 .

Элементы подгруппы криптона- криптон Kr, ксенон Xe, радон Rn характеризуются меньшей энергией ионизации атомов, чем типичные элементы неона и аргона VIIIB группы. Поэтому элементы подгруппы криптона дают соединения обычного типа. И в этом направлении элементы подгруппы криптона отличаются от других благородных газов большими размерами атомов (молекул) и большой поляризуемостью в ряду атомов He-Ne-Ar-Kr-Xe. Вследствии большой устойчивости электронной структуры атома (энергия ионизации 15,76эВ) соединения валентного типа для аргона не получены.

Для He, Ne и Ar устойчивые соединения неизвестны [6]. А следующий благородный газ – криптон имеет химические соединения, но их значительно

меньше, чем у ксенона. Помимо KrF_2 , KrF_4 образование первых соединений, содержащих связи Kr-O, было зафиксировано [7] методом ЯМР-спектроскопии (^{19}F , ^{17}O) для контроля за синтезом устойчивого соединения $[\text{Kr}(\text{OTeF}_5)_2]$:



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Рисунок 1 - Дополнение к длинному варианту периодической системы предложенной Б.В. Некрасовым

Имея относительно больший размер атома, аргон более склонен к образованию межмолекулярных связей, чем гелий и неон. Поэтому, наиболее известны клатраты, образованные Ar, Kr и Xe с гидрохиноном $1,4\text{-C}_6\text{H}_4(\text{OH})_2$ и водой. Клатраты могут служить для хранения запасов благородных газов.

Можно предположить что железо является связующим элементом между подгруппой VIIIB и подгруппой VIIIA при максимальной валентности (+8). Fe и Ar при максимальной валентности (+8)

соединены мелким пунктиром (рис.1). Для остальных III, IV, V, VI, VII, Iи II групп четвертого периода связующими элементами являются Sc, Ti, V, Cr, Mn, Cu, Zn [1, 8, 9].

Вещества, образованные элементами главных и побочных подгрупп, в ряде случаев отличаются своими свойствами. Однако в высшей степени окисления их свойства близки. Например, VIIA – подгруппа – галогены-окислители, VIIB – подгруппа – металлы-восстановители, где они проявляют низкую валентность (Cl_2O - кислотный окисел, MnO -основной), отличия были резко выражены. Однако в своей высшей степени окисления эти элементы в составе соответствующих соединений близки по свойствам [9]. Так, галогены и металлы VII группы в высшей степени окисления образуют сильные кислоты: тетраоксохлорат (+7) водорода HClO_4 и тетраоксоманганат (+7) водорода HMnO_4 , которые являются также сильнейшими окислителями.

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**А.С. Буканова, Ф.Б.Қайрлиева, Л.Б.Сақипова,
О.Ю.Панченко, Н.А.Қарабасова, Р.Н. Насиров**

Х.Досмұхамедов атындағы Атырау мемлекеттік университеті

Д.И.МЕНДЕЛЕЕВТІҢ ПЕРИОДТЫҚ ЖҮЙЕСІНДЕГІ IV ПЕРИОДЫНЫҢ БАЙЛАНЫСТЫРУШЫ d -ЭЛЕМЕНТТЕРІ

Аннотация. Мақалада Д.И.Менделеевтің периодтық жүйесінің IV-периодындағы I–VIII топтардың негізгі және қосымша топтарындағы элементтер қарастырылды. Мұнда VIII А негізгі және VIII В қосымша топша элементтерінің электрондық құрылымы және қасиеттері салыстырылды.

Ал, егер VIIA негізгі тобы элементтері аргонды, криптонды VIIB тобының элементі темірмен салыстырсақ, онда олардың электрондық құрылымын салыстыру нәтижесінде 0, +2, +6 тотығу дәрежелері үшін криптон аргонның аналогы, ал +8 тотығу дәрежесі үшін олар аналог еместігі белгілі. Оған керісінде бұл максимал валенттілікте темір аргонның аналогы. Міне, бұл бізге темір металы VIII А және VIIB топтарын байланыстырушы элемент екендігіне күмән келтірмейді (+8 тотығу дәрежесінде).

XeO_4 толығымен зерттелген жоқ, бірақ электронография және ИҚ-спектроскопиялық зерттеулер оның молекуласы изоморфизм негізінде FeO_4 , OsO_4 , RuO_4 сияқты тетраэдрлік құрылымға ие болатындығын көрсетті.

Түйін сөздер: ауыспалы металдар, тотығу дәрежесі, байланыстырушы элемент, Ключковскийдің ережелері, сипаттамалық элементтер, изоморфизм.

Сведения об авторах:

Буканова Айгуль Сокеевна – к.т.н., доцент, зав.кафедрой «Химия и химическая технология»;
Қайрлиева Фазилат Басаровна – к.т.н., ст. преподаватель кафедры «Химия и химическая технология»;
Сақипова Лидия Бағитжановна – магистр, ст. преподаватель кафедры «Химия и химическая технология»;
Панченко Ольга Юрьевна - магистр, ст. преподаватель кафедрой «Химия и химическая технология»;
Қарабасова Нағима Асылбековна - магистр, ст. преподаватель кафедры «Химия и химическая технология»;
Насиров Рахметулла – д.х.н., профессор кафедры «Химия и химическая технология».

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O.A. Nurkenov^{1,2}, M.K. Ibrayev², S.D. Fazylov¹,
A.T. Takibayeva², I.V. Kulakov³, A.E. Tuktybayeva²

¹Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan;²Karaganda State Technical University, Karaganda, Kazakhstan;³Dostoevsky Omsk State University, Omsk, RussiaE-mail: nurkenov_oral@mail.ru, altynarai81@mail.ru

CHALCONES-SYNTHONS IN SYNTHESIZING BIOLOGICALLY ACTIVE MATTERS

Abstract. The review paper summarizes and systematizes the literature data of recent years, as well as the results of the authors' research in the field of functionally substituted chalcones. The most common natural chalcones, methods of production, reactivity and biological properties of synthetic chalcones are given.

Keywords: substituted aromatic aldehyde, chalcone, pyrazoline, flavonone, cytokine, NF-κB transcription factor.

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О.А. Нуркенов^{1,2}, М.К. Ибраев², С.Д. Фазылов¹,
А.Т. Такибаева², И.В. Кулаков³, А.Е. Туктыбаева²

¹Қазақстан Республикасының органикалық синтез және көмірхимия институты, Қарағанды, Қазақстан;²Қарағанды мемлекеттік техникалық университеті, Қарағанды, Қазақстан;³Ф.М.Достоевский атындағы Омск мемлекеттік университеті, Омск, Ресей

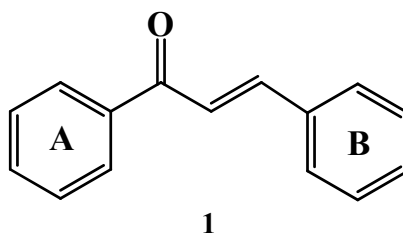
ХАЛКОНДАР–БИОЛОГИЯЛЫҚ БЕЛСЕНДІ ЗАТТАР СИНТЕЗІНДЕГІ СИНТОНДАР

Аннотация: бұл шолу мақаласында соңғы жылдардағы әдеби мәліметтер, сондай-ақ функционалды орынбасқан халкондароблысындағы авторлардың зерттеулер нәтижелері жинақталып, жүйеленген. Кең таралған табиғи халкондар, синтетикалық халкондардың алу әдістері, реакциялық қабілеті мен биологиялық қасиеттері келтірілген.

Түйін сөздер: орынбасқан ароматты альдегид, халкон, пиразолин, флавонон, цитокин, транскрипционды фактор NF-κB

Препаративті мәні бар органикалық қосылыстардың маңызды өкілдері ретінде α,β-қанықпаған карбонильді қосылыстарболып табылады, олардың арасында бензилиденацетофенондар (халкондар) елеулі орын алады. 1896 ж. Халконның ашылғанынан [1] бастап, оның орынбасқан және гетероциклді аналогтарының химиясына қызығушылық жоғалмайды. «Халкон» атауын поляк химигі Станислав Костанеки (Stanisław Kostanecki) ұсынды. Ол «мыс» деп аударылатын гректің «халкос» (χαλκός)сөзінен шыққан.

Халкондар - 1,3-дифенил-2-пропен-1-ондар (1) α,β-қанықпаған карбонильді жүйесінің үш көміртек атомдарымен байланысқан екі ароматты ядросы бар қосылыстарға жатады [2]. Халкондардацис- және транс- формаларыболуы мүмкін, бірақ транс- формасы термодинамикалық тұрақтырақ.



1. Кеңтаралғантабиғи халкондар

Халкондар табиғатта кеңінен таралған: гүлдер, жеміс, тұқым және ағаш құрамында болады. Олар флавоноидтар классына жататын бір қатар заттармен – флавонондар, флавонондар, флавонолдармен тығыз байланысты.

Халкондар өкілдерінің көпшілігі өсімдіктердің барлық органдарында агликон және гликозидтер түрінде кездеседі және А сақинасындағы орынбасарлардың санымен ерекшеленеді. Осылайша, мысалы, күрделі түстілер тұқымдасында жиі кездесетін халкон бутеин орналасқан түріндегі *Coreopsis gigantea* кореопсиннің 4-гликозиді түрінде, ал халконарингенин *Salix purpurea* изосалипурпозидінің 2-гликозиді түрінде кездеседі [3, 4].

Осы уақытқа дейін 200-ден астам түрлі табиғаты халконды агликандар белгілі. Өсімдіктерде құрамында тотықсызданған қосарланған байланысы болатын үшкөміртекті фрагменті бар дигидрохалкондар жиі кездеседі.

Олар гликозидирленген форма, сондай-ақ, метокси - және пирантуындылары ретінде ғана белгілі. Мәселен, кейбір алма түрлерінің құрамында адам ағзасында глюкозаның қарқынды бөлінуін тудыратын (флюридзиндік диабет) флоридзиннің гликозиді (2'-глюкозид, 4', 2', 4, 6-тетраоксидигидрохалкон), сонымен қатар сиболдин (3-оксифлоретин-4'-глюкозид), азебогенин түрінде 2'-азеботиннің гликозиді болады [4].

Халкондар биосинтез кезіндегі флавоноидты қосылыстардың әр түрлі топтардың бастапқы заттары болып саналады. Көктемде, жазда және күзде планетамыздың өсімдіктер дүниесінің көптеген жарқын бояулары бір флавоноидты класстың қосылыстары – халкондар себепші болады. Оларды «антихлоропигменттер» деп атайды, бұл – аммиак буында қызыл сары болатын гүлдің сары пигменттері. Түстің өзгертуін атап айтқанда, халкон құрамды препаративті формалар фармацевтика саласында, мысалы, фенил-3-метокси-4-гидроксистирилкетон және 3-(4'-гидрокси-3'-метокси) 1-фенилпроп-2-ен-1-он ауыз қуысын күтудің түс өзгертетін компоненті ретінде қолданылады [5].

Халкондар салыстырмалы жиі бір тұқымдаста – *Compositae*, әсіресе *Coreopsis* және *Dahlia* кездеседі. Сонымен қатар, кейбір *Leguminosae* (*Butia*, *Cylicodiscus*, *Glycyrrhiza*, *Plathymenia*, *Ulex*) және *Dihymocarpus* (*Gesneriaceae*) табылды. 1-кестеде табиғи шикізаттан бөліп алынған кейбір халкондар мен олардың туындылары келтірілген.

2. Синтетикалық халкондарды алу әдістері

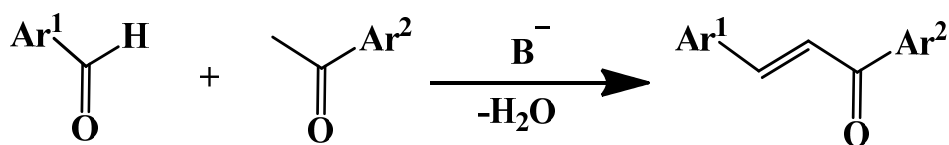
Синтетикалық халкондар химиктер мен фармацевттер үшін айтарлықтай қызығушылық тудырады, бұл бірнеше факторларға негізделген: олардың негізінде алуан түрлі жоғары фармакологиялық белсенділігі бар молекулаларды синтездеуге мүмкіндік беретін салыстырмалы химиялық құрылысының қарапайымдылығы, сонымен қатар, бағалы синтетикалық интермедиаттар ретінде, мысалы, әр түрлі гетероциклді қосылыстар синтезінде пайдалану мүмкіндігі. Айта кету керек, халкондардың көптеген байқалатын биологиялық қасиеттері α, β -қанықпаған кетондық топтардың болуына байланысты, өйткені барлық биологиялық белсенді молекулаларда бұл топтар бар, ал оларды жою белсенділіктің төмендеуіне әкеледі [25]. Көптеген авторлар бұл фрагменттің болуын орынбасқан халкондардың әр түрлі биологиялық белсенділігімен байланыстырады: қабынуға қарсы [26], туберкулезге қарсы [27], антиоксидантты, вирусқа қарсы, микробқа қарсы, зең ауруына қарсы және басқа да көптеген белсенділік түрлері [28, 29]. Орынбасқан халкондар перспективалы ісікке қарсы препараттар болып табылады [30, 31]. Сондай-ақ, дерматофиттерге қарсы селективті белсенділікке ие препарат ретінде назар аудартады [32]. Орынбасқан халкондар күн батареялары [33], ион-селективті электродтар, молекулалық құрылғылар мен фотофункционалдық материалдар үшін компоненттер ретінде қызығушылық тудырады [34-38].

1 кесте - Табиғи шикізаттан алынған халкондар және олардың туындылары

№ пп	Халкондар және олардың туындылары	Табиғи шикізат	Сілтеме
1	2'-гидрокси-2,4,6-триметоксихалкон	<i>Andrographis lincate</i> (<i>Acanthaceae</i>)	[6]
2	2',4'-дигидрокси-4-метоксидигидрохалкон (давидигенин)	<i>Artemisia dracunculifolia</i> L. (<i>Asteraceae</i>)	[7]
3	2',4',4'-тригидрокси-3'-[6-гидрокси-3,7-диметил-2(E)-7-октадиенил]халкон	<i>Artocarpus nobilis</i>	[8; 9]
4	2',4',6',4'-тетрагидрокси-халкон (изосалипурпол); 2',4',4'-тригидрокси-халкон (изоликвиригенин)	<i>Arabidopsis thaliana</i> (<i>Angiosperm</i>)	[10; 11; 12; 13]
5	халкононарингениннің 2'-О-β-D-глюкозид-4'-О-β-гентиобиозиді; халкононарингениннің 2',4'-ди-О-β-D-глюкозиді	<i>Asarum canadense</i> (<i>Aristolochiaceae</i>)	[14]
6	2',6'-дигидрокси-4'-метоксихалкон; 2'-гидрокси-4,4',6'-триметоксихалкон	<i>Boesenbergia pandurata</i> (<i>Robx.</i>)	[15]
7	2',3',4',5',6'-пентагидрокси-халкон	<i>Brassica alba</i> (<i>Cruciferae</i>)	[16]
8	2'-гидрокси-2,3,4',6'-тетраметоксихалкон	<i>Caesalpinia pulcherrima</i> L.	[17]
9	4-гидрокси-2',4'-диметоксидигидрохалкон; изоликвиригенин	<i>Crinum bulbispermum</i> bulbs.	[18]
10	4,4'-бис-α-0-глюкозил-4,2',4'-тригидрокси-6'-метоксихалкон (агликон)	<i>Derodendron phlomidis</i> (<i>Vcrbenaceae</i>)	[19]
11	3'-(3"-метил-3"-гидроксибутил)-2',4,4'-тригидрокси-6'-метоксихалкон; 4'-0-глюкуронил-2,4-дигидрокси-6'-метокси-3'-пренилхалкон; 1-[(2',4'-дигидрокси-3'-изопренил-6'-метокси)-фенил]-[3-(4-гидроксифенил)]-2,3-эпоксипропан-1-он; 4-ацетокси-2',4'-дигидрокси-6'-метокси-3'-пренилхалкон; 1-[(2',4'-дигидрокси-3'-изопренил-6'-метокси)-фенил]-[3-(4-гидроксифенил)]-2,3-эпоксипропан-1-он; 4-ацетокси-2',4'-дигидрокси-6'-метокси-3'-пренилхалкон	<i>Humulus lupulus</i> L. (<i>Cannabaceae</i>)	[20; 21]
12	4',6',4'-тригидрокси-5-метоксихалкон; 4',6'-дигидрокси-4,5-диметоксихалкон	<i>Iryanthera polyneura</i> (<i>Myristicaceae</i>)	[22]
13	2',4',6'-тригидрокси-4-метоксидигидрохалкон; 2'-метокси-4',6',4'-тригидрокси-дигидрохалкон; 2',4'-диметокси-4',6'-дигидрокси-дигидрохалкон; 2'-глюкозид-4',6'-дигидрокси-4-метоксидигидро-халкон; 4',6',4'-тригидрокси-5-метоксидигидро-халкон; 2',4,5-триметокси-4',6'-дигидрокси-дигидрохалкон; 4',4'-диметокси-6'-α-дигидрокси-дигидрохалкон	<i>Iryanthera virola</i> (<i>Myristicaceae</i>)	[22]
14	Ди-2',4',6'-тригидрокси-4-метоксидигидрохалкон	<i>Iryanthera sagotiana</i> (<i>Myristicaceae</i>)	[22]
15	2',4',6',4'-тетрагидрокси-халкон (нарингенин)	<i>Marchantia paleaceae</i>	[10]
16	2',4',6'-тригидрокси-халкон (пиносембрин); 2',4',6',4'-тетрагидрокси-халкон (нарингенин)	<i>Medicago sativa</i> L.	[10; 12]
17	4'-геранилокси-4,2'-дигидрокси-халкон	<i>Melletia ferruginea</i> (<i>Fabaceae</i>)	[23]
18	2',4',6'-тригидрокси-халкон (пиносембрин); 2',4',6',4'-тетрагидрокси-халкон (нарингенин); хлороген қышқылы (5-О-каффеилкюин қышқылы)	<i>Vitis vinifera</i> (<i>Angiosperm</i>)	[12; 24]

Халкондарды синтездеудің ең маңызды әдісі [39] формил- және ацетилқұрамды қосылыстардың қатысуымен жүретін кротонды конденсация болып табылады. Кляйзен-Шмидт реакциясы бойынша 32 орынбасқан ацетофенон мен 40 ароматты бензальдегидтерден комбинаторлы синтез әдісімен 1280 орынбасқан халкондар алынды.

Осы халкондарды 9 конденсация және циклизация реакцияларында пайдалану 74000 бес- және алтымүшелі циклді қосылыстардың түзілуіне әкелді [40].

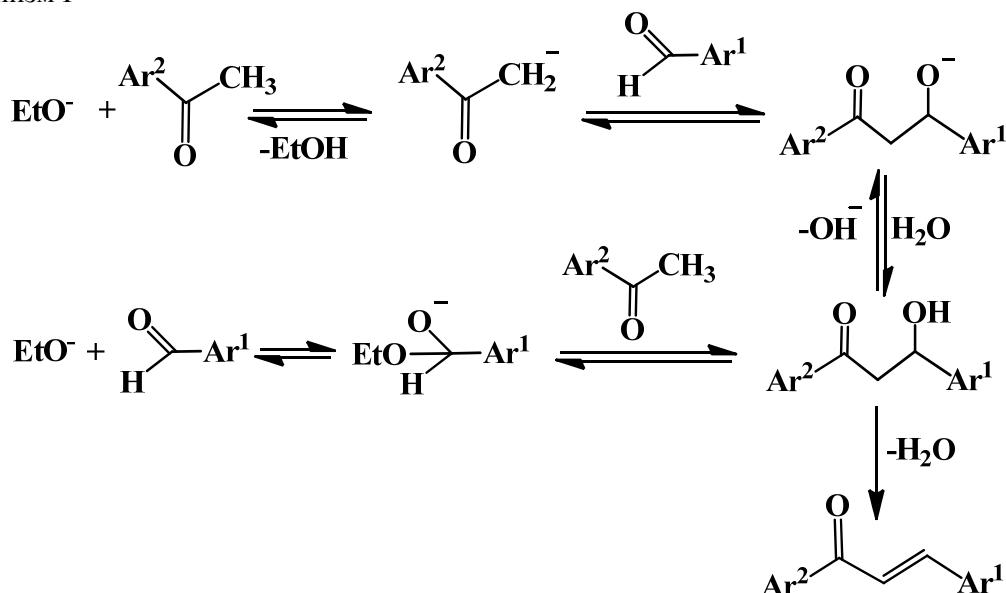


$\text{Ar}^1, \text{Ar}^2 = \text{Ph}$, орынбасқан фенилдер, гетероциклдер

Кляйзен-Шмидт реакциясын УК спектроскопия әдісі арқылы зерттеу кезінде орынбасқан бензальдегидтердің ацетофенонмен өзара әрекеттесуі екінші ретті жылдамдық теңдеуімен сипатталатыны анықталды. Осыған байланысты авторлар [41] реакциялардың екі механизмін ұсынды. Біріншісі – ацетофенонның метилді тобынан протонды негізбен алу (механизм I), екіншісі – альдегидтің карбонилді тобының көміртегіне этилат анионның шабылдауы (механизм II).

Ұсынылған механизмдердің әрбір сатысын термодинамикалық параметрлерді пайдалана отырып талқылау кезінде, авторлар механизм II тиімдірек деген қорытындыға келді [41]:

механизм I

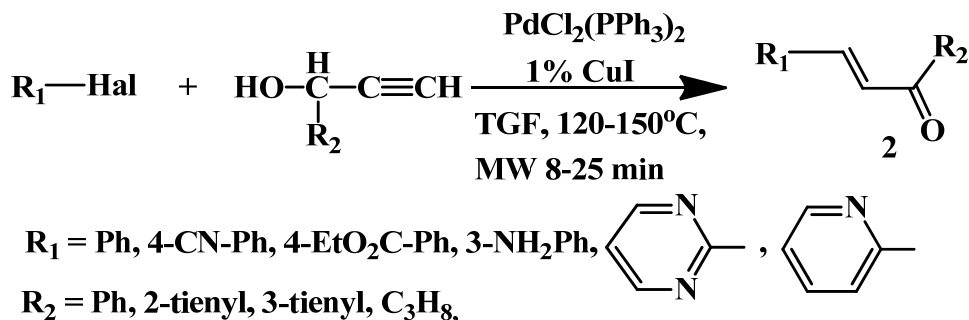


$\text{Ar}^1, \text{Ar}^2 = \text{Ph}$, орынбасқан фенилдер, гетероциклдер

Алайда, кейбір жағдайларда, орынбасқан халкондар пайдалану кезінде бұл әдіс шайырлану мен белгіленген өнімнің шығымының төмендеуіне әкелетін жанама тотығу-тотықсыздану процестерімен қатар жүреді.

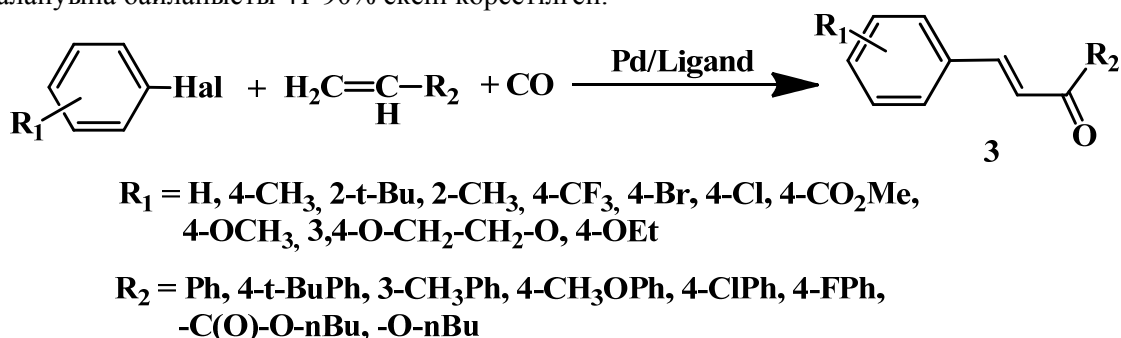
Әдебиеттерде халкондар синтезінің гомогенді және гетерогенді катализ [42, 43], тәсілдерін пайдаланатын сан алуан әдістемелері, олардың арасында белсендірілген барий гидроксидімен катализі [44], SOCl_2 абсолютті EtOH [45], $\text{BF}_3\text{-Et}_2\text{O}$ [46] SOCl_2 өзара әрекеттесуі кезінде *in situ* түзілген тұз қышқылымен, ультрадыбыстық сәулелену, иондық сұйықтармен қоса [47, 48] $\text{KF-Al}_2\text{O}_3$ жағылған калий гидроксидімен катализдері сипатталған. Еріткіштерсіз $\text{I}_2\text{-Al}_2\text{O}_3$, металл оксидтерін қолдану арқылы микротолқынды сәулеленуді пайдалану жұмыстары белгілі, бұл реакция уақытын 3 сағаттан 80 секундке дейін қысқартуға мүмкіндік берді [49, 50]. Бұл шарттар қаламаған реакция өнімдерінен [51] құтылуға, реакция шығымын арттыруға және уақытын бірнеше минутқа дейін қысқартуға мүмкіндік береді. Кляйзен-Шмидт реакцияларынан басқа әдебиеттерде орынбасқан халкондар синтезінің қатаң емес жағдайларда жоғары шығыммен алуға мүмкіндік беретін альтернативті жолдары сипатталады. Кейбір жағдайларда әдістер қаламаған тотығу-тотықсыздану процестері немесе классикалық Кляйзен-Шмидт реакциясы үшін қол жетімді емес қосылыстардың түзілуін болдырмауға мүмкіндік береді. Алайда, бұл ретте, әдетте қымбат реагенттер, микротолқынды немесе ультрадыбыстық әсер ету мен инертті атмосфера пайдалану қажет. Мәселен, халкондар **2** синтезі үшін арилгалогенид және орынбасқан пропаргил спирті арасындағы микротолқынды жағдайда белгіленген өнімдерді жоғары шығыммен аз уақыт арасында алуға мүмкіндік беретін Соногашир үйлестіру реакциясы пайдаланылған [26].

Реакция R_1 ароматты ядроға орынбасушы ретінде электроноакцепторлы топ болған жағдайда ғана жүретіні көрсетілген.

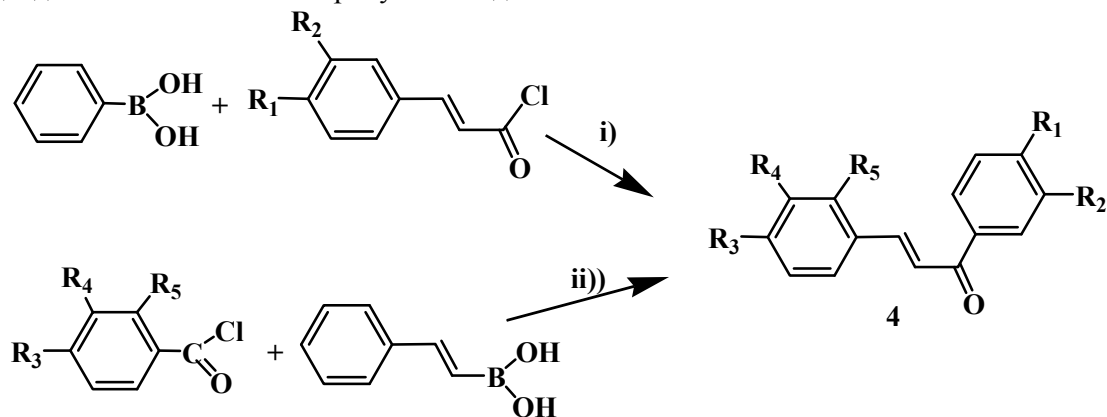


[52] көміртектің монооксиді қатысында палладий катализаторын пайдаланып, халкондар 3 түзілуіне әкелетін арилгалогенид және стирол немесе орынбасқан винилдің Хектің үйлестіру-карбонилдеу реакциясы бойынша мәліметтер келтірілген.

Өнім 3 шығымы халконның ароматты сақинасында лиганда мен орынбасарының пайдалануына байланысты 41-90% екені көрсетілген.



Жұмыстыңавторларымен [53] катаңемесжағдайдаСузукиреакциясыныңбірнеше нұсқаларын пайдалана отырып, халкондар 4 алынды: біріншісінде – циннамоилхлоридімен фенил борқышқылы, екіншісінде – бензоилхлоридпенфенилвинил борқышқылы пайдаланылады. Екі реакцияда белгілен ген өнім 4 түзілуіне әкелді.

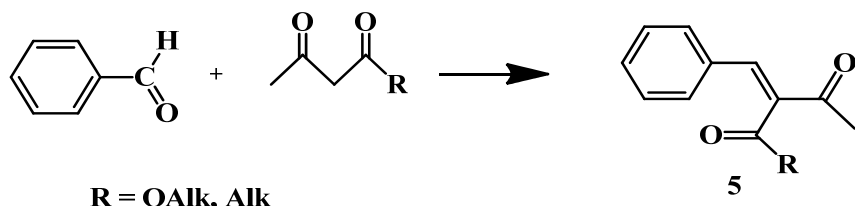


$R_1 = H, OCH_3; R_2 = H, NO_2, OCH_3;$
 $R_3 = H, OCH_3; R_4 = H, CF_3, NO_2, OCH_3; R_5 = H, CF_3$

i): $(PPh_3)_4Pd(o), Cs_2CO_3, toluol.$ Yield 40-50%

ii): $(PPh_3)_4Pd(o), Cs_2CO_3, toluol.$ Yield 70-95%

Сондай-ақ, халкондарды Кневенагель конденсациясымен, яғни альдегиднемесе кетонның белсенді метилденді компоненті бар қосылыстармен, мысалы, негіздік катализ жағдайында ацетосірке эфирімен (АСЭ) әрекеттесуі арқылы алуға болады [39]. Бензальдегидтің АСЭ-мен әрекеттесу кезінде реакция халкон 5 түзілуіне әкеледі.

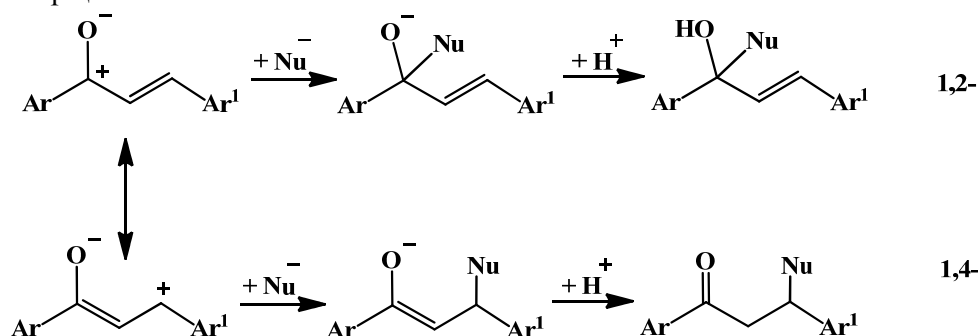


Халкондарды синтездеу әдістерін оңтайландыруға арналған әдебиеттің сан алуандылығына қарамастан, көптеген авторлар тек қана дәстүрлі синтез әдісін - Кляйзен-Шмидтконденсациясын (негіздік жағдайда этанолда 3-48 сағат араластыру) пайдаланады [31, 34-37, 54].

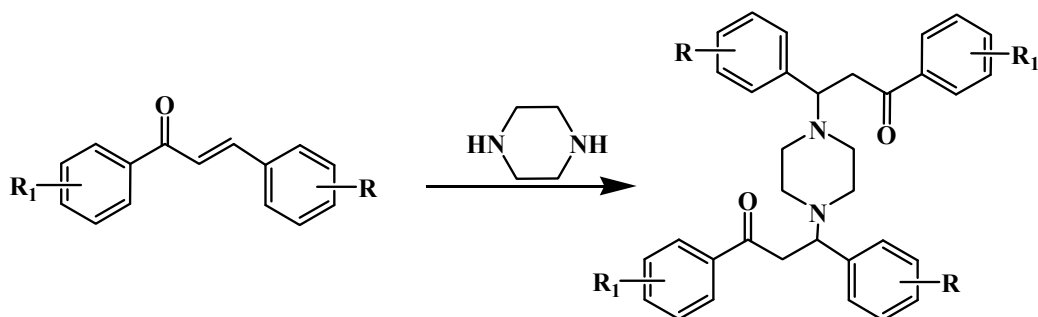
3. Халкондардың реакциялық қабілеттілігі

Халкондар жоғары реакциялық қабілеттілікке ие. Бұл олардың молекуласындағы екі электрофильді орталықтардың – карбонильді топпен онымен қосарланған көміртектің β -атомының болуына байланысты [1]. Халкондар $C=C-C=O$ қосарланған жүйесінде электрондық тығыздықтың делокализациясы нәтижесінде амбидентті электрофилдер секілді әрекет ете алады. Халконның әрекеттесу кезінде нуклеофил немесе карбонильді тобының көміртек атомы (1,2-қосылу), немесе көміртектің β -атомы (1,4-қосылу) шабуыл жасайды, реакция механизмі 1-сызбанұсқада келтірілген. Халкондардың осы екі электрофильді орталықтарының табиғаты әр түрлі, бұл моно- және динуклеофилдермен реакцияларының жоғары региоселективтілігінде байқалады.

1 - сызбанұсқа



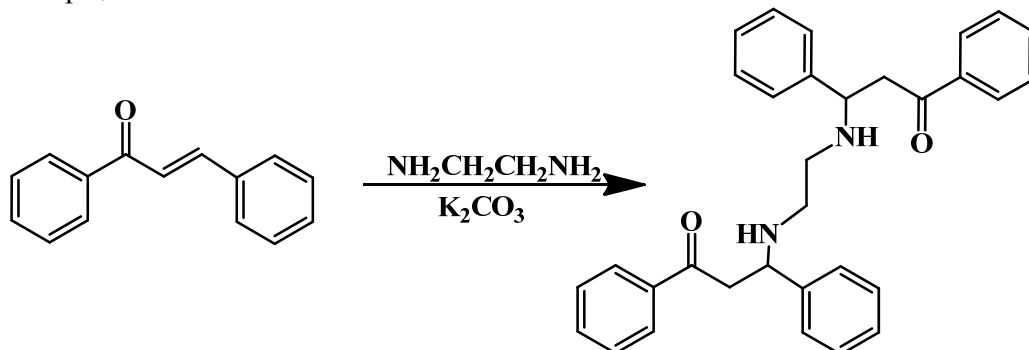
Халкондардың пиперазинмен әрекеттесуі әдетте Михаэлдің бис-аза-аддуктарының түзілуіне әкеледі. Әр түрлі жағдайларда жүргізілетін бұл реакциялар әдебиетте көміртек-азот байланысын түзу мысалы ретінде бірнеше рет сипатталған [55-57]. Мәселен, халкондар, сондай-ақ орынбасқан халкондар толуолдағы пиперазинмен Михаэлдің бис-аза-аддуктарын түзе отырып, әрекеттеседі [55]. Дәл осылай қыздырылған калий карбонаты қатысындағы циклогексан-эфир (1:2) қоспасының реакциясы өтеді [56]. Ультрадыбыс сәулеленукезінде халкон судағы пиперазинмен жоғары шығыммен Михаэлдің бис-аза-аддуктарын түзе отырып, әрекеттеседі [57] (2-сызбанұсқа).



$R_1=R=H$; $R_1=H$, $R=3-NO_2$; $R_1=H$, $R=2-Cl$; $R_1=4-Cl$, $R=H$; $R_1=H$, $R=4-Cl$; $R_1=R=4-Cl$;
 $R_1=4-Br$, $R=H$; $R_1=H$, $R=4-Me$; $R_1=4-Me$, $R=H$; $R_1=H$, $R=4-OMe$; $R_1=R=4-Me$;
 $R_1=4-Me$, $R=4-OMe$; $C_6H_5CH_3$.

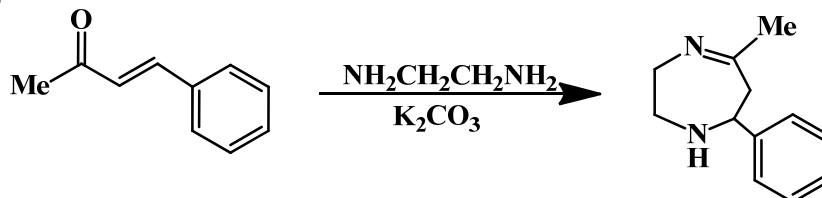
Халкондардың этилендиаминмен әрекеттесуі Михаэлдің бис-аза-аддукттарын [56] немесе диазепиндердің [58, 59] түзілуіне әкелу мүмкін. Мәселен, полярлығы аз еріткіштерде орынбаспаған халконның этилендиаминмен әрекеттесуі көміртектің β -атомына қосылумен жүреді және Михаэлдің бис-аза-аддукттарының [56] түзілуіне әкеледі (3-сызбанұсқа).

3-сызбанұсқа

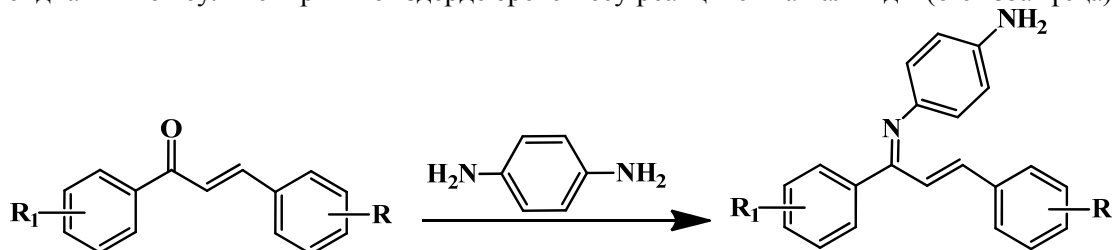


Алайда, Михаэлдің бис-аза-аддукттарының түзілуі реакция жүруінің жалғыз жолы болып табылмайды. [58] жұмысында халкон мен этилендиаминнің өзара әрекеттесуінен 59% шығыммен тетрагидродиазепин алынды.

4-сызбанұсқа



Әдебиетте аталған реакция механизмі келтірілмеген, бірақ ол екі сатыда жүретінін болжауға болады – алдымен Михаэлдің аза-аддукты түзіледі, кейін карбонилді топтың көміртек атомына екінші амин тобының шабуылдауы арқылы оның циклденуі жүреді. Халкондардың *p*-фенилендиаминмен әрекеттесуі кейін флавоидар синтезінде қолданылуы мүмкін Шифф негіздерінің түзілуіне әкеледі. Флавоидар және олардың туындыларының синтезі олардың жоғары антиоксидантты [60-63], ангиолитикалық [64], ісікке қарсы [65] және қабынуға қарсы [66, 67] белсенділіктердің болуына байланысты айтарлықтай назар аудартады. [68] жұмысында халкониминдердің тотығу циклденуі арқылы иминофлавоидар синтезі жайында баяндалған. Бұл синтездің сатыларының бірі халкондардың орын басқан анилинмен, атап айтсақ, *p*-фенилендиаминмен әрекеттесуі және жоғары шығыммен сәйкес иминнің түзілуі болып табылады. Сондай-ақ, бактерияға қарсы белсенділікке ие Шифф негіздері [69] жұмысында халкондардың *p*-фенилендиаминмен сулы-спиртті негіздерде әрекеттесу реакциясынан алынды (6-сызбанұсқа).



$R_1=2\text{-OH}, 5\text{-Br}, R=4\text{-OMe}$.

$R_1=R=\text{H}, R=\text{H}, R=4\text{-OMe}; R_1=2\text{-OH}, R=4\text{-NMe}_2; R_1=\text{H}, R=4\text{-NMe}_2; R_1=2\text{-OH}, 5\text{-Cl}, R=4\text{-OMe};$

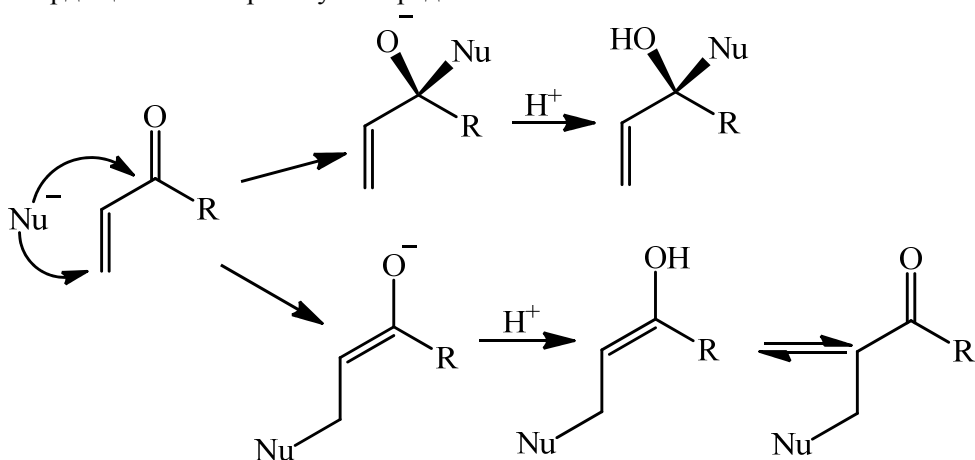
$R_1=2\text{-OH}, 5\text{-Cl}, R=\text{H}; R_1=2\text{-OH}, 5\text{-Cl}, R=4\text{-NMe}_2; R_1=2\text{-OH}, 5\text{-Me}, R=4\text{-NMe}_2$.

α, β -қанықпаған карбонилді қосылыстар әр түрлі орынбасушылары бар үш-, төрт, бес-, алты-, жеті мүшелі карбо- және гетероциклдерді түзудегі синтетиктің кез келген фантазиясын

қанағаттандыратын мүмкіндігі кең екені белгілі [1]. Сондықтан халкондар комбинаторлық химияда негізгі интермедиаттар ретінде ерекше белгілі [70]. Халкондарда екі электрофилді орталықтардың болуы динуклеофилдермен әрекеттесуі кезінде гетероциклдердің, олардың ішінде аннелирленген гетероциклдердің түзілуіне әкеледі [1].

Халкондар қатыса алатын көптеген реакциялар арасынан әр түрлі карбо- және гетероциклді қосылыстардың, оның ішінде биологиялық белсенділіктің кең спектріне ие орынбасқан циклогексанон мен пиримидиннің түзілуіне әкелетін динуклеофилді реагенттермен әрекеттесуі ерекше қызығушылық тудырады.

α,β -қанықпаған карбонилді қосылыстардың (альдегид, кетон (халкон), қышқыл, эфирлер) нуклеофилдермен әрекеттесуі жаңа C-C немесе C-N байланыстың түзілуіне әкеледі. Жаңа байланыс донор мен акцептордың екінші немесе төртінші көміртек атомы арасында түзіледі. Реакцияның бірінші типіретінде карбонилді топ бойынша қарапайым қосылуды, ал екінші жағдайда нуклеофилдің қосылуын қарастырады, электронды жұпдонордың көміртегінен акцептордың оттегіне орын ауыстырады.



Аталған процестің бағытын анықтайтын факторлар – бұл қышқылдар мен негіздердің қаттылығы мен жұмсақтылығы түсініктерімен тығыз байланысты зарядтардың өзара әрекеттесуі және орбиталды сәйкестігі. Қатты қышқылдың қатты негізбен әрекеттесуі зарядтардың әрекеттесуімен анықталады, ал жұмсақ қышқылдың жұмсақ негізбен әрекеттесуі орбиталды бақылауда жүреді [71]. 1,2- және 1,4-қосылу реакцияларында карбаниондардың салыстырмалы реакциялық қабілеттілігі молекулалық орбиталдардың ұйытқу теориясы бойынша қарастырылған. Бұл теория бойынша фрагменттің электронды құрылысын ескере отырып, максималды оң эффективті заряд – карбонилді көміртекте, максималды ТБМО локализациясы – β -көміртек атомында екені көрсетілген. Карбонилді топ бойынша қосылу – зарядты, ал 1,4-қосылу орбиталды бақылауда жүреді. Бірдей шарттарда карбонилді топ бойынша нуклеофилдің қосылу процесіне нуклеофилді орталықтағы заряд локализациясы, ЖБМО энергиясының төмендеуі қолайлы әсер етеді. Керісінше, зарядтың делокализация дәрежесінің өсуі, нуклеофилдің ЖБМО деңгейінің жоғарлауы орбиталды-бақыланатын 1,4-қосылу жүруіне жағдай жасайды.

Реакцияның екі бағыты арасындағы баланс шарттары әр түрлі әсерлерге (еріткіш, катализатор, температура) сезімталдылығы сонша, процестердің бірін доминантты ету үшін салыстырмалы кішігірім өзгерістердің өзі жеткілікті

Сондықтан берілген реакцияның артылықшылығы да, кемшілігі де нуклеофилді орталықтардың әр түрлі реакциялық қабілеттілігі болып табылады, себебі шарттарға реакция өнімдерінің құрылысы ғана емес, сонымен қатар олардың шығымы мен тазалығы тәуелді болады. Соңғы жылдары синтетиктердің назары реакция шартына байланысты әр түрлі өнімдерді алудың тәсілдерінің дамуына бағытталған. Бұндай процестерді «ауыстырылатын селективтілігі бар реакциялар» деп атайды. Олар соңғы уақытта, әсіресе биологиялық белсенді қосылыстар синтезі үшін кең қолданыс тапты. «Ауыстыру» әдістеріне жоғары айтылғандардан басқа (еріткіш, катализатор, температура) микротолқынды немесе ультрадыбыс әсерлері жатады [72, 73].

4. Халкондар туындыларының биологиялық белсенділігі

Халконды фрагменті бар қосылыстар әр түрлі биологиялық белсенділікке ие. Мысалы, олар әр түрлі ісіктерге айтарлықтай белсендік көрсетеді және хемотректорлы қасиеттерге ие. Бұны олардың антиоксидантты белсенділігімен байланыстыруға болады [74-77].

Халкондардың басқа маңызды қасиеттері бактериялардың өсуін ингибирлеу қабілеті [78], зең ауруына қарсы және вирусқа қарсы белсенділік көрсетуі [79] болып табылады. Сонымен қатар, олар капиллярларды қатайту қабілетіне ие және қабынуға қарсы заттар ретінде қолданылуы мүмкін [80]. Аталған белсенділік түрлерінен басқа безгекке қарсы [81-85], қатерлі ісікке қарсы [86-88], ларвицидты [89], иммунотүрлендіруші [90], антигипергликемиялық, туберкулезге қарсы [91], антипротозойлы және антимицетикалық белсендіктер [92], сонымен қатар олардың бактерияға қарсы [93, 94] және зең ауруына қарсы [95, 96] заттар ретінде қолданылуы мүмкіндігі анықталды.

Ферменттерге, әсіресе сүтқоректілердің альфа-амилазасы [97], циклооксигеназа (ЦОГ) [98], моноаминоксидаза (МАО) [99], лейкотриен В [100], тирозиназа [101], редуктаза альдозасына [102] және т.б. ингибирлеу әсері көрсетілген. Халкондарға тән жоғары биологиялық белсенділік бұл қосылыстардың әр түрлі биологиялық нысаналармен әрекеттесуі бойынша зерттеулердің дамуына әсер етті. Халкондардың өсімдіктер құрамындағы функциясы жайында көптеген тәжірибелік мәліметтер бар, олар халкондар өсімдік ағзасында белсенді физиологиялық рөл атқаратынын тұжырымдауға мүмкіндік береді. Олар салыстырмалы оңай тотығады немесе тотықсызданады және олардың тотығу-тотықсыздану потенциалы зат алмасуда қатысатынын көрсетеді. Кейбір халкон құрылыстық қосылыстар қорғаныштық функциясын [95], тынысалу катализаторлары функцияларын атқарады және өсімдік жасушаларының тынысалу кезіндегі тотығу-тотықсыздану процестеріне қатысады.

Электрондонорлы орынбасушылары, мысалы метокси-, гидроксид- топтары, бар қосылыстар, ең жоғары микробқа қарсы белсендік көрсетеді [103]. Құрамында бір-екі хлор немесе фтор атомы бар халкондар зең ауруына және микробқа қарсы жоғары белсенділік көрсетеді. Құрамында оксатиолон [104] фрагменті бар халкондар арасында адамның қатерлі ісік жасушаларына, сонымен қатар *Micrococcus luteus*, *Staphylococcus aureus*, *Micobacterium tuberculosis* HRv қатысты цитоуыттылық көрсететін қосылыстар табылды.

Сондай-ақ, халкондардың қызығушылық тудыратын қасиеттеріне қатерлі ісік жасушалар апоптозасының иницирлеуі [105], олардың митохондриялы тынысалуын ауырлатуы жатады. Мақала авторлары [106] А және В сақиналарында гидроксил топтары аз халкондар құрамында гидроксил топтары көп халкондармен салыстырғанда едәуір тиімді екені көрсетілген. Осындай белсенділік айырмашылығын фенолды ОН-топтарының қышқылдылығымен түсіндіруге болады. Халкондар цитоуыттылық белсенділігін көрсететін кеңінен белгілі механизмдердің бірі халкондардың митоз фазасында әрекеттесуі болып табылады. Nam N.H. авторлар ұжымымен [106] 2',5'-дигидрокси халконның туындыларының белсенділігін зерттеді, халкондардың көпшілігі қатерлі ісік жасушаларының әр түрлі қатарларына қарсы цитоуыттылық белсенділік көрсететінін анықтады.

Халкондардың дигидрокситуындылары қосылыстың құрылысына байланысты антиоксидантты белсенділік көрсетеді [107]. Халкондардың антиоксидантты белсенділік механизмі [108] жұмысында сипатталған. Халкон молекуласының радикалмен әрекеттесуі кезінде феноксидті радикал түзіледі, сонымен қатар бензол сақинасының *орто*- және *пара*- дигидроксилденген жүйелері делокализацияланған электрондары бар жүйелер болып табылады, сондықтан олардан түзілетін феноксидті радикалдар тұрақты семихинонды радикалдарға оңай ауысады, кейін олар хинондарға айналады. Бензол сақинасының *мета*-дигидроксилденген жүйесі электрондардың делокализациясы үшін тиімділігі төменірек, сондықтан феноксидты радикалдар кейінгі айналуларға ұшырай алмайды.

Орто-(яғни 2',3'- мен 3',4'-) және *пара*-(яғни 2',5'-) орынбасушылары бар халкондар өте жоғары антиоксидантты белсенділік (50 μ M концентрациясындағы бақылаумен салыстырғанда 80–90 %), аскорбин қышқылы мен α -токоферолдың белсенділігімен шамалас, көрсететіні анықталды. Екінші жағынан, *мета*-(яғни 2',4'-пен 3',5'-) орынбасушылары бар халкондар (бақылаумен салыстырғанда 25 %) 200 μ M концентрацияда ($IC_{50} > 200 \mu$ M) белсенділіктің едәуір кенет төмендеуін көрсетеді. Бұл мәліметтер В ядросында екі гидроксил топтарының орналасуы маңызды

антирадикалды белсенділігінің құрылыстық факторы болып табылатынын, *орто*-орынбасқанмен салыстырғанда *пара*-орынбасқан қосылыстар жоғары белсенділікке ие екенін көрсетеді. А сақинасында орынбасушылардың *пара*-жағдайына ауысуы антирадикалды белсенділікке қатты әсер етпейді. Бұл бензолсақинасының *пара*-орынбасушыдың электрондық эффектілері антирадикалды белсенділікке әсер етпейтінін көрсетеді.

Кейбір гидроксихалкондардың потенциалды антиоксидантты белсенділігі 1,1-дифенил-2-пикрилгидразил және босгидроксил радикалдарын [108] ингибирлеу қабілеттілігі арқылы бағаланды. Нарингенин мен флоретин үшін (MCF-7) сүт бездерінің қатерлі ісік жасушалар қатарына қатысты антипролиферативті белсенділік анықталмады. Алайда басқа халкондар (2'-гидроксихалконды қоса қарастырғанда) жоғары концентрацияларда (10,50 μM) антипролиферативті белсенділік көрсетті, ал төмен концентрацияларда (0,01–1 μM) жасушалық өсуді үдетті.

Халкондардың қабынуға қарсы белсенділік көрсетуіне α,β -қанықпаған карбонилді функционалдық тобы жауапты. H.L. Yadav ұжымымен [109] халкондардың бес туындысынан тұратын серияны синтездеді де, артқы аяқтың каррагенинді ісінуі болған егеуқұйрықтарға қабынуға қарсы белсенділігін зерттеді. 25 мг/кг дозасында пероралды енгізілген халкондар туындылары ісінудің өршуін едәуір тежеді. Сонымен қатар халкондардың қабынуға қарсы белсенділігін зерттеудің нәтижелері [50] мақаласында келтірілген. Белсендірілген макрофагтар қабынуға қарсы түрлерінде және әр түрлі медиаторларды, соның ішінде лейкоциттер миграциясы мен ісінудің түзілуін, сонымен қатар лейкоциттер активтілігі мен цитокин түзілуін жеңілдететін потенциалды тамыр кеңейтетін агент болып табылатын азот оксидін (NO), босатып алудан егізгі рөл атқарады. В-сақинаның электрондық тығыздығын артыратын орынбасушылары, мысалы MeO- , BuO- , Me N- топтары бар халкондар NO түзілу процесін ингибирлеуде айтарлықтай белсендік көрсетпейді [110].

S.J. Won ұжымымен [111] 2',4-дигидроксихалкон, 2'-гидрокси-2-тиенилхалкон, 2'-гидрокси-3-тиенилхалкон және 2',5'-дигидрокси-индол-3-ил-халкон потенциалды қабынуға қарсы агенттер болып табылатынын көрсетті.

[112] жұмысында халкондардың гипергликемиялық белсенділігі зерттелді. Инсулин тәуелді емес диабет (II типті диабет) инсулин-тұрақтылық, гипергликемия және гиперинсулинемиямен сипатталатын созылмалы метаболитикалық ауру болып табылады. *Broussonetia papyrifera*-дан протеинтирозин фосфатаза (PTP1B) және альдозаның редуктаза ферменттерін селективті ингибирлейтін орынбасқан халкондар алынды. Олардың антиоксидантты қасиеттері гипергликемиялық агенттер ретінде қарастыруға мүмкіндік береді, себебі диабеттерде тотығу стресс маңызды рөл атқарады. 3,4-Диметокси туындылар едәуір жоғары антигипергликемиялық эффект, ал монометокси туындылар төмен белсенділік көрсетеді.

Хлорқұрамды халкондар едәуір жоғары антиплазмодиалды белсенділік, триазолды, пирролды және бензотриазолды сақиналары бар халкондар – антипаразиттік белсенділік көрсетеді. Морфолинді сақинасы бар халкондардың хлортуындылары ең төмен белсенділікке ие екені анықталды. Құрамында триазолды сақина мен хлор бар қосылыстар ең жоғары антиплазмодиалды белсенділікке ие, бұл пішіні бойынша үлкен емес құрамында бір немесе бірнеше азот атомы бар липофилді топтар безгекке қарсы белсенділікті *in vitro* артыратынын растайды.

Орынбасқан халкондардың [(4-Cl, 4-MeO, 3,4,5-(MeO)₃] антиплазмодиалды белсенділікті *in vitro* зерттеуі пішіні бойынша ацетофенон фрагментінде азот атомы немесе амин бар үлкен емес және орташа липофилді топтар потенциалды безгекке қарсы агенттер болып табылатынын көрсетті. Осындай қосылыстар энзима цистеинпротеазаның белсенді орталығында болатын гистидин қалдығымен сутек байланысы есесінен қосымша байланысуын қамтамасыз етуі мүмкін.

Гидрофилді сипаттағы халкондарға, яғни халкондардың ОН-туындыларына, А ядросында нафталин және пиридин фрагменті бар халкондар үшін антилейшманиалды белсенділік [113,114] тән. Халкондар қатарының тиразиазаны меланин түзілу реакциясына қатысты ингибирлеу белсенділігі және антиоксидантты мүмкіндігі зерттелді [115]. А және В ароматты ядроларында ОН-топтарының орналасуы маңызды болып табылады, себебі А сақинасы бойынша гидроксилдеумен салыстырғанда В сақинасы бойынша гидроксилдеу тиразиазаны едәуір жоғары ингибирлеу қабілеттілікке әкеледі.

5. Қорытынды

Табиғи халкондардың кең спектрлі биологиялық әсері бар бағалы фармакологиялық қасиеттері осы класстың биологиялық белсенділігін арттыру міндеттерін шешуге арналған жаңа тәсілдерді жетілдіруін болжауға жағдай туғызады және мүмкіндіктерін кеңейтеді.

Халкондар молекулаларының құрылысын өзгерту арқылы олардың биологиялық сынақтарда белсенділік абсолюттік көрсеткіштерін арттыруға болады.

Халкондар, β -канықпаған кетондар ретінде, қосылыстардың басқа класстарының қолжетімділігі төмен туындыларды алу үшін бастапқы заттар ретінде қызығушылық тудырады, бұл екі электрофильді орталықтардың - карбонильді тобының көміртегі атомы мен көміртектің β -атомының болуына байланысты.

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О.А. Нуркенов^{1,2}, М.К. Ибраев², С.Д. Фазылов¹, И.В. Кулаков³, А.Т. Такибаева², А.Е. Туктыбаева²

¹Институт органического синтеза и углехимии Республики Казахстан, Караганда, Казахстан;

²Карагандинский государственный технический университет, Караганда, Казахстан;

³Омский государственный университет им. Ф.М. Достоевского, Омск, Россия

ХАЛКОНЫ - СИНТОНЫ В СИНТЕЗЕ БИОЛОГИЧЕСКИ АКТИВНЫХ ВЕЩЕСТВ

Аннотация: в обзорной статье обобщены и систематизированы литературные данные последних годов, а также результаты исследований авторов в области функционально замещенных халконов. Приведены наиболее распространенные природные халконы, методы получения, реакционная способность и биологические свойства синтетических халконов.

Ключевые слова: замещенный ароматический альдегид, халкон, пиразолин, флавонон, цитокин, транскрипционный фактор NF-κB.

Сведения об авторах:

Нуркенов Оралгазы Актаевич, Институт органического синтеза и углехимии Республики Казахстан, заведующий лабораторией «Синтез биологически активных веществ», профессор;

Ибраев Марат Киримбаевич, Карагандинский государственный технический университет, профессор кафедры «Химия и химические технологии», профессор;

Фазылов Серик Драхметович, Институт органического синтеза и углехимии Республики Казахстан, заместитель директора по научной работе, член-корр. НАН РК;

Такибаева Алтынарай Темирбековна, Карагандинский государственный технический университет, доцент кафедры «Химия и химические технологии»;

Кулаков Иван Вячеславович, Омский государственный университет им. Ф.М. Достоевского, профессор кафедры «Органическая химия», доцент;

Туктыбаева Арайлым Ермековна, Карагандинский государственный технический университет, преподаватель кафедры «Химия и химические технологии».

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P.Zh. Zhanymkhanova, E.M. Gabdullin, A.Zh. Turmukhambetov, S.M. Adekenov

JSC International Research and Production Holding “Phytochemistry”,
4 M. Gazaliev str., 100009, Karaganda, Kazakhstan,
tel./fax: +7(7212) 433127, e-mail: phyto_pio@mail.ru

ALKALOID-BEARING SPECIES OF THE GENUS *ACONITUM* L.

Abstract. Analytical review of alkaloid-bearing plants of the genus *Aconitum* L. has been carried out. The obtained data will serve as a basis for scientific research of some plantspecies in the genus *Aconitum* L., isolation of alkaloids including high purity aconitine to create a new drug substance.

By identifying specific habitats of species of this genus in the flora of Kazakhstan, it is established that most herbarium materials have been collected in mountainous floristic regions of the flora of Kazakhstan, which justifies the need to study samples of the genus *Aconitum* L. from the indicated floristic areas. The herbarium fund of the International Research and Production Holding “Phytochemistry” JSC (KG) includes herbarium materials of 9 species of the genus *Aconitum* L., of which the most common species are *Aconitum leucostomum* Worosch. and *Aconitum monticola* Steinb. forming large thickets in the nature.

Keywords: *Aconitum* L., alkaloids, chemical study, herbarium materials, cameral treatment.

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П.Ж. Жанымханова, Е.М. Габдуллин, А.Ж. Турмухамбетов, С.М. Адекенов

АО «Международный научно-производственный холдинг «Фитохимия», г. Караганда, 100009,
ул. М. Газалиева, 4, тел./факс: 8(7212)433127, e-mail: phyto_pio@mail.ru

АЛКАЛОИДОНОСНЫЕ ВИДЫ РОДА *ACONITUM* L.

Аннотация. Проведен аналитический обзор алкалоидоносных растений рода *Aconitum* L. Полученные данные послужат основой для научных исследований некоторых видов растений рода *Aconitum* L., выделению алкалоидов, в том числе аконитина высокой чистоты для создания нового лекарственного вещества.

По выявлению конкретных мест произрастания видов данного рода во флоре Казахстана, установлено, что большинство гербарных материалов собраны в горных флористических районах флоры Казахстана, что свидетельствует о необходимости изучения образцов рода *Aconitum* L. из указанных флористических районах. В гербарном фонде АО «Международный научно-производственный холдинг «Фитохимия» (KG) имеется гербарные материалы 9 видов рода *Aconitum* L., из них наиболее часто встречаются виды рода *Aconitum leucostomum* Worosch. и *Aconitum monticola* Steinb., образующие большие заросли в природе.

Ключевые слова: *Aconitum* L., алкалоиды, химическое изучение, гербарные материалы, камеральная обработка.

Представители рода *Aconitum* L. относятся к одним из наиболее ценных алкалоидоносных растений семейства лютиковых (*Ranunculaceae*) и являются богатым источником полифункциональных гетероциклических соединений - дитерпеновых алкалоидов. Растения рода *Aconitum* L. доступны и широко распространены в Казахстане, в странах СНГ, на территории

Китая и Средней Азии, но в зависимости от места произрастания различаются по качественному составу и количественному содержанию. Усиленное внимание исследователей к дитерпеновым алкалоидам обусловлено известной сложностью их строения и вытекающего из этого широкого спектра фармакологической активности. Дитерпеновые алкалоиды обладают широким спектром биологической активности: противовоспалительной, местноанестезирующей, антиаритмической, спазмолитической, противоопухолевой, миорелаксантной, что позволяет рассматривать их как источник перспективных фармакологических соединений.

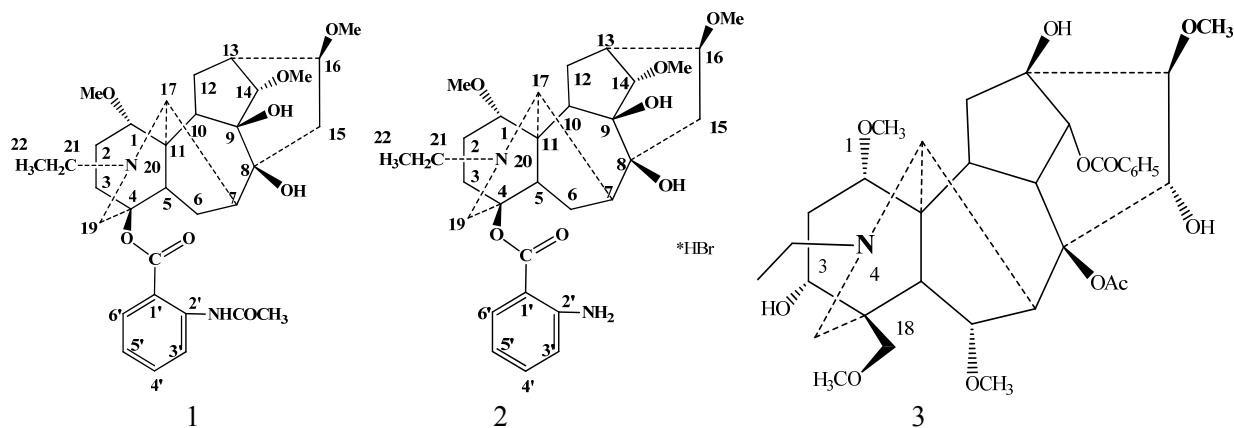
При фармакогностическом изучении растений рода *Aconitum* L. выявлено, что во время цветения очень ядовиты все надземные части – стебли, листья, цветки. Но самым смертельно опасным являются корневища и клубни растения, когда идет накопление алкалоидов. Установлено, что в корнеклубнях данного вида растения количество алкалоидов увеличивается в течении всего вегетационного периода и достигает максимума осенью.

Виды *Aconitum* представляют интерес в качестве лекарственных растений, потому что они обладают многочисленными изопреноидными соединениями в качестве главных вторичных метаболитов: тетрациклические дитерпеноидные алкалоиды. Структура изопреноидов рода *Aconitum* является необычной, так как в этих растениях низшие терпеноиды (моно - C-10 и сескви-терпены C-15) присутствуют только в незначительных количествах, главным образом в цветах, тогда как все части накапливают дитерпеноидные соединения своеобразных структурных типов.

Более 70% современных гомеопатических средств получают из лекарственного растительного сырья. Растения рода *Aconitum* L. являются одним из наиболее используемых в гомеопатии. В Гомеопатические Фармакопеи ведущих стран мира (Германия, Франция, США и другие) включены препараты аконита, получаемые из следующих видов растений: *Aconitum napellus* L. (борец аптечный), *Aconitum ferox* Wall. (борец ядовитый), *Aconitum lycoctonum* L. (борец волчий).

По данным «Флоры СССР» во всем мире насчитывается более 300 видов аконита, из них 70 видов - на территории бывшего СССР. В свою очередь 14 видов встречается во флоре Казахстана. Произрастают в горах на лесных и субальпийских лугах, среди кустарников [1-2]. В работе Гемеджиевой Н.Г. [3-4] отмечается, что все 14 видов относятся к алкалоидоносным растениям.

Учеными ряда стран проводятся интенсивные исследования растений рода *Aconitum* L. Большой вклад в исследование растений видов рода *Aconitum* внесли узбекские ученые С.Ю. Юнусов, М.С. Юнусов, В.А. Тельнов, Э.Ф. Ахметова, И.А. Бессонова, а также зарубежные ученые Takayama H., Pelletier W.S. и др., которыми был определен основной состав алкалоидов. Ими разработаны экономически выгодные и экологически безопасные технологии производства препарата «Аллапинин» на основе субстанции лаппаконитина **1** из корневищ и корней *Aconitum leucostomum* Worosch. (борец белоустый) и *Aconitum septentrionale* Koelle. (борец северный), «Антиаритмина» **2** из отходов производства аллапинина, суммарных препаратов антиаритмического действия «Аклезин» из надземной части *Aconitum leucostomum* Worosch. и «Аксапитмин» из корневищ *Aconitum septentrionale* Koelle. Разработана технология производства субстанции биореактива «Аконитина» **3** из клубней *Aconitum soongaricum* Stapf. (борец джунгарский) [5-12].



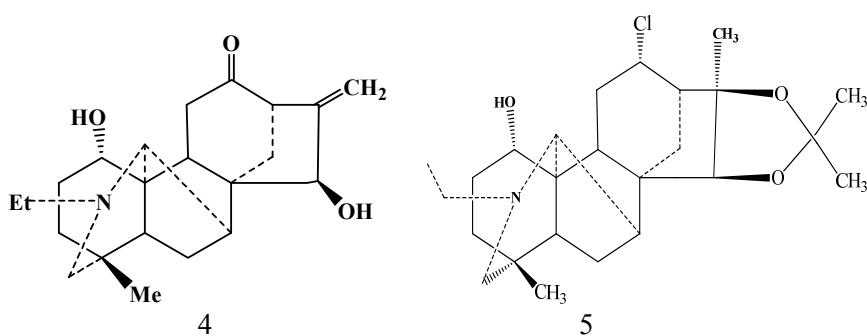
Благодаря исследованиям академиков - химиков С.Ю. и М.С. Юнусовых и академика - кардиолога Е.И. Чазова алкалоид лаппаконитин занял в виде препарата «Аллапинин» прочное место в ряду антиаритмических средств. Он рекомендован при наджелудочковой и желудочковой экстрасистолии, пароксизмах мерцания и трепетания предсердий, тахикардии. Лаппаконитин интересен тем, что он оказался подвластным синтетическим трансформациям, итогом которых стали вещества с сохраненной фармакологической активностью, но существенно потерявшие вредные побочные свойства. Следует отметить, что введение атома брома в молекулу лаппаконитина привело к соединению, в 5 раз менее токсичному и в 10 раз более активному как антиаритмическое средство. Лаппаконитин продуцируют два вида аконита - *Aconitum lycoctonum* L. (борец волчий) и *Aconitum septentrionale* Koelle. (борец северный). Как показали исследования известного ботаника Н.И. Федорова, только на территории Башкирии эксплуатационный запас корней *Aconitum lycoctonum* L. достаточен для обеспечения потребности здравоохранения России.

Несколько видов аконитов, среди которых наиболее перспективным продуцентом считается *Aconitum soongaricum* Stapf, содержат аконитин. Из-за высочайшей токсичности этот алкалоид применения в медицине не нашел. Однако, без него не мыслится экспериментальная фармакология. В отличие от других антиаритмиков, воздействующих только на кальциевые каналы и охватывающих одновременно кальциевые и натриевые каналы аритмии, аконитин селективен в отношении блокирования натриевых каналов. Без применения аконитина исследование антиаритмических средств некорректно.

На наличие в листьях *Aconitum* аконитина впервые указал Пешье в 1820 году. Гейгер и Гессе выделили аконитин из частей растения *Aconitum* в 1838 г., а Морзон - в 1839 г., Плаита в 1850 г. предложил для аморфного аконитина химическую формулу [13]. Аконитин – является одним из мажорных алкалоидов, относится к числу очень ядовитых алкалоидов, содержащихся в некоторых видах аконита [14].

Более «уравновешенную» в смысле функционализации структуру имеет алкалоид зонгорин **4**, обладающий действием на центральную нервную систему. Продуцирует его распространенный на Алтае *Aconitum barbatum* Pers., который может быть введен в культуру.

При химическом изучении растений *Aconitum karakolicum* Rapaics. (борец каракольский), *Aconitum altaicum* Steinb. и *Aconitum kirinense* Nakai. (борец киринский) выделены алкалоиды аконитин, мезаконитин, напеллин, аконифин, 8-ацетилэксельзин. Из *Aconitum karakolicum* Rapaics. и *Aconitum altaicum* Steinb. впервые выделен альтаконитин, а также новый алкалоид акофин **5**. Виды *Aconitum soongaricum* Stapf. и *Aconitum karakolicum* Rapaics. морфологически очень близки между собой [15-20].

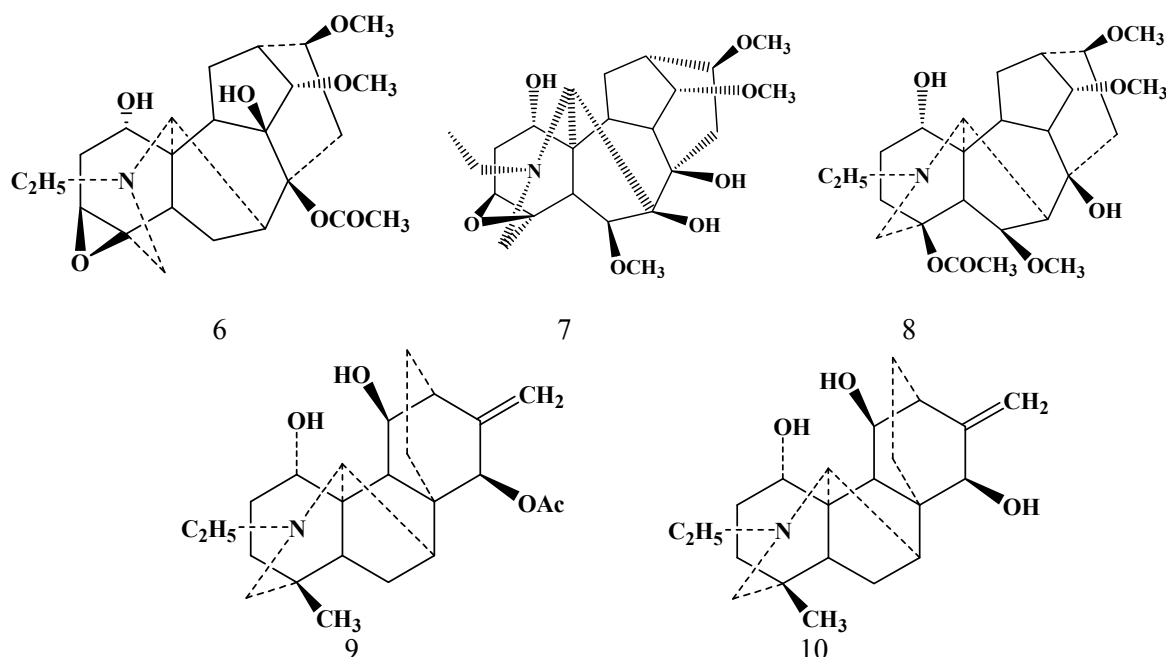


Из *Aconitum talassicum* M. Pop. (борец таласский) исследователями выделены алкалоиды талассамин, талатизамин, 14-*O*-ацетилталатизамин, изоталатизидин, изоболдин, талатизидин, гидрохлорид кристаллина. Экстракцию *Aconitum talassicum* M. Pop. проводили хлороформом, предварительно подщелачивая сырье Na_2CO_3 , после чего подкисляли экстракт с помощью серной кислоты и отделяли алкалоиды хлороформом. Сумму алкалоидов элюировали смесью хлороформ-метанол (100:1) на колонке с силикагелем, при последующей перекристаллизации метанолом [21-23].

Исследователи Института органической химии УрО РАН (г. Уфа) из *Aconitum neosachalinense* H.Lev. (борец новосахалинский) выделили 6 ранее известных алкалоидов гипаконитин,

мезаконитин, неолин и три апорфиновых алкалоида глауцин, N-метиллауротетанин и изоболдин. Экстракцию проводили водой в присутствии ацетона с последующим разделением на колонке [24].

Российскими учеными [25] разработан способ выделения дитерпеновых алкалоидов из *Aconitum kirinense* Nakai. (борец киринский), произрастающего на территории Приморского края. Алкалоиды разделяют с помощью методов газовой и высокоэффективной жидкостной хроматографии (ГХ и ВЭЖХ) с масс-спектрометрическим детектированием разделенных пиков и фрагментацией в режимах химической ионизации при атмосферном давлении (ХИАД), ионизации при атмосферном давлении - электрораспылением (ИАД-Э), электронного удара. Методом газовой хроматографии – масс спектрометрии (ГХ-МС) с фрагментацией в режиме ХИАД и ИАД-Э в *Aconitum kirinense* Nakai. идентифицировано 6 дитерпеновых алкалоидов: 8-ацетилэксельзин 6, тугиаконитин 7, акирамин 8, киринин 9, лепенин 10.



При исследовании каллусообразования *Aconitum barbatum* Pers. (борец бородастый) подобраны оптимальные условия для получения культуры клеток данного растения, определена жизнеспособность каллусной культуры, получена сумма алкалоидов из каллусной массы сырья интактного растения, выделены и очищены индивидуальные дитерпеновые алкалоиды с использованием жидкостной колоночной хроматографии. Установлено, что в культуре тканей содержатся алкалоиды зонгорин, зонгорамин, напеллин, N-окись 12-эпинапеллин и мезаконитин [26].

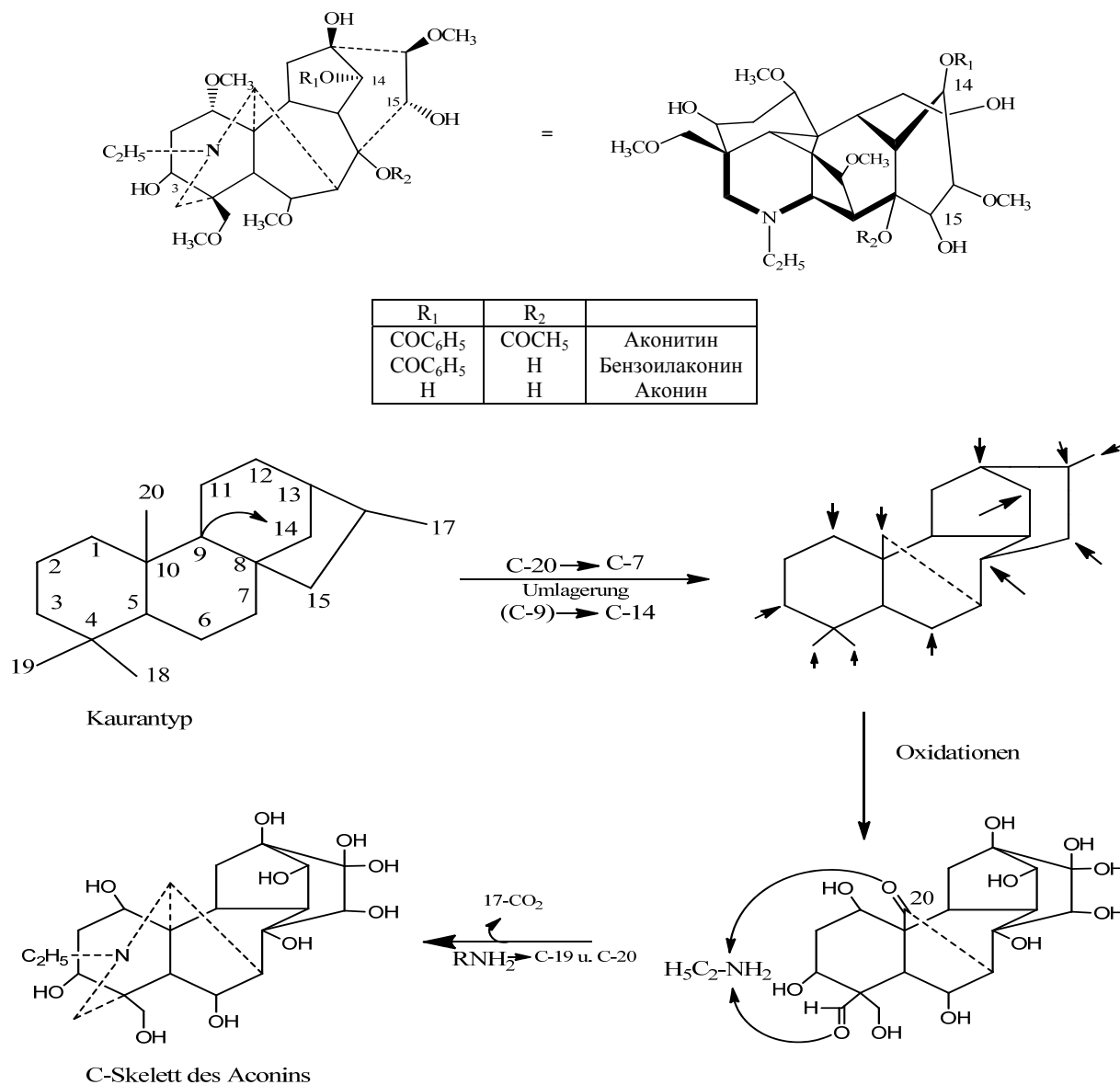
Китайскими учеными удалось впервые выделить C₁₉- дитерпеновые алкалоиды из *Aconitum habaense* W.T.Wang. (борец гавайский) габанин С, вилморрианин, классикаулин С [27].

Учеными Грузии проведено химическое изучение подземных органов *Aconitum orientale* Mill. (борец восточный) и *Aconitum nasutum* Fisch. ex Reichenb (борец носатый). Установлено, что в обоих видах *Aconitum* L. флоры Грузии присутствуют алкалоиды: аконитин, лаппаконитин, караколин. В *Aconitum orientale* Mill. присутствуют основания: ранаконитин, гигахтонин, ликоктонин, а в *Aconitum nasutum* Fisch. ex Reichenb. - талитизамин, каммаконин, аконисин [28-29].

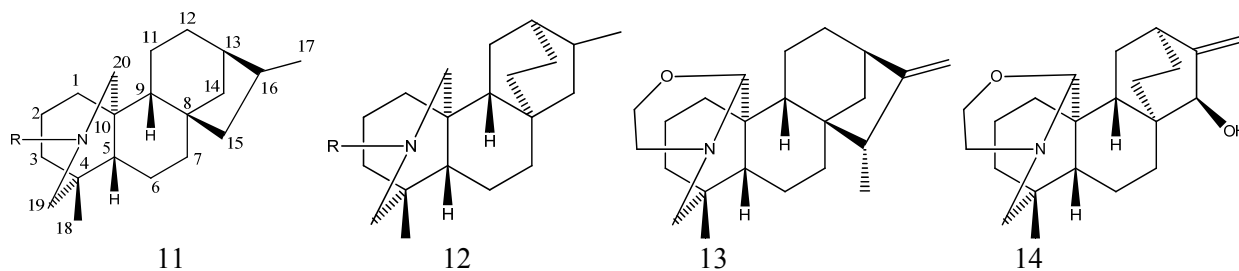
Все дитерпеновые алкалоиды аконитов отличаются высокой плотностью кислородсодержащих функциональных групп, но безусловным рекордсменом является молекула аконитина. Не исключено, что именно высочайшей насыщенностью упомянутыми группами объясняется особая токсичность аконитина.

Биосинтез, фармакологическая активность, а также, динамика накопления дитерпеновых алкалоидов некоторых видов растений рода *Aconitum* не до конца изучен. Биогенетические акониновые основания, скорее всего, являются производными тетрациклических или

пентациклических дитерпенов, в которых атом азота метиламина, этиламина или β-аминоэтанола связывается с C₁₇ и C₁₉ в C₁₉ дитерпеноидном скелете и с C₁₉ и C₂₀ в C₂₀ дитерпеноидном скелете, чтобы сформировать замещенное пиперидиновое кольцо. Вот почему соединения аконитинового типа считаются «своеобразными» алкалоидами, так как их азот не получен в результате метаболизма аминокислот. Они относятся к «псевдоалкалоидам». Совсем немного известно о том, как растения синтезируют данные алкалоиды, и почти ничего не известно о том, как этот биосинтез регулируется.

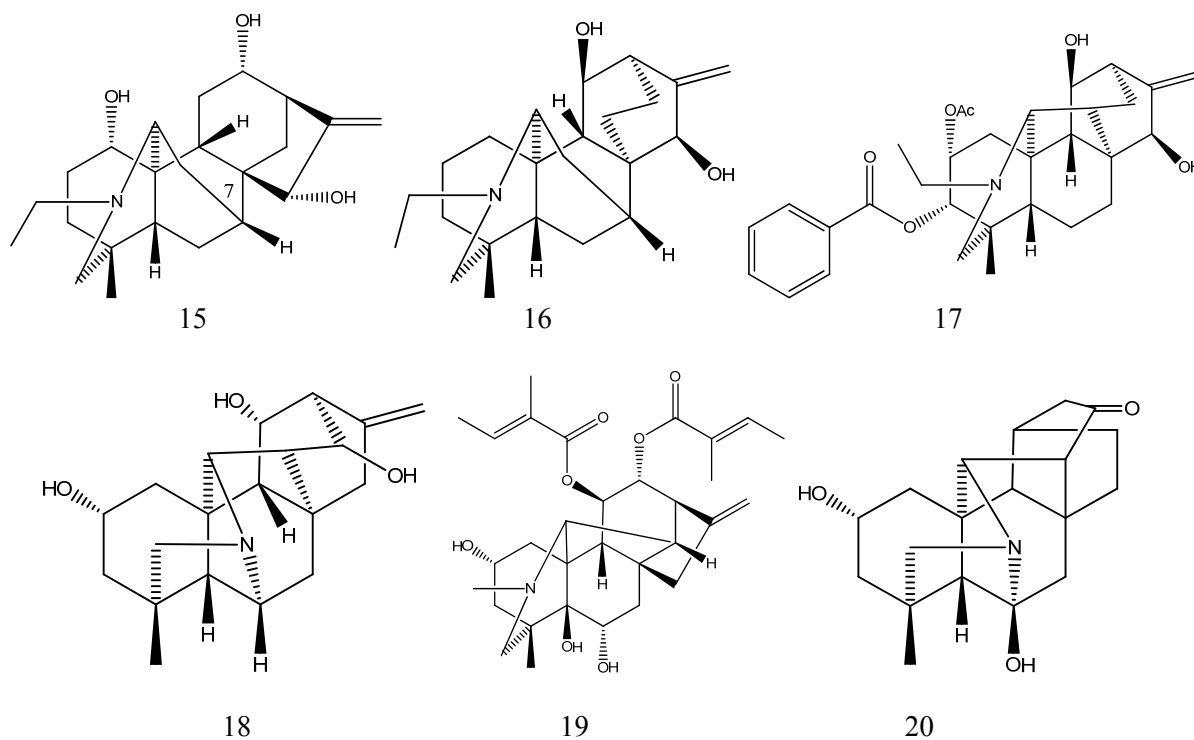


Биогенетическими предшественниками их служат дитерпеноиды рядов *энт*-каурана и атизирана. В обоих случаях в ходе биосинтеза образуется дополнительный азотсодержащий цикл таким образом, что гетероатом становится мостиком между атомами C₁₉ и C₂₀. При этом различают два структурных подтипа, C₂₀ и C₁₉, обозначаемых так по числу углеродных атомов циклического скелета. В свою очередь, C₂₀ алкалоиды бывают производными от двух углеродных каркасов **11** и **12**. У конкретных веществ эти углеродные остовы обычно обрамлены кислородсодержащими заместителями, как у веатхина **13** и атизина **14**, давших названия соответственным подгруппам C₂₀-ряда. В обеих из них часты случаи образования добавочных гетеро- или карбоциклов в дополнение к уже имеющимся в структурах **13** и **14**.

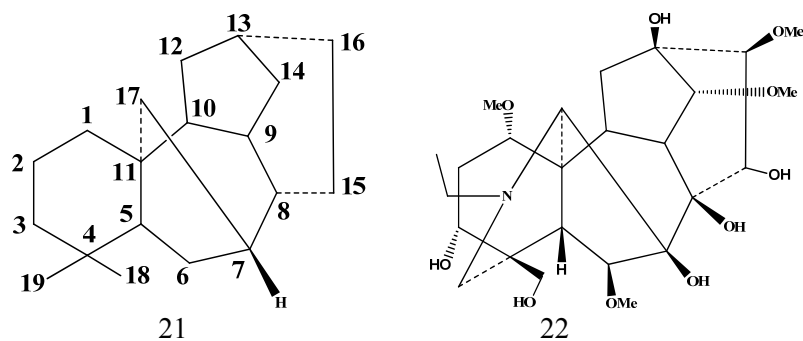


R = H, Me, Et

Дополнительные циклы могут возникать путем установления связей между атомами C20 и C7, а также атомами C20 и C14. В первом случае конструируется циклическая система, имеющаяся в алкалоидах напеллине **15** и денудатине **16**. Второй вариант реализуется в молекуле хеда-гина **17**. В структурах последнего типа возможно образование еще одного цикла путем связывания атома азота с углеродом C6, как в гетизине **18**. Все соединения с углеродно-азотным остовом относят к группе гетизина. В небольшом семействе аноптерина **19** углерод-углеродной связью соединены атомы C20 и C14 в скелете *энт*-кауранового типа. Алкалоид делнудин **20** также принадлежит к C₂₀-ряду. Его молекула возникла в результате перегруппировки гетизинового предшественника.



Основой структуры дитерпеноидных алкалоидов C₁₉-ряда служит перегруппированный углеродный скелет каурана **21**, называемый аконановым. Как и в C₂₀-соединениях, азотный мостик образуется между атомами C17 и C19. По названию алкалоида ликоктонина **22** углеродно-азотный остов, лежащий в его основе, называют ликоктонановым. Внутри семейства C₁₉-алкалоидов различают две основные подгруппы. Имея одинаковый углеродно-азотный скелет, они отличаются друг от друга характером замещения при атомах C6 и C7. К подгруппе ликоктонина принадлежат основания с гидроксильным заместителем в положении C7 и β-метоксильным - у атома C6. Для этой подгруппы веществ характерно также наличие α-гликольной группировки. Аконитин - представитель другой подгруппы C₁₉-алкалоидов, названной его именем. Здесь отсутствуют заместители при атоме C7, а метоксильная группа при атоме C6 имеет α-ориентацию.

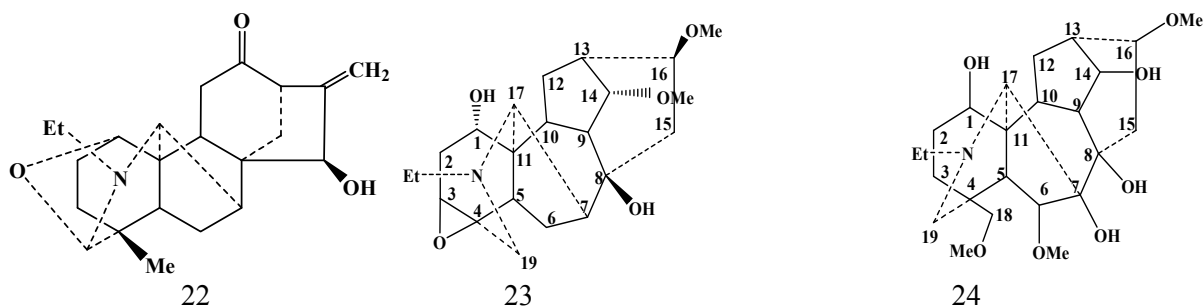


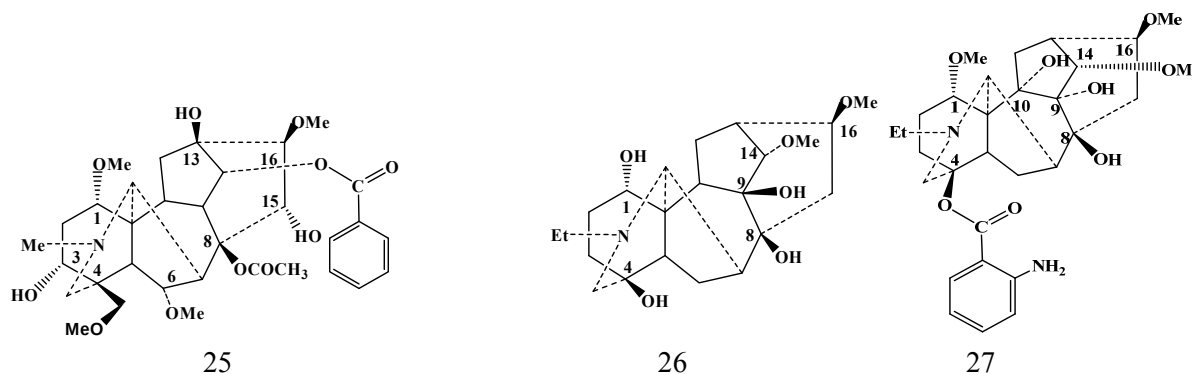
Группа C_{19} -дитерпеноидных алкалоидов достаточно многочисленна. К 1987 году было известно 175 ее природных представителей. Из них более 150 выделены из растений родов *Aconitum* L. и *Delphinium* L.

C_{19} - и C_{20} -дитерпеноидные основания в большинстве своем сильно ядовитые вещества. Так, ЛД 50 аконитина составляет всего 0,22 мг/кг. Из-за этого акониты и живокости относятся к самым ядовитым растениям умеренных широт. Для токсического действия их азотистых метаболитов характерно нарушение деятельности нервной системы и сердца. В малых дозах многие из этих веществ проявляют противовоспалительные, обезболивающие, противоаритмические, противоэпилептические свойства. При этом у разных алкалоидов имеется свой спектр физиологических эффектов. Так, например, аконитин - эффективный обезболивающий агент, а ликоктонин вовсе лишен этого действия. Практическое применение дитерпеноидных алкалоидов как лекарств ограничено из-за опасности отравлений при передозировке. Тем не менее, препарат аллапинин (гидробромид лаппаконитина) производится в России и применяется как одно из лучших противоаритмических средств.

В течение ряда лет в АО «МНПХ «Фитохимия» проводятся работы по выделению и изучению алкалоидов из видов рода *Aconitum* L. Разработана общая технология получения алкалоидов из растительного сырья, с применением классических методов экстракции и колоночной хроматографии. Методики выделения каждого алкалоида индивидуальны и имеют свои особенности, что позволяет в результате наработать алкалоиды с чистотой 95-99,9% по данным ВЭЖХ анализа [30, 31].

При химическом изучении корней *Aconitum monticola* Steinb. нами выделены и идентифицированы алкалоиды зонгорин **4** (выход 0,1%), сопутствующий ему алкалоид зонгорамин **22**, монтикамин **23**, делькозин **24**. Делькозин из аконита горного выделен впервые. Изучен химический состав *Aconitum leucostomum* Worosch. и выделены четыре соединения основного характера мезаконитин **25**, лаппаконидин **26**, сепаконитин **27**, лаппаконитин **1**. С целью установления пространственного строения молекулы лаппаконитина впервые проведен его рентгеноструктурный анализ [32-34].





Подобраны оптимальные условия для разделения и анализа алкалоидов зонгорина, лаппаконитина и сопутствующих компонентов методом ВЭЖХ, разработана методика количественного определения исследуемых соединений в растений *Aconitum soongaricum* Stapf., *Aconitum anthoroideum* DC. и *Aconitum villosum* Reichenb. произрастающих на территории Казахстана. Содержание алкалоидов в данных исследуемых растениях по данным ВЭЖХ колеблется: зонгорин от 0.01%-0,23%, лаппаконитин от 0.01%-0,04% в пересчете на воздушно-сухое сырье [35].

Фитохимический скрининг, собранных в природных условиях образцов рода *Aconitum* L. позволил установить выраженную антибактериальную активность суммарного экстракта *Aconitum anthoroideum* DC., анальгетическую активность суммарного экстракта *Aconitum leucostomum* Worosch. и *Aconitum villosum* Reichenb. и цитотоксическую активность экстрактов *Aconitum monticola* Steinb., *Aconitum anthoroideum* DC., *Aconitum leucostomum* Worosch. и *Aconitum villosum* Reichenb. Fl. Alt. Впервые обнаружена выраженная противовирусная активность лаппаконитина и суммы алкалоидов аконита горного и аконита противоядного в отношении вируса чумы плотоядных и инфекционного ринотрахеита, что делает их перспективными для разработки нового лекарственного средства [36].

Выявлено что основным компонентом *Aconitum monticola* Steinb. является – зонгорин **4**, зонгорамина **22**, *Aconitum soongaricum* Stapf. – аконитин **3**, делькозин **24**, *Aconitum leucostomum* Worosch. – лаппаконитин **1**.

В гербарном фонде АО «Международный научно-производственный холдинг «Фитохимия» имеются гербарные сборы 9 видов рода *Aconitum* из них наиболее часто встречаются *Aconitum leucostomum* Worosch. и *Aconitum monticola* Steinb., образующие большие заросли в природе.

По выявлению конкретных мест произрастания видов данного рода во флоре Казахстана, нами проведена камеральная обработка гербарных материалов видов *Aconitum* в гербарном фонде АО «МНПХ «Фитохимия» (KG).

***Aconitum monticola* Steinb.** in Fl. URSS. 7 (1937) 730, 209. – Gamajun. in Фл. Казах. 4 (1961) 52, tab. 6, fig. 1. – Vorosch. in Бюлл. Главн. бот. сада, 72 (1969) 37. – *A. pallidum* auct. non Rchb.: Kar. et Kir. in Bull. Soc. Nat. Mosc. 15 (1842) 138. – *A. lycoctonum* auct. non L.: O. et B. Fedtsch. in Тр. Об-ва ест. Казан. Унив. 33, 3 (1899) 79, quoad var. *pallidum*. – O. et B. Fedtsch. Consp. Fl. Turk. 1 (1906) 22, quoad var. *pallidum*. Тип в Ленинграде. – Борец горный.

Гербарные сборы: ВКО, хр. Коксуйский, лесная поляна. 14.VIII.2014; Алматинская обл, Жунгарский Алатау, окр. пос. Лепсинск, нижняя часть ущ. Русачка. 10. VII.2000.

***Aconitum leucostomum* Worosch.** Бюлл. Гл. бот. сада, 11 (1952) 62. – *A. excelsum* p. p. non Rchb. Фл. СССР, VII (1937) 201; Крыл. Фл. Зап. Сиб. V (1931) 1151. – *A. vulparia* C.A. Mey. ex Ldb. Fl. Alt. II (1830) 287, non Rchb. Тип в Вене. – Борец белоустый.

Гербарные сборы: Карагандинская обл., Каркаралинские горы, окрестности озера Пашенное, в пойме у ручья. 16.VI.1976 (KG); ВКО, окрестности Лениногорска, хребет Ивановский, листовничная посадка. 21.VII.1976 (KG); Карагандинская обл, Каркаралинский р-н, окрестности озера Шайтан-куль, берег у ручья. 7.VII. 1984 (KG); ВКО, окрестности Лениногорска, линейный белок полевая яма, подошва горы 23.VIII. 1985 (KG); ВКО, дорога Усть-Камень - Лениногорск, окрестности села Быструха, склоны гор. 23.VIII.1985 (KG); Семипалатинская обл, окрестности села Алексеевка, горы Тарбагатай. 10.VII.1994 (KG); Алматинская обл., Аксайское ущелье Зайлийского Алатау 2200 м, вдоль реки Аксай, 12.VII.2000 (KG); ВКО, хребет Листвяга, район Верх. Катунь разнотравные луга подножья гор, 2100 м над. ур. м. 26.VII.2004 (KG); ВКО, Западный Алтай,

хребет Ивановский, разреженный лиственнично-кедровый лес. Н=1800 м. 11. VIII.1997(KUZ); Казахстан, Восточно-Казахстанская область, Западный Алтай, хребет Ивановский. Пихтово-березовый лес. Н=1700 м. 08.VII.1997 (KUZ); ВКО, Западный Алтай, Ивановский хребет, берег временного водотока. Высокотравный альпийский луг. Н=1900 м. 11.VIII.1997 (KUZ); ВКО, Западный Алтай, Ивановский хребет, 4 км сев.-вост. вершины Вышеивановский Белок. Альпийский луг. Н=1900 м. 08.VII.1997 (KUZ); ВКО, Западный Алтай, Ивановский хребет, берег временного водотока. Высокотравный альпийский луг. Н=1900 м. 27.VII.1997 (KUZ).

***Aconitum septentrionale* Koelle.** 1786, Spicil. Observ. Acon. : 22; Фризен, 1993, Фл. Сиб. 6.: 138. – Борец северный.

Гербарные сборы: Казахстан, Павлодарская область, горы Баянаул, поляны в предгорной части. 08.VIII.2006. (KUZ).

***Aconitum anthoroideum* DC.** in Syst. nat. 1 (1818) 366. – Gamagun. in Фл. Казах. 4 (1961) 53, tab. 7, fig. 3. – Vorosch. in Бюлл. Главн. Бот. сада АН СССР. 72 (1969) 37. – A. Anthora var. anthoroideum Rgl. in Ind. Sem. Hort. Petropol. (1861) 41. – Kryl. Fl. Sib. Occid. 5 (1931) 1147. – A. anthora auct. non L.: O. et B. Fedtsch. in Тр. Об-ва ест. Казан. Унив. 33, 3 (1899) 79. – O. et B. Fedtsch. Consp. Fl. Turk. 1 (1906) 22. – Steinb. in Fl. URSS.7 (1937) 190, quoad pl. ex Dshung. et Tarb. Тип в Лондоне. – Борец противоядный.

Гербарные сборы: ВКО, окр. г. Лениногорска дорога на Богданиху. 06. VIII.1963 (KG); ВКО, Альпийские луга рядом с речкой Тополёвкой (окр. пос. Катунь) 28. VII.2004 (KG); ВКО, окр. пос. Заводинка. 01.VIII.2012 (KG); ВКО, Западный Алтай, хребет Ивановский, восточное подножие верш. Вышеивановский Белок. Морена. Н=2000 м. 26.VII.1997. VII (KUZ); ВКО, Западный Алтай, хребет Ивановский, северные отроги вершины Вышеивановский Белок, тундра. Н=2100 м. 22.VII.1997 (KUZ).

***Aconitum soongaricum* Stapf.** in Ann. Bot. Gard. (Calcutta) 10 (1905) 141. – Steinb. in FL. URSS.7 (1937) 232. – Gamagun. in Фл. Казах. 4 (1961) 54, tab. 7, fig. 6, excl. pl. e Alat. Transil. – Gamajun in Vorosch. in Бюлл. Главн. Бот. сада, 72 (1969) 39, pro max. p. (excl. plantis floribus et pedunculis appressi pubescentibus). – A. alatavicum Vorosch. in Бот. Журн. 30, 3 (1945) 137, fig 11, b; fig. 12, a. – Vorosch. in Бюлл. Главн. бот. сада, 72 (1969) 38. – A. Napellus auct. non L.: Trautv. in Bull. Soc. Nat. Mosc. 33, 1 (1860) 83 (incl. formae 1,2,3). – O. et B. Fedtsch. in Тр. Об-ва ест. Казан. Унив. 33, 3 (1899) 80, quoad pl. e Tarb. Alat. Dshung., p. p. et Tian-Schan, p.p. - O. et B. Fedtsch. Consp. Fl. Turk. 1 (1906) 23, quoad pl. e Tarb., Alat. Dshung., p.p. et Tian-Schan, p.p. et e excl. syn. – A. karakolicum auct. non Rapes.: Vorosch. in Бюлл. Главн. Бот. сада 72 (1969) 39 pro min. p. (quoad plantas floribus et pedunculus patenter pilosis). Котип в Ленинграде. – Борец джунгарский.

Гербарные сборы: Алматинская обл., Заилийский Алатау, Каскеленское ущелье, 1955 м н.у.м. N=43°00'38.8'' E= 076 °37'21,8''. 8.X.2017 (KG); Алматинская обл., Заилийский Алатау, Аксайское ущелье, вдоль реки Аксай. 1800-2000 м н.у.м. Разнотравно-кустарниковое сообщество. 12. VII.2000 (KG); Алматинская обл., Жунгарский Алатау, ущелье Угентас. 2200 м н.у.м. 26.VIII.2014 (KG); Казахстан, Алматинская область, Алакольский район, Жонгар-Алатауский ГНПП, верховья р. Сарымсақты, субальпийская зона. 45° 24,229' с.ш., 80° 49,662' в.д., A=2226. 24.VIII.2014.; Казахстан, Алматинская область, Алакольский район, Жонгар-Алатауский ГНПП, верховья р. Сарымсақты, моренные озера, альпийский луг. 45° 21,175' с.ш., 80° 48,442' в.д., A=2600. 25.VIII.2014.

***Aconitum villosum* Reichenb.** Fl. Alt. II, 282; Ldb. Fl. Ross. I, 68. – A. ciliare β. polytrichum DC. Syst. I (1818) 378. – A. flaccidum Rchb. Uebers. (1819) 39 nom nud. – Фл. СССР, VII (1937) 213. - A. volubile var. villosum Rgl. Ind. Sem. Horti Bot. Petropol (1861) 43; Крыл. Фл. Зап. Сиб. V (1931) 1150. Тип в Вене. – Борец мохнатый.

Гербарные сборы: ВКО, хр. Листвяга, 15 км ниже села Кеги, кустарниково – разнотравная опушка леса. 02.08.2004.

***Aconitum altaicum* Steinb.** Фл. СССР, VII (1937) 731, 222. - A. napellus var. alpinum Rgl. Ind. Sem. Hort. Bot. Petropol. (1861) 45 p. p.; Крыл. Фл. Зап. Сиб. V (1931) 1149. Тип в Ленинграде. - Борец алтайский.

Гербарные сборы: ВКО, хр. Нарымский, окр.с. Новоберезовка, дол. реки Теректы. 1120 м н.у.м. 26.VIII.1976 (KG); ВКО, окр. г. Лениногорска. 09.IX.1982 (KG).

***Aconitum volubile* Pall. ex Koelle,** Spicil. Acon. (1788) 21; Фл. СССР, VII (1937) 213; Крыл. Фл. Зап. Сиб. V (1931) 1150. Тип в Лондоне. – A. tortuosum Willd. Enum. Hort. Berol. (1809) 576. – Борец выющийся.

Гербарные сборы: ВКО, отделение совхоза Улановский, урочище Кэтре.

27.VIII.1985(KG); ВКО, г. Риддер. окрестности поселка Кедровка. 05.VIII.2012 (KG); ВКО, Западный Алтай, северное подножье хребта Ивановский, урочище Серый Луг, пойма р. Белая Уба. Н=1200 м. 14.VIII.1997 (KUZ).

Aconitum barbatum Pers. Syn. Pl.II (1807) 83; Фл. СССР, VII (1937) 204; Крыл. Фл. Зап. Сиб. V (1931) 1153 – *A. sibiricum* Poir. Encycl. meth. Suppl. I (1810) 113 – *A. hispidum* DC. Syst. Nat. I (1818) 367. – *A. Gmelini* Rchb. Uebers. Gatt. *Aconitum* (1819) 63. – *A. ochranthum* C. A. M. in Ldb. Fl. Alt. II (1830) 285. – *A. lycoctonum* var. *barbatum* Rgl. Bull. Soc. Nat. Mosc. XXXVI, 3 (1861) 77. Тип в Лондоне. – Борец бородатый.

Гербарные сборы: Семипалатинская обл., окрестности поселка Южный, южный склон сопки. 08. VII.1994 (KG).

Таким образом, по итогам камеральной обработки гербарных материалов в гербарном фонде АО «МНПХ «Фитохимия» (KG), установлено, что большинство гербарных материалов собраны в горных флористических районах флоры Казахстана, что свидетельствует о необходимости изучения образцов рода *Aconitum* из указанных флористических районов. В гербарном фонде имеются гербарные материалы 9 видов рода *Aconitum*, из них наиболее часто встречаются виды рода *Aconitum leucostomum* Worosch. и *Aconitum monticola* Steinb., образующие большие заросли в природе.

Проведенный аналитический обзор послужит основой для фитохимического изучения растений рода *Aconitum*. В ходе исследований планируется выделение алкалоидов из некоторых растений рода *Aconitum* и химическая трансформация растительных алкалоидов с целью получения новых веществ, характеризующихся улучшенными физико-химическими свойствами, более выраженной биологической активностью, пониженной токсичностью, пролонгированностью действия по сравнению с исходными природными аналогами. Перспективным источником для получения биологически активных алкалоидов, в том числе аконитина, является *Aconitum soongaricum* Stapf., *Aconitum monticola* Steinb. и *Aconitum leucostomum* Worosch., произрастающие на территории Казахстана.

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П.Ж. Жанымханова, Е.М. Ғабдуллин, А.Ж. Тұрмұхамбетов, С.М. Әдекенов

«Фитохимия» халықаралық ғылыми-өндірістік холдингі» АҚ, Қарағанды қ., 100009, М. Ғазалиев көш., 4,
тел./факс: 8(7212)433127, e-mail: phyto_pio@mail.ru

ACONITUM L. ТУЫСТАС ӨСІМДІКТЕРДІҢ АЛКАЛОИДТЫ ТҮРЛЕРІ

Аннотация. *Aconitum* L. туыстас өсімдіктердің алкалоидты түрлеріне талдамалы шолу жүргізілді. Алынған деректер *Aconitum* L. туыстас өсімдіктердің бірқатар түрлерін ғылыми зерттеу, сондай-ақ жаңа дәрілік зат жасауға арналған алкалоидтарды, соның ішінде тазалығы жоғары аконитинді бөліп алу үшін негіз болады.

Аталған өсімдік түрлерінің Қазақстан флорасындағы нақты өсу орындарын анықтау бойынша кеппешөп материалдарының басым бөлігі Қазақстан флорасының таулы флоралық аудандарында жиналғаны белгілі болды. Бұл аталған флоралық аудандардағы *Aconitum* L. туыстас өсімдіктердің үлгілерін зерттеу қажеттілігін көрсетеді. «Фитохимия» халықаралық ғылыми-өндірістік холдингі» АҚ-да (KG) *Aconitum* L. туыстас 9 өсімдік түрінің кеппешөп материалдары бар, олардың ішінде табиғатта үлкен тоғайларды құрайтын *Aconitum leucostomum* Worosch. және *Aconitum monticola* Steinb. өсімдік түрлері неғұрлым жиі кездеседі.

Түйін сөздер: *Aconitum* L., алкалоидтар, химиялық зерттеу, кеппешөп материалдары, камералық өңдеу.

МАЗМҰНЫ

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