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SYNTHESIS AND CHARACTERIZATION OF CARBOXYMETHYLATED CORNSTARCH

Abstract. The aim of this study is preparation and characterization of carboxymethylated cornstarch (CMCS) for potential application as water based drilling fluids. The cornstarch was modified by sodium monochloroacetate. The structure of cornstarch and CMCS was established by H^1 NMR and FTIR spectroscopy. The degree of carboxymethylation of cornstarch determined by H^1 NMR spectroscopy was equal to 80%. The viscosity-average molecular weights (M_η) of pristine cornstarch and CMCS calculated from Mark-Kuhn-Houwink equation $[\eta]=K_\eta \cdot M^a$ are equal to $2.15 \cdot 10^3$ g·mol^{-1} and $2.75 \cdot 10^5$ g·mol^{-1} respectively. The temperature dependent viscosity of CMCS was measured in water by Ubbelohde viscometer, while the rheological properties of CMCS in dependence of polymer concentration and ionic strength of the solution were evaluated by rheoviscometer. The thermal characteristics of samples were determined by differential scanning calorimeter (DSC) and thermogravimetric (TGA) and differential thermal analyzer (DTA). The morphological properties of cornstarch and CMCS were studied by scanning electron microscopy (SEM). The structural-mechanical, filtration and filter cake forming properties of drilling fluids and fluid loss indicators of CMCS were found.

Keywords: cornstarch, modification, carboxymethylated cornstarch, degree of substitution, viscosity-average molecular weight, viscosity, rheology, drilling fluids.

Introduction

The interest in natural polysaccharides has increased considerably in recent years, as they are candidates for many commercial applications in different industrial sectors like food, textile, paper, petroleum, and pharmaceuticals [1]. Products made from starch have attracted the interest of researchers and companies due to the abundance of starch in nature, its low cost and biodegradability [2-5]. The carboxymethylation of starch in alkaline solution with sodium monochloroacetate was first carried out in 1924 [6]. Currently many papers concerning the carboxymethylation of starch were published with the aim to optimize the reaction conditions, to increase the yield of product and to increase the degree of substitution (DS) [7]. Starch is unique raw material resources due to high biocompatibility and annual renewability (potatoes (5%), corn (82%), wheat (8|%), etc.) that distinguish it from cellulose derived from wood, which period of maturing is 18-20 years for fast-growing wood [2, 8-9]. Starch is a carbohydrate consisting of linear and helical amylose molecules and branched amylopectin molecules with general chemical formula $(C_6H_{10}O_5)_n$ [10-12].

Starch was the first polymer reagent used for the drilling muds in 1939 [13]. However, with the introduction of polymer reagents based on cellulose ethers widespread use of starch started to reduce. This was primarily due to the need to use bactericides and low thermostable starch reagents [2].

Currently, the natural starch is not used in drilling fluids. Instead of it, the following types of modified starch such as carboxymethyl, hydroxyethyl, as well as oxidized starch are applied to regulate the filtration and rheological characteristics of drilling muds. The chemical modification of cornstarch is performed to overcome the insolubility in water, hardly controlled viscosity after gelatinization, the turbidity of aqueous solutions [14]. Carboxymethylated starch (CMS) is the most commonly used material among the modified starch reagents. It is a starch derivative in which the –OH groups is partially substituted by ether group (-O-CH_2COOH) [15]. It is characterized by good resistance to high content of salt, high durability to thermal and bacteriological affect [16]. The CMS has a wide applicability due to water-solubility, high viscosity and stability as a fluid loss reducing agent in drilling fluid [10, 17]. The application of CMS in enhanced oil recovery is also growing [18].

The main objective of this work is to synthesize and characterize CMCS with potential application as additives in water-based drilling fluids. These materials were also evaluated regarding their thermal resistance and rheological behavior in the presence of various salts. Starch is a perspective material from practical point of view because it is non-toxic, contains easily modifiable functional groups and is ecologically friendly [19].

Experimental part

Materials

Cornstarch was purchased from LLP "Zharkent Starch-Factory". Sodium monochloroacetate (Na-MCA) $ClCH_2COONa$ was obtained from Merck-Schuchardt (Hohenbrunn, Germany). The chemical reagents used in this investigation (NaOH, CH_3CH_2OH, NaCl, KCl, $MgCl_2$, $CaCl_2$, HCl, LiBr, d_6-DMSO, and d_1-TFA were purchased from Sigma Aldrich (Finland) and used as received.

Synthesis of carboxymethylated cornstarch (CMCS)

Modification of cornstarchwas carried out in two steps [19]. Firstly, alkalization was performed by mixing of 0.4 g cornstarch, 1.2 mL ethanol and 0.28 mL aqueous 11.5 M NaOH solution at 25ºC, the mixture was stirred for 20 min. In the second step, 0.28 g Na-MCA was added and the reaction mixture was heated to 58ºC and stirred during 100 min. The precipitated in ethanol CMCS was filtered and dried under vacuum at 50ºC.

Methods

^{1}H NMR of cornstarch and CMCS were recorded on a Bruker Avance III 500 spectrometer at 70ºC according to procedure [20]. The viscosity-average molecular weights of the cornstarch and CMCS were determined by Mark-Kuhn-Houwink equation, $[\eta]=K_\eta \cdot M^a$, where M_η is the viscosity-average molecular weight and the parameters K_η and *a* are related to local stiffness of the polymer and depend on the nature of polymer, solvent and temperature. The Fourier Transform Infrared (FTIR) spectra of the starch samples were registered by FTIR spectrometer Carry 660 (Agilent, USA).The viscosity of cornstarch and CMCS solutions was measured by Ubbelohde viscometer at 25±0.1 °C. The rheological behavior of CMCS solutions was monitored with the help of Rheolab QC, Anton Paar (Austria). The thermal characteristics of samples were determined with the help of DSC 131 EVO Setaram and TGA «Labsys EVO» Setaram (France). The samples were heated from 25 to 500 ºC at heating rate 10ºC/min. The size and ζ-potential of CMSC was determined with the help of Dynamic Light Scattering (DLS) device Malvern Zetasizer Nano ZS90 (UK). Scanning electron micrographs were obtained with the help of SEM (Jeol JSM-6490LA, Japan). Static shear stress (SSS) measurements after 1 min and 10 min (SSS_1 and SSS_{10}) were performed by means of the instrument SNS-2 (Russian Federation). Water yield of the drilling muds (W) was determined by VM-6 instrument (Russian Federation). The thickness of the filter cake (δ) was measured by the instrument WIKA IV-2 (Russian Federation).

Results and Discussion.

Modification of cornstarch

The carboxymethylation of cornstarch proceeds by two steps:

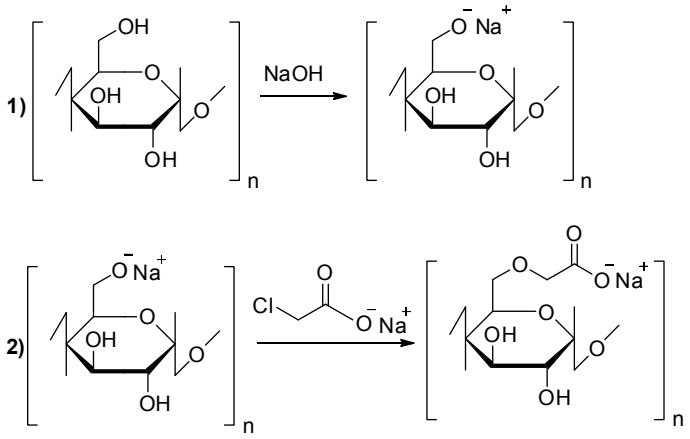


Figure 1 -Modification of corn starch with sodium monochloroacetate

In the first step (1) the OH groups are transformed to O^-Na^+, then on the second step (2) the Na^+ ions are eliminated by chlorine of sodium monochloroacetate by the following reaction:

— O^-Na^+ + Cl-CH_2COONa → —O-CH_2COONa + NaCl

As a result a fully water-soluble carboxymethylated cornstarch (CMCS) with DS = 80% was obtsined.

Identification of the CMCS structure by H^1 NMR and FTIR spectroscopy

^{1}H NMR spectrum of CMCS registered at 70 ºC is shown in Figure 2.

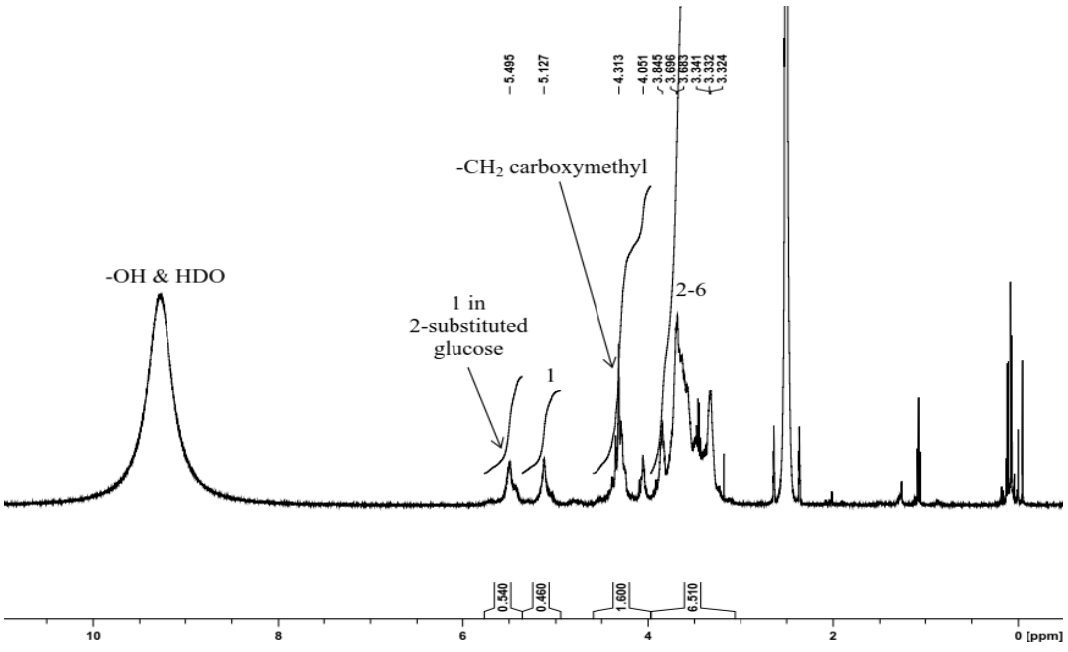


Figure 2 - ^{1}H NMR spectrum of CMCS in d_6-DMSO

The substitution degree of CMCS determined from the methylene signal of the carboxymethyl substituent (4.31 ppm) and the anomeric protons of glucose (5.13 and 5.50 ppm) was equal to 80%.

FTIR spectra of pristine and modified cornstarch are compared in Figure 3.

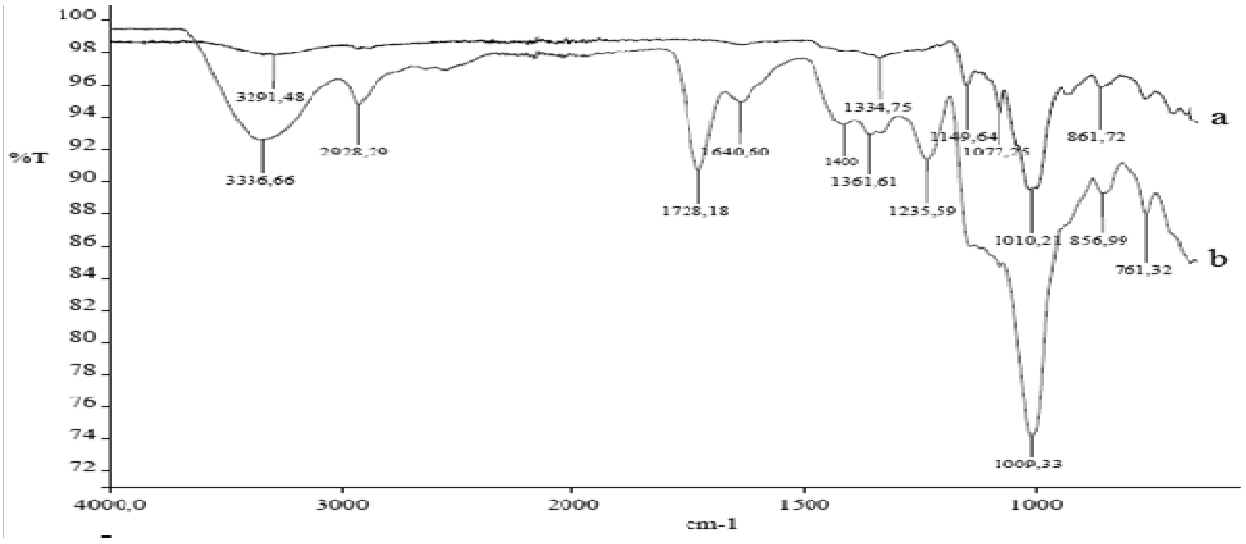


Figure 3 - FTIR spectra of cornstarch (a) and CMCS (b)

The broad bands between 3336 and 3291 cm^{-1} is assigned to OH stretching vibrations due to hydrogen bonding between the hydroxyl groups. The band around of 2928 cm^{-1} belongs to CH_2 symmetrical stretching vibrations. A new peak at 1728 cm^{-1} is specific for ester groups, the bands at 1640 and 1400 $cm^{-1}$are related to asymmetric and symmetric vibrations of carboxylate ions (COO^-). At 1200-1360 cm^{-1} the vibrations of CH_2, CH, and C-OH groups are observed. An absorption band at 1009 cm^{-1} corresponds to stretching vibrations of ether groups -OCH-O-CH_2. Low intensive bands in the range of 860-760 cm^{-1} correspond to out-of-plane vibrations of OH-group of glucopyranose ring. Thus, both H^1 NMR and FTIR spectra of CMCS reveal that the modification by Na-MCA takes place to obtain the water-soluble derivatives of cornstarch.

Viscosity-average molecular weight (M_η) of CMCS

The viscosity-average molecular weight (M_η) of the CMCS was calculated by the Mark-Kuhn-Houwink relationship $[\eta]=K_\eta \cdot M^a$ taking into account that $K_\eta=2.0\cdot10^{-4}$ and a=0.75 for a standard starch in 0.1 M aqueous NaCl at 25°C [2].

The viscosity-average molecular weights (M_η) of cornstarch and CMCS were found to be $2.15\cdot10^3$ $g\cdot mol^{-1}$ and $2.75\cdot10^5$ $g\cdot mol^{-1}$ respectively. A significant increase in the M_η of the cornstarch after carboxymethylation is due to the presence of bulkier carboxymethyl groups in modified cornstarch.

Viscosity measurements

The influence of temperature on solution behavior of CMCS is shown in Figure 4.

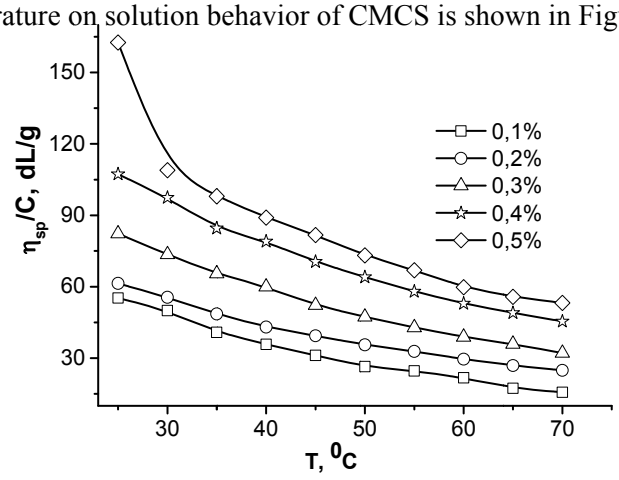
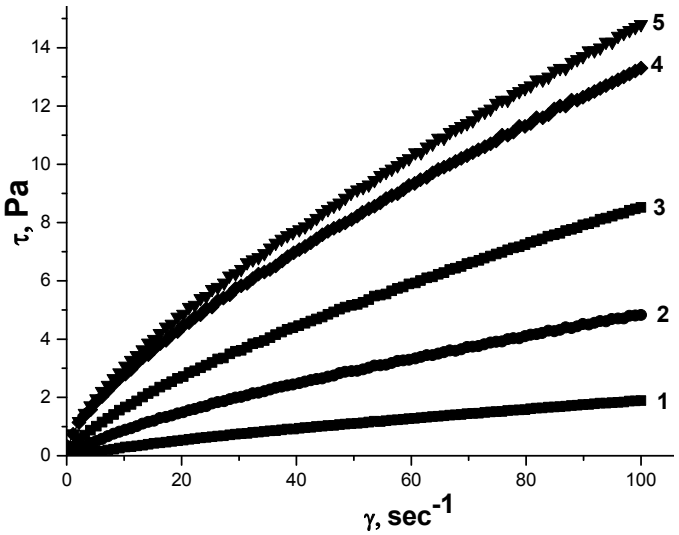


Figure 4 – Temperature dependent reduced viscosity of aqueous solutions of CMCS

The reduced viscosity of aqueous solutions of CMCS gradually decreases with increasing of the temperature. This may be connected with a gradual disaggregation of macromolecular associates due to destruction of hydrogen bonds.

Rheological characteristics of CMCS solutions

Rheological properties are considered as important parameters to evaluate the applicability of the CMCS as drilling fluids. The CMCS solutions represent the pseudo plastic liquids and are suitable for the formulation of drilling fluids.



(1) 0.25, (2) 0.5, (3) 1, (4) 2, (5) 1.5 wt.%

Figure 5 – Concentration dependent shear stress-shear rate curves of aqueous solutions of CMCS

As the polymer concentration increases the solution viscosity increases as well. However, increasing of the polymer concentration higher than 1.5 wt.% is not efficient. Therefore it is expected that the optimal concentration of CMCS for shear rate is 1.5 wt.%.

Dependences of shear stress on shear rate for CMCS solutions in the presence of NaCl, KCl, $MgCl_2$ and $CaCl_2$ are shown in Figure 6.

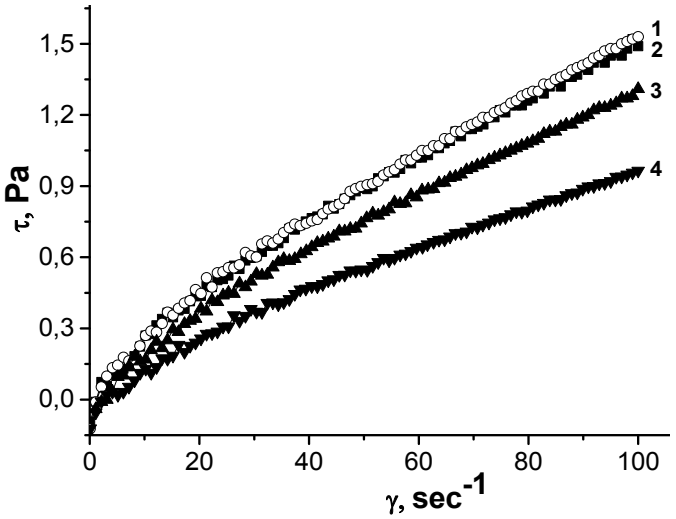


Figure 6 - The shear stress-shear rate curves of 0.5% wt.% CMCS solutions at the ionic strength of μ=0.01 adjusted by NaCl (1), KCl (2), $MgCl_2$ (3) and $CaCl_2$ (4)

Aqueous solutions of CMCS behave polyelectrolyte character that is suppressed upon addition of low-molecular-weight salts. The viscosity resistant behavior of CMCS in saline water provides the stability of drilling muds in a wide range of salt concentrations.

Thermal characteristics of cornstarch and CMCS

Thermal properties of cornstarch and CMCS derived from DSC are shown in Figure 7. The appearance of exothermic peaks at 80.2 and 83.3 ºC is probably due to removal of residual moisture. The broad endothermic peaks at the interval of temperature 285.85-392.77 and 251.3-326.87 ºC probably reflect the crystallization of cornstarch and CMCS, respectively.

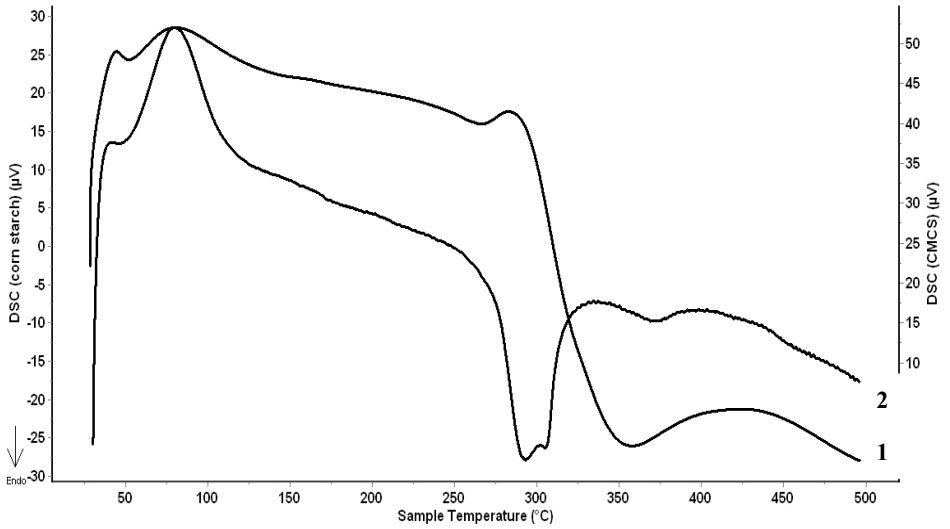


Figure 7 - DSC curves of cornstarch (1) and CMCS (2)

Mass loss percentages for cornstarch and CMCS were calculated from TGA data (Figure 8). TGA studies reveal high heat resistance for CMCS as compared to the cornstarch. CMCS loses 38.47 % of the mass, while cornstarch – 45.83

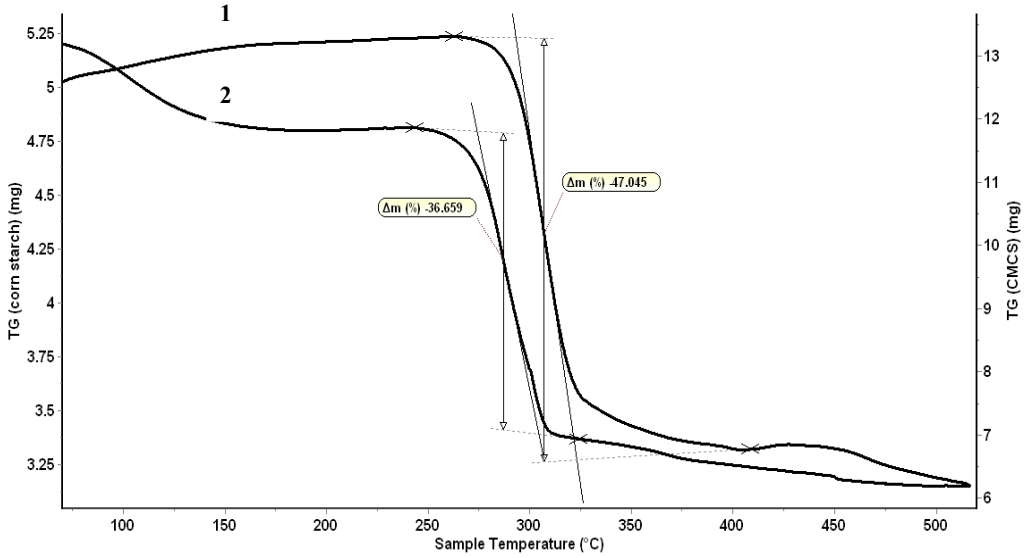


Figure 8 - TGA curves of cornstarch (1) and CMCS (2)

DLS measurements

Table 2 shows the average sizes and ζ-potentials of CMCS. The size distribution of CMCS is varied from 235 nm to 1034 nm. The negative values of the ζ-potentials of CMCS in water confirm the substitution of hydroxyl groups of cornstarch by carboxymethyl moieties.

Table 1 – The average sizes and ζ-potentials of CMCS in water

C, wt.%	Size, nm	ζ-potential, mV
0.1	1034	-85
0.2	633	-60
0.3	235	-56
0.4	487	-50
0.5	552	-53

Morphology of cornstarch and CMCS

The SEM images of cornstarch and the CMCS are compared in Figure 9. SEM showed the carboxymethylation to change the structure of starch granules, compared with native cornstarch. Cornstarch granules are smooth, round in shape with sizes ranging from 5 to 15 μm. After carboxymethylation the granules of cornstarch are bigger in size (400-500 μm) and the granular surface becomes rough and scaly. Probably these changes are due to modification of cornstarch affected by strong alkaline environment and heat treatment.

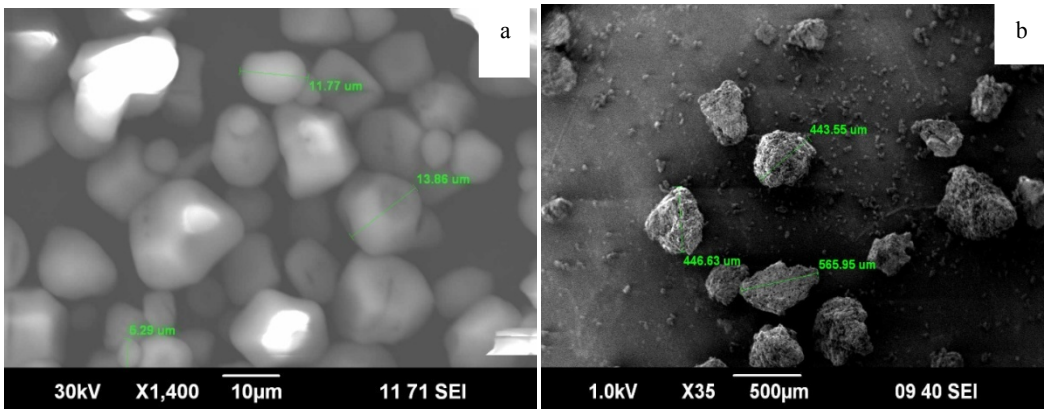


Figure 9 - SEM images of cornstarch (a) and CMCS (b)

Formulation of drilling fluids

The drilling fluids (DF) composed of gellan, xanthan, CMCS, Polyanionic cellulose (PAC), KCl and bentonite were formulated to obtain an appropriate DF with optimal solution density (ρ), relative viscosity (η_{rel}), dynamic shear stress (DSS), fluid loss indicator (W), thickness of mud cake (δ), and ratio of static shear stress (SSS_1/SSS_{10}).

Properties of drilling fluids

The structural-mechanical, filtration and filter cake forming properties of model system, consisting of 0.1% gellan, 0.2% xanthan, 0.25-0.35% CMCS at the interval of pH 9.2-10.0 are summarized in Table 2. Analysis shows that all drilling fluids based on CMCS possess good structural-mechanical and filtration characteristics. The thickness of filter cake may be increased by adding 4 wt.% of bentonite. The thixotropic characteristics of drilling fluids are improved with increasing of CMCS concentration. Moreover, the CMCS with high DS due to good water-solubility and high viscosity is more beneficial than industrial starch that is applied for formulation of drilling fluids.

Table 2 – Composition and characteristics of drilling fluids

№	Ratio DF*, %						pH	ρ, g/cm^3	η_{rel}, sec	DSS, Pa	W, cm^3	δ, mm	SSS_1/SSS_{10}, dPa
	gellan	xanthan	CMCS	PAC	KCl	bentonite							
1	0.1	0.2	1**	0.5	0	4	10	1.03	54	1.2	5	0.4	8/15
2	0.1	0.2	1**	0.5	1	4	9.8	1.04	52	1.4	5	0.4	7.5/14
3	0.1	0.2	1**	0.5	3	4	9.6	1.05	52	1.7	5	0.4	7/13
4	0.1	0.2	0.25	0.5	0	1	9.2	1.02	33.6	1.7	6	0.4	3.3/5.3
5	0.1	0.2	0.25	0.5	0	2	9.4	1.06	35.7	1.7	5.5	0.4	5/7
6	**0.1**	**0.2**	**0.25**	**0.5**	**1**	**4**	**9.6**	**1.08**	**32.8**	**1.6**	**5**	**0.5**	**9.8/11.5**
7	**0.1**	**0.2**	**0.35**	**0.5**	**2**	**4**	**9.7**	**1.08**	**35.3**	**1.5**	**5**	**0.5**	**12.3/13.9**
*The rest is water													
** Industrial CMCS													

Samples No. 6 and 7 containing gellan, xanthan, CMCS and PAC in the presence of 4% bentonite exhibit the best SSS_1/SSS_{10} characteristics that are applicable as drilling fluids [21].

Conclusion

Water-soluble CMCS were prepared by carboxymethylation of cornstarch. The introduction of carboxymethyl groups into the structure of cornstarch was detected by FTIR and H^1 NMR spectroscopy. The viscosity-average molecular weight of CMCS is much higher than unmodified cornstarch. Aqueous solutions of CMCS show a high viscosity that decreases upon increasing of temperature and salt addition. The thermal, morphological and rheological properties of CMCS have been evaluated. Water-based optimal drilling fluids composed of various polysaccharides, salt and bentonite have been formulated and suggested for application.

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КАРБОКСИМЕТИЛДЕНГЕН ЖҮГЕРІ КРАХМАЛЫН СИНТЕЗДЕУ ЖӘНЕ СИПАТТАУ

Аннотация. Бұл жұмыстың мақсаты карбоксиметилденген жүгері крахмалын (КМЖК) алу, сипаттау және бұл үлгілерді су негізіндегі бұрғылау ерітінділерінде қолдану мүмкіндігін бағалау болып табылады. Жүгері крахмалын натрий монохлорацетатымен модификациялады. Жүгері крахмалы мен КМЖК құрылысы ЯМР және ИҚ-спектроскопия көмегімен анықталды. ЯМР-спектроскопиясы көмегімен анықталған жүгері крахмалының карбоксиметилдену дәрежесі 80% тең болды. Марк—Кун—Хаувинк теңдеуімен $[\eta]=K_\eta \cdot M^a$ табылған таза жүгері крахмалы мен КМЖК ортамассалық молекулалық массасы (M_η) сәйкесінше $2.15 \cdot 10^3$ г/моль және $2.75 \cdot 10^5$ г/моль тең болды. КМЖК температураға тәуелді тұтқырлығы суда Уббелоде вискозиметрі көмегімен өлшенді, КМЖК реологиялық қасиеттері полимер концентрациясы және ерітіндінің иондық күшіне тәуелділігі реовискозиметрмен бағаланды. Үлгілердің жылу сипаттамалары дифференциалды сканирлеуші калориметрі (ДСК), термогравиметриялық (ТА) және дифференциалды термиялық анализаторы (ДТА) арқылы Eva Setaram (Франция) анықталды. Жүгері крахмалы мен КМЖК морфологиялық қасиеттері сканирлеуші электрондық микроскоп (СЭМ) арқылы зерттелді. Бұрғылау ерітінділерінің құрылымдық – механикалық, фильтрациялық және қабат түзу қасиеттері, КМЖК фильтрация көрсеткіші табылды.

Түйін сөздер: жүгері крахмалы, модификация, карбоксиметилденген жүгері крахмалы, орынбасу дәрежесі, ортамассалық молекулалық масса, тұтқырлық, реология, бұрғылау ерітінділері.

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СИНТЕЗ И ХАРАКТЕРИСТИКА КАРБОКСИМЕТИЛИРОВАННОГО КУКУРУЗНОГО КРАХМАЛА

Аннотация. Целью данной работы является подготовка и исследование карбоксиметилированного кукурузного крахмала (КМКК) для потенциального применения в качестве буровых растворов. Кукурузный крахмал модифицировали монохлорацетатом натрия. Структура кукурузного крахмала и КМКК была установлена с помощью ЯМР и ИК-спектроскопии. Степень карбоксиметилирования кукурузного крахмала, определенная с помощью ЯМР-спектроскопии, была равна 80%. Средневязкостные молекулярные массы (M_η) чистого кукурузного крахмала и КМКК, рассчитанные по уравнению Марка-Куна-Хаувинка $[\eta]=K_\eta \cdot M^a$, равны $2{,}15 \cdot 10^3$ г/моль и $2{,}75 \cdot 10^5$ г/моль соответственно. Зависимость вязкости КМКК от температуры измерялась в воде с помощью вискозиметра Уббелоде, а реологические свойства КМКК в зависимости от концентрации полимера и ионной силы раствора оценивались реовискометром. Термические характеристики образцов определялись дифференциальным сканирующим калориметром (ДСК) и термогравиметрическим (ТГА) и дифференциальным термическим анализом (ДТА). Морфологические свойства кукурузного крахмала и КМКК были изучены сканирующей электронной микроскопией (СЭМ). Определены структурно-механические, фильтрационные и коркообразующие свойства буровых растворов и показатели потери жидкости КМКК.

Ключевые слова: кукурузный крахмал, модификация, карбоксиметилированный кукурузный крахмал, степень замещения, средневязкостная молекулярная масса, вязкость, реология, буровые растворы.

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RECYCLING OF WASTES OF PETROLEUM REFINING INDUSTRY BY USING THEM IN THE MANUFACTURE OF TIRE RUBBERS

Abstract: The important scientific direction of petrochemistry is manufacture of plasticizers, softeners, vulcanizing agents, fillers on the basis of industrial wastes.This allows expand the raw-material base, use heavy stocks of refinery wastes, reduce technogenic influence on the environmentand solve the problem of manufacture of import-substituting softeners for the rubber-processing industry of Kazakhstan. The feature of Kazakhstan petroleum is high concentration of sulfur compounds, in consequence of which much sulfuric wastes are formed, which are environmentally hazardous in open storage. Optimization of a receipt for developed rubber compounds for manufacture of a filler strip for passenger car tire beads was carried out in our work by serial analysis of influence of content of each of the components separately (sulfur and oil sludge) at the fixed amount of other ingredients on the rubber properties. In order to identify optimal amount of organic share of the oil sludge in the content of rubber compounds, rubber compounds with different content of organic share of the oil sludge were gained. Plasticizers and softeners were substituted to the organic share of the oil sludge. Also polymeric and colloidal sulfur mixture of Tengiz field was used as a vulcanizing agent in the receipts of rubber compounds. The results of comprehensive tests showed replaceability of traditionally used in the rubber compounds softeners to the organic share of the oil sludge and use of Tengiz sulfur as a vulcanizing agent.

Key words:organicshareofoilsludge, oilsludge, softeners, vulcanizingagent, Tengizsulfur, vulcanizing system, rubber compound, filler strip, bead.

Introduction

The rubber industry in Kazakhstan has very limited assortment of ingredients for rubber compounds. The important scientific direction of petrochemistry is manufacture of plasticizers, softeners, vulcanizing agents, fillers on the basis of industrial wastes. This allows expand the raw-material base, use heavy stocks of refinery wastes, reduce anthropogenic stress on the environment and solve the problem of manufacture of import-substituting softeners and vulcanizing agents for the rubber-processing industry of Kazakhstan. The feature of Kazakhstan petroleum is high concentration of sulfur compounds, in consequence of which much sulfuric wastes are formed [3-6].

Vulcanization plays an important role on rubber industry by offering the rubber products containing three-dimensional net work of rubber molecules. By this mean, the significant improvement innumerous properties including tensile and tear properties, set, resilience and abrasion of rubber vulcanizates is resulted. The vulcanization could generally be divided into 3 main systems, i.e., sulfur, peroxide, and metal oxide systems. The sulfur vulcanization system is generally preferential because of its superiority in mechanical properties and ease of cure behavior adjustment [5, 6]. Typically, the sulfur used in rubber industry originates from 2 main resources, i.e., natural resource and petroleum refinery. Basically, the

sulfur from natural resource is more prefer able because of its certain chemical structure in conjunction with its high sulfur content (99 %)[7].

The generally accepted is application of organic and inorganic low-molecular compounds in the receipts of rubber compounds. By theefficacy, polymers and products of low-molecular compounds are divided into softeners and plasticizers. The softeners are low-molecular compounds, which reduce yield temperature and not influence on vitrification temperature of rubber substances. The plasticizers are low-molecular compounds, which reduce vitrification temperature and yield temperature of the rubber substances.The important requirement to the plasticizers and softeners is their low cost. The great significance is also given to the availability of initial raw material used for their manufacture. Different other requirements to the plasticizers and softeners (absence of leachability by water, oils, etc.) are set by specific conditions, in which a manufactured product, containing the plasticizer and softener, will operate.

Experimental part. Sulfur is used in the rubber compounds as the vulcanizing agent, therefore in our work we offer to use refined Tengiz sulfur, gained from the wastes of oil production and refinery wastes, in the vulcanizing system.

Earlier we carried out experiments of the organic share of the oil sludge, gained from the oil sludge of "PetroKazakhstanOilProducts" LLP in the receipts of the rubber compounds on the basis of rubber substances of general assignment as the softeners, with substantiation of traditionally used softeners – oil PN-6SH and softener ASMG. The results of measurement of processing properties established -that the organic share of the oil sludge causes the plasticizing effect [8-11].

Optimization of the rubber compounds receipts. Optimization of the developed rubber compounds for manufacture of a filler strip for passenger car tire beads wascarried out by serial analysis of influence of content of each of the components separately (sulfur and oil sludge) at the fixed amount of other ingredients on the rubber properties.

In order to identify optimal amount of the organic share of the oil sludge in the content of rubber compounds, the rubber compounds with different content of the organic share of the oil sludge were gained. The plasticizers and softeners were substituted to the organic share of the oil sludge. Also polymeric and colloidal sulfur mixture of Tengiz field was used as the vulcanizing agent in the receipts of the rubber compounds.The rubber compounds' receipts used at the manufacture of the chafer strip are given in Table 1.

Fine mineral fraction of the oil sludge (1-5 mcm) was used in the receipt of the rubber compound for rubberizing of thefiller strip for passenger car tire beads.

Table 1 – Receipt of the optimal rubber compound for the rubberizing of thefiller strip for passenger car tire beads

Ingredients	Per 100 mass shares of the rubber substance					
	Control variant	Studied variant				
1	2	3	4	5	6	7
SKI-3	40,0	40,0	40,0	40,0	40,0	40,0
Butyl	60,0	60,0	60,0	60,0	60,0	60,0
Technical sulfur	2,4	-	-	-	-	-
Tengizsulfur	-	1,2	1,6	2,0	2,2	2,4
Sulfonamide "Ts"	1,2	1,2	1,2	1,2	1,2	1,2
Santogard PVI	0,4	0,4	0,4	0,4	0,4	0,4
Zinc oxide	5,0	5,0	5,0	5,0	5,0	5,0
Stearinic commercial acid	2,0	2,0	2,0	2,0	2,0	2,0
Softener ASMG	4,0	4,0	4,0	4,0	4,0	4,0
Organic share of the oil sludge	-	4,0	5,0	6,0	6,5	7,0
Oil PN-6SH	4,0	-	-	-	-	-
Acetone anil R	2,0	2,0	2,0	2,0	2,0	2,0
Diaphene FP	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 share of the oil sludge	-	10,0	15,0	20,0	25,0	30,0

Methods. Vulcanizing features of the rubber compounds, gained on "Monsanto" rheometer, proved the fact that different dosages of the organic share of the oil sludge and sulfur have direct influence on the rubber compounds' vulcanizing kinetics. Addition of the organic share of the oil sludge into the rubber compounds results in reduction of minimal viscosity and stiffness of the elastomeric matrix system. This reduction is directly proportional to the percentage composition of the organic share of the oil sludge.Application of Tengizsulfur allows preserve duration of the plateau effect, hence preventing over-vulcanization of the filler striprubber.

Results and their discussion. Optimal ratio of the components, resulting in reduction of the minimal viscosity and increase in the beginning of vulcanizing, characterizing the best processing properties of the rubber compounds, is observed at 7 and 8 mass shares of the organic share of the oil sludge for the rubber compounds, meant for the filler strip. Analysis of the rubber compounds' vulcanometric curves shows that the optimal time for attaining the vulcanizing of the rubber compound for the rubber compound of the filler strip consists 23 minutes.

Physical-mechanical tests of the experimental rubbers have led to the conclusion about the highest appropriateness of using the organic share of the oil sludge in the receipts of the rubber compounds for the filler strip of the boardside panels, as when substituting traditionally used softeners to the organic share of the oil sludge, the rubber properties meet the rates of inspection. The best results are observed at the dosage of 8-10 mass shares of the organic share of the oil sludge for the rubber compounds, meant for the filler strip. Dependencies of the main physical-mechanical indicators of thevulcanized rubbers of the filler strip on the dosage of the organic share of the oil sludge and Tengizsulfurare given in Table 2.

Table 2 – Properties of the vulcanizates on the basis of rubber substances of general assignment for the filler strip with additives of the organic share of the oil sludge and Tengiz sulfur

Indicators	Inspection rates	1-v	2-v	3-v	4-v	5-v
Nominal tensile strength, kgf/cm^2, at least	92	107	104	109	111	111
Relative tensile elongation, %, at least	270	270	300	310	310	295
Shorehardness, c.u.	70	75	77	77	78	75

Conclusions

Insignificant reduction in the tensile indicators and increase in the elastic properties of the rubbers when increasing the organic share of the oil sludge dosage can be explained by plasticization effect mechanism of the organic share of the oil sludge low-molecular compounds, which permeate between macromoleculesby the same token reducing the rubber substance macromolecules' intermolecular interaction. Insignificantreductioninthestrengthpropertiesofthesidepanelrubbersis not fundamental, as the main strength for the board side panel structure is given by bead rings from a brass plated wire. Application of Tengiz sulfur allowed preserve the vulcanizing kinetics, which could be reduced when using the organic share of the oil sludge.AlsoapplicationofTengiz sulfur allowed increase hardness of the rubbers which is necessary to increase stiffness of the tire bead.

Thus, the results of the comprehensive tests showed the possibility of substitution of traditionally used in the rubber compounds softeners to the organic share of the oil sludge and use of Tengiz sulfur as the vulcanizing agent. The fillers in the receipts of the rubber compounds for formation of the filler strip can be partially substituted to the mineral share of the oil sludge.

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МҰНАЙ ӨНДІРУ МЕН МҰНАЙ ӨҢДЕУ 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 45-50^{0}С дейін) мен басқа да факторлардың әсерінен, адам денсаулығы мен қоршаған ортаға зиянды әсерін тигізетін күкірттің көп қоспалары түзіледі. Жұмыста күкіртті резина қоспасын вулкандаушы аген 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 вулкандау 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 вулкандаушы агент ретінде қолданылатын тенгиз күкірті 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, резеңке, резеңке қоспалар, вулканизаттар, вулканизациялау агенті, вулкандау жүйесі, протекторлық резеңке қоспалар, брекерлық резеңке қоспалар.

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УТИЛИЗАЦИЯ ОТХОДОВ НЕФТЕПЕРЕРАБАТЫВАЮЩЕЙ ПРОМЫШЛЕННОСТИ ПУТЕМ ИСПОЛЬЗОВАНИЯ ИХ В ПРОИЗВОДСТВЕ ШИННЫХ РЕЗИН.

Аннотация. Важным научным направлением нефтехимии является производство пластификаторов, мягчителей, вулканизующих агентов, наполнителей на основе техногенных отходов. Это позволяет расширить сырьевую базу, использовать большие запасы отходов нефтепереработки, уменьшить техногенное воздействие на окружающую среду и решить проблему производства импортозамещающих мягчителей для резиновой промышленности Казахстана. Особенностью казахстанскихнефтей является повышенной содержание соединений серы, вследствие чего образуется много серных отходов, являющимися экологически опасными при открытом хранении. В нашей работе путем последовательного изучения влияния на свойства резин содержания каждого из компонентов в отдельности (серы и нефтешлама) при фиксированных количествах других ингредиентов была проведена оптимизация рецептур разработанных резиновых смесей для изготовления наполнительного шнура борталегковых шин. С целью выявления оптимального количества органической части нефтешлама(ОЧН) в составе резиновых смесей были получены резиновые смеси с различным содержанием ОЧН. Пластификаторы и мягчители были заменены на ОЧН. Также в рецептурах резиновых смесей в качестве вулканизующего агента была использована смесь

полимерной и коллоидной серы тенгизского месторождения. Результаты расширенных испытаний показали возможность замены традиционно используемых в резиновых смесях мягчителей на органическую часть нефтешлама и использования тенгизской серы в виде вулканизующего агента.

Ключевые слова: органическая часть нефтешлама (ОЧН), нефтешламы, мягчители, вулканизующий агент, тенгизская сера, вулканизующая система, резиновая смесь, наполнительный шнур, борт.

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RESEARCH OF THE POSSIBILITY OF THE USING OF WASTES ENRICHMENT OF GOLD-CONTAINING ORES IN THE PROCESS OF RECEIVING SILICOPHOSPHATE FERTILIZERS BY MECHANOCHEMICAL ACTIVATION

Abstract. The material and phase composition of the wastes enrichment of the gold-bearing ore of the Pustynoye deposit were studied and it was shown that quartz and silicon compounds are their main productive phase, their content in recalculate on silicon dioxide is 75.13 mass.%. With the using of the mechanochemical activation (MCA)method by dry process a silicon-phosphate material was obtained with the component ratio of Karatau phosphorite: enrichment waste = 1: 1. It has been established that mechanically activated phosphorite mixture with wastes of ore enrichment of "Pustynoye" deposit contains 1.4% of water-soluble form of phosphorus pentoxide and 51.7% of citrate-soluble P_2O_5. In this case, the product is completely soluble in citric acid. While the original phosphorus does not contain a water-soluble form of phosphorus pentoxide, and the content of citrate- and citron-soluble forms of P_2O_5 is (rel. %) 8.6 and 58.5, accordingly. Mechanochemical activation of mixtures of natural phosphates with waste of enrichment of gold-bearing ore promotes the appearance in the aqueous extract of assimilable compounds of silicon in the form of monosilicic acid in the amount of 62.5 mg / l, whereas in the original phosphorus these compounds are absent. Also it has been shown that in the silicophosphative-containing product after MCA the fluorine content significantly reduces, from 3.11 to 1.21 wt%. The carried out researches have shown the possibility of using of wastes enrichment of gold-bearing ore of "Pustynoye" deposit in the processes of obtaining silicophosphate fertilizers by the method of mechanochemical activation.

Keywords: silicophosphate fertilizers, wastes of enrichment, mechanochemical method.

Introduction

Over the past century, the population of the Earth has increased from 1.5 to 5.5 billion people and it is expected that by 2020 it will reach 8 milliards. The feed of so many people is the most important problem that has arisen before humanity [1]. Therefore, recently the priority scientific direction in the whole world is the intensification of agricultural production with the using of new science intensive technologies of the application of mineral fertilizers, which are improve the structure of the soil and increasing its fertility and quality of agricultural products. The existing technologies for the production of mineral fertilizers, in particular phosphorus fertilizers, lead to the formation of a huge amount of wastes (phosphogypsum, off-balance ores, waste rock), overphosphating and salinization of soil in the regions of the location of phosphate plants, which lead not only to the loss of a large number of valuable components that remain in the waste, but also it worse the environmental conditions of these areas.

In addition, currently produced single- and two-component mineral fertilizers have a relatively low coefficient of use of nutrients by plants. Thus, the authors of [2-4] showed that the coefficient of nitrogen using of single-component fertilizers does not exceed 40%, phosphorus pentoxide 20%, and potassium

dioxide 50-60%. Consequently, from 1000 kilograms of inputed nutrients from 400 to 850 kilograms pollute the soil, water and atmosphere, and also it increase economic costs for the production of agricultural products.

It should also be noted that with the existing acid methods of natural phosphate raw materials processing, the degree of utilization of fluorine compounds in the production of superphosphate does not exceed 20-50%, and it is even less in the production of complex fertilizers. The content of fluorine in superphosphate reaches 1-1.5, in ammophos 3-5%. On average, with each ton of necessary for plants phosphorus about 160 kg of fluorine is fed to the fields [4]. In addition, in fertilizers, unlike natural phosphate ores, fluorine is in the form of soluble compounds and easily enters the plant. Increased accumulation of fluorine in plants disrupts metabolism, enzymatic activity (inhibits the effect of phosphatase, etc.), negatively affects the photo and biosynthesis of the protein, the development of fruits.

Based on the aforesaid, certain scientific and practical interest in this regard is development of technologies of production of new and effective fertilizers, which are decide question of increasing of soil fertility and improve of the environmental situation of agricultural regions. In our view, a promising technological solution for the production of new phosphoric fertilizers is the mechanochemical activation of natural phosphates with various additives associated with solid-phase reactions in grinding machines [5-10]. This method contains a huge innovative potential, as it provides a comparative simplicity of the process and the ability to conduct reactions in the absence of aggressive liquid reagents - mineral acids, alkalis, which in turn is important from an environmental point of view.

As additives that increase the effectiveness of phosphate fertilizers, we proposed to use silicon-containing wastes of the enrichment of ore raw materials of Kazakhstan, since it is known that silica-phosphate fertilizers introduced into the soil significantly improve its structure and increase fertility [12-15]. It is also known that the presence in the soil of available forms of silicon is very important for plants, as it enhances the assimilability of phosphorus, potassium, magnesium, influencing the growth and metabolic processes of the plant, creates conditions for expanding the feeding zone, strengthening drought resistance, increases resistance to frost, radiation, toxic substances, pest damage [11]. It is also known that the presence in the soil of available forms of silicon is very important for plants, as it enhances the assimilability of phosphorus, potassium, magnesium, influencing the growth and metabolic processes of the plant, creates conditions for expanding the feeding zone, strengthening resistance to frosts, increases resistance to frost, radiation, toxic substances, pest damage [11].

Methods

The research objects in this work are Karatau phosphorites (phosphate component) and wastes of enrichment of gold-bearing ore of the “Pustynoye” deposit, which are a light-yellow material without any inclusions. A study of the material composition of the enrichment wastes and the initial Karatau phosphorites was carried out by electron-probe analysis with using of electron microscope of JEOL-733 firm with X-ray analyzer. The phase composition was studied by X-ray diffractometric analysis, which was carried out on an automated diffronometer DRON-3 with CuK_{α} radiation, β-filter. X-ray phase analysis on the semi-quantitative basis was carried out according to diffractograms of powder samples using the method of equal weights and artificial mixtures. Quantitative ratios of crystalline phases were determined. Interpretation of the diffractograms was carried out using the ICDD file data: powder diffractometry database PDF2 (Powder Diffraction File) and diffractograms of minerals free of impurities.

Results

The average material composition of Karatau phosphorites and ore wastes from the "Pustynoye" deposit are presented in Tables 1-2, and the results of semi-quantitative X-ray phase analysis of crystalline phases of the objects of investigation are given in Tables 3-4.

Table 1 – The average material composition of the initial phosphatites of Karatau

Content of component in reculculations on oxides, wt.%										
F	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	MnO	FeO	total
3.17	4.14	3.53	20.83	25.17	0.94	1.12	38.58	0.47	2.05	100.00

From the results it follows that the wastes of the gravity concentration of the ore at the "Pustynoye" deposit are mainly represented by silicon compounds, whose content in terms of SiO_2 is 75.13% by weight. There are no harmful impurities (plumbum, cadmium, arsenic, antimony, barium) in the wastes studied, which allows us to recommend them as an initial silicon-containing component for the production of silicophosphate fertilizers.

Table 2 – The average material composition of wastes of gravitational enrichment of gold-bearing ore of the “Pustynoye” deposit

Content of component in reculculations on oxides, wt.%								Total
Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	
2.13	0.74	12.22	75.13	3.19	2.11	0.58	3.90	100.00

Table 3 – Results of semi-quantitative X-ray phase analysis of Karatau samples

Phase name	Chemical formula	Content, wt.%
Fluoropatite	$Ca_5(PO_4)_3F$	51.6
Quartz	SiO_2	20.0
Dolomite	$CaMg(CO_3)_2$	22.9
Albite	$Na(AlSi_3O_8)$	2.0
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	2.1
Calcite	$CaCO_3$	1.3

Table 4 – Results of semi-quantitative X-ray phase analysis of crystalline phases of wastes of gravity concentration of gold-bearing ore of "Pustynnoe" deposit

Mineral	Chemical formula	Content, wt.%
Quartz	SiO_2	79.1
Albite	$Na(AlSi_3O_8)$	9.4
Calcite	$CaCO_3$	6.9
Mica	$KAl_2(AlSi_3O_{10})(OH)_2$	4.6

Silicophosphate fertilizers were obtained by the dry process by mechanochemical activation of mixtures of initial phosphorites with silicon-containing wastes with the ratio of components 1: 1. The activation was carried out in a planetary ball mill of the "Activator 2S" type for 5 minutes. For comparison, a known fertilizer, phosphorite flour, was used. The phosphorus content available for plants (water-soluble, citrate- and citric-soluble P_2O_5) was carried out in accordance with standard methods [16]. Extraction of the assimilable silicon compounds was carried out with distilled water with stirring and a ratio S: L = 1: 100. The concentration of monosilicic acids in the filtrates was determined by a known method [17]. The results are shown in Table 5.

Table 5 – Results of analytical determination of phosphorus and silicon compounds assimilated by plants in silicophosphate fertilizers, obtained by dry method MCA

Composition of fertilizer	The content of assimilable forms of P_2O_5, rel.%			Content of assimilable silicon compounds, mg / l
	water-soluble	citrate-soluble	citron-soluble	
The initial phosphorite of Karatau (phosphorus)	0.0	8.6	58.5	0.0
Mechanoactivated Phosphorite of Karatau	1.2	30.5	65.8	20.5
Mechanoactivated mixture of phosphorite with wastes of ore enreachment of "Pustynoye" deposit with component ratio 1: 1	1.4	51.7	100.0	62.5

From the obtained results, it follows that the mechanically activated phosphorite mixture with the ore enreachment wastes of "Pustynoye" deposit at component ratio equal to 1: 1 contains 1.4% by weight of the water-soluble form of phosphorus pentoxide and 51.7% by weight of citrate-soluble P_2O_5. In this case, the product is completely soluble in citric acid. While the original phosphorus does not contain a water-soluble form of phosphorus pentoxide, the content of citrate- and citron-soluble forms of P_2O_5 is (rel.%) 8.6 and 58.5, respectively. In mechanically activated phosphoryte, a water-soluble form of P_2O_5 (1.2 rel.%) appears, the content of citrate-soluble form increases 3.5 times and the content of citrate-soluble phosphates slightly increases. The main difference between the mechanically activated phosphorite mixture and the wastes of ore ereachment of "Pustynoye" deposit from mechanoactivated and initial phosphorite is the presence of assimilable silicon compounds 62.5 mg/l in the form of monosilicic acid, whereas in the original phosphate flour these compounds are absent, and after mechanochemical activation their content in the aqueous extract is 20.5 mg / l. In addition, as follows from the results of the physical analysis of the mechanically activated (MCA) mixture of the Karatau phosphorite with wastes of gold-containing ore enrichment of "Pustynoye" deposit (Table 6), the fluorine content decreased significantly from 3.11 to 1.21 mass.% in the silicon phosphate product.

Table 6 – The average material composition of mechanically activated (MCA) Karatau phosphorite and its mixture with wastes of enrichment of gold-bearing ore of "Pustynoye" deposit

Content of component in reculculations on oxides, mass.%											
	F	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	MnO	FeO	TiO_2
MCA phosphorite	3.11	3.82	2.53	25.53	24.06	0.90	0.97	36.82	0.39	1.82	0.0
MCA mixture of phosphorite with wastes	1.21	2.98	8.84	46.87	12.49	0.51	2.50	10.12	0.27	2.28	0.36

Thus, the conducted studies showed that the mechanochemical activation of mixtures of Karatau phosphorites with wastes of gold-containing ore enrichment of "Pustynoye" deposit leads to destruction of the initial phosphorite, accompanied by defluorination of MCA products and the appearance in the solution of not only assimilable forms of P_2O_5, but also the formation of silicon compounds assimilated by plants. In addition, involving large-tonnage siliceous wastes from the enrichment of ore raw materials into the production of silicophosphate fertilizers will not only expand the range of phosphate fertilizers, but it will also solve the problem of solid waste storage and environmental protection.

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Discussion

The carried out researches have shown the possibility of using wastes of enrichment of gold-bearing ore of "Pustynoye" deposit in the processes of obtaining of silicophosphate fertilizers by the method of mechanochemical activation. In this process, natural phosphates are degraded, resulting in the reduction in the fluorine content of the final product. Acid-free method of used ultrafine grinding allows obtaining completely soluble in citric acid silicophosphate materials containing water (1.4% by weight) and citrate-soluble (51.7 rel.%) forms of P_2O_5, as well as plants assimilated by silicon compounds (62.5 mg/l).

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МЕХАНОХМИЯЛЫҚ АКТИВАЦИЯЛАУ ТӘСІЛМЕН КРЕМНЕФОСФАТТЫ ТЫҢАЙТҚЫШТАР АЛУ ҮРДІСІНДЕ АЛТЫН ҚҰРАМДЫ КЕНДЕРІНІҢ БАЙЫТУ ҚАЛДЫҚТАРЫН ҚОЛДАНЫЛУ МҮМКІНДІГІН ЗЕРТТЕУ

Аннотация. Берілген жұмыста «Пустынное» кенорының алтын құрамды кенін байыту қалдықтарының заттық және фазалық құрамы зерттелген және олардың негізгі фазасы - кварц пен кремний қосылыстары (кремний диоксидіне қайта есептегенде 75.13 масс.%) болып келетіні дәлелденген. Механохимиялық активациялау әдіс (МХӘ) қолданумен Қаратау фосфориті:байыту қалдықтары компоненттердің 1:1 тең қатынаста кремнийқұрамды фосфаттық материал алынған. Фосфорит және «Пустынное» кенорындағы алтынқұрамды кенінің байыту қалдықтарынан тұратын механобелсендірілген қоспада фосфор пентаоскиді суда еритін түрінде 1.4 сал.% және цитрат ерігіш түрінде 51.7 сал.% P_2O_5 бар. Алынған өнім лимон қышқылында толық ериді. Алайда бастапқы фосфорит үні пентаоксидтің суда еримейтін формалар жоқ, ал P_2O_5 цитратты- және лимонды-ерігіш формалары (сал.%) 8,6 және 58,5 сәйкесінше құрайды. Табиғи фосфаттары мен алтынқұрамды кенінің байыту қалдықтарының қоспаларды механохимиялық активациялау кезінде сулы сүзіндіде монокремний қышқылы 62,5 мг/л мөлшерде болатын кремнийлі сіңірімді қосылыстар пайда болады, ал бастапқы фосфоритті үнда бұл қосылыстар жоқ. Сонымен қатар, МХА-дан кейін кремнефосфатты өнімдегі фтордың мөлшері айтарлықтай – 3,11-ден 1,21 масс.%-ға дейін азаяды. Жүргізілген зерттеулер «Пустынное» кенорының алтын құрамды кенін байыту қалдықтарын механохимиялық активация арқылы кремнефосфатты тыңайтқыштар алу үрдісінде қолданылу мүмкіндіктері көрсетілген.

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ИССЛЕДОВАНИЕ ВОЗМОЖНОСТИ ИСПОЛЬЗОВАНИЯ ОТХОДОВ ОБОГАЩЕНИЯ ЗОЛОТОСОДЕРЖАЩИХ РУД В ПРОЦЕССЕ ПОЛУЧЕНИЯ КРЕМНЕФОСФАТНЫХ УДОБРЕНИЙ МЕХАНОХИМИЧЕСКИМ СПОСОБОМ

Аннотация. В работе изучен вещественный и фазовый состав отходов обогащения золотосодержащей руды месторождения «Пустынное» и показано, что их основной продуктивной фазой являются кварц и соединения кремния, содержание которых в пересчете на диоксид кремния составляет 75.13 масс.%. С использованием метода механохимической активации (МХА) сухим способом получен кремнефосфатный материал с соотношением компонентов фосфорит Каратау:отходы обогащения = 1:1. Установлено, что механоактивированная смесь фосфорита с отходами обогащения руды м. «Пустынное» содержит 1,4 отн.% водорастворимой формы пентаоксида фосфора и 51,7 отн.% цитратнорастворимой P_2O_5. При этом продукт полностью растворим в лимонной кислоте. Тогда как исходная фосмука не содержит водорастворимой формы пентаоксида фосфора, а содержание цитратно- и лимоннорастворимой форм P_2O_5 составляет (отн.%) 8,6 и 58,5 соответственно. Механохимическая активация смесей природных фосфатов с отходами обогащения золотосодержащей руды способствует появлению в водной вытяжке усвояемых соединений кремния в виде монокремниевой кислоты в количестве 62,5 мг/л, тогда как в исходной фосмуке эти соединения отсутствуют. Также показано, что в кремнефосфатном продукте после МХА существенно снижается содержание фтора – с 3,11 до 1,21 масс.%. Проведенные исследования показали возможность использования отходов обогащения золотосодержащей руды м. «Пустынное» в процессах получения кремнефосфатных удобрений способом механохимической активации.

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FEATURES OF HYDROCHEMICAL AND GEOCHEMICAL INDICATORS OF THE NORTH-EASTERN PART OF THE CASPIAN SEA (ZONES, OIL AND GAS FIELDS OF THE KAZAKHSTAN SECTOR)

Abstract. Changes in hydrometeorological conditions that play a major role in the life of the Caspian Sea are combined with the impact on its ecosystem of economic activity, one of the types of which is pollution of the marine environment. Much attention is paid to environmental safety in the search and exploration of hydrocarbon deposits in the North Caspian, because without it, neither its high biological productivity, nor the fishery value can be maintained. The Caspian Sea, and especially its northern shallow part, is a highly productive body of water. Such extremely high productivity of the Caspian is combined with the relative poverty of the biological diversity of this reservoir. A significant part of the Caspian hydrobionts is relict. This part of the sea is the richest in biological productivity. And it is not by chance that the rich nutrients and the organic substrate of the waters of the Northern Caspian have a great influence on the diversity of the flora and fauna of the entire Caspian. However, at present, the Caspian Sea and especially the Northern Sea, like the other seas of the world, are experiencing increasing anthropogenic impact, which is manifested in pollution with oil products and heavy metals, as well as in active shipping and hydro-construction.

Keywords: heavy metals, concentration, salinity of water, dissolved oxygen, pH, hydro chemical and geochemical indicators.

INTRODUCTION

The Eastern section of the North Caspian Sea adjacent to the Kazakhstan coast was selected as the study area. The study area is characterized by a gentle slope of the bottom and a slow increase in the depths. The soils here are predominantly silty and silty - sandy.

Seasonal fluctuations in the level of the Caspian Sea do not exceed a few dm. For the northeastern coast of the Caspian Sea, high surge levels are characteristic.

MAIN PART

The study site is unique in its geochemical and hydrological and hydrochemical conditions, as well as its hydrobiological characteristics. Comprehensive studies of the main geochemical, hydrological and hydrochemical characteristics were carried out at stations located near the surface and bottom of the sea.

Heavy metals in bottom sediments. The main statistical parameters are shown in table 1.

Associations of chemical elements that form anomalies in areas of oil and gas fields are determined by the primary presence of mobile elements in soils that can move and concentrate on the corresponding barriers. Most often they include Pb, Zn, Mn, Cu, Ba, Co, Ni, Cr.

Table 1 - The main statistical characteristics of the content of heavy metals (mg / kg) in bottom sediments.

parameter	maximum	average	minimum
Cu	9,00	6,80	5,00
Zn	22,00	16,68	10,00
Cd	4,70	2,28	0,80
Fe	8300,00	3468,00	600,00
Mn	421,00	168,48	63,00
Co	19,00	12,84	6,00

Such associations of chemical elements arise from the fact that gaseous products from hydrocarbon deposits periodically enter the soil. These primarily include the hydrocarbons themselves, hydrogen, carbon dioxide, and inert gases. Their bacterial decomposition, accompanied by various chemical reactions, leads to the formation of numerous and diverse geochemical barriers (hydrogen sulfide, acid, alkaline, sorption, and biogenic) in soils above the deposits. Redox reactions occurring on such sites (with the participation of bacteria that decompose hydrocarbons) can increase the mobility of the regenerating elements of variable valence, often leading them to "distillation" from the central parts of the sites. As a result of all these processes, redistribution anomalies are formed in the soils, accompanying areas of oil and gas fields.

The observation of the bottom sediments of the eastern part of the Northern Caspian was carried out in the autumn and spring, and it was found that the concentration of heavy metals in the bottom sediments in the autumn decreases as compared with the summer period.

From monitoring observations, it follows that the average concentration of zinc and cadmium in bottom sediments on the Kashagan structure in 2003-2006 turned out to be lower than in 2000-2002. (Table 2). These changes occurred both on the main test site and on the structure as a whole, but did not affect manganese, the average concentration of which in the surface layer of bottom sediments increased, unlike other heavy metals, and more so on the main test site. It is unlikely that the reason for this is to carry out drilling operations, since when discharging drilling waste the pollution of the marine environment is complex. Most likely, the difference in the rate of manganese accumulation between the landfill and the background area as a whole was due to the specific behavior of this microelement in the bottom sediments, its close connection with redox conditions and the acidity of these sediments, in which by myself.

Table 2 - The average concentration of heavy metals in the bottom sediments on the Kashagan structure in 2000-2006

Indicator	Area observations	years	
		2000-2002	2003-2006
Manganese, mg / kg	polygon	122,5	405,0
	background	113,6	175,4
Zinc, mg / kg	polygon	20,74	12,87
	background	19,28	16,94
Cadmium, mg / kg	polygon	2,07	< 1
	background	2,87	< 1

The main sources of iron and copper in the Caspian Sea are surface and underground runoff. In river water, these elements are usually concentrated in unstable minerals or migrate in the form of solutions. As a result, after entering the sea, iron and copper are actively involved in biogenic migration and the formation of various forms of fine mineral and organic matter, which is deposited mainly in deep-sea halistatic areas.

The concentration of iron in the bottom sediments on the main site was on average slightly higher than on the Kashagan structure as a whole. However, both of these areas turned out to be very similar in the dynamics of iron content in bottom sediments, since here and there in 2003-2006. it decreased relative to 2000-2002. (Table 2). The difference in the level and dynamics of iron content between the studied water area as a whole and the main landfill may be due to different depths. It is known that the iron

content in the bottom sediments of the Caspian Sea increases with depth. At the same time, unlike deep-water areas, where iron is concentrated in the thin-melt fraction, iron is often found in shallow water and, especially, near river mouths in aleuritic and larger fractions of the surface layer of bottom sediments.

According to environmental monitoring in 2000-2002. Copper concentration in bottom sediments at the main test site was on average somewhat higher than on the structure as a whole. However, both of these areas turned out to be very similar in terms of copper content in bottom sediments, since here and there it decreased from 2000–2002. (Table 3.). The difference in the level and dynamics of copper content between the studied water area as a whole and the main range is explained by the greater depth of the latter, because the copper content (as well as iron) in the bottom sediments of the Caspian Sea increases with depth. At the same time, unlike deep-water areas, where copper is concentrated in the fine-grained fraction of bottom sediments, coarse-grained fractions of bottom sediments are not rarely found in the estuaries of river basins, as confirmed by environmental monitoring data.

Table 3 - Comparative characteristics of the concentration of iron and copper in the bottom sediments of the Kashagan structure and the background area

Indicator	Area Of observations	years	
		2000-2002	2003-2006
Iron, mg / kg	Main polygon	3600	3120
	background	3340	2490
Copper, mg / kg	Main polygon	13,61	12,20
	background	14,20	9,36

Salinity of water.

The determination of the salinity of water in the water area of the structure revealed its gradual increase from the north of the water area to the south throughout the entire water mass. The smallest salinity (0.37-2.53) in spring was observed in the western and central parts of the water area, the eastern part of the license area was occupied by salinity up to 5-9.

In the fall in the north of the central part of the structure water area, the minimum salinity of water was 0.54 in the surface layer, 2.96 - in the bottom layer. The maximum value of salinity (11.89 ‰ in the surface layer and 12.00 in the bottom layer) was recorded in the south of the central part of the structure.

Dissolved oxygen. In a large part of the sea area, the surface water layer is saturated with oxygen or is in a state close to saturation. The exceptions are the western part of the Northern Caspian and local areas in the central and south-eastern part of the water area, where water saturation in the surface layer from 76 to 95% (in the western part) and from 90 to 98% (in local areas). In the bottom layer, the degree of saturation of water with oxygen in its value and nature of distribution differed from those in the surface layer. In the western, central and southern regions of the water area, local areas are registered, in which oxygen deficiency is noted in the bottom layer. Practically in most of the Northern Caspian water area, the degree of oxygen saturation in the bottom layer did not exceed 100%, with the exception of local zones in the southern and northern regions.

Hydrogen indicator (pH).

The values of the pH in the license area in the spring and autumn periods are presented in Table. four.

Table 4 - Hydrogen indicator (pH) of surface and bottom waters of the northeastern part of the Caspian Sea

Horizon	Spring	Autumn
Surface	8,17-9,44 8,48	8,06-8,86 8,50
Bottom floor	8,20-9,44 8,47	8,20-8,84 8,49

Over the entire water area of the structure, the pH values on the surface and at the bottom are close in magnitude. The distribution of pH values is homogeneous - a smooth decrease in pH values from northwest, north to south, southeast is observed throughout the water mass. This distribution of pH is typical for the water area under consideration in the spring, characterized by the onset of spring flood

waters of the Volga and Ural rivers, and in the summer-autumn period, characterized by a decrease in the influence of river runoff and an increase in salinity as one moves south.

In the hydrological and hydrochemical terms, the area is distinguished by extremely unstable salt and temperature regimes over the seasons.

During the summer period of studies, the water temperature was marked by elevated values and ranged from 20.95 - 29.03 ° C at the bottom and 26.10 - 29.20 ° C on the surface. In the autumn - winter period, the range of water temperature fluctuations was 6.32 - 12.13 ° C at the bottom and 6.10 - 12.00 ° C at the surface. The temperature values at the surface and at the bottom indicate a uniform heating of water along the vertical (homothermy), which is associated with the shallowness of the studied water area.

The research zone was distinguished by low and constantly fluctuating salinity (in the summer period it was 3.84-10.5% o at the bottom and 3.81-10.3% oat the surface with average values of 7.5 and 6.98% o, respectively; in the winter period - 2.4 - 12.5% o and 2.39 - 12.5% 0, respectively, with average values of 9.85 and 7.49).

One of the most important hydrochemical characteristics is the oxygen content in water. The oxygen regime in the studied water area, due to hydrological, hydrochemical, and geomorphological features of individual regions of the structure, was characterized by significant contrast in time and space.

The summer O2 content was 6.86-8.56 mg O2 / l at the bottom and 6.80 - 8.86 mg at the surface with average values of 7.75 and 8.04 mg O 2 / l, respectively; autumn-winter period. - 9.89 - 12.0 mg 0 2 / l and 10.17 - 12.38 mg O2 / l, respectively, with average values of 10.8 at the bottom and 11.4 mg O2 / l at the surface. The oxygen regime was formed under conditions of increased hydrodynamic activity and low temperature - salinity stratification of water masses. In a large part of the water area, the surface water layer was saturated with oxygen. The exception was local areas where the oxygen saturation of water in the surface layer ranged from 89 to 97%. In the bottom layer, the degree of saturation of water with oxygen in its value and nature of distribution was slightly different from those in the surface layer.

CONCLUSION

Localized areas with relatively low oxygen content, identified by surveying materials, were confined to lower, deep-water parts of the bottom topography. Apparently, they were carried out by the influx of oxygen-depleted sea waters from the Middle Caspian, as evidenced by the materials of a synchronous survey of currents, which revealed in these areas of the water area the total transfer of sea waters to the north.

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КАСПИЙ ТЕҢІЗІНІҢ СОЛТҮСТІК-ШЫҒЫС БӨЛІГІНІҢ ГИДРОХИМИЯЛЫҚ ЖӘНЕ ГЕОХИМИЯЛЫҚ КӨРСЕТКІШТЕРІНІҢ ЕРЕКШЕЛІКТЕРІ (ҚАЗАҚСТАН СЕКТОРЫНЫҢ ЗОНУ, МҰНАЙ ЖӘНЕ ГАЗ ӨНДІРІСІ)

Аннотация. Каспий теңізінің өмірінде маңызды рөл атқаратын гидрометеорологиялық жағдайлардағы өзгерістер оның экожүйесіне әсер етуімен біріктіріледі, олардың бірі теңіз ортасын ластау болып табылады. Солтүстік Каспийде көмірсутегі шикізатын іздестіру мен барлауда экологиялық қауіпсіздікті сақтауға көп көңіл бөлінеді онсыз биологиялық өнімділігі де, балық аулау құндылығы да сақталмайды. Каспий теңізі, әсіресе оның солтүстік қалың бөлігі - судың жоғары өнімділігі. Каспийдің мұндай жоғары өнімділігі осы резервуардың биологиялық әртүрлілігінің салыстырмалы кедейлігімен біріктірілген. Каспий гидробионттарының маңызды бөлігі реликті болып табылады. Теңіздің бұл бөлігі биологиялық өнімділіктегі ең бай. Және Каспий теңізінің флорасы мен фаунасының алуан түрлілігіне Солтүстік Каспийдің суының бай қоректік заттар мен органикалық субстраты әсер етпейді. Алайда қазіргі уақытта Каспий теңізі, әсіресе Солтүстік теңіз, әлемнің басқа да теңіздері сияқты, мұнай өнімдері мен ауыр металдардың ластануымен, сондай-ақ белсенді жүк тасымалдау және гидроқұрылыста көрініс тапқан антропогендік әсерді бастан өткеруде.

Түйін сөздер: ауыр металдар, шоғырлану, судың тұздылығы, еріген оттегі, pH, гидрохимиялық және геохимиялық көрсеткіштер.

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ОСОБЕННОСТИ ГИДРОХИМИЧЕСКИХ И ГЕОХИМИЧЕСКИХ ПОКАЗАТЕЛЕЙ СЕВЕРО-ВОСТОЧНОЙ ЧАСТИ КАСПИЙСКОГО МОРЯ (ЗОНЫ, НЕФТЕГАЗОВЫХ МЕСТОРОЖДЕНИЙ КАЗАХСТАНСКОГО СЕКТОРА)

Аннотация. Изменения гидрометеорологических условий, играющие главную роль в жизни Каспийского моря, сочетаются с воздействием на его экосистему хозяйственной деятельности, одним из видов которого является загрязнение морской среды. Большое внимание уделяется экологической безопасности при поиске и разведке месторождений углеводородного сырья на Северном Каспий, т.к. без этого не удается сохранить ни его высокую биологическую продуктивность, ни рыбохозяйственную ценность. Каспийское море, и особенно его Северная мелководная часть, является высокопродуктивным водоемом. Такая исключительно высокая продуктивность Каспия сочетается с относительной бедностью биологического разнообразия этого водоема. Значительная часть гидробионтов Каспия является реликтовой. Именно эта часть моря является самой богатой по биологической продуктивности. И не случайно, что богатые биогенными элементами и органическим субстратом воды Северного Каспия оказывают большое влияние на разнообразие флоры и фауны всего Каспия. Однако в настоящее время Каспий и особенно Северный, как и другие моря земного шара, испытывает усиливающееся антропогенное воздействие, которое проявляется в загрязнении нефтепродуктами и тяжелыми металлами, а также в активном судоходстве и гидростроительстве.

Ключевые слова: тяжелые металлы, концентрация, соленость воды, растворенный кислород, водородный показатель, гидрохимические и геохимические показатели.

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CHEMICAL CONSTITUENTS OF THE ROOTS OF *FRITILLARIA PALLIDIFLORA*

Abstract. The roots of *F.pallidiflora* collected in Kazakhstan were investigated for chemical constituent. The quantitative and qualitative analysis of the medicinal plant have been made. Biological active constituents such as organic acid (1.08%), flavonoids (0.17%) together with moisture content (7.13 %), ash (20.796%), and extractives (12.85%) of plant *F.pallidiflora* were determined. By using the method of multi-element atomic emission spectral analysis in theash of the plantwas found 8 macro-micro elements, in which the main contents were Potassium (440.420 mcg/ml) and Sodium (33.7475 mcg/ml). In addition, twenty amino and eight fatty acids were identified from *F.pallidiflora*. The results showed that the major contents of amino acids were glutamate (2650 mg/100g), aspartate (1185 mg/100g) and alanine (802 mg/100g), and fatty acids were linoleic (24.2%) and oleic acids (48.4%), respectively.

Key words: *Fritillaria pallidiflora,* bioactive constituents, macro-micro elements, amino-, fatty acids.

Introduction

Fritillaria - is a genus of about 130−165 species within the monocot family Liliaceae, and is native to temperate regions of the Northern Hemisphere. *Fritillaria* is a botanical source for various pharmaceutically active components which have been used in traditional Chinese medicine for thousands of years. Many species (such as *F. cirrhosa*, *F.thunbergii* and *F. verticillata*) are used in traditional Chinese cough remedies. Increasing interest in *Fritillaria* medicinal resources has led to additional discoveries of steroidal alkaloids, saponins, terpenoids, glycosides and many other compounds in various *Fritillaria* species, and to investigations on their chemotaxonomy, molecular phylogeny and pharmacology [1]. *Fritillaria pallidiflora Schrenk* belongs to the *Fritillaria* genus of *Liliaceae* family widely distributed in Xinjiang province of China and finds widespread applications as antitussive, antiasthmatic and expectorant medicine [2]. The chemical constituents of *F. pallidiflora* have been studied, and steroidal saponins and alkaloids are regarded as their main ingredients [3]. In recent years, steroidal saponins have attracted more attention for their significant bioactivities, including their anti-tumor [4], anti-thrombotic [5], anti-inflammatory [6], anti-fungal [7] activities.

In the steppe zones, meadow places, on the slopes of the alpine and subalpine belt of Kazakhstan, there are 5 species of growing [8]. In addition, the bulbs contain organic acids, terpenoids, phytosterols and some vitamins. In small doses, the alkaloids contained in the bulbs have a therapeutic effect. Thus, in Chinese medicine, on the basis of the alkaloids contained in the bulbs, expectorants and soothing agents are made. In large doses of hazelnut bulbs are dangerous to health [9].

Proteins are large, complex molecules that are critical for the normal functioning of the human body. They are essential for the structure, function, and regulation of the body's tissues and organs. Proteins are made up of hundreds of smaller units called **amino acids** that are attached to one another by peptide bonds, forming a long chain. First point of investigation was on amino acids, which is organic (carboxylic) acids, the molecules of them contain one or more amino groups (NH_2-groups), the basic structural elements of protein molecules [10].

It is known that fatty acids - components of lipids exist in plants, animals, and microorganisms. Lipids are necessary for our body, because without them, metabolism cannot be carried out normally, and toxins and toxins accumulate in cells and tissues, as purification processes are slowed down. Many of fatty acids

cannot be synthesize in human organism. Those fatty acids are required, however, for cellular processes and the production of other necessary omega-3 and omega-6 fatty acids. In addition fatty acids have a wide range of commercial applications, for example, they are used not only in the production of numerous food products but also in soaps, detergents, and cosmetics. Soaps are the sodium and potassium salts of fatty acids [11].

In the present study, the quantitative and qualitative analysis of bioactive components such as moisture, total ash, and extractives contents of *F.pallidiflora* have been carried out, as well as amino-fatty acid contents were determined. Determination of main bioactive constituents, macro, micro elemts and amin-, fatty acid contents of the root of *F.pallidiflora* which growing in Almaty region of Kazakhstan were reported for the first time.

Materials and Methods

The root part of plant *F.pallidiflora* was collected in May 2017 from the piedmont steppe of the Toraigir Mountains of Almaty region and identified by Dr. AlibekYdyrys. Plant was 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 *F.pallidiflora* were cut into small pieces and stored at room temperature.

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

In the "Center of Physico-Chemical methods of research 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 *F.pallidiflora* 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 hydrolysate 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 NH_4OH 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 thenevaporated 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 triethyl amine, 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 by using GC/MS device. GC/MS analysis: amino acid content of the roots part of *F.pallidiflora* 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 fishing of exit of all amino acids. The chromatogram is counted according to an external standard.

Results and discussion

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

The ash of plant raw materials is the balance of inorganic substances obtained after burning the raw material and then calcining the residue to a constant mass. The ash of plants consists of a mixture of various inorganic substances characteristic of the plant, and mineral impurities that can get into the raw material during collection and drying. The moisture of plant materials is the loss in the mass due to hygroscopic moisture and volatile substances detecting when plant material is dried till constant weight. The moisture content in medicinal plant raw materials serves as one of the numerical indicators characterizing its quality. Medicinal plant raw materials should not contain moisture above the permissible standards, because with high humidity, during storage conditions are created that contribute to a decrease in its quality. For most types of medicinal plant raw materials, the permissible moisture limit is usually 12-15%.

Table-1 - Quantitative analysis of bioactive constituents of the root *F.pallidiflora*

Content, %				
Moisturecontent	**Ash**	**Extractives**	**Organicacids**	**Flavonoids**
7.13	20.7	12.8	1.08	0.17

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 *F.pallidiflora* there were determined eight macro- and micro elements, shown in Table 2 and major of them are Potassium (440.420 mcg/ml) and Sodium (33.7475 mcg/ml). One of the main factors of nutrition, affecting health, working capacity and active longevity, are micronutrients - macro- and micro elements. The body does not produce microcircuits and should receive them in ready form, for example, with food. The ability to store these substances in the body is absent. Sodium is the maintains the osmotic pressure and pH of the medium, participates in the formation of gastric juice, activates the enzymes of saliva and pancreatic juice, together with potassium, forms the electrical potential of cell membranes, through which a signal is transmitted in nerve cells, muscle cells, etc. Potassium is the most important component of intracellular fluid, controlling acid-base balance, muscular activity, and synthesis of proteins and glycogen [12].

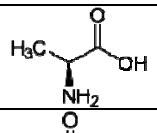
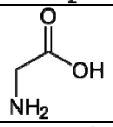
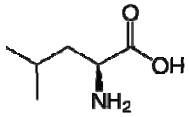
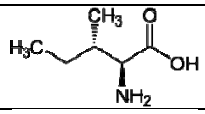
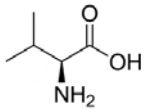
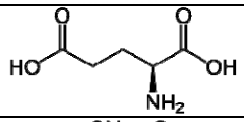
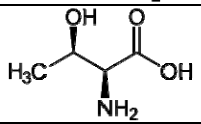
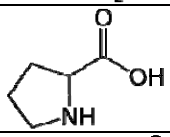
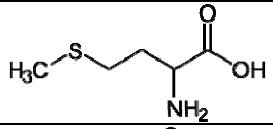
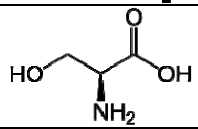
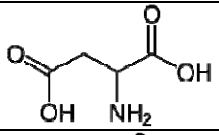
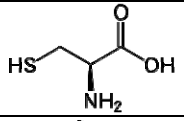
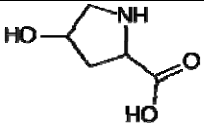
Table 2 - Composition of macro-micro elements in the ash of *F.pallidiflora ash*

Element	**K**	**Mg**	**Ca**	**Mn**	**Fe**	**Zn**	**Cu**	**Na**
mcg/ml	440.4200	25.6850	28.0300	0.4254	3.4152	5.8052	0.1731	33.7475

Determination of fatty acid composition of raw material, and dried plant *F.pallidiflora* 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 "CARLO-ERBA-420" allocated the Kazakh Academy of Nutrition for 1 hour. 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.

Quantitative composition of fatty acids in *F.pallidiflora* mostly were linoleic acid (24.2%) and oleic acid (48.4%). Linoleic acid has received much attention in recent years because of its interesting biological benefits. The main health effects described for linoleic acid include reduction of carcinogenesis, atherosclerosis, inflammation, obesity, diabetes, as well as growth promoting and bone formation-promoting properties [13]. 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 [14].

Table 3 - Amino acids from the root of *F.pallidiflora*

№	Amino acids	Molecular formula	Structure	MW	Amount in plant, mg/100g
1	2	3	4	5	6
1	Alanine	$C_3H_7NO_2$		89	802
2	Glycine	$C_2H_5NO_2$		75	326
3	Leucine	$C_6H_{13}NO_2$		131	415
4	Isoleucine	$C_6H_{13}NO_2$		131	402
5	Valine	$C_5H_{11}NO_2$		117	328
6	Glutamate	$C_5H_9NO_4$		147	2650
7	Threonine	$C_4H_9NO_3$		119	290
8	Proline	$C_5H_9NO_2$		115	652
9	Methionine	$C_5H_{11}NO_2S$		149	75
10	Serine	$C_3H_7NO_3$		105	480
11	Aspartate	$C_4H_7NO_4$		133	1185
12	Cysteine	$C_3H_7NO_2S$		121	50
13	Oxyproline	$C_5H_9NO_3$		131	1

Окончание таблицы

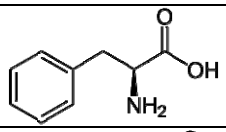
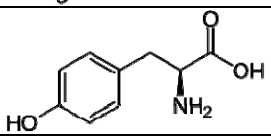
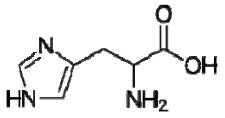
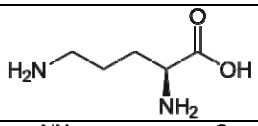
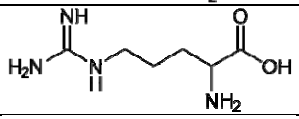
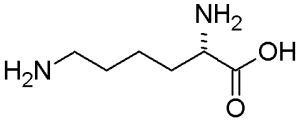
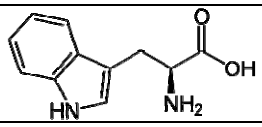
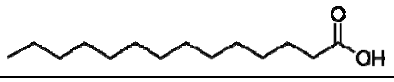
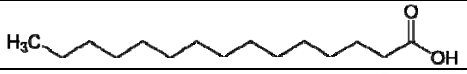
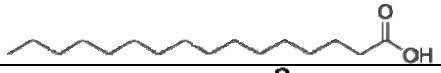
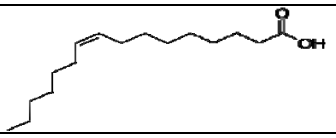
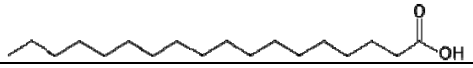
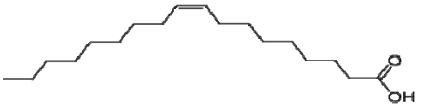
1	2	3	4	5	6
14	Phenylalanine	$C_9H_{11}NO_2$		165	303
15	Tyrosine	$C_9H_{11}NO_3$		181	348
16	Histidine	$C_6H_9N_3O_2$		155	200
17	Ornithine	$C_5H_{12}N_2O_2$		132	2
18	Arginine	$C_6H_{14}N_4O_2$		174	498
19	Lysine	$C_6H_{14}N_2O_2$		146	160
20	Tryptophan	$C_{11}H_{12}N_2O_2$		204	90

Table 4 - Fatty acids from the root of *F. pallidiflora*

№	**Fatty acids**	**Molecular formula**	**Structure**	**MW**	**Amount in plant, %**
1	Meristic acid $C_{14:0}$	$C_{14}H_{28}O_2$		228	2.1
2	Pentadecanoic acid $C_{15:0}$	$C_{15}H_{30}O_2$		242	1.2
3	Palmitic acid C $_{16:0}$	$C_{16}H_{32}O_2$		256	18.3
4	Palmitoleic acid $C_{16:1}$	$C_{16}H_{30}O_2$		254	0.9
5	Stearin acid $C_{18:0}$	$C_{18}H_{36}O_2$		284	3.8
6	Oleic acid $C_{18:1}$	$C_{18}H_{34}O_2$		282	48.4
7	Linoleic acid $C_{18:2}$	$C_{18}H_{32}O_2$		280	24.2
8	Linolenic acid $C_{18:3}$	$C_{18}H_{30}O_2$		278	1.1

In the composition of amino acids mainly were glutamate (2650 mg/100g), aspartate (1185 mg/100g) and alanine (802 mg/100g). Glutamate is replaceable amino acid, which plays the role of a neurotransmitter with high metabolic activity in the brain, stimulates redox processes in the brain, the exchange of proteins. Normalizes the metabolism, changing the functional state of the nervous and endocrine systems [15]. 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 [16]. Alanine plays a significant role in metabolic processes, as well as to regulate the level of sugar in the bloodstream. This amino acid protects against the development of cancer of the pancreas and prostate gland, it is an important part of sports nutrition, increases physical endurance and allows to build muscle mass [17].

Conclusion

Quantitative and qualitative analysis of bioactive constituents and the moisture, total ash and extractives contents of roots *F.pallidiflora* were determined. Besides, macro-micro elementsin the ash of the medicinal plant were investigated, and total eight macro-micro elements were identified by the method of multi-element atomic emission spectral analysis. Meanwhile, twenty amino and eight fatty acids were determined from *F.pallidiflora*. The results showed that the major contents of amino acids were glutamate (2650 mg/100g), aspartate (1185 mg/100g) and alanine (802 mg/100g), and fatty acids were linoleic (24.2%) and oleic acid acids (48.4%), respectively.

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АҚШЫЛ СЕПКІЛГҮЛ ТАМЫРЫНЫҢ ХИМИЯЛЫҚ ҚҰРАМЫН ЗЕРТТЕУ

Аннотация. Қазақстанда жиналған *F. pallidiflora* тамырының химиялық құрамы зерттелді. Дәрілік өсімдіктің сандық және сапалық талдауы жүргізілді. Өсімдіктің ылғалдылығы (7,13%), күлділігі (20,796%) және экстрактивтілігі (12,85%),сонымен бірге органикалық қышқыл (1,08%), флавоноидтар (0,17%) сияқты биологиялық активті компоненттер құрамы анықталды. Атомдық эмиссия спектральды талдау әдісін қолдана отырып, өсімдіктің күліндегі 8 микро және макро элементері анықталдыжәне оның негізгі құрамы калий (440.420 мкг / мл) және натрий (33.7475 мкг / мл) элементтерінен тұратыны анықталды. Бұдан басқа, *F.pallidiflora*-дан жиырма амин және сегіз майлы қышқыл анықталды. Алынған нәтижелер бойынша аминқышқылдардың негізгі құрамы глутамат (2650 мг / 100 г), аспартат (1185 мг / 100 г) және аланин (802 мг / 100 г) және май құрамында линол (24,2 %) және олеин қышқылдары (48,4 %).

Түйін сөздер: *Fritillaria pallidiflora*, биоактивті құрамдастар, макро-микро элементтер, амино-майлы қышқылдар.

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ИССЛЕДОВАНИЕ ХИМИЧЕСКОГО СОСТАВА РЯБЧИКА БЛЕДНОЦВЕТКОГО

Аннотация. Был исследован химический состав корней *F. pallidiflora*, собранного в Казахстане. Сделан количественный и качественный анализ лекарственного растения. Определены биологически активные компоненты, такие как органические кислоты (1,08%), флавоноиды (0,17%), а также содержание влаги (7,13%), зольность (20,796%) и экстрагенты (12,85%) растения *F.pallidiflora*. При использованием метода многоэлементного атомно-эмиссионного спектрального анализа в золе растения было найдено 8 макро-микро элементов, основными веществами из которых были калий (440.420 мкг / мл) и натрий (33.7475 мкг / мл). Кроме того, из корней *F.pallidiflora* были идентифицированы двадцать аминокислот и восемь жирных кислот. Результаты показали, что основным содержанием аминокислот являются глутамат (2650 мг / 100 г),

аспартат (1185 мг / 100 г) и аланин (802 мг / 100 г), а среди жирных кислот - линолевые (24,2%) и олеиновые кислоты (48,4%) соответственно.

Ключевые слова: *Fritillaria pallidiflora*, биоактивные компоненты, макро-микро элементы, амино-, жирные кислоты.

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STUDYING THE PROCESS OF OBTAINING PHOSPHATES OF METALS BASED ON THE PHASE EQUILIBRIA OF FOUR COMPONENT SYSTEMS

Abstract. In this article the literature data on phase equilibria in four-component reciprocal systems are given and the solubility in the mutual quaternary systems $FeCl_2$-H_3PO_4-H_2O was determined in the range of concentrations of phosphoric acid from 5 to 55% H_3PO_4 at temperatures of 25, 60 and 80ºC.

The calculated data on the construction of the crystallization fields of salts in the studied system, taking into account the possible formation of one- and two-substituted iron phosphates, are given. The optimum consumption of phosphoric acid solution to obtain the desired product is defined. The maximum possible yield of the finished product in these conditions of the process from a unit mass of ferric chloride is also established.

The consumption of phosphoric acid was determined according to the diagram according to the lever rule as the ratio of the segments BM5 and M5D. The excess acid ratio over the stoichiometric norm was calculated for the formation of monosubstituted phosphates for the $FeCl_2$-H_3PO_4-H_2O system.

Keywords: multicomponent system, phase equilibrium, phase diagrams, phosphatizing, isothermal method, Yeneke diagram.

Introduction

The study of state diagrams of multicomponent systems, depicting the relationship between the property (temperature) and composition is of scientific interest. The interest and importance of the study of such state diagrams is not only to establish the presence of phases in the system, but also to clarify the nature and nature of the interaction between the components of the system, as far as possible, on the basis of studying the type of obtained diagrams [1].

For complex systems consisting of many phases and components, the construction of a state diagram is the only method that allows one to determine in practice how many phases and what phases form the system for given values of state parameters. Each real-life state of a system in a state diagram is depicted by a so-called figurative point; areas of existence of one phase correspond to sections of space [2-3].

The theoretical basis for the construction and interpretation of state diagrams of equilibrium systems are phase equilibrium condition, according to which the chemical potentials of each component in all phases at equilibrium are equal; the condition of chemical equilibrium, according to which the sum of the chemical potentials of the reacting substances at equilibrium is equal to the same amount for the reaction products; phases of the Gibbs rule [4-5].

In order to construct state diagrams by calculation, it is necessary to know the dependencies of the chemical potentials of all components of the system. The study of state diagrams is the main content of physico-chemical analysis.

Up to date the problem of anticorrosive protection of metals is still extremely topical one, and it requires fast decision. Herewith one of directions of development of effective phosphate protective coatings is using waste of chemical-metallurgical productions for that purpose.

In work [6], the possibility of using the electrochemical method - cyclic voltammetry for determining the applying the phosphate coatings on brass samples from phosphating solutions was considered.

The proposed voltammetric method is based on measuring the amount of current (amount of electricity) for cathode maxima of electroreduction of ionization products of disk brass electrodes in the absence of a phosphate coating and coated with a wide potential range against a background of 0.3 M Na_2SO_4. In work [7], the influence of zinc phosphonat ZnHTΦ and sodium lingosulphate on speed of a steel corrosion is studied. It is established, that the greatest inhibitory effect is observed at a ratio 1:1.

Phosphatizing of non-ferrous metals, in particular brass, is used less frequently than phosphatization of ferrous metals. However, in the case of applying paint coatings, the preliminary application of a phosphate layer leads to a significant increase in the resistance of the applied coating, which is very important for non-ferrous metals with low adhesive properties [8-20].

Determining the optimal phosphatizing conditions for brass samples — the composition and nature of phosphating solutions, temperature, phosphating time, hydrodynamic conditions is associated with conducting a large number of laborious tests using chemical and physical methods [6, 21-24].

The use of such methods does not always allow to obtain unambiguous information about the physico-chemical characteristics of phosphate coatings. To establish the optimal conditions for monitoring and controlling the phosphating process on the samples used, the most informative method may be an electrochemical method based on fixing cyclic current-voltage curves.

For determination of the reactivity and conditions of applying the phosphate coatings on metals and alloys of different nature, chemical optical and physicochemical methods are widely used. Among electrochemical methods, the most widely used method is a method, based on the measurement of the potential of time. Using this method, the time of formation of phosphate coatings on the studied samples can be estimated.

It is known that chloride sublimates of oxidizing-chloridizing roasting of lead-zinc ore contain 28.9% of chloride-ions, including 38.3% of $ZnCl_2$ and 6.85% of $FeCl_2$ and 6,75% $PbCl_2$ [25]. When phosphoric-acid processing of these sublimates to obtain phosphating anticorrosive coatings four-component (quaternary) $FeCl_2$-H_3PO_4-H_2O systems is formed. Formation of five-component (quinary) $FeCl_2$-$ZnCl_2$-H_3PO_4-H_2O system is possible as well. Researched processes represent complex chemical-technological systems, including both chemical and phase transformations in equilibrium conditions. Therefore the technology of processing of chloride sublimates with a certain composition using phosphoric acid is impossible to develop without complex physical-chemical analysis of these mutual systems and setting regularities of phenomena taking place in the systems. The analysis is performed by studying properties of a heterogeneous system depending on its composition and parameters and imaging these dependences on state diagrams.

The analysis of the latest news from literature sources for the question of phase equilibrium in pointed systems testifies that similar investigations weren't conducted. There are data only about composition and properties of two-component systems $FeCl_2$-H_2O and $ZnCl_2$-H_2O in the literature [26], but those don't correspond with composition of waste under investigation. Acid-containing ternary systems like $FeCl_2$-HCl-H_2O and $ZnCl_2$- HCl-H_2O, $Fe_3(PO_4)_2$-H_3PO_4-H_2O and $Zn_3(PO_4)_2$-H_3PO_4-H_2O aren't studied. Phase equilibrium in a system Fe_2O_3-P_2O_5-H_2O is established only, and this system has absolutely another composition with crystallization of iron (III) phosphates.

The system FeO-P_2O_5-H_2O is researched at temperature 70ºC in the interval of diluted solutions only (less than 5,54% FeO and 15,1% P_2O_5) forming amorphous products like $2FeO{\cdot}P_2O_5{\cdot}3H_2O$ in solid phase. Hence, information about solubility in the given system is limited and it doesn't correspond to conditions of process behavior.

Phase equilibrium in quaternary mutual systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O, as well as in quinary system $FeCl_2$-$ZnCl_2$-H_3PO_4-H_2O aren't studied. There isn't data about solubility and crystallization fields in given systems even at standard temperature.

In this connection, it is necessary to study the state diagrams of the above-mentioned four-component systems, which are the basis for the development of the theoretical foundations of technological processes occurring during the phosphoric acid processing of chloride sublimates.

METHODS

The solubility was studied by an isothermal method, the essence of which is to mix the solution at a constant temperature with an excess amount of solid phase until equilibrium is established. In the studied systems, chemical interaction of the initial reagents - a solution of phosphoric acid of a certain concentration and ferric (II) chloride proceeds until equilibrium is established in accordance with the reaction equation:

$$3FeCl_2 + 2H_3PO_4 = Fe_3(PO_4)_2 + 6HCl \quad (1)$$

Depending on the degree of saturation of the acid with the cation, one-, two-, or three-substituted phosphates are formed; however, in order to reach the saturation state and determine the equilibrium composition of the system at a certain temperature, it is necessary to introduce chlorides in an amount exceeding the stoichiometric rate for the indicated reactions.

The experiments were carried out in a thermostated reactor, equipped with a refrigerator, a mixer with a water seal and a thermometer. The temperature was maintained using a contact thermometer with an accuracy of +/- 0.5 ° C. Due to the release of hydrogen chloride as a result of the reaction, the process was carried out in a fume hood, and a reflux condenser and an absorber with cold water were used to remove the formed gas. Removal of gas from the reactor to the absorber is provided by connecting it to a water jet pump.

In a solution of phosphoric acid (chemical pure) of a certain concentration was added a portion of ferric chloride in an amount to saturate the solution with salt after the reaction, which is determined by the remaining excess salt in the solid phase. Upon reaching saturation every half hour using a thermostated sampler, samples were taken of the liquid phase for analysis on the content of chloride ions. About the time to reach equilibrium was judged by the constancy of the content of chloride ions in the last two or three selected samples. The content of chloride ions was determined by argentometric method.

Solubility was calculated on the basis of 3-4 parallel experiments results at allowable discrepancy less than 0.5% between two parallel analyses of liquid phase in every experiment. It is established experimentally that equilibrium in systems $FeCl_2$-H_3PO_4-H_2O is reached in 2.5 hours at any temperature [27]. Solubility is studied in phosphoric acid concentration interval from 5 to 55% of H_3PO_4 at temperatures 25, 60 and 80ºC. The last ones correspond to conditions of chloride sublimate processing.

RESULTS AND DISCUSSION

In order to construct solubility isotherms for mutual quaternary systems on flat square Yeneke diagram the ionic salt composition of the system is expressed in Yeneke indexes, which are determined on the basis of the equality of the sum of the number of moles of cations and anions. So for the system $FeCl_2$-H_3PO_4-H_2O the sum of cation moles $3Fe^{2+}$ (bounded as chlorides and phosphates in the solution) and $6H^+$ (bounded as phosphoric and hydrochloric acids) is to be equal to the sum of anion moles $6Cl^-$ and $2PO_4^{3-}$, are also in the composition of the corresponding salts and acids. Based on this, the ionic composition of the system at any point in the diagram is defined as the molar ratio of one of the anions to the sum of anions and the molar ratio of $6H^+$ to the sum of cations [28].

For this purpose, the data on the composition of the equilibrium system obtained as a result of the studies carried out are recalculated taking into account the proceeding chemical reaction (1). The content of chloride ions in the solution takes into account their presence both in the form of ferric chloride and hydrogen chloride, and the high content of these ions in dilute phosphoric acid solutions (5-15% H_3PO_4 at 25 °C) indicates that in equilibrium with a stable pair salts of $Fe_3(PO_4)_2$-6HCl is also a salt of $FeCl_2$, and H_3PO_4 is absent. For higher temperatures, the region of such a composition of the equilibrium system expands to 20 and 25% H_3PO_4 at 60 and 80 °C, respectively. In the $FeCl_2$-H_3PO_4-H_2O system, the temperature dependence is traced: with increasing temperature, the solubility increases, and the point of triple eutonics shifts to the area of higher concentrations.

Recalculation of the content of system components with regard to the reactions taking place shows that, starting from the inflection point, phosphoric acid is in equilibrium with a stable pair of salts up to the maximum concentration of this acid, which indicates a wide crystallization range of iron phosphates.

Next, we calculated the number of moles of compounds and the number of moles of individual ions in the composition of these compounds, and then the total number of moles of like ions. Based on the obtained data, the coordinates of the points on the solubility isotherms were calculated in accordance with the above method. The composition of the solid phase, equilibrium with the solution in the $FeCl_2$-H_3PO_4-H_2O system is given in table 1.

Table 1 - The composition of the solid phase, equilibrium with the solution in the $FeCl_2$-H_3PO_4-H_2O system

Composition of the initial acid,%	Content of P_2O_5/Cl^- in solid phase, %, at temperatures of			The composition of the equilibrium solid phase at temperatures of		
H_3PO_4	25ºC	60ºC	80ºC	25ºC	60ºC	80ºC
5	0/37,2	0/39,1	0/42,2	$FeCl_2 \cdot H_2O$	$FeCl_2 \cdot H_2O$	$FeCl_2 \cdot H_2O$
10	0/45,1	0/40,4	0/47,7	$FeCl_2 \cdot H_2O$	$FeCl_2$	$FeCl_2$
15	3,0/43,5	0/46,9	0/50,3	$FeCl_2$+ $Fe_3(PO_4)_2$	$FeCl_2$	$FeCl_2$
20	29,2/16,1	0/51,2	0/50,2	$FeCl_2$+ $Fe_3(PO_4)_2$	$FeCl_2$	$FeCl_2$
25	38,7/1,3	28,7/12,1	0/48,9	$FeCl_2$+$Fe_3(PO_4)_2$+ $FeHPO_4$	$FeCl_2$+ $Fe_3(PO_4)_2$	$FeCl_2$
30	50,3/0	42,0/0	27,7/10,4	$Fe_3(PO_4)_2$+ $FeHPO_4$	$Fe_3(PO_4)_2$+ $FeHPO_4$	$FeCl_2$+ $Fe_3(PO_4)_2$
35	51,9/0	52,1/0	40,9/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe_3(PO_4)_2$+ $FeHPO_4$
40	54,3/0	55,0/0	50,5/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$
45	53,8/0	53,5/0	53,7/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$
50	53,0/0	53,9/0	54,4/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$
55	54,1/0	54,0/0	53,1/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$

Applying certain compositions of saturated solutions (X_{PO4}, X_H) on the Jeneke diagram, we obtain the line of solubility isotherms in the studied system at temperatures of 25, 60 and 80ºC.

Based on the obtained data, salt crystallization fields were constructed in the studied system, taking into account the possible formation of one- and two-substituted iron phosphates, which compositions are indicated by points F_1 and F_2, respectively (Fig. 1).

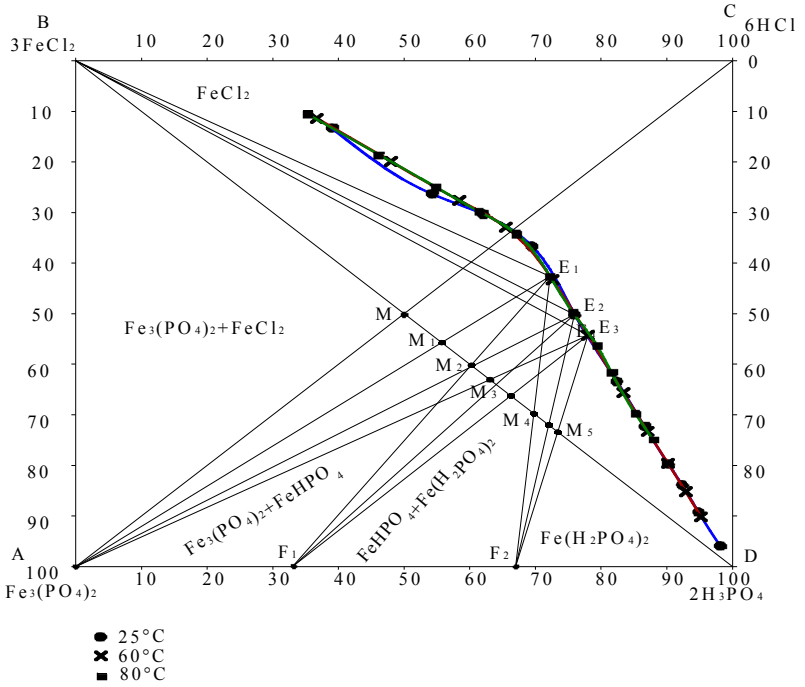

Figure 1 - Diagram of the $FeCl_2$-H_3PO_4-H_2O phase system

From Fig. 1 it is seen that in the $FeCl_2$-H_3PO_4-H_2O system, the displacement of triple eutonics, the increase in solubility and the expansion of the co-crystallization region of $Fe_3(PO_4)_2$ and $FeCl_2$ and $FeCl_2$ salts with increasing temperature are traced. The fields of crystallization of iron phosphate are reduced, which affects the choice of optimal conditions for obtaining monosubstituted iron phosphates. The points of the triple eutonic E_1, E_2 and E_3 are determined by the extreme point in the composition of the saturated solution at a given temperature and confirmed by the composition of the solid phase determined by the content of phosphate ions and chloride ions in it (Table 1).

According to the rule, the connecting direct process of the interaction of chlorides with phosphoric acid is depicted in the diagram by the BD line, connecting the composition points of the initial pure reagents [29]. At their equimolecular ratio, the figurative point of the composition of system M will be in the region of the joint crystallization of the $Fe_3(PO_4)_2$ and $FeCl_2$ salts, which does not allow to obtain the desired product in the solid phase. In order to achieve the maximum yield of the product, the initial reagents should be taken in such a ratio that the figurative point of the system composition is on the crystallization beam, connecting the point of the salt composition, for example, $Fe_3(PO_4)_2$, and the eutonic point corresponding to the process temperature - E_1, E_2 and E_3, determining the composition of the solutions, saturated simultaneously with three salts, for temperatures of 25, 60 and 80ºC, respectively. These are respectively points M_1, M_2 and M_3. In this case, the crystallization of the production salt occurs over a longer segment, which makes it possible to isolate the maximum amount of the product in the solid phase. For the formation of the target product - iron dihydrogen phosphate, the process must be carried out at such a ratio of initial compounds that the figurative point of the system composition is on the crystallization line of $Fe(H_2PO_4)_2$ salt connecting the points of their composition F1 and the eutonic point. In the case of carrying out the process at a temperature of 80 °C, the desired point M5 is located at the intersection of the line of interaction between the initial reagents and the crystallization beam F_1E_3, which ensures the maximum yield of the product.

In order to obtain the specified composition of the system, the consumption of phosphoric acid solution is determined according to the lever rule and, more precisely, by the method of compiling the material balance of the process [30]. As a result of its decision, the yield of the finished product, the $Fe(H_2PO_4)_2$ salt, is also determined.

The consumption of phosphoric acid is determined according to the diagram according to the lever rule as the ratio of the segments BM_5 and M_5D. For the $FeCl_2$-H_3PO_4-H_2O system, the excess acid ratio over the stoichiometric norm for the formation of monosubstituted phosphates is calculated as 98: 43 = 2.28. Then the consumption of a phosphoric acid solution, taking into account its concentration of 45% for the interaction with the initial 5 grams of chloride in accordance with the equation of reaction (1) is determined as (5·196:381)·2.28):0.45 = 13.02 g per reaction with iron chloride. Taking into account the density of the solution of a given concentration, equal to 1.293 g/cm^3, the volume flow of the phosphoric acid solution will be 13.02:1.293 = 10.07 cm^3. We will carry out a refined calculation of the optimal consumption of phosphoric acid for carrying out the reaction by preparing a complete and partial equation of the material balance of the process per unit mass of the initial chloride. The complete material balance equation for the process of the interaction of pure ferric chloride and phosphoric acid on the salt mass of the system is determined as follows:

$$1\ FeCl_2 + X\ H_3PO_4 = Y\ Fe(H_2PO_4)_2 + Z\ \text{solution}\ E_3 \qquad (2)$$

Substituting into the equation the composition of the solution E_3, calculated when constructing solubility isotherms for extreme points (table 2-4), we get:

$$1FeCl_2 + XH_3PO_4 = YFe(H_2PO_4)_2 + Z(0{,}426PO_4^{3-} + 0{,}574Cl^- + 0{,}772H^+ + 0{,}228Fe^{2+}) \qquad (3)$$

Table 2 - Results of the recalculation of data by Jeneke at 25 °C

The initial system 25°C		The composition of the solution in the equilibrium system, %				The number of moles of components			
H_3PO_4	$FeCl_2$	$Fe_3(PO_4)_2$	6HCl	$3FeCl_2$	$2H_3PO_4$	$Fe_3(PO_4)_2$	6HCl	$3FeCl_2$	$2H_3PO_4$
5	29,71	-	5,59	43,43	0	0,0255	0,0255	0,114	-
10	23,54	9,13	11,17	22,67	0	0,0510	0,051	0,0595	-
15	23,54	-	16,76	12,95	0	0,07654	0,07653	0,03399	-
20	21,07	27,40	21,66	0	0,62	0,09891	0,0989	-	0,00316
25	18,58	35,41	19,10	0	7,90	0,08723	0,0872	-	0,04031
30	14,87	24,99	15,29	0	16,32	0,0698	0,0698	-	0,0833
35	12,39	20,82	12,74	0	23,60	0,05816	0,05817	-	0,1204
40	9,91	16,66	10,19	0	30,88	0,04654	0,0465	-	0,1576
45	8,67	14,57	8,92	0	37,02	0,0407	0,0407	-	0,1889
50	6,19	10,41	6,37	0	44,30	0,0291	0,0291	-	0,226
55	2,48	4,16	2,55	0	52,72	0,01162	0,01164	-	0,269

Table 3 - Results of recalculation of data by Jeneke at 60 ° C

The initial system 60°C		The composition of the solution in the equilibrium system, %				The number of moles of components			
H_3PO_4	$FeCl_2$	$Fe_3(PO_4)_2$	6HCl	$3FeCl_2$	$2H_3PO_4$	$Fe_3(PO_4)_2$	6HCl	$3FeCl_2$	$2H_3PO_4$
5	35,93	9,13	5,59	54,55	-	0,0255	0,0255	0,143	-
10	33,45	18,26	11,17	40,40	-	0,051	0,051	0,106	-
15	28,50	27,40	16,76	21,81	-	0,0765	0,0765	0,0572	-
20	26,02	36,53	22,35	7,66	-	0,102	0,102	0,0201	-
25	22,30	37,48	22,93	-	4,48	0,105	0,105	-	0,0229
30	19,82	33,32	20,38	-	11,76	0,093	0,093	-	0,060
35	16,11	27,07	16,56	-	20,18	0,0756	0,0756	-	0,103
40	13,63	22,91	14,01	-	27,46	0,064	0,064	-	0,140
45	11,20	18,82	11,51	-	34,70	0,0526	0,0526	-	0,177
50	8,68	14,57	8,92	-	42,02	0,0407	0,0407	-	0,214
55	6,19	10,40	6,37	-	49,30	0,0291	0,0291	-	0,252

Table 4 - Results of recalculation of data by Jeneke at 80 ° C

The initial system 80°C		The composition of the solution in the equilibrium system, %				The number of moles of components			
H_3PO_4	$FeCl_2$	$Fe_3(PO_4)_2$	6HCl	$3FeCl_2$	$2H_3PO_4$	$Fe_3(PO_4)_2$	6HCl	$3FeCl_2$	$2H_3PO_4$
5	39,65	9,13	5,59	61,20	-	0,0255	0,0255	0,161	-
10	37,17	18,26	11,17	47,05	-	0,051	0,051	0,125	-
15	34,69	27,40	16,76	32,90	-	0,0765	0,0765	0,0864	-
20	32,34	36,53	22,35	18,97	-	0,102	0,102	0,0498	-
25	29,74	45,66	27,93	4,59	-	0,128	0,128	0,012	-
30	27,26	45,82	28,03	-	4,92	0,128	0,128	-	0,025
35	26,12	43,91	26,86	-	10,96	0,123	0,123	-	0,056
40	24,78	41,65	25,48	-	17,20	0,116	0,116	-	0,088
45	23,54	39,57	24,20	-	23,34	0,111	0,111	-	0,119
50	19,82	33,32	20,38	-	31,76	0,093	0,093	-	0,162
55	17,35	29,16	17,84	-	39,04	0,081	0,081	-	0,199

Next, we compose the partial equations for the individual components - ions, taking into account their mass fraction in the anhydrous compound, and solve them with respect to the unknowns:

$$\text{By } Fe^{2+}: 1\cdot 0{,}441 = Y\cdot 0{,}224 + Z\cdot 0{,}228 \quad (4)$$

$$\text{By } Cl^{-}: 1\cdot 0{,}559 = Z\cdot 0{,}574 \quad (5)$$

$$\text{By } PO_4^{3-}: X\cdot 0{,}969 = Y\cdot 0{,}776 + Z\cdot 0{,}426 \quad (6)$$

Hence the mass of the eutonic solution E_3 is Z = 0.974; the mass of production dihydrogen phosphate of iron is Y = 0,977; mass of phosphoric acid is X = 1.210 per unit mass of $FeCl_2$, or 2.69 in terms of 45% phosphoric acid. On 5 grams of this reagent, the consumption of the acid solution will be 13.44 g, and taking into account its density, 13.44: 1.293 = 10.4 cm^3, which is slightly more than the volume flow, calculated using the lever rule.

Conclusion

Thus, the optimal consumption of a phosphoric acid solution to obtain a specified product from a unit mass (1 kg) of iron chloride — 2.69 kg was determined. The maximum possible yield of the finished product in these conditions of the process from a unit mass of iron chloride - 0.977 is also established. Also, the studied phase diagram of the $FeCl_2$-H_3PO_4-H_2O system at temperatures of 25, 60 and 80ºC represents new scientific data on solubility in reciprocal four-component systems, which significantly expand the area of knowledge in the physico-chemical analysis of multicomponent systems and provide a theoretical basis for the analysis and justification of the optimal conditions of the processes occurring in the studied systems.

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ТӨРТ КОМПОНЕНТТІ ЖҮЙЕЛЕРДІҢ ФАЗАЛЫҚ ТЕПЕ-ТЕҢДІГІ НЕГІЗІНДЕ ТЕМІР ФОСФАТЫН АЛУ ҮРДІСІН ЗЕРТТЕУ

Аннотация: Бұл мақалада өзара әрекеттесетін төрт компонентті жүйелердегі фазалық тепе-теңдігі туралы әдебиеттік мәліметтердің талдауы келтірілген, сонымен қатар фосфор қышқылының шоғыры 5 және 55% H_3PO_4 аралығында 25, 60 және 80ºС температураларда $FeCl_2$-H_3PO_4-H_2O жүйесінің ерігіштігі қарастырылған.

Сондай-ақ зерттеліп отырған жүйеде бір немесе екі негізді темір фосфатының түзілуін ескере отырып, тұздардың кристалдану алаңдарын тұрғызудың есептік мәліметтері келтірілген. Аталған өнімді алу үшін қажетті фосфор қышқылының тиімді шығыны анықталған. Сонымен қатар, үрдістерді жүргізудің берілген шарттарында темір хлоридінің бір бірлігінен дайын өнімнің мүмкін максималды шығымы тағайындалған.

Фосфор қышқылының шығыны диаграмма бойынша иінтірек ережесіне сәйкес, BM_5 және M_5D кесінділерінің қатынасы ретінде анықталды. $FeCl_2$-H_3PO_4-H_2O жүйесі үшін бір орын басқан фосфаттардың түзілуіне стехиометриялық нормадан жоғары қышқылдың артық мөлшерінің коэффициенті есептелді.

Түйін сөздер: Көп компонентті жүйе, фазалық тепе-теңдіктер, фазалық диаграммалары, фосфаттау, изотермиялық әдіс, Йенеке диаграммасы.

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ИЗУЧЕНИЕ ПРОЦЕССА ПОЛУЧЕНИЯ ФОСФАТА ЖЕЛЕЗА НА ОСНОВЕ ФАЗОВЫХ РАВНОВЕСИИ ЧЕТЫРЕХКОМПОНЕНТНЫХ СИСТЕМ

Аннотация: В данной статье приведен анализ литературных сведений по фазовым равновесиям в четырехкомпонентных взаимных системах, также изучена растворимость системы $FeCl_2$-H_3PO_4-H_2O в интервале концентраций фосфорной кислоты от 5 до 55% H_3PO_4 при температурах 25, 60 и 80ºС.

Приведены расчетные данные по построению полей кристаллизации солей в изучаемой системе с учетом возможного образования одно- и двухзамещенных фосфатов железа. Определено оптимальный расход раствора фосфорной кислоты на получение заданного продукта. Установлен также максимально возможный выход готового продукта в данных условиях проведения процесса из единицы массы хлорида железа.

Расход фосфорной кислоты определяли по диаграмме согласно правилу рычага как отношение отрезков BM_5 и M_5D. Рассчитывали коэффициент избытка кислоты сверх стехиометрической нормы для образования однозамещенных фосфатов для системы $FeCl_2$-H_3PO_4-H_2O.

Ключевые слова: многокомпонентая система, фазовое равновесие, фазовые диаграммы, фосфатирование, изотермический метод, диаграмма Йенеке

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Pt- AND Pd-CATALYSTS ON MODIFIED KAOLINITES IN THE REACTION OF N-HEXANE ISOMERIZATION

Abstract. The article presents the data on synthesis and properties of Pt and Pd catalysts supported on modified Ti^{4+} and Zr^{4+} kaolinites of two of Kazakhstan fields- Sarymsak, Ermakov (KS and KE), their catalytic activity in n-hexane isomerization, depending on temperature and composition of the catalyst. The elemental and phase composition of the synthesized catalysts, as well as their textural properties, are determined. It was indicated that the studied catalysts showed high activity and selectivity in the reaction isomerization of n-hexane with formation of mono- and disubstituted isohexanes and isoheptanes. The Pt catalysts supported on modified Zr^{4+} and Ti^{4+} kaolinites were exhibit higher isomerization activity compared to Pd-catalysts. Maximum conversion of n-hexane, equal to 43.2% and a yield of $C_6 + C_7$ isomers of 36.0% with selectivity for isomers of 93.3%, was observed on 0.35% Pt / Zr (5.0) HKS catalyst at 400 °C which can be recommended for further improvement.

Keywords: kaolinite, platinum, palladium, n-hexane, isomerization, selectivity, isomer yield, mono- and disubstituted isohexanes.

Introduction. Among the most important minerals are clays, which are widely used in various industries, agriculture and medicine [1]. It is known that the bentonite clays themselves are natural catalysts widely used in various refining processes [2, 3]. A characteristic feature of aluminosilicate catalysts (natural and synthetic) are their acidic properties. It is established that the catalyst activity increases with increasing the acidity.

Currently, montmorillonite (MM) - a natural layered aluminosilicate, is being successfully used in matrix of the cracking catalysts in Russia [4]. In addition to participating in formation of porous structure of the catalyst and primary cracking of hydrocarbon molecules of the raw material, MM provides mechanical strength of the catalyst and removal of the heat from the zeolite crystals, helping to preserve its structure and catalytic activity. Modification of MM allows you to optimize its properties for use in the composition of cracking catalysts. In industrial practice, the ion exchange method is used to remove sodium from MM, which negatively affects on activity and stability of the catalyst. Intercalation of MM with oxides of various metals (Al_2O_3, ZrO_2) allows to obtain microporous materials with comparable in structure and acidity of zeolites [5]. It is possible to use methods of influencing the dispersion of MM, for example, ultrasonic processing, since dispersity of the components is important for the formation of porous structure of the catalyst and its mechanical properties [6]. Since indirect indicator of the sorption and catalytic activity of the minerals is value of their exchange capacity, not only the clay minerals, montmorillonite, hydromica, kaolinite and others can be catalysts for the process of organic matter conversion. Clay is a binder in the production of zeolite catalysts, which have found wide application in petrochemistry and oil refining. In addition to improving the strength properties of the catalyst during its transportation and operation, clays also affect chemistry of the processes [7]. By changing amount and composition of the clay binder, you can directly influence selectivity of the contact. It was established that zeolite Y synthesized from kaolin with modulus 4.9 after exchanging 60% Na^+ for H* in it has a high catalytic activity in the reaction of oligomerization of α-octene [8].

Kazakhstan has sufficient reserves of bentonite clays [9], which are widely developed in Kazakhstan. The greatest practical interests are the fields of Southern and Eastern Kazakhstan. In South Kazakhstan, these are the Darbazin and Kelesk deposits with total reserves of 58 million tons, as well as the Andreev, Dzerzhin, Ildersay with total reserves of more than 100 million tons. In East Kazakhstan, the Manrak group of bentonite clay deposits is known with a total estimated resource of about 50 million tons. The high quality of bentonite is allocated Tagan (10.6 million tons) and Dinosaur (about 4 million tons) deposits [10]. Of particular importance is the use of bentonite clays and synthetic zeolites as contacts and carriers for various processes, since they are characterized by a developed surface, porosity and high adsorption capacity.

Kaolinite - a clay mineral from the group of aqueous aluminum silicates. The chemical composition of $Al_4[Si_4O_{10}]$ $(OH)_8$ contains 39.5% Al_2O_3, 46.5% SiO_2 and 14% H_2O. Kaolinite is a widespread clay mineral, the composition of aqueous aluminosilicate (monoclinic), has a layered structure, in nature it occurs in the form of hexagonal or irregular-shaped scales about 1 micron in size. The crystalline structure of kaolinite is based on infinite sheets of Si – O_4 tetrahedral having three common oxygen and connected in pairs through free tops with aluminum and hydroxide [11]. Syntheses of highly dispersed and granulated zeolite types of LTA and FAU without binders, which are based on crystallization of metakaolin in solutions of sodium hydroxide and sodium silicate, respectively, have been developed [12, 13].

Modification of layered silicates with a rigid structural cell, which kaolinites are attributed due to the strong hydrogen bonding of individual layers of kaolinite to each other, makes it possible to synthesize a new generation of three-dimensional microporous structures with high specific surface (up to 240 m^2/g) and a significant increase in acid sites due to surface silanol groups [14]. The introduction of catalytically active metals (Pt, Pd, Ni) into the layered structure silicates are leads to the formation of redox centers on the surface, which allows them to act simultaneously as acid and oxidative catalysts [15,16]. Studies conducted previously at the Institute of Organic Catalysis and Electrochemistry named after D.V. Sokolsky using Tagan montmorillonite, which pillared with aluminum and zirconium, showed perspective use of layered clays in the processes of hydrocarbon conversion [17-19]. Previously, with the use of XRD, IR spectroscopy, EPR, we studied the physicochemical properties of Ermak layered kaolinites (KE) and Sarymsak (KS) deposits of Kazakhstan [20]. It has been established that the studied clays along with kaolinite contain montmorillonite, quartz, cristobalite and muscovite impurities. The pore size in the original kaolinites varies between 12-60Å, and most of them are mesopores. Acid treatment of KE and KS contributes to the expansion of the area of mesopores and the growth of their number.

The purpose of this report is to create isomerization catalysts for light n-alkanes based on the modified Ti and Zr natural kaolinites of the Ermak and Sarymsak deposits to produce environmentally friendly high-octane additives to motor fuels.

Experimental part

Methods have been developed for modifying the activated forms of the Sarymsak and Ermak kaolinites (HKS and HKE) with Zr^{4+}, Ti^{4+} cations using $ZrOCl_2$ and $TiCl_4$.

Modified kaolinites of the Sarymsak and Ermak deposits were studied by elemental and X-ray phase analysis (XRF), BET, electron microscopy. Elemental analysis of the samples was performed using an electronic micro analyzer Superprobe 733, Geol (Japan). The synthesized modified clays were studied by X-ray diffraction (XRD) using DRON 4 * 0.7 with CoKα radiation. The specific surface area, pore volume, and pore size distribution were determined by the BET method using low-temperature N_2 adsorption at 77 K (ACCUSORB).

Pt (0.35 wt. %) from H_2PtCl_6 was supported onto the modified kaolinites by impregnation method, followed by washing out of chlorine ions, drying and calcining.

The isomerization reaction was carried out in a flow-type installation in a hydrogen atmosphere and temperatures of 250-400 °C, a molar ratio of H_2:C_6H_{14} = 3.5, and a space velocity of n-hexane - 0.82 h^{-1}. Liquid products were analyzed by GLC with a Tsvet chromatograph on a 120-m capillary column. The analysis of gas phase was carried out with an LHM chromatograph on an alumina-packed column. The yield of isomers was accepted as activity of the catalysts.

Result and discussions

The elemental and phase composition of initial, activated and modified kaolinite of Pavlodar deposits was determined by XRD method. The main reflexes of the Sarymsak and Ermak kaolinites (KS and KE) are retained when activated by acid and modifying with Zr^{4+} and Ti^{4+}, while the content of alkaline components of clay (Na_2O, K_2O, MgO) decreases, and reflections of the corresponding oxides appear on the diffractograms: ZrO_2; TiO_2 (anatase) (Table 1, Figure 1). The amount of ZrO_2 in Yermak kaolinite after introduction of ZrO_2 is 4.30%, in Sarymsak -2.41%.

The modification of titanium and zirconium oxides by kaolinites of the Sarymsak and Ermak deposits leads to a decrease in the content of not only oxides of alkali and alkaline earth metals, but also oxides of Fe_2O_3, Al_2O_3 and SiO_2. The ratio of SiO_2/Al_2O_3 with the introduction of TiO_2 increases from 4.4 to 4.6 in the case of HKE and from 4.4 to 4.8 for HKS (Table 1). According to the analysis, amount of TiO_2 increases from 0.4 and 0.6% in the initial kaolinite KS and KE to 36.65 and 34.54%, respectively, after treatment with a solution of titanium oxochloride.

Table 1 - Composition of acid-activated and pillared Zr and Ti clays from the Sarymsak and Ermak deposits

Sample	Quantity, wt.%										Σ,%
	Na_2O	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	K_2O	TiO_2	SO_3	ZrO_2	
KS	1.0	2.5	27.0	60.0	0.8	5.0	3.0	0.4			
HKS	1.11	1.32	16.36	72.08	0.33	4.48	3.16	1.07			100
Zr(7.5)HKS	1.02	0.98	18.59	68.81	0.26	3.59	3.31	1.04		2.41	100
Ti(7.5)HKS	0.61	0.66	10.16	48.54	0.55	2.91	2.02	34.54	-		100
KE	0.8	3.0	15.0	>60.0	3.0	6.0	1.5	0.6			
HKE	0.60	1.18	16.41	71.91	0.33	5.95	2.39	0.97	0.25		100
Zr(7.5)HKE	0.74	0.94	14.93	70.04	0.18	5.69	2.29	0.89		4.30	100
Ti(7.5)HKE	0.33	0.88	9.96	46.02	1.28	3.23	1.66	36.65	-		100

According to the XRF data, the Sarymsak and Ermak clays are among the kaolinite clays. The clearest reflexes of the original Sarymsak and Ermak clays belong to the phases: α-quartz, montmorillonite, kaolinite, and muscovite (Fig. 1). The main reflexes of kaolinites in these two clays are the same, therefore, Fig. 1 shows the diffraction pattern of Ermak kaolinite, and the XRD of the Sarymsak kaolinite is shown earlier in [20].

Intensity, (o.e.)

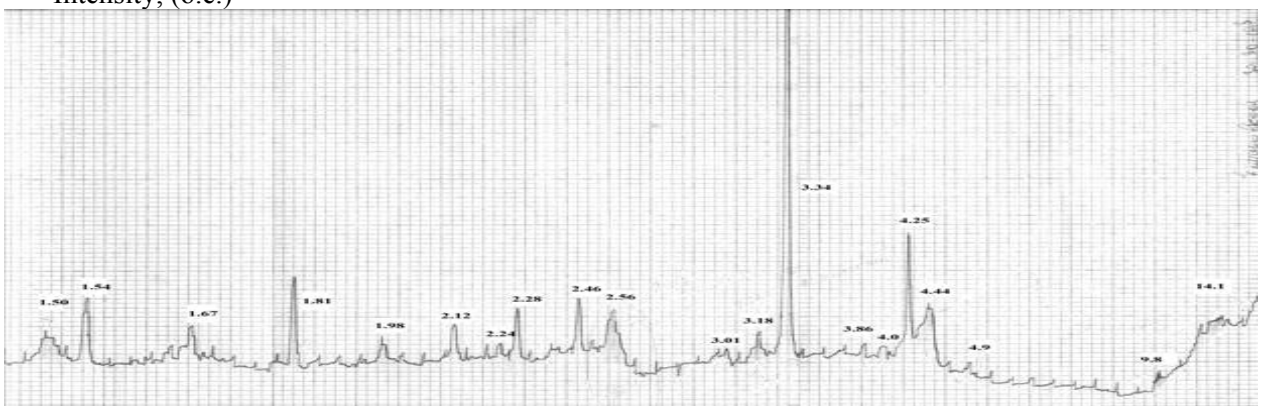

Figure 1 - Diffractogram of the original Ermakov kaolinite (KE)

The defining reflexes in kaolinite are: 7.01-7.02; 3.58-3.60; 3.15-3.18Å. The content of montmorillonite in kaolinites is determined by reflexes: 14.2; 4.44; 1.5Å. The 3.34Å reflex is quartz, and the low-intensity reflexes are 9.80-9.82Å and 4.9Å are the admixtures of muscovite. Acid treatment leads to partial destruction of the structures of kaolinite, muscovite, monorillonite, which is manifested in a decrease in the intensity of reflexes.

The diffractograms of HKE and HKS kaolinites treated with Ti^{4+}, Zr^{4+} ions are almost unchanged compared with the H – form of kaolinite. For illustration, Fig.2 shows the diffractogram of Zr (2.5) HKE.

The main reflexes of KS and KE are preserved when activated by acid and modified with Zr^{4+}, Ti^{4+} ions, while the content of alkaline components of clay (Na_2O, K_2O, CaO) decreases and reflections of the corresponding oxides appear on the diffraction patterns: ZrO_2; TiO_2 (anatase). The appearance of these oxides is also confirmed by the results of elemental analysis (Table 1).

Intensity, (o.e.)

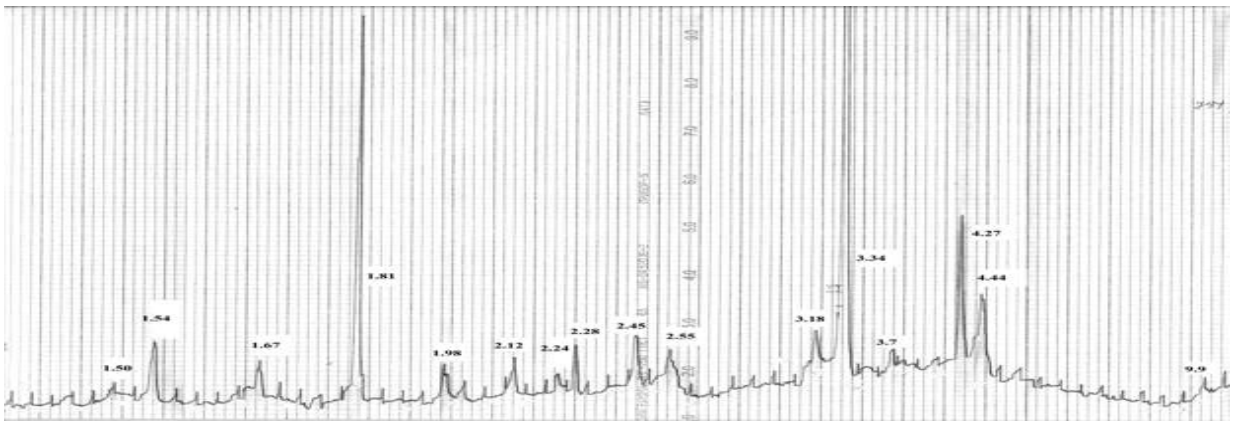

Figure 2 - Diffractogram of modified Zirconium oxide the activated Yermakov kaolinite Zr (2.5) HKE

Textural characteristics of the Ermak and Sarymsak kaolinites change significantly with the introduction of ZrO_2 and TiO_2 into the composition of kaolinites (Table 2, Figure 3). The total pore volume and average pore diameter increase with transition from initial to the modified samples. The original KS sample is characterized by a relatively wide set of pores with radius of 10–80Å. The maximum number of pores has radius of 40–80 Å, less than 10–30 Å. Acid treatment reduces the number of micropores, while the number of pores with a diameter of 20 - 80 Å increases to 91.6%. In modified Ti^{4+} samples, the effective pore radius are 12.5–50.0 Å. Thus, the modified KS samples are more uniform and more porous than the original clay.

Table 2 - Changes in specific surface area, pore volume, and pore size distribution with an increase the content of Zr and Ti in HKE and HKS

Sample	S, $м^2/г$	Total pore volume, cm^3 / g	Relative content, pores,%	
			Micro -(<20Å)	Mezo -(20-80Å)
KE	92.1	0.287	10.8	89.2
HKE	177.3	0.240	22.8	77.2
Zr(2.5)HKE	135.7	0.147	14.8	85.2
Zr(5.0)HKE	150.9	0.128	37.1	62.9
Zr(7.5)HKE	127.8	0.120	48.5	51.5
Ti (2.5)HKE	150.7	0.298	16.0	84.0
Ti (5.0) NKE	137.4	0.295	19.0	81.0
Ti (7.5) HKE	136.3	0.318	10.0	90.0
KS	49.1	0.119	25.0	74.9
HKS	73.6	0.345	8.4	91.6
Ti (2.5) HKS	123.6	0.203	18.0	82.0
Ti (5.0) HKS	145.0	0.314	7.0	93.0
Ti (7.5) HKS	156.5	0.288	13.0	87.0

Ermak kaolinite has a stable porous structure. Acid treatment and pillaring lead to a slight increase in the specific surface area and proportion of mesopores. Acid activation and modification of Zr leads to a significant increase in the specific surface area of HKE-177.3-127.8 m^2/g (Table 2). The relative content of micropores increases to 48.5% for Zr (7.5) HKE compared to 10.8% for the original kaolinite. The content of mesopores in the modified Zr catalyst decreases from 89.2 to 51.5%.

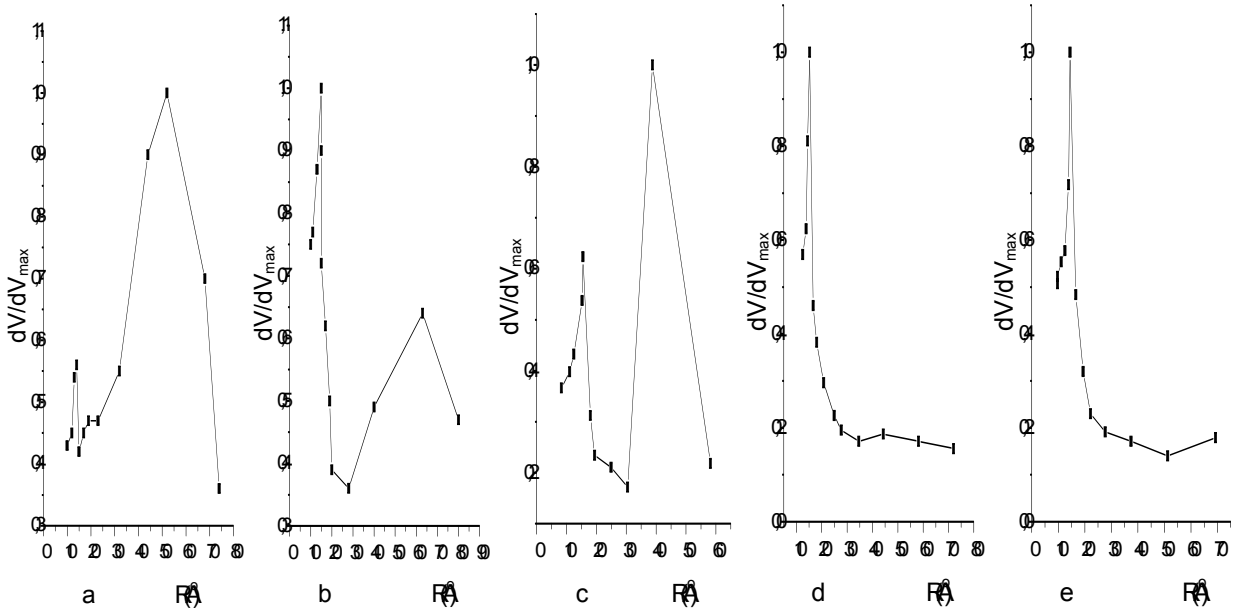

Figure 3 - Pore size distribution in KE kaolinites: a) KE; b) HKE; c) Zr (2.5) HKE; d) Zr (5.0) HKE; e) Zr (7.5) HKE

With introduction of TiO_2 into the composition of kaolinites, a significant change in textural characteristics of the original clays is observed, which is associated with a significant decrease in number of micropores and corresponding increase in number of mesopores as compared results on samples modified with Zr^{4+}.

The isomerizing activity of Pt and Pd catalysts supported on Zr pillared kaolinite from the Yermak field (ZrHKE) are depends on the content of Zr in the carrier and temperature (Table 3). Conversion of n-hexane on the Pt/Zr (2.5) HKE-catalyst is decreases from 18.7 to 15.1% with an increase in temperature from 250 to 400 °C. At this catalyst at all temperatures only C_6, C_7-isomers are formed. The C_6 isomer selectivity decreases with increasing temperature due to the presence of isobutane in the products. With an increase in content of Zr in the HKE to 7.5 mmol/g, the conversion of n-hexane in the temperature range 250-350 °C varies a little, but appeared small amounts of gaseous C_1-C_4 hydrocarbons, which are in the products of disproportionation and hydrocracking reaction.

Table 3 - Isomerization of n-hexane on the Pt-and Pd-catalysts supported on ZrHKE with different zirconium contents

The amount of Zr, mmol / g	T,°C	α,%	S_{C4+}	S_{C6}	Products, wt.%						
					ΣC_1-C_3	Iso-C_4	Iso-C_5	2,2-DMB	2-MPEN	3-MPEN	Iso-C_7
Pt/2.5	250	18.7	100	87.7	-	-	-	-	13.7	2.7	2.3
	300	13.2	100	84.1	-	-	-	-	8.7	2.4	2.1
	350	16.1	100	88.2					11.6	2.6	1.9
	400	15.1	100	77.5		1.3		2.8	5.1	3.8	2.1
Pt/7.5	250	14.2	100	84.5	-	-	-	-	9.5	2.5	2.2
	300	12.4	95.2	68.5	0.6	0.9	0.6	1.6	4.7	2.2	1.8
	350	15	94	55.3	0.9	2.0	1.3	1.5	3.5	3.3	2.5
	400	34.9	94.8	63.3	1.8	3.5	5.2	0.8	16.7	4.6	2.3
Pd/2.5	250	9.0	100	71.1					3.5	2.9	2.6
	300	15.7	100	77.7		0.9			9.3	2.9	2.6
	350	15.4	94.2	57.8	0.9	1.4	1.4	1.6	4.1	3.2	2.8
	400	22.2	95.5	69.4	1.0	1.6	2.4	1.9	8.1	5.4	1.8
Pd/7.5	250	10.5	100	81.0					6.0	2.5	2.0
	300	12.0	100	70.8		1.3			6.0	2.5	2.2
	350	15.4	94.8	62.3	0.8	1.2	1.3	1.4	4.9	3.6	2.2
	400	20.2	88.1	64.5	2.4	0.2	2.9	0.7	7.3	5.0	1.7

The maximum conversion of n-hexane on the Pt/Zr (7.5) HKE was observed at 400° C (34.9%). Under these conditions, the selectivity for C_6 and C_{4+} isomers is 63.3 and 94.8%, respectively. Close patterns of effect of the temperature and Zr content on the isomerization activity are also observed on the Pd/Zr (7.5) HKE catalyst at 400 °C (Table 3).

Tests of Pt and Pd catalysts deposited on Zr pillared kaolinite from the Sarymsak deposit (ZrHKS) showed (Table 4) that the isomerizing activity of these catalysts is significantly higher than Pt and Pd catalysts on ZrHKE (Table 3).

Table 4 - Isomerization of n-hexane on the Pt catalysts supported on ZrHKS with different zirconium contents

Amount of Zr, mmol / g clay	T,°C	α,%	S_{C4+}	S_{C6}	The composition of products, wt.%						
					ΣC_1-C_3	Iso-C_4	Iso-C_5	2.2-DMB	2-MPEN	3-MPEN	Iso-C_7
Pt/2.5	250	14.3	100	88.1	-	-	-	-	10.3	2.3	1.7
	300	7.7	93.5	72.7	0.5	-	-	-	3.5	2.1	1.6
	350	15.2	93.4	57.9	1.0	0.9	2.7	0.5	4.9	3.4	1.8
	400	22.7	95.6	61.7	1.0	1.4	3.0	0.5	8.3	5.2	3.3
Pt/5.0	250	29.0	100	100	-	-	-	-	13.9	15.1	
	300	33.9	100	73.7	-	-	-	-	13.9	11.1	8.9
	350	40.5	100	78.0	-	3.2	-	3.9	7.4	20.3	5.7
	400	43.2	93.3	71.1	2.9	5.2	-	3.1	21.6	6.0	4.4
Pt/7.5	250	9.6	100	78.1	-	-	-	-	5.1	2.4	2.1
	300	8.9	95.5	71.9	0.4	0.4	-	0.4	4.0	2.0	1.7
	350	27.5	94.9	72.7	1.4	3.8	-	1.3	5.3	13.4	2.3
	400	36.9	98.4	70.7	0.6	1.1	4.2	3.4	7.1	15.6	4.9

On the Pt/ZrHKS catalysts with different Zr content, conversion of n-hexane increases with increasing temperature, and the selectivity for C_6 and C_{4+} isomers decreases. The best results on isomerizing activity were obtained on a Pt catalyst supported on ZrHKS with a content of Zr = 5.0 mmol / g. The conversion of n-hexane on this catalyst at 400 °C is 43.2% with a selectivity for isomers of 93.3%, and the yield of isohexanes is 30.7%. It should be noted that on the Pt / Zr (5.0) HKS catalyst in the temperature range 250-350° C, the conversion of n-hexane increases from 29.0% to 40.5% with 100% selectivity for isomers. The gaseous products of n-hexane hydrocracking on this catalyst appear only at 400 ° C. On Pt catalysts deposited on kaolinites with a large (7.5) Zr content, 100% isomer selectivity is observed only at 250° C, and at higher temperatures, the isomer selectivity decreases due to the appearance of gaseous hydrocarbons in the reaction products.

Regularities of effect of the temperature and amount of zirconium modified kaolinite HKS on speed and direction of the process of isomerization of n-hexane on Pd / ZrHKS catalysts (Table 5) are close to those found on Pt / ZrHKS catalysts (Table 4), but selectivity of overall isomers and isohexanes are significantly higher on Pd catalysts compared to results on Pt catalysts. The maximum yield of isohexanes, equal to 31%, was also obtained on a Pd catalyst supported on Zr (5.0) HKS, at 400 °C. The conversion of n-hexane on this catalyst is ~ 5% lower than on the Pt catalyst, however, the yield of isohexanes is slightly higher, due to the higher isomer selectivity. The yield of gaseous C_1-C_3-hydrocarbons on the Pd-catalyst is reduced to 0.5% compared with 2.9% in the same conditions on the Pt-catalyst (Table 4). On a Pd catalyst supported on Zr (7.5) HKS, the conversion of n-hexane varies from 8.3-20.1% depending on the temperature, while the selectivity for all isomers is 100%, and as a result of the reaction mainly 2- and 3-methylpentanes and small amounts (1.5-2.3%) of isoheptanes are formed.

Catalysts based on activated titanium-modified kaolin clay were also tested in the isomerization of n-hexane at various temperatures. For this purpose, catalysts with the composition of 0.35% Pt/Ti (2.5) HKE, Pt/Ti (2.5) HKS, Pd/Ti (2.5) HKE, Pd/Ti (2.5) HKS were prepared. Data on the activity and composition of products resulting from the hydroconversion of n-hexane on Pt- and Pd/Ti HKE catalysts are presented in Table 6 and Fig. 4 and 5.

Table 5 - Isomerization of n-hexane on the Pd-catalysts supported on ZrHKS with different zirconium contents

Amount of Zr, mmol / g clay	T, ^{o}C	α,%	S_{C4+}	S_{C6}	The composition of products, wt.%						
					ΣC_1-C_3	Iso-C_4	Iso -C_5	2,2-DMB	2-MPEN	3-MPEN	Iso - C_7
Pd/2.5	250	9.8	100	67.3	-	1.3	-	-	4.2	2.4	1.9
	300	10.8	100	85.2	-	-	-	3.2	4.1	1.9	1.6
	350	15.2	93.4	77.6	1.0	0.7	-	2.8	6.9	2.1	1.7
	400	28.6	98.3	78.3	0.5	0.5	2.5	1.8	17.5	3.1	2.7
Pd/5.0	250	12.3	100	90.2	-	-	-	1.3	5.6	4.2	1.2
	300	19.5	100	85.1	-	1.1	-	3.1	8.3	5.2	1.8
	350	32.8	100	88.4	-	1.3	-	4.7	16.5	7.8	2.5
	400	38.3	98.7	80.9	0.5	3.2	1.2	5.6	17.1	8.3	2.4
Pd/7.5	250	10.1	100	79.2	-	-	-	-	5.5	2.5	2.1
	300	8.3	100	78.3	-	-	-	-	4.4	2.1	1.8
	350	20.0	100	92.5	-	-	-	-	16.7	1.8	1.5
	400	20.1	100	86.6	-	0.4	-	-	15.2	2.2	2.3

Table 6 - Isomerization of n-hexane on Pt- and Pd/Ti (2.5) HKE – catalysts

Catalyst	T T^{o},C, ^{0}C	α, %	S_{C4+}, %	S_{C6}, %	The yield of reaction products,%						
					C_1-C_3	Iso-C_4	n-C_5	2,2-DMB	2MP	3MP	Iso- C_7
Pt/Ti(2.5)HKE	250	25.0	99.4	98.1	0.5	0	0.1	-	8.5	10.1	0
	300	21.6	99.3	97.8	0	0	0.1	0.1	8.7	12.3	0.1
	350	13.0	98.6	95.8	0	0	0.2	0.1	10.0	2.3	0.1
	400	10.4	99.7	94.9	0	0	0.1	0.4	8.1	1.4	0.2
Pd/Ti(2.5/HKE	250	25.7	100	85.7	0	0	0	0	18.4	3.6	2.7
	300	15.2	81.8	70.9	0	0	2.7	0	4.2	6.6	1.5
	350	10.5	82.2	52.4	0.6	0.6	1.2	0	3.1	2.4	1.8
	400	15.4	81.5	55.6	0.7	0.7	2.2	0	5.5	3.0	2.0

The n-hexane conversion on Pt/Ti HKE catalyst is decreases with increasing temperature, selectivity to isomers at all temperatures remains high (98.6 - 99.7%). The maximum conversion of n-hexane is observed at 250°C and equal to 25.0 %. At 400°C, the conversion is reduced to 10.4% with selectivity for all isomers of 99.7%. No hydrocracking products were detected on this catalyst in the temperature range of 350-400 °C. The 2- and 3-methylpentanes and small amounts of 2,2-DMB, n-pentane and isoheptanes are formed from n-hexane.

On the catalyst Pd/Ti HKE at 250 °C, the conversion of n-hexane is maintained at 25.7% with a selectivity of 100% for isomers (Table 6). With increasing temperature decrease in the conversion of n-hexane is observed with a simultaneous decrease in selectivity for all isomers and C_6 - isomers (Table 6, Fig. 5). Thus, the selectivity of Pd/TiHKE-catalyst on C_{4+} decreases from 100% at 250 °C to 81.5% at 400 °C, while on the Pt/TiHKE catalyst the selectivity for C_{4+} does not change. A similar pattern was observed on the effect of temperature on the selectivity of Pt and Pd catalysts for isohexanes (S_{C6}). On Pt/TiHKE, the isohexane selectivity decreases from 98.1% at 250 °C to 95.0% at 400 °C, while on Pd/TiHKE, the isomer selectivity decreases from 85.7% at 250 °C to 55.6% at 400 °C (fig. 4 and 5). Isohexanes, small amounts of isoheptane (2,4-dimethylpentane), n-pentane were detected in the reaction products, and gaseous C_1-C_3 - hydrocarbons appeared at 350 and 400 °C. The absence of a hydrocracking process at temperatures of 300–400 °C is noted for the Pt / TiHKE catalyst.

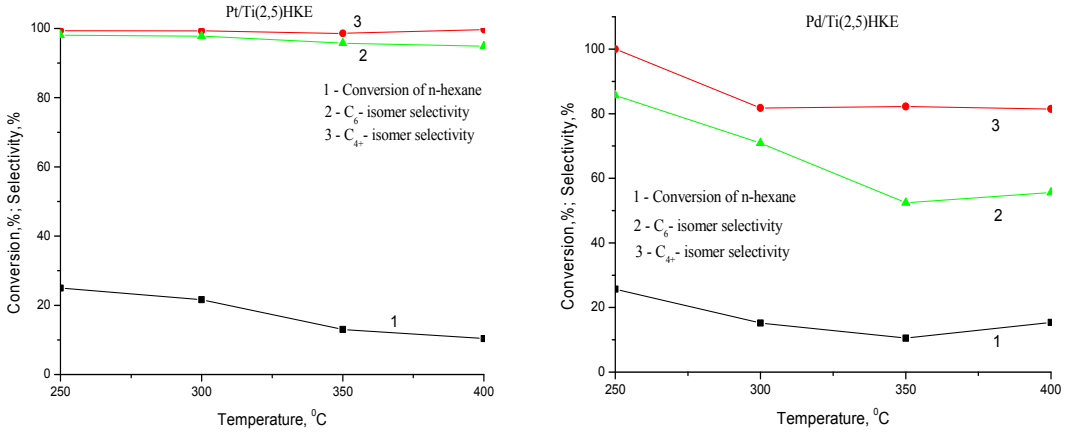

Figure 4 - Conversion of n-hexane and the selectivity of C_6 and C_{4+} - isomers on the catalysts Pt/TiHKE and Pd/TiHKE at different temperatures

In Table 7 presents the data on isomerization of n-hexane on composite catalysts (Pt/Ti/HKS and Pd/Ti/ HKS) based on kaolinite from Sarymsak clay at different temperatures.

Table 7 - Isomerization of n-hexane on Pt- and Pd/Ti (2.5) HKS – catalysts

Catalyst	T,^{0}C	α, %	S_{C4+}, %	S_{C6}, %	The yield of reaction products, %						
					C_1-C_3	Изо-C_4	н-C_5	2.2-DMB	2MP	3MP	Iso-C_7
Pt/Ti(2.5)/HKS	250	9.5	96.1	79.2	0	0	0.4	0	5.3	2.2	2.4
	300	11.1	87.0	50.4	0.5	1.0	0.9	0	3.3	2.3	2.7
	350	22.2	89.5	47.3	0.7	2.7	1.6	0	6.6	3.8	5,2
	400	37.1	86.5	40.6	2.4	4.2	2.5	0.4	9.3	5.7	8.4
Pd/Ti(2.5)/HKS	250	15.3	100	89.0	0	0	0	0	11.2	2.4	1.7
	300	8.9	100	84.4	0	0	0	0	6.5	1.8	1.5
	350	8.4	78.1	53.3	0.4	0.5	1.0	0	2.6	1.9	1.6
	400	17.5	84.6	68	0.5	0.5	1.5	0.7	4.0	7.0	1.7

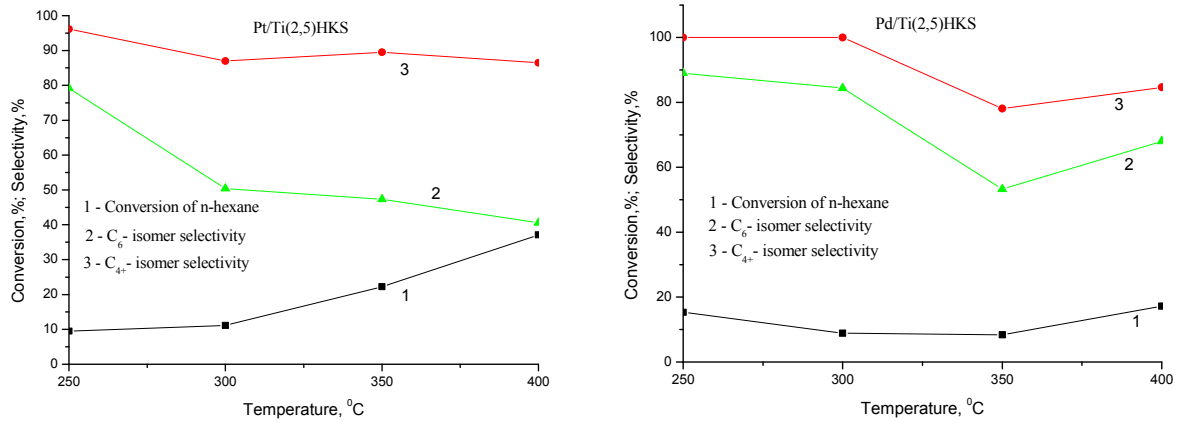

Figure 5 - Conversion of n-hexane and the selectivity of C_6 and C_{4+} - isomers on the catalysts Pt/TiHKS and Pd/TiHKS at different temperatures

From the analysis of the results (Table 7 and Figure 5) it can be seen that the degree of conversion of

n-hexane on the Pt/Ti/HKS - catalyst increases from 9.5 to 37.1% with increasing temperature from 250 to 400 °C. The maximum conversion of n-hexane equal to 37.1%, was observed at 400 °C. In contrast to the catalyst on Ermak clay with Pt / TiHKS, increasing temperature, the selectivity for all isomers and for isohexanes is significantly reduced (Fig. 5). At this catalyst, at elevated temperatures (300 and 400 °C), significant amounts of hydrocracking products are formed (Table 7): C_1-C_3 - hydrocarbons (0.5 and 2.4%); isobutane (1.0 and 4.2%); n-pentane (0.9 and 2.5%). In addition to isohexanes, in the reaction products were found isoheptanes: 2,4-DMP (4.0 and 6.0%) and 3,3-DMP (1.2 and 2.4%) at 350 and 400 °C.

The conversion of n-hexane on the Pd/Ti/HKS catalyst is significantly lower than over the Pt/TiHKS (Table 7, Figure 5). High selectivity for isomers is maintained only at 250 and 300 °C, and with increasing temperature, the selectivity for all isomers and isohexanes decreases. Unlike the Pt/Ti HKS catalyst, the amount of hydrocracking products formed at 350-400 °C is significantly lower on the Pd/TiHKS catalyst (Table 7). The amount of isoheptanes formed in the process of hydroconversion of n-hexane on Pd /TiHKS is also lower than over the Pt/Ti/HKS catalyst.

Thus, on the basis of studies performed, it can be concluded that the Pt and Pd catalysts supported on zirconium or titanium modified activated kaolinite exhibit high isomerization activity.

Analysis of results of the n-hexane isomerization on metal catalysts deposited on pillared clays showed that the studied catalysts are distinguished by high selectivity for isomers and insignificant yield of hydrocracking products only at temperatures of 350 and 400 °C. Two of Pt/TiHKE and Pd/TiHKE catalysts showed high activity (conversion of 25.0 and 25.7%) and selectivity (99.4 and 100%) in the isomerization of n-hexane at 250° C.

To reduce the conversion of n-hexane (in parentheses) at 400 °C, the studied Pt and Pd catalysts on modified kaolinites can be arranged in a row: Pt / Zr (5.0) HKS (43.2%)> Pd / Zr (5.0) HKS (38.3%)> Pt / TiHKS (37.1%)> Pt / Zr (7.5) HKE (34.9%). The yield of C6 + C7 isomers in this series of catalysts decreases in sequence: 36% –33.4% –23.9% –24.4%.

The isomer selectivity for the listed catalysts ranges from 93.3-98.7%. The maximum conversion of n-hexane is equal to 43.2% with an isomer selectivity of 93.3%, was observed on 0.35% Pt/Zr (5.0) HKS catalyst at 400° C, which can be recommended for further improvement of process in isomerization of light n-alkanes with obtaining high-octane additives to motor fuel.

Comparison of isomerization results of the n-hexane on metal-supported catalysts showed that the Pt catalysts deposited on modified Zr^{4+} and Ti^{4+} kaolinite is exhibit higher isomerization activity compared to Pd.

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Қ-ГЕКСАНДЫ ИЗОМЕРЛЕНУ РЕАКЦИЯСЫНДАҒЫ ТҮРЛЕНДІРІЛГЕН КАОЛИНИТТЕРДІҢ Pt- ЖӘНЕ Pd-КАТАЛИЗАТОРЛАРЫ

Аннотация. Мақалада екі Қазақстандық – Сарымсақ және Ермаковский кен орындарының Ti^{4+} және Zr^{4+} түрлендірілген каолиниттеріне енгізілген Pt- мен Pd- катализаторларының синтезделуі және қасиеттері бойынша мәліметтері, олардың катализатор құрамы мен температураға тәуелді қ-гексан изомеризациясындағы каталитикалық белсенділіктері көрсетілген. Синтезделген катализаторлардың элементтік және фазалық құрамы, сондай-ақ текстуралық қасиеттері анықталды. Қ-гександы изомерлеу реакциясында зерттелген катализаторлар моно- және қосорынбасарлы изогександар мен изогептандардың пайда болуы нәтижесінде жоғары белсенділік пен селективтілік көрсетті. Ti^{4+} және Zr^{4+} түрлендірілген каолиниттеріне енгізілген Pt-катализаторлары Pd-катализаторларына қарағанда жоғарырақ белсенділік танытты. 400°C кезінде 0.35%Pt/Zr(5.0)HKS –катализаторында өлшемдері бойынша селективтілігі 93.3% болғанда C_6+C_7-изомерлер шығымы 36,0% және қ-гексанның максималды конверсиясы 43.2% болды.

Түйін сөздер: каолинит, платина, палладий, қ-гексан, изомерлеу, селективтілік, изомерлер шығымы, моно- және қосорынбасарлы изогександар.

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Pt- И Pd-КАТАЛИЗАТОРЫ НА МОДИФИЦИРОВАННЫХ КАОЛИНИТАХ В РЕАКЦИИ ИЗОМЕРИЗАЦИИ Н-ГЕКСАНА

Аннотация. В статье представлены данные по синтезу и свойствам Pt- и Pd- катализаторов, нанесенных на модифицированные Ti^{4+} и Zr^{4+} каолиниты двух Казахстанских месторождений - Сарымсакском и Ермаковском (KS, KE), их каталитической активности в изомеризации н-гексана в зависимости от температуры и состава катализатора. Определен элементный и фазовый состав синтезированных катализаторов, а также их текстурные свойства. Показано, что изученные катализаторы проявили высокую активность и селективность в реакции изомеризации н-гексана с образованием моно- и дизамещенных изогексанов и изогептанов. Более высокую изомеризующую активность проявляют Pt-катализаторы, нанесенные на модифицированный Zr^{4+} и Ti^{4+} каолинит по сравнению с Pd. Максимальная конверсия н-гексана, равная 43,2% и выходом C_6+C_7-изомеров 36,0% при селективности по изомерам, равной 93,3%, наблюдалась на 0,35%Pt/ Zr(5.0)HKS -катализаторе при 400^{o}C.

Ключевые слова: каолинит, платина, палладий, н-гексан, изомеризация, селективность, выход изомеров, моно- и дизамещенные изогексаны.

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SYNTHESIS AND BIOPROTECTIVE PROPERTIES OF HYBRID MONTMORILLONITE-POLYSACCHARIDE COMPOSITES

Abstarct. Polysaccharide-silicate composites based on pectin (PC) and Tagansorbent (TS) - montmorillonite of the Tagansky deposit – have been synthesized. The calculated amount of pectin in the composites was 5, 10, 20, and 40%. Viscosimetric method showed the degree of fixation of pectin on the surface of the inorganic sorbent Samples of the prepared pectin-containing composites have been studied by various physicochemical methods (IR-spectroscopy, scanning electron microscopy, X-ray diffraction). The data of IR – spectroscopy and scanning electron microscopy showed the presence of polysaccharide in the prepared composites. The IRS method has confirmed the shifting absorption bands of the pectin functional groups in the polymer fixed to Tagansorbent. SEM images has demonstrated modification of the surface of inorganic sorbent after treatment with pectin.

The adsorption of lead ions (Pb^{2+}) on the developed polysaccharide-silicate composites has been studied for further their testing as enterosorbents. The optimum adsorption activity was observed in the presence of the composite with a pectin content of 9.4%. The polysaccharide-silicate composites have shown bioprotective properties at the study of the total proteolytic activity (TPA) of the intestinal walls of lead-intoxicated rats.

Keywords: Pectin, polysaccharides, tagansorbent, organo-inorganic composite, sorption activity, bioprotective properties.

Introduction

Recently a wide variety of new technologies on syntheses of polymer-inorganic nanocomposites is being developed. One of the most potentially complementary applications of the hybride composites is the creation of new materials with improved properties. Polysaccharides as the components of the composites are in the focus of the researchers [1-6] due to biodegradability, environmental friendliness and renewability of ssuch kind of polymers [7-14]. Hybrid sorbents consisting of biocompatible components can be used in medicine (as enterosorbents) for removing toxic substances from living organisms [15-18].

In the present work, pectin and montmorillonite of the Taganskii deposit are used to develop polysaccharide-silicate composites. It is known [19] that Tagansorbent is an effective detoxicant, which is used as a preparation for removing toxic substances from the human body. Pectin is also one of the most important and recognized sorbents. It is known [20] that pectin substances are extremely effective and absolutely harmless natural detoxicants. Pectin is very important for the stabilization of metabolism, It reduces the cholesterol in the body, improves peripheral circulation, as well as intestinal peristalsis. But, nevertheless, its most valuable property is the ability to purify living organisms from harmful substances: heavy metals, radionuclides, nitrates, pesticides and other toxins [21, 22].

The object of the paper is to determine the sorption capacity of lead ions on pectin-montmorillonite composites for further their testing as enterosorbents.

Experimental part

Montmorillonite of the Tagansky deposit produced by LLP "Sorbent" (Tagansorbent), pectin (PC, Mw = 15000, the content of the uronide components is 91.3%, the degree of esterification is 64.3%, pure

for analysis), lead nitrate (II), pyridylazo-resorcinol (PAR, pure for analysis.) were used without further purification.

Synthesis of pectin-containing hybrid materials based on Tagansorbent (TS) was carried out by adsorption of pectin on this inorganic sorbent at room temperature and constant stirring for 2 hours. The precipitate was then kept in the mother liquor within 24 hours. The amount of polymer injected to 1.0 g of Tagansorbent was ranged from 0.05 to 0.67 g.

The completeness of the fixing of polymers to Tagansorbent was evaluated by the method of a calibration curve by measuring the viscosity of the mother liquor before and after pectin sorption. The viscosity of solutions was determined in a cryostatic cell KRIVOVIST-01 at a temperature of 20±0.1°C using Ubellode viscometer (k = 0.001077 mm^2/s^2).

IR spectra were obtained using a Karl Zeiss Specord-IR-75 with a resolution of 3 cm^{-1} in the 4,000-400 cm^{-1} region. Pellets for infrared analysis were prepared by grinding a mixture of 1 mg sample with 100 mg dry KBr, followed by pressing the mixture into a mold. Instrumental errors at frequency determining were: 4000-2500 cm^{-1} ± 3 cm^{-1}; 2000-400 cm^{-1} ± 1 cm^{-1}.

Diffractograms of TS-containing samples were examined on a PANalytical X'Pert MPD PRO diffractometer in copper filtered radiation with a wavelength of 0.154 nm. Preparation of the samples for analysis was carried out by pipetting the aqueous suspension of the sample onto a glass plate, followed by drying in air until the water was completely removed.

The morphology and structure of the initial Tagansorbent and the pectin-containing composites were examined by a scanning electron microscope JEOL JSM-6610 LV (Japan).

The sorption properties of polysaccharide-silicate composites were studied by the following procedure: 10 ml of water were added to 0.1 g of the sorbent and mixed until a homogeneous suspension has been formed. A hydrochloric acid solution (0.01 N) was added dropwise to the resulting suspension to reach pH of 2.5 and then 10 ml of a lead nitrate solution (100 mg Pb^{2+}/l) were added. Adsorption was carried out for 4 hours. After filtration the precipitate was analyzed by SF-2000 spectrophotometer using a PAR reagent according to the procedure [23].

The detoxification properties of the developed polysaccharide-silicate composites were evaluated on the lead intoxicated rats (190-220 g) by testing changes in total proteolytic activity (TPA). The TPA index was determined in the acute experiments under Nembutal anesthesia (4 mg/100g body weight, intramuscularly). An abdominal cavity of rats was opened over the white line, blood was taken from the venous vessel and intestinal samples were prepared for further experiments. The tissue (200 mg) were taken, then tissue samples were homogenized with an Ultra-TurraxT8 dispersant. The level of total proteolytic activity of homogenates of the small intestine wall was determined by precipitation of proteins with ethyl alcohol. The calibration curve was plotted using amino acid phenylalanine and the obtained data were presented in μg of phenylalanine (Fen) per 1 mg tissue (for homogenates) for 1 hour of incubation. The control was samples without incubation.

Results and discussion

The amount of pectin adsorbed on Tagansorbent was determined using a calibration plot of the viscosity of the polysaccharide solution versus its concentration (Fig. 1).

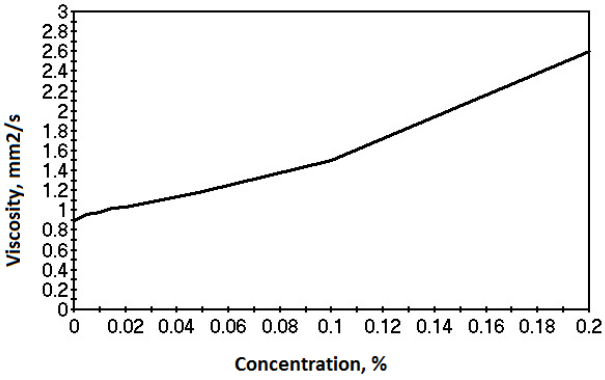


Figure 1 - Calibration chart for determination of pectin concentrations in solutions

Using the graph, the amount of adsorbed polymer was determined based on the difference in the values concentrations. The results of calculations on the content of polysaccharide in composites are presented in Table 1

Table 1 - Adsorption of pectin on Tagansorbent

The amount of pectin injected to 1 g of TS		ν (sol-n) after sorption, мм^2/s	m(PC) in sol-n after sorption, g	m(PC) adsorbed., g	Degree of adsorb., %	Comp-n of PC, %
m(PC), g	w(PC)*, %					
0.0526	5	0.9750	0.0025	0.0501	95.2	4.8
0.1111	10	1.0498	0.0078	0.1033	93.0	9.4
0.2500	20	1.2560	0.0247	0.2253	90.1	18.4
0.6666	40	2.5980	0.1047	0.5619	84.3	36.0
Note: * - the mass fraction of the injected polymer according the sum of the masses of all injected components of the composite (PC + TS), %						

It has been established that the degree of adsorption of the polysaccharide on Tagansorbent decreased with increasing amount of the biopolymer introduced. As a result, PC/TS composites were obtained, the content of pectin in which was slightly different from the calculated data (5, 10, 20% and 40%) and were 4.8, 9.4, 18.4% and 36.0%, respectively (Table 1).

The presence of pectin in the composites obtained was confirmed by IR spectroscopy (Table 2). The wide band in the area of 2800-3000 cm^{-1} is characteristic of the asymmetric and symmetric stretching vibrations of -CH- groups of pectin. The shifts of stretching (3000-3700 cm^{-1}) and bending (1200-1400 cm^{-1}) of the -OH as well as C = O groups of pectin indicated their interaction with the surface hydroxyl groups of Tagansorbent. A slight shift of some bands characteristic of Al-O and Si-O of TS was also observed confirming bonding of the polymer to TS.

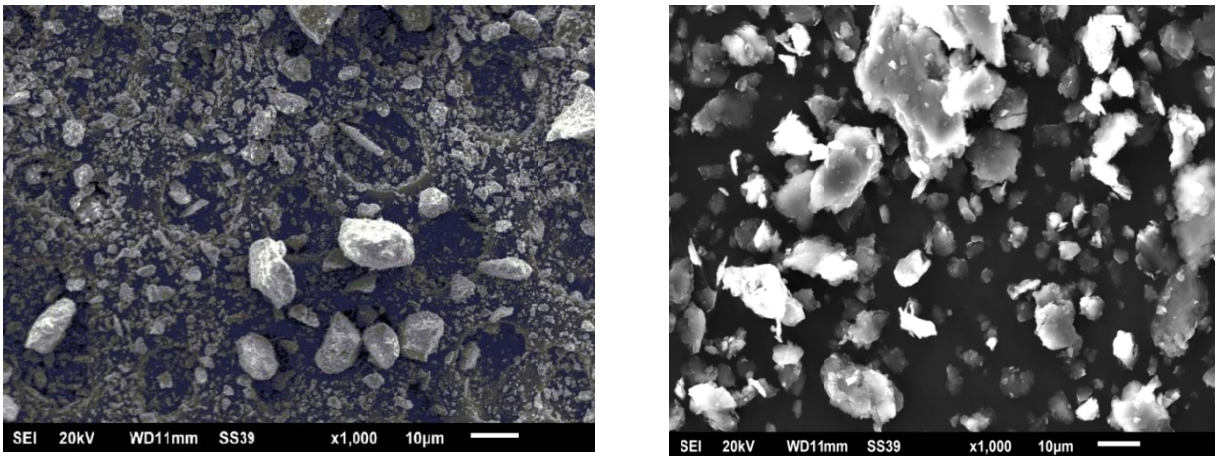
Table 2 - IRS data of the examined samples

Sample	νOH	νCH	νC=O	δCH δOH	νC-O-C νC-C νC-O	δOH(TC) νSi-O νAl-O
Pectin	3429	2933 2857	1762 1638	1445 1348 1248	1123 1076 1060	
TS	3630 3430	-	-		-	1030 914 527 472
9.4%PC/TS	3631 3408 3169	2925 2847	1758 1635	1408 1340	Overlapped by a PC signal	1039 925 529 468

Thus, the conducted studies indicate the possibility of creation of hybrid materials by adsorption of the polysaccharide on Tagansorbent. The results of IR spectroscopy have indicated the formation of polysaccharide-silicate composites through chemisorption of the polymer on the surface of the aluminosilicate.

The study of synthesized composites by scanning electron microscopy (SEM) showed that modification of the clay mineral with pectin promoted the aggregation of the aluminosilicate into larger particles to compare with initial TS (Figure 2).

It is known that the X-ray diffraction method is widely used in the study and identification of clay minerals and their composites by determining the position of basal reflection (001).



a) b)

Figure 2 - Micrographs of SEM of Tagansorbent (a) and 9.4% of PC/TS composite (b)

The diffraction pattern is represented by a wide reflex at 2θ = 7.06 ° (d001 = 12.55 Å) and with two second order reflexes at 2θ = 12.10 ° (d002 = 7.31 Å) and 14.20 ° (d002 = 6.26 Å), which indicate that the pectin-modified sodium montmorillonite is in a partially intercalated state (d001 = 14.62 Å) (Figure 3) [17]

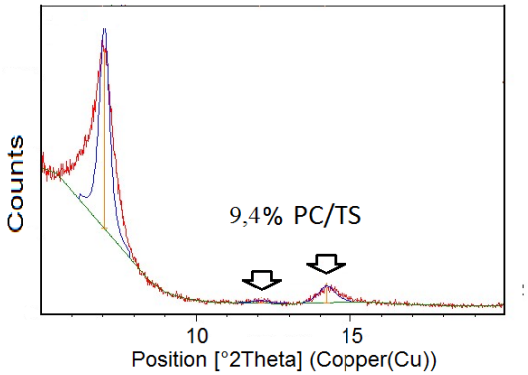


Figure 3 - Diffractogram 9.4% of PC/TS

The sorption properties of the developed polysaccharide-silicate composites towards lead ions (Pd^{2+}) were studied by spectrophotometry.

It was shown (Table 3) that the modification of Tagansorbent with pectin led to an increase in the sorption capacity of composites. The sorption capacity of PC/TS with a pectin content of 4.8% was 9.2 mg/g versus 8.4 mg/g for the original TS. A further increase in the content of biopolymer (up to 9.4%) in PC/TS led to a slight increase in sorption capacity (Table 3). In the presence of 36.0% PC/TS composite, the amount of the adsorbed lead was reduced to a level corresponding to the unmodified montmorillonite. Thus, the maximum adsorption of lead (93%) was achieved on the hybrid PC/TS composite with 9.4% polysaccharide content (Table 3).

Table 3 - Sorption of lead on PC/TS composites as a function of polymer content

PC comp-n, %	Mass of sorb., мg	C(Pb^{2+}) in sol-n before sorpt-n, мg/l	C(Pb^{2+}) in sol-n before sorpt-n, мg/l	Degree of sorption, %	Sorbent capacity, мg/g
0	102.3	50	7.0	86.0	8.4
4.8	101.6	50	3.7	92.6	9.1
9.4	101.0	50	3.5	93.0	9.2
18.4	101.4	50	4.9	90.2	8.9
36.0	102.0	50	7.1	85.8	8.4

To study the bioprotective effect of the developed polysaccharide-silicate composites, a control test was conducted. The activity of proteolytic enzymes in the intestinal part of experimental rats has been compared for the lead-intoxicated, PC/TS taken and the control group of animals (Table 4).

Table 4 - Data of total proteolytic activity of the intestinal wall after lead intoxication against the background of pectin-containing composites

№	Index	Guts μgFen/mg * hr
1	Control	465.50 ±15.72
2	$Pb(NO_3)_2$	1213.88±18.60
3	4.8% PC/TS+ $Pb(NO_3)_2$	787.45 ± 23.21*
4	9.4% PC/TS+ $Pb(NO_3)_2$	747.91 ± 12.80*
5	18.4% PC/TS+ $Pb(NO_3)_2$	714.99 ± 14.62*
Note: * - p≤0,001; compared with the data of a group of rats subjected to lead intoxication.		

The results of the experiment showed a 2.6-fold increase in the activity of proteolytic enzymes in the intestines of rats subjected to lead intoxication, as compared to control animals. The increase in proteolysis demonstrates the increased process of digestion and deep purification of body from conformationally altered lead-intoxicated proteins. It reflects the significant aggressiveness of the xenobiotic damaged intestinal wall. The enzymatic activity decreased by 1.5-1.7 times with the injection of PC/TS hybrid composites, indicating protective function of the obtained materials. A more pronounced protective effect is achieved in the presence of sorbents with a pectin content of 9.4% and 18.4%.

Thus, PC/TS composites protected the wall of the small intestine of rats from the toxic effect of lead nitrate. With an increase in the content of pectin from 4.8% to 18.4%, the activity of proteolysis decreased from 70% to 50% compared to the data for the group subjected to lead nitrate poisoning. The active removal of toxic substances from the body in the presence of composites is probably due to the synergistic effect of combining the complexing properties of pectin with the sorption ability of Tagansorbent.

Conclusions

The results of this work have shown the possibility to synthize polysaccharide-silicate composites by a simple and environmentally friendly approach through adsorption of pectin on Tagansorbent (Kazakhstan natural montmorillonite). Fixation of pectin to the surface of the inorganic sorbent with partial formation of intercalated structures has been confirmed by physico-chemical methods. The results of the study showed high sorption and bioprotective properties of the developed hybrid enterosorbents based on natural components such as pectin and Tagansorbent.

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ГИБРИДТІ МОНМОРИЛЛОНИТ-ПОЛИСАХАРИДТІ КОМПОЗИТТЕРДІҢ СИНТЕЗІ ЖӘНЕ БИОПРОТЕКТРЛІК ҚАСИЕТТЕРІ

Аннотация. Пектин (ПК) және Таған кен орнының монтмориллониті - Тагансорбент (ТС) негізінде полисахарид-силикатты композиттер алынды. Композициядағы пектиннің есептелген көлемі 5, 10, 20 және 40% құрады. Вискозиметриялық әдісі арқылы бейорганикалық сорбенттің бетіндегі пектиннің бекітілу дәрежесі көрсетілді. Құрамында 4,8, 9,4, 18,4 және 36,0% пектині бар ПК/ТС жүйелер алынды. Алынған құрамында пектин бар композиттердің үлгілері әртүрлі физикалық-химиялық әдістері (ИКС, сканерден

өтетін электрондық микроскопия, рентген дифракциясы) арқылы зерттелген. ИК-спектроскопия, сканерлеу электрондық микроскопиясының деректері композит құрамында полисахаридтің болуын растады. ИКС әдісі арқылы пектинді Тагансерорбентке отырғызған кезде полимердің функционалдық топтарының жұтылу жолақтарының ығысуы байқалынады. Бейорганикалық сорбентті пектинмен модификациялағаннан кейін СЭМ микрофографияларында алюмосиликаттың бетінде өзгерістер байқалады.

Энтеросорбент ретінде әрі қарай қолдану мақсатында өндірілген полисахарид-силикатты композиттерде қорғасын иондарының (Pb^{2+}) адсорбциясы зерттелді. Оңтайлы сорбциялық кабілеттілікке ие болып құрамында 9,4% пектині бар композит екені анықталды.

Композиттерді қолдану аясында қорғасынның интоксикациясынан кейін егеуқұйрықтардың ішек қабырғасының жалпы протеолитикалық белсенділігін (ОРА) зерттеу барысында полисахарид-силикат сорбенттерінің қорғаныш қасиеттері бар екені көрсетілген.

Түйін сөздер. Пектин, полисахаридтер, тагансорбент, органикалық-бейорганикалық композит, сорбциялық белсенділік, биопротекторлық қасиеттер.

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СИНТЕЗ И БИОПРОТЕКТРНЫЕ СВОЙСТВА ГИБРИДНЫХ МОНМОРИЛЛОНИТ-ПОЛИСАХАРИДНЫХ КОМПОЗИТОВ

Аннотация. Синтезированы полисахарид-силикатные композиты на основе пектина (ПК) и Тагансорбента (ТС) - монтмориллонита Таганского месторождения. Расчетное количество пектина в составе композитов составляло 5, 10, 20 и 40%. Вискозиметрическим методом показана степень закрепления пектина на поверхности неорганического сорбента. Были получены ПК/ТС системы с содержанием пектина 4,8, 9,4, 18,4 и 36,0%. Образцы полученных пектин-содержащих композитов были изучены различными физико-химическими метдами (ИКС, сканирующая электронная микроскопия, рентгеновская дифракция). Данные ИК-спектроскопии, сканирующей электронной микроскопии подтвердили наличие полисахарида в составе композитов. Методом ИКС установлено, что при нанесении пектина на Тагансорбент происходит смещение полос поглощения функциональных групп полимера. На микрофотографиях СЭМ после модификации неорганического сорбента пектином наблюдается изменение поверхности алюмосиликата.

Исследована адсорбция ионов свинца (Pb^{2+}) на разработанных полисахарид-силикатных композитах с целью дальнейшего их тестирования в качества энтеросорбентов. Установлено, что оптимальной сорбционной способностью обладает композит с содержанием пектина 9,4%. При исследовании общей протеолитической активности (ОПА) стенки кишечника крыс после свинцовой интоксикации на фоне применения композитов показано, что полисахарид-силикатные сорбенты проявляют протекторные свойства.

Ключевые слова. Пектин, полисахариды, тагансорбент, органо-неорганический композит, сорбционная активность, биопротекторные свойства.

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OBTAINING AND RESEARCH OF THE SUPRAMOLECULAR COMPLEXES OF ALKALOID SALSOLINE WITH CYCLODEXTRINS BY NMR SPECTROSCOPY

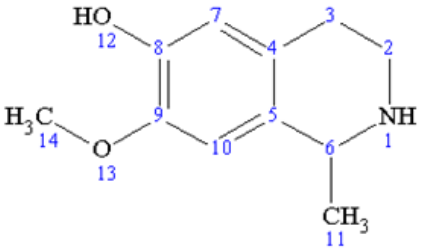
Abstract. One-dimensional NMR ^{1}H, ^{13}C and DEPT and two-dimensional spectroscopy COSY (^{1}H-^{1}H), ^{1}H-^{1}H TOCSY, ^{1}H-^{1}H ROESY, HMQC (^{1}H-^{13}C) and ^{1}H-^{13}C HMBC were used to study the alkaloid salsoline, as well as its supramolecular components, and the supramolecular components of the HMBC spectroscopy polysaccharides α- and γ-cyclodextrins. Schemes of proton correlation with protons through three carbon atoms (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C) in the initial state of the alkaloid under study. The use of the possibilities of two-dimensional spectroscopy COSY (^{1}H-^{1}H), ^{1}H-^{1}H TOCSY, ^{1}H-^{1}H ROESY, HMQC (^{1}H-^{13}C) and ^{1}H-^{13}C HMBC when studying the alkaloid under study correctly and uniquely identify the structure of the substrate of supramolecular self-assembly with cyclic fields. Homonuclear and heteronuclear correlation NMR COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C) are also used to confirm the structure and structure of the cyclic polysaccharides of α- and γ-cyclodextrins. The chemical shifts of the aliphatic and hydroxyl protons of the inner and outer surfaces of the receptors were determined. A comparative analysis of the ^{1}H and ^{13}C NMR spectra of salsoline, α- and γ-cyclodextrins and their supramolecular complexes was carried out. Certain changes have the chemical shifts of ^{1}H and ^{13}C nucleus of salsoline, as well as α- and γ-cyclodextrins in supramolecular complexes. The proton integral intensities of the substrate and receptors in the ^{1}H NMR spectra were definitely that the supramolecular self-assembly with alpha and γ-cyclodecrins occurs with the formation of complexes without including (external) due to the intermolecular interaction of hydroxyl groups from both the alkaloids and cyclodextrins . The water-soluble aggregates formed during this process are capable of solubilizing the required substrate through non-inclusive complexation.

Keywords: alkaloid salsoline, cyclodextrins, supramolecular complexes.

Introduction

Supramolecular self-assembly of alkaloids complexes with cyclodextrins (CD) allows to increase the solubility of a substance in water, to improve their bioavailability and physical and chemical stability, to protect against biodegradation and to reduce toxicity [1-5]. CDDs are relatively affordable compounds, produced from renewable raw materials - starch. The most common are α-, β-, γ-CDA-containing, containing, respectively, 6, 7 and 8 glucopyranose units. The increased interest in CD-us is due to their cyclic structure and the ability, due to the internal hydrophobic cavity, to form supramolecular inclusion complexes of the host-guest type (receptor-substrate) in an aqueous medium [6–8].

The choice of salsoline 1 as a substrate for the supramolecular self-assembly of complexes with α- and γ-CD is determined by the presence of a wide spectrum of biological activity of the alkaloid and its poor solubility in water [9-12].



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Supramolecular complexes 1 with α- and γ-CD were obtained by interaction of equimolecular amounts of substrate 1 with α- and γ-CD receptors in ethanol solutions of the reactants at 65-70°C for 7 hours, followed by separation of the supra complexes by drying.

Results and discussion

The NMR spectroscopic study of supramolecular inclusion complexes 1, obtained on the basis of CDs, is based on determining the difference in the chemical shifts of the ^{1}H and ^{13}C substrates (1) and receptors (CDs) in the free state and in the complexes as a result of intermolecular interaction. In terms of the magnitude of the change in chemical shifts of internal or external protons of CDDs, it is possible to judge the formation of internal (inclusion complexes) or external (without inclusion) complexes, respectively. The change in the chemical shifts of ^{1}H and ^{13}C in the spectra of the substrate makes it possible to determine the direction of the latter's entry into the cavity of the CDs [1–8].

The structure of compound 1 was established on the basis of the results of ^{1}H and ^{13}C NMR spectroscopy obtained in DMSO-d_6 (Tables 1 and 2). The correctness of the assignment of one-dimensional ^{1}H and ^{13}C 1 NMR spectra was confirmed by the data of two-dimensional correlations of the ^{1}H-^{1}H TOCSY NMR spectra, ^{1}H-^{1}H ROESY, ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC.

The ^{1}H and ^{13}C NMR spectra of α- and γ-CDA in the free state and the supramolecular complexes based on them with 1, obtained in DMSO-d_6, are presented in Tables 1 and 2.

Table 1 – Chemicalshifts ^{1}H and ^{13}C NMR of compound 1 and α-CD-na in the free state (δ_0) and in the composition of the supramolecular complex (δ)

Atomnumber C	Group	$\delta_{0,\ ppm}$		δ, ppm		Δδ=δ-δ_0, ppm	
		^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
Connections**1**							
2	CH_{ax} CH_{eq}	2.76 2.83	38.85	2.76 2.81	38.94	0 -0.01	0.09
3	CH_{ax} CH_{eq}	3.14 3.28	24.87	3.15 3.23	24.97	0.01 -0.05	0.10
4	C		124.28		124.28		0
5	C		124.87		124.97		0.10
6	CH	4.32	50.46	4.34	50.58	0.02	0.12
7	CH	6.55	115.51	6.54	115.55	-0.01	0.04
8	C		146.47		146.48		0.01
9	C		147.22		147.25		0.03
10	CH	6.75	110.36	6.74	110.39	-0.01	0.03
11	CH_3	1.53	19.74	1.52	19.81	-0.01	0.64
14	CH_3	3.69	56.31	3.70	56.35	0.01	0.04
12	OH	9.17		9.09		-0.08	
α-Cyclodextrin							
1	CH	4.76	102.48	4.76	102.46	0	-0.02
2	CH	3.24	72.64	3.23	72.60	-0.01	-0.04
3	CH	3.73	73.78	3.73	73.78	0	0
4	CH	3.34	82.59	3.34	82.60	0	0.01
5	CH	3.53	72.64	3.54	72.60	0.01	-0.04
6	CH_2	3.60	60.55	3.60	60.50	0	-0.05
2	OH	5.44		5.49		0.05	
3	OH	5.38		5.41		0.03	
6	OH	4.42		4.47		0.05	

Table 2 – Chemical shifts ^{1}H and ^{13}C NMR of compound 1 and γ-CD-na in the free state (δ_0) and in the supramolecular complex (δ)

Atomnumber C	Group	$\delta_{0,\ ppm}$		δ, ppm		Δδ=δ-δ_0, ppm	
		^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
Connections**1**							
2	CH_{ax} CH_{eq}	2.76 2.83	38.85	2.77 2.82	38.93	0.01 -0.01	0.08
3	CH_{ax} CH_{eq}	3.14 3.28	24.87	3.16 3.28	24.95	0.01 0	0.08
4	C		124.28		124.28		0
5	C		124.87		124.93		0.06
6	CH	4.32	50.46	4.34	50.58	0.02	0.12
7	CH	6.55	115.51	6.54	115.55	-0.01	0.04
8	C		146.47		146.49		0.02
9	C		147.22		147.25		0.03
10	CH	6.75	110.36	6.74	110.39	-0.01	0.03
11	CH_3	1.53	19.17	1.52	19.80	-0.01	0.63
14	CH_3	3.69	56.31	3.70	56.35	-0.01	0.04
12	OH	9.17		9.09		-0.08	
γ-Cyclodextrin							
1	CH	4.83	102.20	4.85	102.18	0.02	-0.02
2	CH	3.28	73.11	3.28	73.10	0	-0.01
3	CH	3.54	73.44	3.54	73.44	0	0
4	CH	3.30	81.46	3.31	81.41	0.01	-0.05
5	CH	3.47	72.69	3.48	72.68	0.01	-0.01
6	CH_2	3.58	60.53	3.58	60.48	0	-0.05
2	OH	5.69		5.75		0.06	
3	OH	5.66		5.72		0.06	
6	OH	4.46		4.51		0.05	

Comparison of the integral intensities of the 1H NMR signals of the salsoline molecule with α- and γ-CDA in supramolecular complexes showed that alkaloid 1 with both CDA forms 1: 1 complexes.

During the formation of supramolecular complexes 1 with α- and γ-CD, we observe insignificant changes in proton chemical shifts Δδ in cyclodextrin molecules to the same extent both for internal hydrophobic protons H-5 and H-6 that are closest to the edge of the cylindrical rim, and for located in the outer hydrophilic surface of protons H-1, H-2 and H-4. In both CD-new molecules, there is no change in the chemical shift of ^{1}H NMR of the internal hydrophobic proton H-3. The greatest change in the proton spectra of cyclodextrins occurs in hydroxyl protons 2-OH, 3-OH and 6-OH. In the alkaloid molecule 1, the change in the proton spectra is also insignificant. The greatest change in the proton spectra is observed at the hydroxyl proton H-12. These results indicate that the supramolecular self-assembly of salsoline with CD-nam leads to the formation of complexes without the inclusion of (external) [3, 13] due to the intermolecular interaction of hydroxyl groups from both the alkaloid and the CD-n (Fig. 1). The water-soluble aggregates formed during this process are able to solubilize the substrate molecule through non-inclusive complexation [14].

As a result of a comparative analysis of the ^{1}H and ^{H}C NMR spectra of salsoline, α- and γ-cyclodextrins and their supramolecular complexes, as well as by the value of the proton integrated intensities of the substrate and receptors in the ^{1}H NMR spectra, it was determined that supramolecular self-assembly of salsoline with α- and γ-cyclodecryns occurs with the formation of complexes without the inclusion of (external) due to the intermolecular interaction of hydroxyl groups from both the alkaloid and cyclodextrins. The water-soluble aggregates formed during this process are capable of solubilizing the substrate molecule through non-inclusive complexation. This allows you to increase the solubility of the substrate in water. The resulting salsoline supra complexes are essentially nanocomplexes of the latter and can be used in nanomedicine in the future.

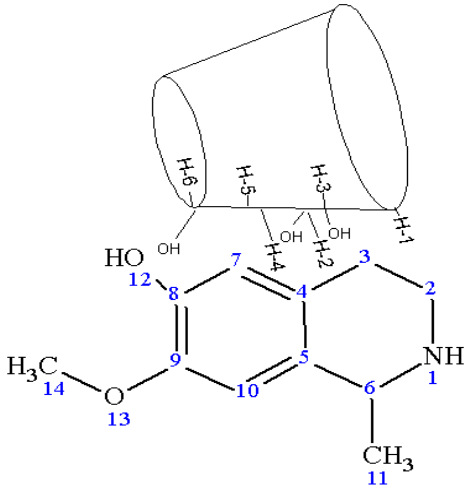

Figure 1 – Estimated supramolecular complexes without the inclusion of molecule **1** with α- and γ-CD-us

Experimental part

α- and γ-CDs were used by Fluka, 99% pure. The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM-ECA 400 spectrometer (399.78 and 100.53 MHz on ^{1}H and ^{13}C cores, respectively) in a DMSO-d_6 solution at room temperature. Chemical shifts are measured relative to the residual signals of protons or carbon atoms DMSO-d_6.

Obtaining the inclusion complexes of salsoline alkaloid with α- and γ-cyclodextrins. We have chosen the coprecipitation method, since this method allows to obtain a very pure preparation of the inclusion complex in crystalline form. To a concentrated solution of salsoline alkaloid in ethanol in the ratio of 1: 1 a saturated solution of cyclodextrin in water was added dropwise. Then stirred with a magnetic stirrer at a temperature of 65-70 ° C. The individuality of the proposed complexes was checked by thin layer chromatography on Silufol UV-254 plates in the system of isopropyl alcohol - 25% ammonia-water solution 7:2:1. The final product must be dried at a temperature of 60°C in a vacuum dryer at an atmospheric pressure of 0.4 kgf / cm^2. The inclusion complexes of salsoline with cyclodextrins were obtained in the form of a powder.

ӘОЖ 547.94 +547.458.68+543.429.2

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ЯМР СПЕКТРОСКОПИЯСЫ ӘДІСІМЕН ЦИКЛОДЕКСТРИНДЕРМЕН САЛЬСОЛИН АЛКАЛОИДТАРЫНЫҢ СУПРАМОЛЕКУЛЯРЛЫ КЕШЕНДЕРІН АЛУ ЖӘНЕ ЗЕРТТЕУ

Аннотация. ^{1}H, ^{13}C және DEPT бір өлшемді ЯМР және COSY (^{1}H-^{1}H), ^{1}H-^{1}H TOCSY, ^{1}H-^{1}H ROESY, HMQC (^{1}H-^{13}C) және ^{1}H-^{13}C HMBC әдістерімен алкалоид сальсолиннің,оның циклдық полисахарид α-және γ-циклодекстриндермен супрамолекулярлық кешендері зерттелді. Зерттелетін алкалоид молекуласында COSY (^{1}H-^{1}H) және HMQC (^{1}H-^{13}C) бір байланыс арқылы көміртекті атомдармен протондар корреляциясының, сондай-ақ үш байланыс арқылы протондары бар протондар корреляциясының схемалары ұсынылған. Зерттелетін алкалоидты сәйкестендіру кезінде COSY (^{1}H-^{1}H), ^{1}H-^{1}H TOCSY, ^{1}H-^{1}H ROESY, HMQC (^{1}H-^{13}C) және ^{1}H-^{13}C HMBC екі өлшемді спектроскопия мүмкіндіктерін пайдалану циклдік полисахаридті рецепторлармен супрамолекулярлық өздігінен жинаудың субстратының құрылымын дұрыс және бір мәнді сәйкестендіруге мүмкіндік берді. Гомоядерлік және гетероядролық корреляция ЯМР COSY (^{1}H-^{1}H) және HMQC (^{1}H-^{13}C) α - және γ-циклодекстриндердің циклдық полисахаридтерінің құрылымы мен құрамын сәйкестендіру және растау мақсатында қолданылды. Рецепторлардың ішкі және сыртқы бетінің алифатикалық және гидроксильді протондарының химиялық өзгерістері анықталды. Сальсолиннің ^{1}H және

^{13}С ЯМР спектрлеріне, α- және γ-циклодекстриндерге және олардың супрамолекулярлық кешендеріне салыстырмалы талдау жүргізілді. Сальсолиннің^{1}Н және ^{13}С ядроларының химиялық ығысуы мәндерінің, сондай-ақ супрамолекулярлы кешендердегі α-және γ-циклодекстриндердің өзгеруі анықталды. Субстрат пен рецепторлардың ЯМР ^{1}Н спектріндегі протонды интегралды қарқындылығының шамасы бойынша α- және γ-циклодекстриндермен сальсолиннің супрамолекулалық өздігінен жинауы алкалоид жағынан да, циклодекстриндер жағынан да гидроксильді топтардың молекулааралық өзара әрекеттесуі (сыртқы) әсерлердің көмегінсіз-ақ, кешендердің пайда болуымен жүреді. Бұл ретте түзілетін суда еритін агрегаттар субстрат молекуласын инклюзивтік емес кешен құру арқылы солюбилизациялауға қабілетті.

Кілт сөздер: сальсолин алкалоиды, циклодекстриндер, супрамолекулярлық кешендер.

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ПОЛУЧЕНИЕ И ИССЛЕДОВАНИЕ СУПРАМОЛЕКУЛЯРНЫХ КОМПЛЕКСОВАЛКАЛОИДА САЛЬСОЛИНА СЦИКЛОДЕКСТРИНАМИ МЕТОДОМ СПЕКТРОСКОПИИ ЯМР

Аннотация. Методами ЯМР одномерной ^{1}Н, ^{13}С и DEPT и двумерной спектроскопии COSY(^{1}Н-^{1}Н), ^{1}Н-^{1}Н TOCSY, ^{1}Н-^{1}Н ROESY, HMQC (^{1}Н-^{13}С) и ^{1}Н-^{13}CHMBC исследованы алкалоид сальсолин, а также его супрамолекулярные комплексы с циклическими полисахаридами α- и γ-циклодекстринами. Представлены схемы корреляций протонов с протонами через три связи и схемы корреляций протонов с углеродными атомами через одну связь COSY(^{1}Н-^{1}Н) и HMQC (^{1}Н-^{13}С) в молекуле исследуемого алкалоида. Использование при идентификациии изучаемого алкалоида возможностей двумерной спектроскопии COSY(^{1}Н-^{1}Н), ^{1}Н-^{1}Н TOCSY, ^{1}Н-^{1}Н ROESY, HMQC (^{1}Н-^{13}С) и ^{1}Н-^{13}CHMBC позволило правильно и однозначно идентифицировать строение субстрата супрамолекулярной самосборки с циклическими полисахаридными рецепторами. Гомоядерная и гетероядерная корреляция ЯМР COSY(^{1}Н-^{1}Н) и HMQC (^{1}Н-^{13}С) применена также для идентификации и подтверждения строения и структуры циклических полисахаридов α- и γ-циклодекстринов. Были определены химические сдвиги алифатических и гидроксильных протонов внутренней и внешней поверхности рецепторов. Проведен сравнительный анализ спектров ЯМР ^{1}Н и ^{13}С сальсолина, α- и γ-циклодекстринов и их супрамолекулярных комплексов. Определены изменения значений химических сдвигов ядер ^{1}Н и ^{13}С сальсолина, а также α- и γ-циклодекстринов в супрамолекулярных комплексах. По величине протонных интегральных интенсивностей субстрата и рецепторов в спектрах ^{1}Н ЯМР было определено, что супрамолекулярнаясамосборкасальсолина с α- и γ-циклодекстринами происходит с образованием комплексов без включения (внешних) за счет межмолекулярного взаимодействия гидроксильных групп как со стороны алкалоида, так и со стороны циклодекстринов. Образуемые при этом водорастворимые агрегаты способны солюбилизировать молекулу субстрата через неинклюзивноекомплексообразование.

Ключевые слова: алкалоид сальсолин, циклодекстрины, супрамолекулярные комплексы.

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