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Д.В. Сокольский атындағы «Жанармай,
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ХАБАРЛАРЫ

ИЗВЕСТИЯ

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

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KINETICS AND MECHANISM OF SORPTION OF COPPER (II) IONS BY ION EXCHANGER

Abstract. In this article the kinetics of the process of sorption of copper (II) ions from aqueous solutions by polymer sulfonic cation exchanger, an elementary unit containing a heterocycle and a sulfonic group, under static conditions at a temperature of 298 K and a copper concentration of 2 mmol / mg is investigated. The sulfonic cation exchanger was preliminarily obtained by the reaction of polycondensation of diphenyl oxide and furfural with further sulfonation to obtain functional ionogenic groups in order to increase the extraction efficiency. The obtained kinetic curves of the dependence of the degree of extraction of copper ions from solution on time were processed using the Boyd, Adamson, and Myers equation, which describes diffusion in a limited volume of solution. The kinetic parameters of the sorption process (effective diffusion coefficient, etc.) are calculated, and the results obtained are compared with the data for the traditionally used industrial cation exchanger, which is a copolymer of styrene and divinyl benzene. It has been established that the process of sorption of copper (II) ions in the sulfonic cation exchanger phase is of an intra diffusion nature and corresponds to second-order kinetic equations.

Key words: kinetics, sorption, copper (II) ions, photometry, diffusion, mechanism.

Introduction. Heavy metal ions are dangerous and widespread pollutants of the hydrosphere that have a toxic effect on the ecosystem. Among them, copper ions are considered especially unfavorable for living organisms, which belong to the group of highly toxic substances with a wide spectrum of toxic effects with diverse manifestations [1, 2].

In this regard, a very promising direction of research is the development of methods for purifying industrial and domestic wastewater from heavy metal ions, in particular, from copper ions. Currently, most enterprises use the ion-exchange method as the main method of water purification from ions of heavy metals, which has significant advantages over other methods, for example, high selectivity with respect to the recovered metal. This allows the process to be carried out with a short duration of the technological cycle, relatively low costs and consumption of chemical reagents [3]. Nevertheless, the use of this method with known ion-exchangers does not allow reducing the content of toxic ions of heavy metals to the norm of the maximum permissible concentration [4]. The solution to this problem can be the use of more efficient cation-exchanger based on polymers modified with various functional groups [5–10], for example, carboxyl [9–12], amine [13], phosphoric acid [7, 14, 15], akylthiophosphoric [16], sulfogroups [17,18], etc. At the same time, to establish the optimal parameters of the sorption of metal ions, it is necessary to know the kinetic laws and the mechanism of the sorption process. In connection with the above, the purpose of this study was to determine the kinetic characteristics of the sorption process of copper (II) ions from aqueous solutions using a new sulfonic cation exchanger of the polycondensation type, to establish the sorption mechanism, and also to compare the obtained parameters with the data for the known cation exchanger used in industry.

Methods. In the study, we used two types of cation exchanger - industrial sulfonic cation exchanger grade KU-2-8 (strongly acidic cation exchanger, copolymer of divinylbenzene and styrene, Anta LLC, Russia) and sulfonic cation exchanger obtained by polycondensation of diphenyl oxide and furfural, followed by sulfonation. The synthesis of the latter is described in [17], where the static exchange capacity for copper was 2.4–3.2 mg-eq/g.

For the determine of the copper ions in the solution used photometric method.The method is based on measuring the optical density (A) of a blue solution of copper (II) ammonia, obtained as a result of the reaction:

$$Cu^{2+} + 4NH_4OH \leftrightarrow [(Cu(NH_3)_4]^{2+} + 4H_2O$$

and using the functional dependence of optical density on the concentration of Cu (II) ions according to the Bouguer-Lambert-Beer law

$$I = I_o\exp\cdot(-\varepsilon\cdot c\cdot \ell),$$

where I_o is the intensity of the incident light, c - is the concentration of the absorbing substance (mol/l), ε - is the molar absorption coefficient (l / mol · cm).

A sample weighing 3.927 g of chemically pure copper sulfate $CuSO_4 \cdot 5H_2O$ was transferred into a volumetric flask with a capacity of 1000 ml, dissolved, added 5 ml of concentrated sulfuric acid (density 1.84 g/cm^3) and brought up to the mark with water. 1 ml of this solution contains 1 mg of Cu^{2+} ion. 5 standard solutions were prepared from standard solution 1. For this purpose, 20, 15, 10, 5, and 2.5 ml of a standard copper salt solution were measured with a burette in five volumetric flasks with a capacity of 100 ml. To each of the flasks, 10 ml of diluted (1: 3) ammonia solution was added and the volume was brought to the mark with distilled water. To plot a calibration graph, 10 ml of diluted (1: 3) ammonia was transferred into a 100 ml volumetric flask, one drop of concentrated sulfuric acid was added and distilled water was brought to the mark (zero solution). A solution with an average concentration was photometrically measured in the wavelength range of 400–750 nm. We chose a light filter at which the absorption maximum of the solution is observed - 670 nm. This light filter was used for further work [19].

Measurement of absorbance A was started with the solution having the highest copper concentration. To do this, the solution from the flask was poured into a cuvette with a working width of 1 cm, the cuvette was closed with a lid, and the absorption of the solution was measured with a yellow filter. Having measured the absorption A of all solutions, a calibration graph was built.

Experiments to determine the kinetics of sorption were carried out at a temperature of 298 K, in a time interval from 1 to 120 min, while the concentration of copper in the solution was 2 mmol / mg.

Results and its discussion. In order to identify the peculiarities of the kinetics of ion exchange in the work, we compared the sorption of copper (II) ions from aqueous solutions by two types of polymer sulfonic cation exchangers - industrial sulfonic cation exchanger based on divinylbenzene and styrene (KU-2-8) and sulfonic cation exchanger, previously synthesized by the polycondensation reaction of diphenyloxide and furfural followed by sulfonation (SKDF) [17]. Figure 1 shows the kinetic curves representing the time dependences of the amount of sorbed copper ions from the solution.

The obtained dependences make it possible to conclude that the achievement of sorption equilibrium on the SKDF cation exchanger occurs within 30 minutes, and on the KU-2-8 cation exchanger, respectively, within 20 minutes. The difference in achieving equilibrium between SKDF and KU-2-8 is small, which indicates the possibility of using the obtained cation exchanger for the extraction of copper ions from wastewater solutions.

Further, the obtained kinetic curves were processed using the Boyd, Adamson and Myers equation [20], which describes diffusion in a limited volume of solution:

$$F = \frac{Q_t}{Q_\infty} = 1 - 6/\pi^2 \sum \frac{1}{n^2}\exp(-Bt\cdot n^2),$$

where F is the degree of ion exchange; Q_t and Q_∞ are the amount of sorbed ion at time t (sampling time) and at the time of reaching equilibrium, respectively; $Bt = \frac{D\pi^2 t}{r^2 Bt}$ - dimensionless parameter or Fourier homochronism criterion; D is the diffusion coefficient (cm^2/g); *r* - is the radius of the ion exchanger grain, cm.

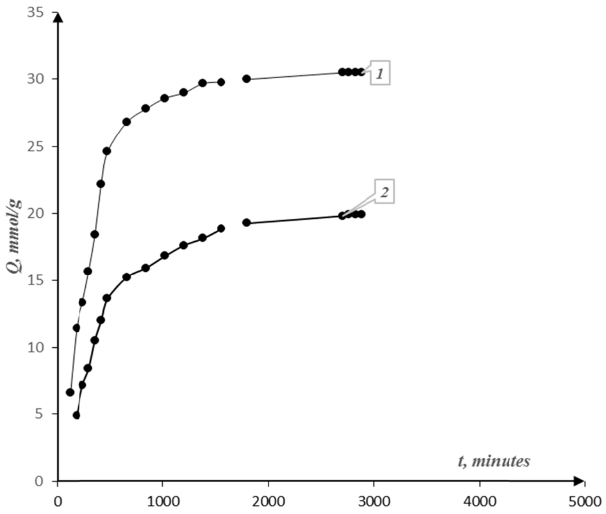


Figure 1 - Kinetic curves of sorption of copper (II) ions from aqueous solutions by industrial sulfonic cation exchanger KU-2-8 (curve *1*) and sulfonic cation exchanger based on a copolymer of diphenyl oxide and furfural SKDF (curve *2*)

The value of *F* was determined experimentally and a graph of the dependence of the degree of exchange of ions *F* on *t* was plotted (figure 2). Then, using the table of dependence of *F* on *Bt* [21], the value of *Bt* was found for the corresponding values of *F* and *t,* and then the diffusion coefficient was calculated according to the method described in the literature [22].

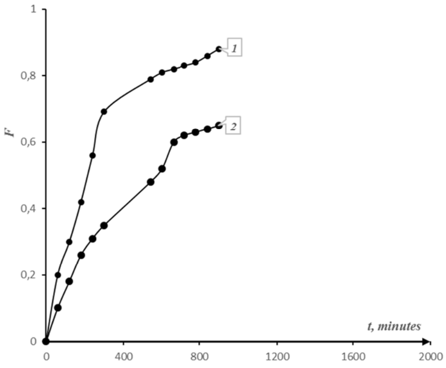


Figure 2 - Dependence of the degree of ion exchange F on time for sulfonic cation exchangers KU-2-8 (1) and SKDF (2)

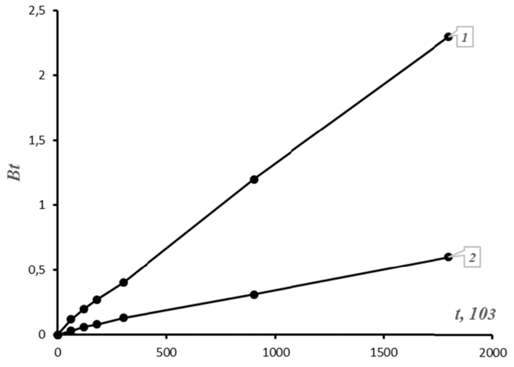


Figure 3 - Dependence of the kinetic coefficient of sorption Bt on time for sulfonic cation exchangers KU-2-8 (1) and SKDF (2)

In figures 2 and 3 the time dependences of the kinetic parameters *F* and *Bt* is shown. As can be seen, in the case of the dependence of the function *F* on time *t* (figure 2) at small values of *F* from 0 to 0.15, the obtained dependences are linear, which indicates the internal diffusion character of the kinetics. The dependences of the parameter *Bt* (kinetic coefficient of sorption) on time *t* (figure 3) are linear, which suggests a "gel" type of kinetics. In figure 4 shows the kinetic curves of the dependence $– \ln(1 – F) = f(t)$.

As can be seen from figure 4, only in the initial sections of the dependence is the linear character of the function $– \ln(1 – F) = f(t)$ observed. At the next time intervals, the kinetic curves do not meet the criteria of a pure "external diffusion" mechanism. This indicates that, at the initial stage, the sorption process on the indicated cation exchangers proceeds according to the external diffusion mechanism, and over time the influence of the external diffusion factor decreases, and the internal diffusion factor, on the contrary, increases. This means that the process as a whole proceeds in a mixed diffusion mode, i.e. controlled by diffusion in the solution film and diffusion in the grain of the cation exchanger [23].

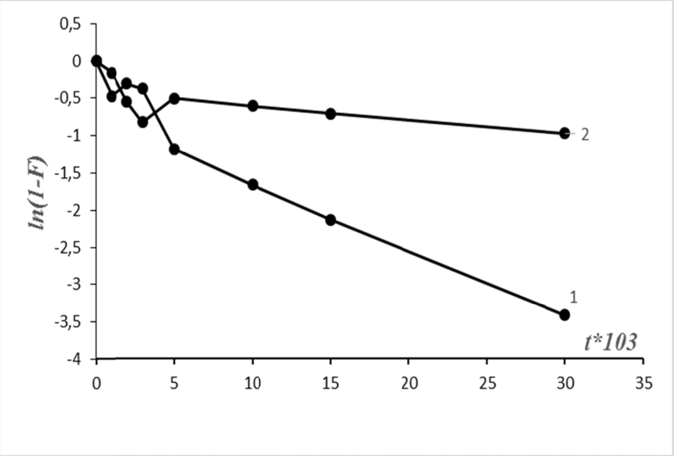


Figure 4 - Dependence –ln (1 – F) = f (t) for the sorption of copper (II) ions by sulfonic cation exchangers KU-2-8 (1) and SKDF (2)

Assigning the kinetic curves to one of the kinetic types makes it possible to calculate the effective diffusion coefficients from the experimental curves, which are kinetic coefficients that take into account both the diffusion features of the transport of molecules in the sorption system and the parallel processes of swelling of the ion-exchange agent, protolysis, and sorbate solvation [24]. Thus, the diffusion coefficients can be calculated using the following formula:

$$D = \frac{Bt \cdot r_0^2}{\pi^2 \cdot t},$$

where D - is the diffusion coefficient, cm^2/s; t - is the contact time of the solution with the ion exchanger; r - is the radius of an ion exchanger grain in a swollen state, cm.

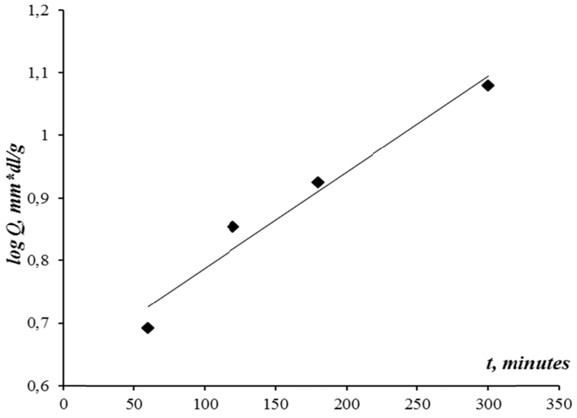


Figure 5 - Dependence of logQ on time of SKDF sulfonic cation exchanger

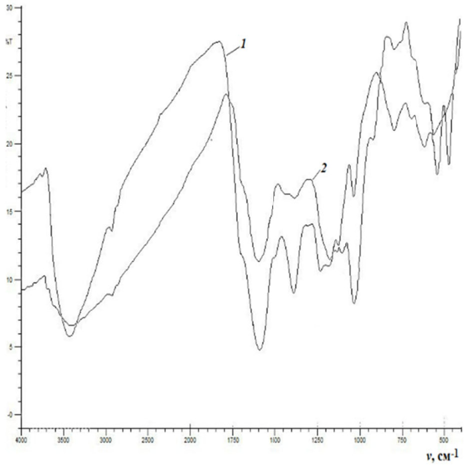
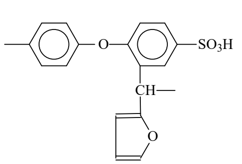
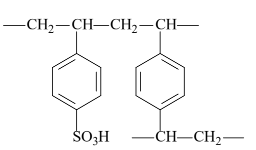


Figure 6 - IR spectra of SKDF sulfonic cation exchanger before (*1*) and after (*2*) sorption of copper (II) ions

Stages 1, 5 and 2, 4 are different in the direction, but not in the nature of the movement of ions. Therefore, we can restrict ourselves to considering only the first three stages. In this case, the third stage proceeds instantly in systems not complicated by side processes, including complexation with ionogenic groups [25]. Sorption kinetics expresses the rate of absorption of copper ions on the sorbent, as well as the time of equilibrium regulation of the rate. Kinetic data were processed using kinetic equations of various orders. Representing the equations for the concentration of the reagent at different times, the values of the rate constant are calculated, which make it possible to reveal the contribution of the chemical interaction stage to the sorption process [26]. Dependences of the processed kinetic data showing the second order in linearized coordinates according to the equation $1/C=k\tau +1/C_0$ showing a high determination value $R^2 = 0.9628$ is shown in Fig. 5. The IR spectrum of sulfonic cation exchanger before and after adsorption is shown in Figure 6.The IR spectrum of the sulfonic cation exchanger is characterized by the presence of intense absorption bands in the range of 3000-3600 $см^{-1}$ (ν_{max}=3406 $см^{-1}$), 1500-1700 $см^{-1}$ (ν_{max}=1599 $см^{-1}$) и 950-1250 $см^{-1}$ (ν_{max}=1031, 1103, 1173 $см^{-1}$). In addition, in the “fingerprint” region, absorption bands are found due to bending vibrations (out-of-plane vibrations) of aromatic fragments [27] with less (at 792, 686, 615 cm^{-1}) and medium intensity (at 920, 539, and 472 cm^{-1}). According to the literature data [28, 29], the absorption band at ν_{max} = 3406 $^{cm-1}$ can be attributed to the stretching vibrations of the OH group of sulfonic acid. A relatively broad absorption band with a maximum ν_{max} = 1599 cm^{-1} is due to in-plane vibrations of aromatic fragments. The characteristic bands of O=S=O groups, caused by symmetric and asymmetric vibrations, usually lie in the range of 1010-1080 and 1150-1260 cm^{-1}, respectively [30]. On this basis, the absorption bands at 1031 and 1173 $^{cm-1}$ can be attributed to symmetric and asymmetric vibrations of O=S=O groups. Difficult to assign is the absorption band at 1103 cm^{-1} in the initial cation exchanger. Since, the cation exchanger contains C-O-C groups of furan and diphenyl oxide, which can give absorption bands at a given frequency [31]. The high sensitivity of this band to the formation of the SO_3- anion makes it possible to assign this band to the C-O-C group of diphenyl oxide, which undergoes a high-frequency shift by 20 cm^{-1} after absorption. After sorption, the relative intensity of the absorption band at 1031 cm^{-1} decreases significantly, the position does not change. The absorption band of sulfonic cation exchanger at 1173 cm^{-1}, caused by asymmetric vibrations of O=S=O groups, undergoes a high-frequency shift (ν_{max} = 1227 cm^{-1}) after sorption. This band of naphthalene-2-sulfonic acid [29] is found at 1189 cm^{-1} and after (sorption of the copper ion) the formation of the SO_3-anion is shifted to the high-frequency region - 1224 cm^{-1}. Similar absorption bands are observed in complexes with the participation of copper (II) ion, cobalt (II) and other metals and aromatic sulfonic acid [32]. In these complexes, the tetraaqua cation $[Me\ (OH_2)_4]^{2+}$ is formed, coordinating with two anions - SO_3^-. A wide absorption band in the region of 3000-3600 cm^{-1} with a maximum at 3431 cm^{-1}, an absorption band in the region of double bonds (in the form of a shoulder at~1700 cm^{-1}), and broad low-intensity absorption bands in the region of 450-900 cm^{-1}. The table lists some parameters that determine the nature of the kinetics of the sorption of copper (II) ions on the used sulfonic cation exchangers [33,34].

Table - Elementary unit structure and kinetic parameters of cation exchangers

Cation exchanger type	Elementary link	Kinetic parameters *		
		R^2	$D\cdot10^{-9}$	k
SKDF		0.9978	31.69 31.69 28.17 27.46 21.834	0.0370 0.0211 0.0298 0.0064 0.0037
КУ-2-8		0.9994	12.67 10.56 9.50 84.52 84.52	0.0317 0.0220 0.0628 0.0096 0.0022

Note: * R^2-values of the coefficient of determination; $D \cdot 10^{-9}$ diffusion coefficient (cm^2 / s); k - second-order sorption rate constant, respectively, g / mmol / min.

Conclusion. Thus, the results of studying the kinetics of sorption of copper (II) ions from aqueous solutions by sulfonic cation exchangers of two types under static conditions, as well as the performed mathematical processing of the kinetic curves, made it possible to establish that the sorption mechanism is of a mixed nature and is determined by the total effect of diffusion and chemical reaction.

The results obtained allow us to conclude that the small difference in reaching equilibrium between the SKDF sulfonic cation exchanger obtained by us and on the KU-2-8 cation exchanger indicates the possibility of using the cation exchanger for the extraction of copper ions from wastewater solutions in certain working time intervals. The peculiarities of the study are represented by the "gel" type of kinetics. The graph constructed according to the experimental data for the obtained sulfonic cation exchanger turned out to be rectilinear to the coordinates logQ = f (τ) shows the second order of kinetics determining the process of ion exchange inside the grain of the ion exchanger.

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СУЛЬФОКАТИОНИТПЕН МЫС (II) ИОНДАРЫН СОРБЦИЯЛАУ КИНЕТИКАСЫ ЖӘНЕ МЕХАНИЗМІ

Аннотация. Сорбция кинетикасын зерттеу практикалық қызығушылық тудырады, өйткені тәжірибе барысында өлшенетін сорбция жылдамдығы сорбцияны жүргізу үшін мынадай шарттарды – сорбент түрін, сорбент түйіршіктерінің мөлшерін, температуралық жағдай және басқа параметрлерді таңдау тәрізді практикалық мәселелерді шешуде үлкен рөл атқарады. Сорбция кинетикасын анықтау бойынша тәжірибелер 298 К температурада 1-120 минут уақыт аралығында жүргізіледі, ерітіндідегі мыс концентрациясы 2 ммоль/мг болады. Иониттер фазасындағы мыс (II) иондарының катиондармен сорбциясын зерттеу үшін келесідей физико-химиялық талдау әдістері қолданылады. Екітипті катиондиттер арқылы мыс иондарының сорбция кинетикасын зерттеу үшін шектеулі көлем әдісі қолданылады. Салмағы 1 г зерттелетін сорбент сынама-ларының өлшенген бөліктеріне 0,1 г/дм3 концентрациясы бар 100 дм3 $CuSO_4$* $5H_2O$ ерітінділері құйылады, колбаларды кезеңімен шайқап, 1-120 минутқа дейін сақтайды. Белгіленген уақыттан кейін ерітіндіні декантирлейді және мыс иондарының қалдық мөлшері анықталады. Кинетикалық қисықтар «А –t» коорди-наттарында құрылады, мұнда А – таңдалған уақыт аралығында байқалатын адсорбция, мг / г, t – фаза арасындағы байланыс ұзақтығы. Алынған мәліметтерді математикалық өңдеу Origin Lab Pro бағдарламасы арқылы жүзеге асырылады. ИК спектрлері Перкин-Элмер (АҚШ) фирмасының System-2000 ИК- Фурье спектрометрінде нығыздалған KBr түйіршіктері түрінде анықталады.

Алдын ала болжағанымыздай, сульфокатионитпен мыс иондарының сорбциялану кинетикасы ион алмасу реакциясының жылдамдығымен анықталады. Ион алмасу процесінің жалпы жылдамдығы ерітіндіде жүретін (дәнге қарсы ион және иониттер дәнінен диффузиясы) және ионитте (ионит дәнінің орталығына жоғарғы бетінен қарсы иондар диффузиясы және қарама-қарсы бағытта; ерітіндіден қарсы иондармен ионитте қарсы иондарының алмасуы) процестердің жиынтығы ретінде ұсынылады. Ион алмасу процесі күрделі, көпсатылы, гетерогенді қатты-сұйық жүйеде жүреді. Осыған байланысты ион алмасу кинетикасы гетерогенді реакциялардың жалпы теориясы тұрғысынан қарастырылады. Бұл теорияға сәйкес, ион алмасу процесі қатты фазада жүретін химиялық өзгерістермен ғана емес, зат массасының бір фазадан екінші фазаға өту процестері, реактив шығынын толтыру және реакция өнімдерін жою негізінде сипатталады. Мыс иондары d-элементтер және қисық сутекті байланыстармен сульфо тобы байланысқан түрлі құрылымдар кешенін құрайды, бұл сульфо тобының оттегі атомдары әсерінің нәтижесі болып саналады.

Өндірістік катиониттермен салыстырғанда синтезделген сульфокатионит үшін орнатылған механизмі мен алынған кинетикалық сипаттамалары көрсеткендей, біріншісінің Cu2 + иондарын алудың технологиялық процестерінде, сонымен қатар оны ауыр металл иондарынан ағынды суды тазарту технологиясында қолдану мүмкіндігінің болашағы бар.

Кестедегі мәліметтерде көрсетілгендей, сорбцияның бастапқы кезеңінде диффузияның тиімді коэффициентінің мәні артады, одан кейін төмендеу негізінде тұрақты мәнге жуықтайды. Диффузия коэффициентінің жоғарылауы сорбцияның бастапқы сатысында ионит бөлшектерінің (катиониттің бастапқы үлгісі құрғақ күйде болады) ісінуі барысында күрделене түсетін сипатын түсіндіреді. Иониттің ісіну уақыты, кезектегі диффузия коэффициентінің өсуі тәжірибелік жағдай, иониттің сорбцияланған иондарының табиғаты, өзара байланысу дәрежесі және басқа факторлармен анықталады. Осы сульфокатиониттерде Н + → Cu2 + иондары алмасқан жағдайда ион алмасудың ұзақтығы 30 минутты құрайды.

Алынған сульфокатиониттің тәжірибелік мәліметтері бойынша құрылған график, logQ = f (τ) координаттарында түзу сызығы ионит дәнінің ішіндегі ион алмасу процесін анықтайтын кинетиканың екінші реттілігін көрсетеді. ИК-спектрлік және әдебиеттер мәліметтеріне негізделген нәтижелерде, сульфокатионитпен мыс (II) иондарының тетраaква кешені түрінде байланысуы – [Cu (OH2) 4] $^{2+}$ • 2SO^{3-} байқалады.

Осылайша, статикалық жағдайда екі түрдегі сульфокатиониттің сулы ерітінділерден мыс (II) иондарын сорбциялану кинетикасын зерттеу нәтижелері, сонымен қатар кинетикалық қисықтарды математикалық өңдеу анықтағандай, сорбция механизмі аралас сипатқа ие және диффузия мен химиялық реакцияның жалпы әсері арқылы анықтауға мүмкіндік береді.

Түйін сөздер: кинетика, сорбция, мыс (II) иондары, фотометрия, диффузия, механизм.

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КИНЕТИКА И МЕХАНИЗМ СОРБЦИИ ИОНОВ МЕДИ(II) СУЛЬФОКАТИОНИТОМ

Аннотация.Исследование кинетики сорбции представляет практический интерес, так как скорость сорбции, измеряемая в ходе эксперимента, играет главную роль при решении таких практических задач, как выбор условий проведения сорбции типа сорбента, размера гранул сорбента, температурных условий и других параметров. Эксперименты по определению кинетики сорбции осуществляли при температуре 298 К, во временном интервале от 1 до 120 мин, при этом концентрация меди в растворе составляла 2 ммоль/мг. Для исследования сорбции ионов меди(II) катионами в фазе ионитов использовали следующие физико-химические методы анализа. Для изучения кинетики сорбции ионов меди с помощью катионитов двух типов использовали метод ограниченного объема. К навескам исследуемых образцов сорбента массой 1 г приливали по 100 дм^3 растворов $CuSO_4{\cdot}5H_2O$ с концентрацией 0.1 г/дм^3 и оставляли в течение времени от 1 до 120 мин, периодически встряхивая колбы. По истечении заданного времени раствор декантировали и определяли в нем остаточное содержание ионов меди. Кинетические кривые строили в координатах «А –t», где А – адсорбция, наблюдаемая в выбранный временной промежуток, мг/г, t – продолжительность контакта фаз. Математическую обработку полученных данных проводили в программе Origin Lab Pro. ИК-спектры были сняты на ИК-Фурье спектрометре System-2000 фирмы Перкин-Эльмер (США) в виде прессованных таблеток с KBr.

Предполагалось, что кинетика сорбции ионов меди сульфокатионитом должна определяться скоростью протекания ионообменной реакции. Общая скорость процесса ионного обмена может быть представлена как совокупность процессов, происходящих в растворе (диффузия противоионов к зерну и от зерна ионита) и в ионите (диффузия противоионов от поверхности к центру зерна ионита и в обратном направлении; обмен противоионов ионита на противоионы из раствора). Процесс ионного обмена является сложным, многостадийным, протекающим в гетерогенной системе твердое тело – жидкость. В связи с этим кинетику ионного обмена следует рассматривать с позиций общей теории гетерогенных реакций. Согласно этой теории процесс ионного обмена должен характеризоваться не только химическим превращением, протекающим в твердой фазе, но и процессами переноса массы вещества из одной фазы в другую, для восполнения расхода реагентов и удаления продуктов реакции. Ионы меди является *d*-элементами и образуют комплексы различного строения, связанные с сульфогруппой искривленными водородными связями, что является результатом влияния атомов кислорода сульфогрупп.

Установленный механизм и полученные кинетические характеристики для синтезированного сульфокатионита по сравнению с промышленным катионитом указывают на перспективность использования первого в технологических процессах извлечения ионов Cu^{2+}, а также возможность его применения в технологии очистки сточных вод от ионов тяжелых металлов.

Из данных таблицы видно, что значения эффективного коэффициента диффузии в начальный период сорбции возрастают, затем, снижаясь, приближаются к постоянной величине. Рост коэффициента диффузии, по-видимому, объясняется тем, что на начальной стадии сорбция осложняется набуханием частиц ионита (исходная навеска катионита была в сухом состоянии). Время набухания ионита, а, следовательно, рост коэффициента диффузии определяется условиями опыта, природой сорбируемых ионов ионита, степени сшивки и другими факторами. В случае обмена ионов $H^+ \rightarrow Cu^{2+}$ на данных сульфокатионитах продолжительность ионного обмена составляет 30 мин.

График, построенный по опытным данным для полученного сульфокатионита, оказался прямолинейным к координатам logQ = f(τ), показывает второго порядка кинетики, обусловливающим процесс ионного обмена внутри зерна ионита. Результаты на основание ИК спектральных и литературных данных можно предположить связывание ионов меди(II) сульфокатионитом в виде тетрааква комплекса – $[Cu(OH_2)_4]^{2+}{\cdot}2SO_3^-$.

Таким образом, результаты исследования кинетики сорбции ионов меди(II) из водных растворов сульфокатионитами двух типов в статических условиях, а также проведенная математическая обработка кинетических кривых, позволили установить, что механизм сорбции носит смешанный характер и определяется суммарным эффектом диффузии и химической реакции.

Ключевые слова: кинетика, сорбция, ионы меди(II), фотометрия, диффузия, механизм.

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SYNTHESIS OF NEW ION EXCHANGE MATERIALS ON THE BASE OF EPOXYACRYLATES

Abstract. The article studies the properties of obtaining anionite based on a triple copolymer of glycidylmethacrylate, styrene and Acrylonitrile and its suction of strontium ions. The composition and structure of the obtained anion was determined by infrared spectroscopy, were also studied basic physicochemical properties of the resulting anion.

Anionite, presented on the basis of GMA-ST-ACN, is promising in the field of ion exchange process and is used for the extraction of strontium ions from aqueous solutions in the field of hydrometallurgy.

The work is devoted to a review of the preparation of cross-linked polyelectrolytes, the extraction of strontium (II) ions using anionites. The possibilities of obtaining new nitrogen-containing anion exchangers based on a copolymer of glycidyl methacrylate (GMA), styrene (St) and acrylonitrile (ACN) have been studied. The optimal synthesis conditions were found and the physicochemical properties of the ion exchanger were investigated. Methods for the preparation of new anionites based on a copolymer of glycidyl methacrylate (GMA) with polyethylene polyimines (PEI) have been developed.

Keywords: glycidyl methacrylate, styrene, Acrylonitrile, polyethylenimine, polyethylene polyamine, heavy metals, strontium (II), ion exchange resins, sorption.

Introduction. Ion-exchange resins are widely used in various fields of human activity. They are used for softening and desalting water in the heat power industry, for treatment of waste and return water, for separation and removal of metal particles in hydrometallurgy, for cleaning substances in the chemical industry, for the regeneration of waste metal processing and electroplating. Therefore, the development of effective methods for obtaining new ion exchangers with improved kinetic, ion exchange, complex-forming properties, increased thermal and chemical resistance, as well as mechanical strength remains an urgent problem. In the case of using ion exchangers for special purposes, their ability to sorb substances with a relatively high molecular weight plays an important role [1]. The most well-known ion exchangers are usually prepared on the basis of styrene and divinylbenzene copolymers. The ability to control the amount of divinyl compound in the initial mixture of monomers during copolymerization and, most importantly, the availability of the resulting copolymers for various polymeranalogical transformations opens up great prospects [2].

In the process of polycondensation of SPL GMA with vinyloxyethylmethacrylate with various polyamines (polyethylenimine, polyethylene polyamine) and acids (concentrated sulfuric, phosphoric and thiodiglicolic acid solution) and subsequent curing, cross-linked anionites and cationites with high exchange capacity and physical and chemical parameters were obtained [3].

The scientific novelty of the article is that the proposed cross-linked anionites (GMA-ST-ACN) can become the first promising anionites in the field of ion exchange process that will be used in the hydrometallurgy of heavy metals [4].

A sulfur - and phosphorus-containing cationite was obtained based on a double copolymer of glycidyl methacrylate α - phenylvinylphosphonic acid and 96% sulfuric acid. This polymer has a high static exchange capacity of 0.1 n NaOH solution, equal to 8.35 mg-EQ/g, thermal stability, increased chemical, and sorption capacity for cobalt and copper ions 49. It can be used in hydrometallurgy as a sorbent for extracting transition metal ions.

An effective method for producing highly permeable ion exchangers with the preservation of the pyridine nitrogen atom in the interaction of glycidyl methacrylate with polyvinyloxyethylamine and its nitrogen-containing copolymers has been developed. Optimal synthesis conditions were determined, and the physic-chemical and sorption properties of the resulting polymers were studied [5].

Glycidyl methacrylate (GMA), whose structural features make it possible to obtain reactive compounds containing side epoxy groups and multiple double bonds, is a promising monomer for the synthesis of various Homo-and copolymers. They have long been successfully used for the synthesis of ion exchange materials for a wide range of purposes [6].

Grafted GMA copolymers can be obtained by combining side epoxigroups of the GMA-MMA copolymer obtained by anionic copolymerization with another "live" macroanion, such as "live" polystyrene or polyisoprene at 30°C in tetrahydrofuran. The polydispersity of the resulting grafted copolymer depends on the nature of the solvent in which the polystyrene and poly isoprene macroanions were obtained. Method preparative gas chromatography (GPC) it is shown that the combination takes place exclusively on epoxypropan without the participation of the carbonyl groups.

The results of quantum chemical studies of the electronic structure of the macromolecule GMA-ST-MA and GMA-ST-MA-H_3PO_4 [7] are presented.

Experimental. *Synthesis of the glycidyl methacrylate copolymer with styrene and Acrylonitrile.* The synthesis of the glycidyl methacrylate copolymer with methyl methacrylate and Acrylonitrile was performed by a radical method in a dioxane solution. Homo-and copolymers of GMA were synthesized by radical polymerization in a solvent (acetone, dioxane) in the presence of a DAA initiator of a concentration of $5 \cdot 10^{-3}$ mol / l at a temperature of 90°C in sealed molybdenum glass ampoules in an atmosphere of inert argon gas. Soluble polymers were purified by double precipitation from acetone to sulfur ether. Cross-linked copolymers (GMA-ST-ACN) were washed from unreacted monomers in 1,4-dioxane. Samples were dried at room temperature in a vacuum-drying cabinet to a constant mass.

Methods of synthesis of anion exchangers and cation exchangers. Condensation of linear and cross-linked GMA copolymers with polyamines (PEI, PEPA) and acids (H_2S0_4, H_3P0_4 (75 %), H_3P0_4 (ml)) was performed in an environment of organic solvents. In a three-neck flask equipped with a mechanical stirrer, a thermometer and a drop funnel, an amine suspension was loaded or acid was added and a copolymer solution was gradually dug in an organic solvent [9]. With intensive stirring, the mixture was heated to 30°C (H2S04, H_3P0_4 (75%), H_3P0_4 (ml)), 80 °C (PEI, PEP) and after the formation of the gel was unloaded into a porcelain cup, cured for a day at (60-120)°C, crushed, sieved, selecting a fraction with a granule size (0.25-1.00) mm. the Ionites were repeatedly washed with a solvent, extracted in the soxlet apparatus with methyl alcohol for removing unreacted substances, dried to a constant weight under vacuum at (25-30)°C.

Results and Discussion. Cations and anions on the basis of various copolymers of epoxyacrylate. Synthetic sorbents, especially selective chelating ionites, attract increasing attention when solving important environmental and technological problems. In the conditions of increasing technological prospects of synthetic ionites, it is very important to expand their range and study their properties. An important task facing the researchers is to create new promising monomers with different chelating groups, linear and cross-linked highly permeable polymer ion exchangers, selective phosphorus-and sulfur-containing ionites, strong and weak acid cation exchangers, anionites, amphoteric, optically active and organo - mineral polyelectrolytes, characterized by high ion exchange rates, thermal and radiation stability, and mechanical strength. Due to the presence of reactive functional groups in the molecule, epoxyacrylates are not only available monomers, but also quite promising [10].

Study of the structure of model epoxy-containing molecular systems by IR spectroscopy. Known polyelectrolytes of gel structure do not solve the problem of sorption of large metal ions and organic compounds. Weakly cross-linked strongly swollen samples have low mechanical characteristics, while macroporous samples [11] are permeable only for ions of limited size in the macropore region, and not for all active groups of the sorbent.

One way to solve this problem is to obtain copolymers with long-chain crosslinking agents. The use of di-and polyvinyl compounds with different distances between multiple bonds makes it possible to regulate the degree of crosslinking of macromolecules during copolymerization [12] and to obtain on their basis mechanically strong and osmotically stable macro-mesh ionites with the necessary size of the spatial grid [13].

Copolymers of GMA-ST-ACN were synthesized by radical polymerization in solution at the ratio of initial monomers [GMA]: [ST]:[ACN]= 60: 20: 20 mol.%.

The structure of the obtained triple copolymers GMA-ST-ACN was determined by IR spectroscopy (figure 1). The absorption frequencies in the copolymer spectra are assigned based on the IR spectra of the original monomers.

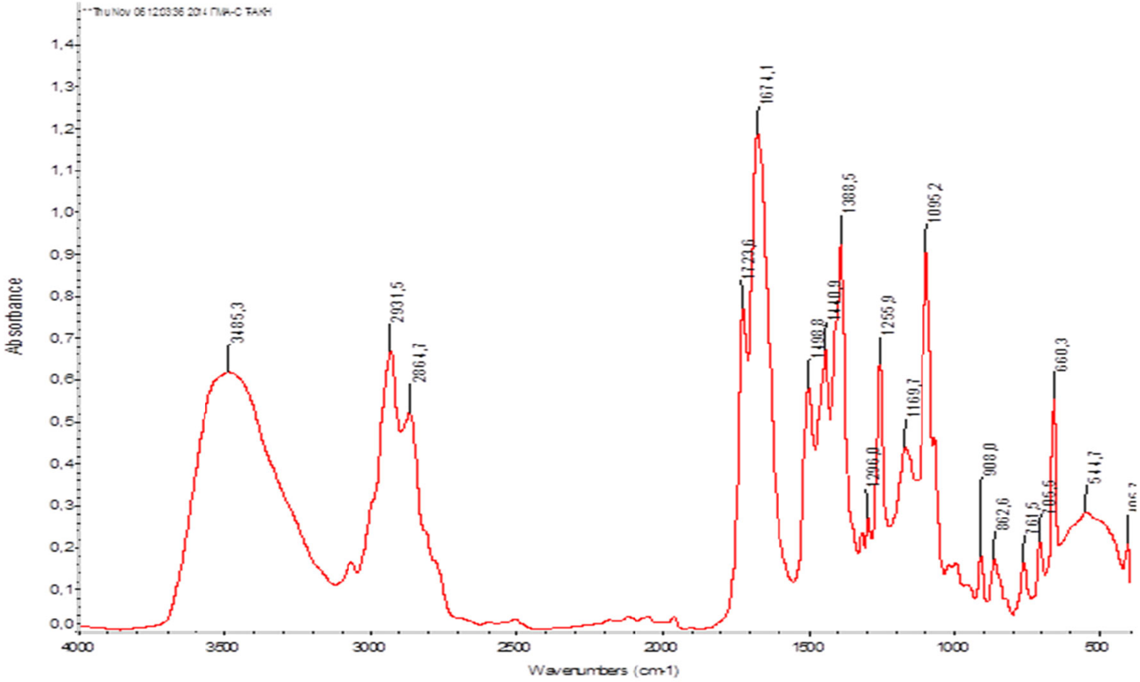

Figure 1 - The IR spectrum of the copolymer of GMA-ST-ACN

Studies of IR spectra of GMA-ST-ACN copolymers have helped to establish that the absorption bands of asymmetric and symmetric valence oscillations of C-O, C-C, C-H bonds of the epoxy cycle are observed at 908.0; 862.6; 761.5 and 705.5 cm^{-1}. The absorption frequency at 1674 cm^{-1} refers to the valence oscillations of the double bond. In the spectrum of the latter, as well as in the spectrum of its analog-isopropyl ether, a triplet structure is manifested in the region of 1169.3 cm^{-1}.

According to IR spectroscopy data, the elementary repeating link of GMA-ST-ACN copolymers is schematically represented (figure 2) can be represented as follows:

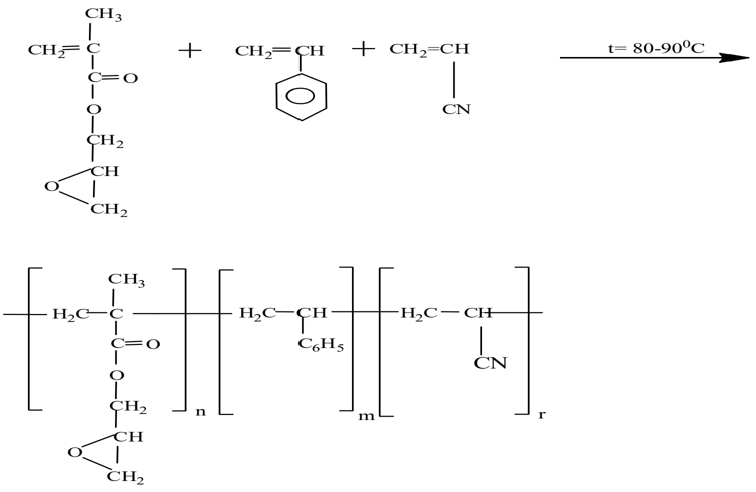

Figure 2 - The structural formula of the copolymer of GMA-ST-ACN

Based on these compounds, methods for the synthesis of highly permeable ion exchangers with improved kinetic characteristics have been developed [14].

Sorption of strontium ions by anion exchanger based on a copolymer of GMA-ST-ACN: PEI. The problem of creating new high-performance sorbents for wastewater treatment and extraction of mercury ions, polyvalent and transition metals in hydrometallurgy, medicine, food industry, water treatment, for sorption and concentration of isotopes, as well as for solving problems of oil spills on the water surface, integrated use of natural and energy-saving resources and environmental protection in the Republic of Kazakhstan remains relevant [15].

In non-ferrous metallurgy and metal processing enterprises, waste water contaminated with heavy metal salts is generated in technological processes, which have a very harmful effect on the ecosystem. In this regard, the study of sorption properties in relation to heavy metal ions of new ionites is of scientific and practical interest [16].

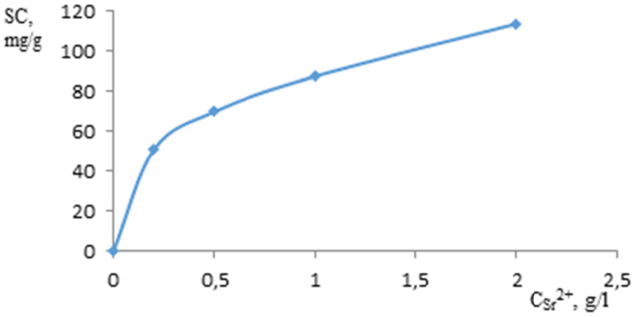

Figure 3 - Isotherms of Sr^{2+} ion sorption by GMA-ST-ACN anionite: PEI contact duration 7 days

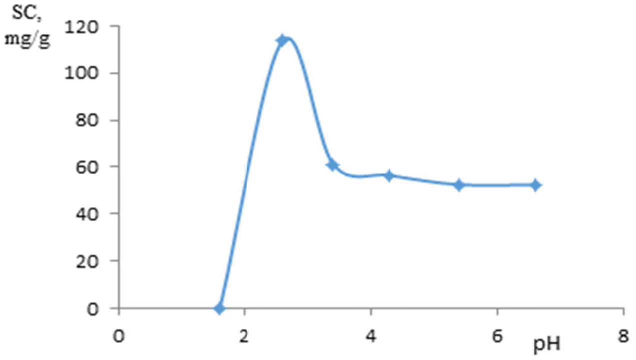

Figure 4 - Dependence of Sr^{2+} ion sorption by GMA-St-ACN anionite: PEI on the pH of $SrCl_2$ solutions (continued. Cohn. 7 days.)

The study of the effect of the pH of the solution on the sorption of the Sr (II) ion, anionite is of great importance. It was found that anionites based on the GMA-St-ACN-PEI copolymer quantitatively extract Sr (II) ions in acidic media at pH 5 (figure 4).Thus, we can say that the resulting sorbent in acidic environments well forms complex compounds.

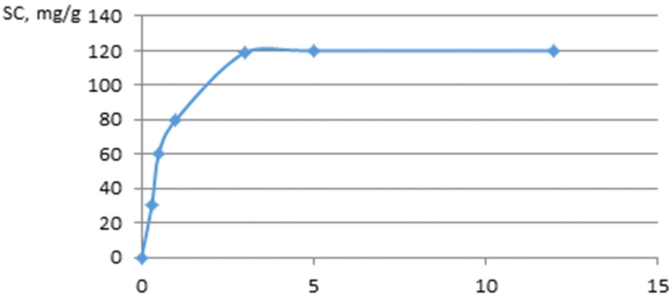

Figure 5 - Kinetic curves of strontium ion sorption with GMA-St-ACN anionite: PEI from $SrCl_2$ solutions (C=2.0 g / l, pH= 2.6)

From figure 5, which shows the dependence of the CE anionite GMA-St-ACN-PEI on the time of its contact with the SrCl2 solution (C=2.0 g / l, pH= 2.6), it follows that the equilibrium is established in 2.5 hours. Therefore, this ion exchanger has high kinetic properties.

Conclusions. This article is devoted to the development of available methods for obtaining new anionites based on triple (GMA-ST-ACN) glycidyl methacrylate copolymers, establishing optimal conditions for their synthesis, and investigating their physical, chemical, and sorption characteristics.

Methods for the synthesis of new highly permeable anionites based on the GMA-ST-ACN copolymer have been developed, optimal synthesis conditions have been found, and their physicochemical and sorption properties with respect to strontium ions have been studied.

It was found that they differ in high values of exchange capacities, increased chemical and thermal stability, and improved sorption capacity in relation to heavy (Sr^{2+}) metal ions.

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ЭПОКСИАКРИЛАТ НЕГІЗІНДЕ ЖАҢА ИОНАЛМАСТЫРУШЫ МАТЕРИАЛДАРДЫ СИНТЕЗДЕУ

Аннотация. Мақалада үштік сополимер глицидилметакрилат, стирол және акрилонитрил негізінде анионит алу және оның стронций иондарын сорып алу қасиеттері қарастырылған. Анионittің құрамы және құрылымы ИҚ-спектроскопия және элементтік анализ әдістерімен анықталды, физико-химиялық қасиеттері зерттелді және синтездің оптималды жағдайлары анықталды.

ГМА-СТ-АКН негізінде ұсынылған анионит ионалмастыру процесі аймағында перспективті болып саналады және гидрометаллургия саласында сулы ерітіндіден стронций иондарын бөліп алуда қолданылады.

Жалпы стронций элементі қоршаған ортаны ластаудың негізгі көзі болып есептеледі, көп жағдайда ядролық қару жасау мен атом өнеркәсібінің жұмыстарымен тығыз байланысты. Тірі организмдердегі стронций иондарының шамадан тыс мөлшері тірі ағза үшін өте қауіпті және көптеген ауруға ұшыратады. Ол туралы авторлар басқа мақаласында толығырақ тоқталған [1].

Органикалық және бейорганикалық қосылыстардың күрделі молекулаларын бөлуге, бөліп алуға және тазартуға байланысты ион алмасу процестері үлкен иондар мен молекулаларды сіңіруге қабілетті сорбенттер жасауды қажет етеді. Сондықтан жоғары өткізгішті ион алмастырғыштарды қолдану аталған мәселені тиімді шешудің алғышарттары болып саналады. Сонымен қатар, мұндай сорбенттер бірқатар экологиялық мәселелерді шешіп, сол арқылы ресурстарды үнемдейтін технологияларды құруға мүмкіндік береді. Бұл сорбенттерді өндірудің тиімді әдістерін әзірлеуге және олардың қасиеттерін зерттеуге, өндіріс технологиясын жетілдіруге және олардың ассортиментін кеңейтетін зерттеулерді жүргізуге қызығушылық тудырады.

Ион алмастырғыштар қалдықсыз экологиялық таза өндіріс схемасын жасауда қажетті компоненттердің бірі болып саналады. Осы мақсатта гельдік және макро торлық құрылым сорбенттерін қолдану әрдайым мүмкін емес, өйткені олар реактивті ортаға сәйкес келмейді, яғни регенерация процесінің қиындығына байланысты агрессивті ерітінділерге тұрақсыз, жеткілікті өткізгіштігі жоқ, ал кейбіреулері химиялық, термиялық ортада тұрақсыз болып келеді.

Соңғы уақытта зерттеушілер қызығушылығы жоғары селективті болып келетін металдың ішкі комплексті қосылыстар түзе алатын полиамин құрамы бар иониттерге артуда.

Полиэлектролиттерді алудың әдістері көпсатылы, олар катализатор ретінде қолжетімділігі аз және қымбат қосылыстарды, күрделі аппараттық дизайнды қажет етеді. Осыған байланысты кинетикалық және физика-химиялық қасиеттері жақсартылған ион алмастырғыштарды синтездеудің перспективалық әдіс жасауға көбірек көңіл бөлінуде.

Зерттеуді тұжырымдау қажеттілігі иониттердің өнеркәсіптік маркаларының үлкен ассортиментіне қарамастан, олардың көпшілігінде пайдалану мүмкіндіктерін шектейтін бірқатар кемшіліктер бар екендігіне байланысты. Сондықтан физика-химиялық және сорбциялық сипаттамалары жақсартылған полифункционалды жоғары өткізгіш иониттерді құрудың бастапқы мономерлері мен перспективалық жолдарын іздеу өзекті мәселе болып саналады. Мақала аталған мәселені шешуге арналған.

Жұмыс тігілген полиэлектролит пен аниониттерді қолдану арқылы стронций (II) иондарын алуға арналған. Құрамында азот кездесетін жаңа аниониттерді глицидилметакрилат (ГМА), стирол (Ст) және акрилонитрил (АКН) сополимері негізінде алу жолдары зерттелді. Синтездің оңтайлы шарттары анықталды

және ионіттің физика-химиялық қасиеттері қарастырылды. Полиэтиленполиминдермен (PEI) глицидилметакрилат (ГМА) сополимері негізінде жаңа аниониттер алу әдістері әзірленді.

Ғылыми-тәжірибелік жұмыстың нәтижесінде гидрометаллургия саласында практикалық тұрғыда қолдану үшін жақсартылған физика-химиялық сипаттамалары бар және жоғарыдағы қатаң талаптарға жауап беретін эпоксиакрилаттардың сополимерлері негізінде аниониттер алуды қамтамасыз етуге болады.

Түйін сөздер: глицидилметакрилат, стирол, акрилонитрил, полиэтиленимин, полиэтиленполиамин, ауыр металдар, стронций (II), ионалмастырғыш шайырлар, сорбция, анионит.

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СИНТЕЗ НОВЫХ ИОНООБМЕННЫХ МАТЕРИАЛОВ НА ОСНОВЕ ЭПОКСИАКРИЛАТОВ

Аннотация. В статье изучены свойства получения анионита на основе тройного сополимера глицидилметакрилата, стирола и акрилонитрила и его отсасывания ионов стронция. Состав и структура анионита определены методами ИК-спектроскопии и элементного анализа, изучены физико-химические свойства и определено оптимальные условия синтеза. Анионит, представленный на основе ГМА-СТ-АКН, является перспективным в области ионообменного процесса и используется для извлечения ионов стронция из водных растворов в области гидрометаллургии. В общем, стронций является основным источником загрязнения окружающей среды, во многом неразрывно связан с созданием ядерного оружия и работой атомной промышленности. Чрезмерное содержание ионов стронция в живых организмах очень опасно для живого организма и приводит к многочисленным заболеваниям. Об этом авторы подробно остановятся в следующей статье [1].

Ионообменные процессы, связанные с разделением, выделением и очисткой сложных молекул органических и неорганических соединений, требуют создания сорбентов, способных поглощать большие ионы и молекулы. Поэтому применение высокочастотных ионообменных устройств является предпосылкой для эффективного решения этой проблемы. Кроме того, такие сорбенты позволят решить ряд экологических проблем и создать на их основе ресурсосберегающие технологии. Это, в свою очередь, вызывает интерес к разработке эффективных методов производства таких сорбентов и изучению их свойств, проведению исследований, предусматривающих совершенствование технологии производства и расширение их ассортимента.

Ионообменники являются одной из наиболее необходимых компонентов при разработке безотходной экологически чистой схемы производства. Для этой цели использование сорбентов гелевой и макропористой структуры не всегда возможно, так как они несовместимы с реагирующей средой, т.е. неустойчивы к агрессивным растворам, недостаточно проницаемы, а некоторые являются нестабильными в химической, термической среде, а также связаны с трудностями процесса регенерации.

В последнее время все большее внимание исследователей привлекают полиаминосодержащие иониты, способные образовывать с целым рядов металлов внутрикомплексные соединения, вследствие их высокой селективности.

Наиболее известные способы получения полиэлектролитов являются многостадийными, требующими использования в качестве катализаторов малодоступных и дорогостоящих соединений, сложного аппаратурного оформления. В связи с этим большое внимание уделяется разработке перспективных методов синтеза ионообменников с улучшенными кинетическими и физико-химическими свойствами.

Необходимость постановки исследования вызвана тем, что, несмотря на большой ассортимент промышленных марок ионитов, многие из них обладают рядом существенных недостатков, которые ограничивают возможности их использования. Поэтому поиск исходных мономеров и перспективных путей создания полифункциональных высокопроницаемых ионитов с улучшенными физико-химическими и сорбционными характеристиками является актуальной задачей. Решению этой задачи и посвящена настоящая статья.

Работа посвящена обзору получения сшитых полиэлектролитов, извлечения ионов стронция (II) с использованием анионитов. Изучены возможности получения новых азотсодержащих анионитов на основе сополимера глицидилметакрилата (ГМА), стирола (Ст) и акрилонитрила (АКН). Найдены оптимальные условия синтеза и исследованы физико-химические свойства ионита. Разработаны методы получения новых анионитов на основе сополимера глицидилметакрилата (ГМА) с полиэтиленполиминам (PEI).

В результате научно-экспериментального работы можно обеспечивать получение анионитов на основе сополимеров эпоксиакрилатов с улучшенными физико-химическими характеристиками для практического применения в области гидрометаллургии.

Ключевые слова*:* глицидилметакрилат, стирол, акрилонитрил, полиэтиленимин, полиэтиленполиамин, тяжелые металлы, стронций (II), ионообменные смолы, сорбция.

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SYNTHESIS AND PHYSICOCHEMICAL CHARACTERISTICS OF MESOPOROUS ALUMINOSILICATES

Abstract. In the article, the synthesis of mesoporous aluminosilicates was carried out according to the developed methods, in which tetraethylorthosilicate $Si(OC_2H_5)_4$ was used as a source of silicon, secondary aluminum butoxide $(sec\text{-}BuO)_3Al$ and aluminum triisopropoxide $Al(i\text{-}OPr)_3$ were used as aluminum's sources. The synthesis of mesostructured aluminosilicate is based on the method of copolycondensation of silicon and aluminum sources in the presence of alcohol. Hexadecylamine (HDA, $C_{16}H_{33}NH_2$) was used as a template for the formation of a porous structure. The physicochemical characteristics of the synthesized structured mesoporous aluminosilicates have been studied. It was found that the synthesized materials MAS-1 and MAS-2 possess high specific surface area from 511 to 1170.0 m^2/g. The presence of a mesoporous and ordered structure in the synthesized aluminosilicates is confirmed by the data of low-temperature nitrogen adsorption/desorption, X-ray diffraction and FT-IR. To determine the relative strength of Brønsted and Lewis acid sites on the surface of mesoporous aluminosilicates, diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) of adsorbed pyridine samples was carried out. DRIFT analysis data demonstrated a majority of Lewis acid sites on the surface of the synthesized materials. We are currently studying the possibility of applying these materials as acidic components of bifunctional catalysts for petrochemical processes.

Key words: Mesoporous aluminosilicates, template, bifunctional catalysts, porosity, Lewis and Brønsted acid sites.

Introduction. More than 20 years ago, the synthesis of catalytically effective ordered mesoporous materials was reported for the first time [1-5]. Ordered mesoporous materials with adjustable pore sizes in the range of 2-50 nm have attracted much attention due to their unique structure with ordered porosity, large surface area and volume of pores, as well as potential applications, mainly in the field of catalysis, adsorption, separation, sensors and fuel cells [6]. Mesoporous aluminosilicates are one of the mesoporous materials that are of great interest for study, since they have become widely used as catalysts for the conversion process of n-alkanes into their branched isomers. Mesoporous aluminosilicates contribute to the high selectivity of the isomerization process (> 90%) at medium degrees of conversion (60-75 %), and also through the use of various methods of their synthesis, it becomes possible to regulate the size of their pores and, as a consequence, to obtain the size of molecules larger than in zeolites and other catalysts [7-10].

Mesoporous aluminosilicates can be synthesized using various "bottom-up" and "top-down" technologies such as co-precipitation, graft copolymerization, and precipitation using a silicon source and an aluminum source [11].

Mesoporous aluminosilicates form three different phases: a hexagonal phase, a cubic phase, and an unstable lamellar phase. Among them, mesoporous aluminosilicates with a cubic phase are widespread, while the other two are of limited use in catalysis [12, 13]. The synthesis of mesoporous aluminosilicates is based on the use of templates and their further removal by calcining at 450-600 °C. The use of nonionic surfactants as templates is of greatest interest for petrochemistry and oil refining. Materials synthesized on the basis of hexadecylamine possess the highest specific surface area (up to 1030 m^2/g) compared with other widely used templates, for example, triblock copolymers of polyethylene and polypropylene oxide (only up to 750 m^2/g) [14]. Another important issue in the synthesis of mesostructured aluminosilicates is the silicon to aluminum ratio (Si/Al). Karakhanov et al. [15] found that the most optimal ratio Si/Al = 10. Thus, mesoporous aluminosilicates with a high aluminum content possess higher specific surface area of 1030 m^2/g in comparison with samples with a Si/Al ratio = 20, 40 (673, 963 m^2/g, respectively), and also provide higher selectivity of n-dodecane hydroisomerization.

In this work, we present the results of a study of the effect of the mesoporous aluminosilicates' synthesis method on their physicochemical characteristics.

Experimental part. Samples of mesoporous aluminosilicates for the synthesis of which hexadecylamine was used as a structure-forming template were prepared by the authors. The synthesis of mesostructured aluminosilicate was based on the method of copolycondensation of tetraethylorthosilicate $Si(OC_2H_5)_4$ and secondary aluminum butoxide $(sec\text{-}BuO)_3Al$/aluminum triisopropoxide $Al(i\text{-}OPr)_3$ in the presence of alcohol. For this, the sources of aluminum were dissolved in alcohol. Then a solution of tetraethylorthosilicate was added dropwise to them under intensive stirring. In parallel, while heating a solution of hexadecylamine with alcohol was prepared. After complete dissolution of the template, distilled water was added to the solution. A solution of silicon and aluminum compounds mixture was added portionwise to the resulting viscous homogeneous mass containing the template solution. Further, after adding water dropwise and with stirring for 10 minutes, the resulting mixture was stirred for 6 hours at room temperature. Then it was kept without stirring at room temperature for a day. Next, the precipitate was filtered on a Buchner funnel, dried at room temperature for 24 hours, and then slowly heated in an oven to 110 °C during 3 hours. The resulting solid-phase substance was placed in a tubular furnace and heated to 600 °C at a heating rate of 1 °C/min, after which the sample was calcined at this temperature for 6 hours in an oxygen flow.

The porous structure of the synthesized samples and the values of the BET surface area were studied using the standard nitrogen adsorption/desorption method on a Quanta Chrome Autosorb-6 sorptometer.

The ordering of the porous structure of the synthesized materials was analyzed using the method of small-angle X-ray scattering. X-ray diffraction patterns were recorded on a Rigaku D/MAX 2200 diffractometer with a Cu K radiation source.

Determination of Lewis/Brønsted acid sites in the synthesized catalysts was carried out using experiments of diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) of adsorbed pyridine using a PerkinElmer Spectrum One FTIR-spectrometer. Before these tests, the samples were pretreated at 110 °C to remove water adsorbed on acid sites. After adsorption of pyridine, the samples were dried at 40 °C before DRIFT analysis. The background spectrum was recorded using KBr. The spectra obtained after pyridine desorption were subtracted from those measured before pyridine adsorption (fresh samples) in order to determine the bands relative to the Lewis and Brønsted acid sites.

The IR spectrum of the samples was obtained on a Thermo Nicolet 8700 FT-IR spectrometer with a spectral resolution of 4 cm^{-1}.

Results and discussion. The nitrogen adsorption/desorption isotherms in both studied samples belong to type IV according to the classification of Brunauer, Emmett and Teller; the presence of a hysteresis loop in them is correlated with capillary condensation occurring in the mesopores. However, they differ in the type of hysteresis loop (figure 1). If on the isotherm of the MAS-1 sample the hysteresis loop belongs to the H1 type, indicating a narrow pore size distribution and ordered structure, then on the isotherm of the MAS-2 sample - to H4 type and indicates narrow slit-shaped pores [16]. The synthesized materials also sharply differ in specific surface area (MAS-1 – 511 m^2/g, MAS-2 – 1170.0 m^2/g), the average pore diameter and pore volume vary from 3.82 nm to 2.19 nm and1.47 cm^3/g to 0.875 cm^3/g (table 1). According to the data shown in figure 2, for both samples the maximum on the pore size distribution curve is observed at 3.5-4.2 nm. The average pore size for all three samples is due to the presence of a small minority of macropores.

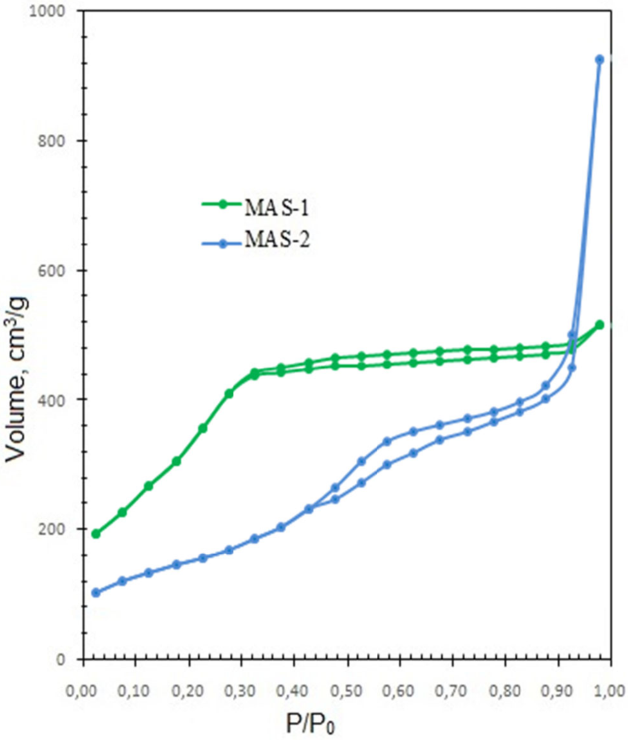

Figure 1 – Nitrogen adsorption/desorption isotherms on MAS-1 and MAS-2 samples

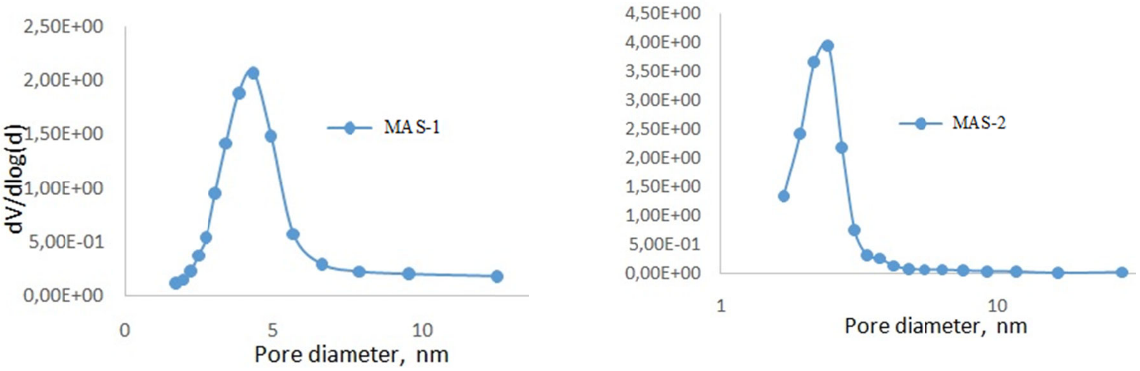

Figure 2 – Pore size distribution for MAS-1 and MAS-2 samples

Table 1 – Physical properties of samples

Sample	Specific surface area, m^2/g	Volume of pores, cm^3/g	Average pore diameter, nm
MAS-1	511.0	1.469	3.82
MAS-2	1170.0	0.875	2.188

To confirm the mesoporosity and orderliness of the porous structure of the synthesized materials, the X-ray scattering method was used.

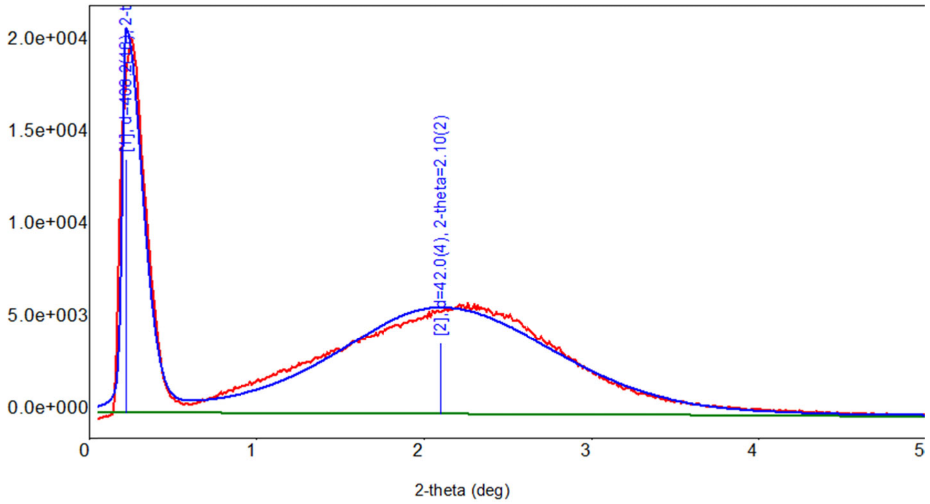

Figure 3 – Small-angle X-ray diffraction pattern of mesoporous aluminosilicate MAS-1

Figure 3 shows an X-ray diffraction pattern of small-angle scattering of a mesoporous sample MAS-1, according to which the presence of a pronounced peak in the 2.1° 2θ angular range indicates the presence of a mesoporous structure. For the MAS-1 sample, the intensity peak is in the 2.1 ° range, which at the wavelength of the radiation used corresponds to an interplanar distance of 4.2 nm.

DRIFT spectroscopy of adsorbed pyridine samples was performed in order to determine the relative strength of Brønsted and Lewis acid sites on the surface of mesoporous aluminosilicates (figure 4).

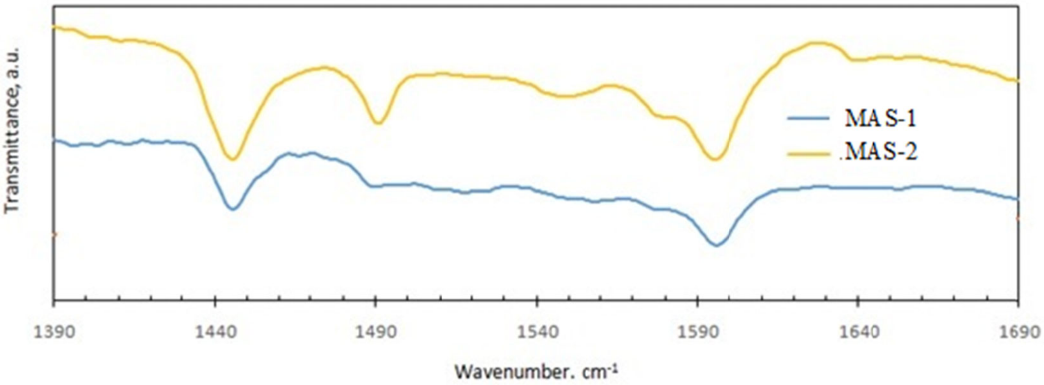

Figure 4 – Diffuse reflectance infrared Fourier transform (DRIFT) spectra of mesoporous aluminosilicates

The studied samples show absorption bands at 1445, 1490 and 1595 cm^{-1}. The observed bands at 1445 and 1595 cm^{-1} in the spectra are explained by the presence of hydrogen-bonded pyridine adsorbed on the centers of Lewis acids [17, 18]. The band observed at about 1490 cm^{-1} is due to the adsorption of pyridine, both at the Lewis centers and at the Brønsted acid sites. It should be noted that the appearance of an absorption band at 1640 cm^{-1} in the spectrum of the MAS-2 sample indicates the presence of Brønsted acid sites.

FT-IR spectroscopy was used to study the retention of crystalline ordering in the synthesized mesoporous aluminosilicates. FT-IR spectra of synthesized samples in the range of 400-4000 cm^{-1} are shown in figure 5. Fourier transform infrared spectroscopy (FTIR) complements X-ray diffraction in the search for modifications in crystallinity by comparing peak intensities in the range from 400 to 1300 cm^{-1} [19]. These bands are grouped into two types of vibrations of TO_4 tetrahedral units (where T = Al or Si): vibrations associated with connections between TO_4 tetrahedra, which are therefore sensitive to structural modifications, and vibrations of TO_4 tetrahedra, insensitive to structural modifications..

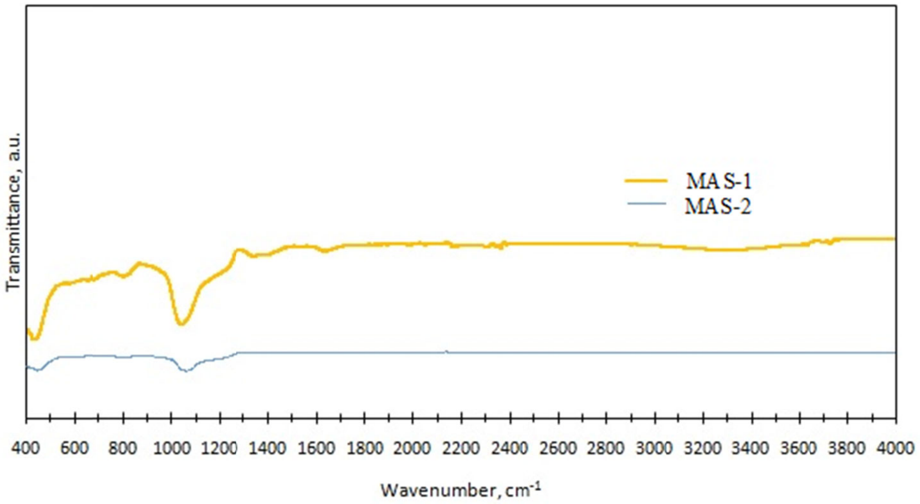

Figure 5 – FT-IR-spectra of synthesized samples

According to the data in Figure 5, the appearance of the 1059 cm^{-1} band can be attributed to asymmetric stretching vibrations of Si–O and Al–O, while the 800 cm^{-1} band in the spectra of the studied materials indicates crystalline ordering [20], i.e., apparently, this is due to the internal vibration of TO_4 tetrahedra containing Al and Si. The absorption band at 450 cm^{-1} corresponds to the deformation vibrations of SiO_4.

Thus, the ordered mesoporous aluminosilicates MAS-1 and MAS-2 were synthesized using various sources of aluminum. The synthesized samples were examined using various physicochemical methods of analysis. The presence of a mesoporous and ordered structure in the synthesized aluminosilicates is confirmed by the data of low-temperature nitrogen adsorption/desorption, X-ray diffraction and FT-IR. According to the DRIFT analysis data, it was shown that the surface of the synthesized materials mainly contains Lewis acid sites. We are currently studying the possibility of using these materials as acidic components of bifunctional catalysts for petrochemical processes.

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МЕЗОКЕУЕКТІ АЛЮМОСИЛИКАТТАР СИНТЕЗІ МЕН ФИЗИКА-ХИМИЯЛЫҚ СИПАТТАМАСЫ

Аннотация. Мақалада мезокеуекті алюминосиликаттарды синтездеу әдісінің физика-химиялық сипаттамасына әсерін зерттеу нәтижелері ұсынылған. Мезокеуекті алюмосиликаттар дайындалып, синтезіне гексадециламин құрылымдық темплат ретінде пайдаланылды. Мезоқұрылымды алюмосиликат синтезі спирт қосылатын тетраэтилортосиликат $Si(OC_2H_5)_4$ және екіншілік алюминий бутоксид (екіншілік-BuO)$_3$Al/алю-миний триизопропилатAl(i-OPr)$_3$ сополиконденсация әдісіне негізделген. Ол үшін алюминий көзі спиртте ерітіліп, қарқынды араластыру барысында тетраэтилортосиликат ерітіндісі тамшылатылып қосылды. Сонымен қатар, қыздыру арқылы гексадециламиннің спиртпен ерітіндісі дайындалды. Темплат ерітіндісі қосылып алынған қою, біртекті массаға бөлме температурасында 6 сағат бойы араластыру арқылы кремний және алюминий қосылыстары қоспасының ерітіндісі бөліктеп қосылып, 1 күн кептірілді. Алынған қатты фазалы қоспа құбырлы пешке салынып, 1°C/мин қыздыру жылдамдығымен 600°C дейін қыздырылып, кейін үлгі осы температурада 6 сағат бойы оттегі ағынында күйдірілді.

Төмен температуралы азот адсорбциясы/десорбциясы әдісіне сәйкес, зерттелген екі үлгідегі изотермалар Брунауэр, Эммет және Теллер классификациясы бойынша IV типке жатады, ондағы гистерезис тұзағы мезокеуекте кездесетін капиллярлық конденсациямен байланысты. Алайда олар гистерезис тұзағы түрімен ерекшеленеді. Егер MAS-1 үлгісінің изотермасында гистерезис тұзағы H1 типіне жататын болса, бұл кеуек өлшемі мен реттелген құрылымы бойынша аз таралғанын көрсетеді, ал MAS-2 – H4 үлгісінің изотермасы тар саңылаулы кеуекті көрсетеді. Сондай-ақ, синтезделген материалдар меншікті бет ауданы бойынша да ерекшеленеді (MAS-1 – 511 м^2/г, MAS-2 – 1170,0 м^2/г), кеуектің орташа диаметрі мен көлемі 3,82 нм-ден 2,19 нм-ге дейін және 1,47 см^3/г-дан 0,875 см^3/г-ға дейінгі аралықты қамтиды. Барлық үш үлгідегі кеуектің орташа өлшемі макрокеуектердің аз мөлшеріне байланысты.

Синтезделген материалдардың кеуекті құрылымының мезокеуектілігі мен реттілігін дәлелдеу үшін рентгендік шашырату әдісі қолданылды. MAS-1 мезокеуекті үлгісінің аз бұрышты шашырау рентгенограммасына сәйкес, 2θ бұрыштарының мәндері аймағында 2,1° айқын шыңның болуы мезокеуекті құрылымның болатынын көрсетеді. Сонымен қатар MAS-1 үлгісі үшін қарқынды шыңы 2,1° аймағында байқалады, ол пайдаланылған сәулеленудің толқын ұзындығында 4,2 нм аралық қашықтыққа сәйкес келеді.

Мезокеуекті алюмосиликат бетіндегі Бренстед және Льюис қышқыл орталығының салыстырмалы беріктігін анықтау үшін адсорбцияланған пиридин үлгілерінің диффузды шағылысын Фурье түрлендіруі арқылы (DRIFT) ИҚ спектроскопиясына талдау жасалды. Зерттелген үлгілерде 1445, 1490 және 1595 см$^{-1}$ кезінде жұтылу жолақтары байқалды. Спектрлердегі 1445 және 1595 см$^{-1}$ байқалатын жолақтар Льюис қышқыл орталықтарында жұтылған сутегімен байланысқан пиридинне қатысты түсіндіріледі. Шамамен 1490 см$^{-1}$ байқалған жолақ Льюис орталықтарында да, Бренстед қышқылы орталықтарында да пиридин адсорбциясымен байланысты. MAS-2 үлгісінің спектрінде 1640 см$^{-1}$ аймағында жұтылу жолағының пайда болуы Бренстедтің қышқыл орталықтарының болатынын көрсетеді.

Синтезделген мезокеуекті алюмосиликаттардағы кристалды реттіліктің сақталуын зерттеу үшін 400-4000 см$^{-1}$ диапазонында FT-ИҚ спектроскопия әдісі қолданылды. Спектрлердегі 1059 см$^{-1}$ жолағының пайда болуы Si–O және Al–O созылуының асимметриялық ауытқуына жатқызылуы мүмкін, ал зерттелген материал спектрінде 800 см$^{-1}$ аймағындағы жолақ кристалды реттілікті көрсетеді, яғни бұл Al және Si бар TO_4 тетраэдрлерінің ішкі діріліне байланысты. 450 см$^{-1}$ жұтылу жолағы SiO_4 деформациялық тербелістеріне сәйкес келеді.

Осылайша түрлі темплаттар мен алюминий көздерін қолдану арқылы MAS-1 және MAS-2 мезокеуекті алюмосиликаттар синтезделіп, түрлі физика-химиялық талдау әдістері негізінде зерттелді. Синтезделген алюмосиликаттардағы мезокеуек пен реттелген құрылым төмен температуралы азот адсорбциясы/десорбциясы және FT-IR деректерімен расталған. DRIFT талдамасына сәйкес синтезделген материалдар бетінде негізінен Льюистің қышқыл орталықтары бар екендігі көрсетілген. Қазіргі уақытта бұл материалдарды мұнай-химия процестеріне арналған бифункционалды катализатордың қышқыл компоненттері ретінде пайдалану мүмкіндігін зерттеп жатырмыз.

Түйін сөздер: мезокеуекті алюмосиликат, темплат, бифункционалды катализатор, кеуектілік, Льюис пен Бренстедтің қышқыл орталықтары.

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СИНТЕЗ И ФИЗИКО-ХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ МЕЗОПОРИСТЫХ АЛЮМОСИЛИКАТОВ

Аннотация. В данной работе представлены результаты исследования влияния метода синтеза мезопористых алюмосиликатов на их физико-химические характеристики. Авторами были приготовлены серии мезопористых алюмосиликатов, для синтеза которых в качестве структурообразующего темплата был использован гексадециламин. Синтез мезоструктурированного алюмосиликата был основан на методе соликонденсации тетраэтилортосиликата $Si(OC_2H_5)_4$ и вторичного бутоксида алюминия (втор-BuO)$_3$Al/триизопропилат алюминия Al(i-OPr)$_3$ в присутствии спирта. Для этого источники алюминия были растворены в спирте. Далее, при интенсивном перемешивании к нему по каплям добавлялся раствор тетраэтилортосиликата. Параллельно готовился раствор гексадециламина со спиртом при нагревании. К полученной густой однородной массе, содержащей раствор темплата, порциями добавляли раствор смеси соединений кремния и алюминия при перемешивании в течение 6 часов при комнатной температуре. Затем

она была высушена в течение суток. Полученное твердофазное вещество поместили в трубчатую печь и нагрели до 600°С со скоростью нагрева 1°С/мин, после чего прокаливали образец при этой температуре в течение 6 часов в потоке кислорода.

По данным метода низкотемпературной адсорбции/десорбции азота, изотермы на обоих изученных образцах относятся к IV типу по классификации Брунауэра, Эммета и Теллера, наличие в них петли гистерезиса связано с капиллярной конденсацией, происходящей в мезопорах. Однако они отличаются по типу петли гистерезиса. Если на изотерме образца MAS-1 петля гистерезиса относится к Н1 типу, свидетельствующая об узком распределении пор по размерам и упорядоченной структуре, то на изотерме образца MAS-2 – Н4, свидетельствующая об узких щелевидных порах. Также синтезированные материалы резко отличаются и по удельной поверхности (MAS-1 – 511 $м^2/г$, MAS-2 – 1170,0 $м^2/г$), средний диаметр пор и объем пор колеблются с 3,82 нм до 2,19 нм и с 1,47 $см^3/г$ до 0,875$см^3/г$. Для обоих образцов максимум на кривой распределения пор по размерам наблюдается при 3,5-4,2 нм. Средний размер пор для всех трех образцов обусловлен присутствием в небольшом количестве макропор.

Для подтверждения мезопористости и упорядоченности пористой структуры синтезированных материалов был использован метод рентгеновского рассеяния. Согласно рентгенограмме малоуглового рассеяния мезопористого образца MAS-1, присутствие выраженного пика в области значений углов 2θ 2,1° свидетельствует о наличии мезопористой структуры. Для образца MAS-1 пик интенсивности находится в области 2,1°, что при длине волны используемого излучения соответствует межплоскостному расстоянию 4,2 нм.

Для определения относительной прочности кислотных центров Бренстеда и Льюиса на поверхности мезопористых алюмосиликатов был проведен анализ ИК-спектроскопии с Фурье-преобразованием диффузного отражения (DRIFT) адсорбированных образцов пиридина. На изученных образцах фиксируются полосы поглощения при 1445, 1490 и 1595 $см^{-1}$. Наблюдаемые полосы при 1445 и 1595 $см^{-1}$ в спектрах объясняются наличием связанного водородом пиридина, адсорбированного на центрах кислот Льюиса. Полоса, наблюдаемая примерно на 1490 $см^{-1}$, обусловлена адсорбцией пиридина как на центрах Льюиса, так и на центрах кислоты Бренстеда. Следует отметить, что появление полосы поглощения в области 1640 $см^{-1}$ на спектре образца MAS-2 свидетельствует о наличии кислотных центров Бренстеда.

Для исследования сохранения кристаллического упорядочения в синтезированных мезопористых алюмосиликатах была использована FT-ИК-спектроскопия в диапазоне 400-4000 $см^{-1}$. Появление на спектрах полосы 1059 $см^{-1}$ может быть отнесено к асимметричным колебаниям растяжения Si–O и Al–O, в то время как полоса в области 800 $см^{-1}$ в спектрах изученных материалов указывает на кристаллическое упорядочение, т.е., по-видимому, обусловлена это внутренней вибрацией тетраэдров TO_4, содержащих Al и Si. Полоса поглощения при 450 $см^{-1}$ отвечает деформационным колебаниям SiO_4.

Таким образом, были синтезированы упорядоченные мезопористые алюмосиликаты MAS-1 и MAS-2 с использованием различных темплатов и источников алюминия. Синтезированные образцы были исследованы с помощью различных физико-химических методов анализа. Наличие мезопористой и упорядоченной структуры в синтезированных алюмосиликатах подтверждены данными низкотемпературной адсорбции/десорбции азота и FT-IR. По данным DRIFT анализа показано, что на поверхности синтезированных материалов в основном присутствуют кислотные центры Льюиса. В настоящее время мы изучаем возможность использования этих материалов в качестве кислотных компонентов бифункциональных катализаторов нефтехимических процессов.

Ключевые слова: мезопористые алюмосиликаты, темплат, бифункциональные катализаторы, пористость, кислотные центры Льюиса и Бренстеда.

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ELECTROCHEMICAL BEHAVIOR OF SILVER IN A SULPHURIC ACID SOLUTION

Abstract. In recent years, alternating current has been widely used in various fields of chemical and electrochemical technology. When a symmetric alternating current passes through an electrochemical cell, in principle there should be no visible changes, since the product restored to the cathode half-period should be oxidized back to the anodic half-period. However, depending on the conditions of electrolysis, electrode material, etc. a purposeful course of the electrochemical process is possible. The paper shows the distinctive features of electrochemical processes occurring on a silver electrode during electrolysis by industrial alternating current in a solution of sulfuric acid by the method of rational mathematical planning. The optimal conditions for the dissolution of silver are determined by studying the effect of current density at the electrodes, the concentration and temperature of the electrolyte, the duration of the electrolysis and the frequency of the alternating current. It is shown that when polarized with an alternating current of silver in a pair with a titanium electrode, the process of passivation of the silver electrode is eliminated, and the rate of dissolution of the metal increases.

Keywords: alternating current, silver, electrode, electrolysis, current density, mathematical planning, current output.

One promising technique now in use is polarization with an alternating current of industrial frequency, which is of interest to researchers in regard to the oxidation with destruction of passivating films. A feature of the processes that occur under the action of alternating current of industrial frequency is that by changing the direction of the current, it is possible to remove oxide films and create conditions for the subsequent dissolution of the metal [1-5].

It is necessary to mark that the detail researches carried out by us on a silver electrode and other researchers studying titanium, chrome, molybdenum, lead, etc. in case of polarization by an alternating current of industrial frequency, showed that the electrode processes proceeding with an electrode involvement by superimposed a. c. technique, sharply differ both on the mechanism, and according to the quantitative characteristics [6-14].

In [15–18], we studied the electrochemical behavior silver of different solutions under polarization with alternating current of industrial frequency. Analysis of the literature data showed there were very few works devoted to the electrochemical behavior of silver. Studying the ionization of silver under the action of industrial alternating current would therefore seem to be relevant and timely.

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

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

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

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

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

Results and discussion. The study of the electrochemical behavior of silver in a in acidic solution was carried out by the method of rational mathematical planning [19]. In accordance with the planning for the six factors, and in each factor of five levels 25 experiments were conducted. The studied factors and their levels are presented in table 1.

Table 1 – Levels of factors under study

Factor	Level				
	1	2	3	4	5
X_1, current density on the silver electrode, A/m^2	200	400	600	800	1000
X_2, current density on the titanium electrode, kA / m^2	60	80	100	120	140
X_3, solution concentration, M	1,0	2,0	3,0	4,0	5,0
X_4, duration of electrolysis, min	15	30	45	60	75
X_5, electrolyte temperature, ° C	40	50	60	70	80
X_6, frequency of alternating current, Hz	50	100	200	300	400

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

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

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

Table 2 – Experimental values of private functions

Function	Level					Average value
	1	2	3	4	5	
Y_1	66,74	62,82	59,63	54,42	50,64	58,85
Y_2	58,44	62,80	65,65	60,40	46,96	58,85
Y_3	63,42	60,85	58,64	56,92	54,42	58,85
Y_4	67,80	63,50	57,82	54,21	50,92	58,85
Y_5	63,36	61,81	58,47	56,64	53,97	58,85
Y_6	61,40	65,30	61,30	55,10	51,15	58,85

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

$$Y - Y_1 = a\,(X - X_1) \quad (2)$$

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

$$Y_2 - Y_1 = a\,(X_2 - X_1) \quad (3)$$

After the final transformation, the equation has the form:

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

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

$$\mathrm{Y} = \mathrm{Y}_1 - \mathrm{a}\,(\mathrm{X} - \mathrm{X}_1)^2 \tag{5}$$

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

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

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

Table 3 – Calculated values of functions at matrix levels

Function	Level					Average value
	1	2	3	4	5	
Y_1 = 93-0,018 (X-300)	64,83	61,17	57,60	54,00	50,40	57,60
Y_2 = 91-0,0037 $(X-70)^2$	55,00	60,63	60,63	57,67	51,75	57,13
Y_3 = 91 – 4,6666 (X-0,75)	62,16	69,83	57,5	55,17	52,83	59,50
Y_4 = 95 - 0,29 (X-22,5)	67,17	62,82	58,47	54,12	49,77	58,47
Y_5 = 92 - 0,2666 (X-25)	63,33	60,67	58,01	55,33	52,67	58,00
Y_6 = 93 - 0,0029 $(X-40)^2$	62,70	62,70	60,39	55,75	48,79	58,06

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

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

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

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

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

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

To describe the statistical multifactor dependencies, the particular functions generalized M.M.Protodyakonov’s equation [20]:

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

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

Based on the equation, we find the correlation coefficient for N = 25 and K = 6. It is equal to 0.5338 and the significance is $t_R = 3.02 > 2$, which indicates the adequacy of the generalized equation.

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

Function	R	t_R	Function significance
Y_1	0,96	19,18	Significant
Y_2	0,73	2,70	Significant
Y_3	0,86	5,65	Significant
Y_4	0,99	85,70	Significant
Y_5	0,94	14,41	Significant
Y_6	0,92	10,28	Significant

Based on the equation, 8 were determined as the optimal conditions for the electrochemical dissolution of silver: the density on the silver electrode was 200 A / m^2, the density on the titanium electrode was 100 kA / m^2, the electrolyte concentration was 1.0-2.0 mol / l, the electrolyte temperature was 40 -60 °C, electrolysis duration - 15-45 minutes, frequency of alternating current - 50 Hz.

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

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

The effect of current density on the titanium electrode on the CO dissolution of silver was studied in the range of 60-140 kA/m^2. The maximum CO value is observed at i_{Ti} = 100 kA / m^2 (figure 1a).

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

When studying the electrolytes concentration effect on the results of electrolysis, it was found that the maximum value of the current efficiency is achieved at a concentration of 1.0 mol/l (figure 1c). With an increase in the electrolyte concentration, the near-electrode space is saturated with SO_4^{-2} anions and, in this connection, the silver dissolution current output decreases.

We found (figure 1d) that when the temperature rises to 60 0C, the value of the apparent current output increases, reaching 136 %, and then remains almost unchanged. It is known from the literature that at 60 ^{0}C in a sulfuric acid solution, metallic silver is dissolved chemically.

Studying the effect of the electrolysis duration on the dissolution process of silver during polarization with industrial alternating current was studied in 1.0 M of sulfuric acid (figure 1e). The current dissolution rate of silver naturally decreases. It should be noted that on the electrode during prolonged experiments the electrode surface is covered with a layer of dark color.

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

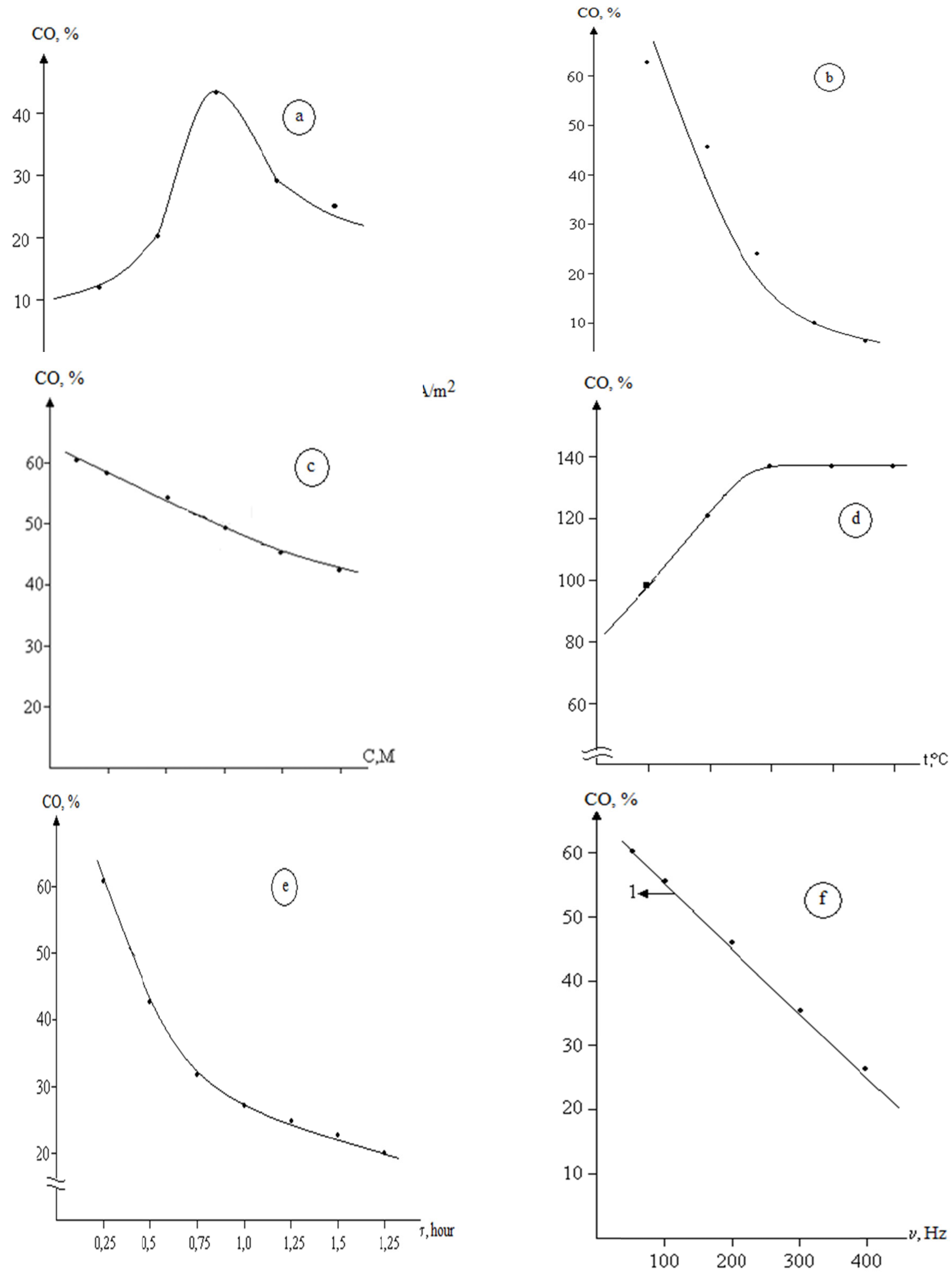

Figure 1 - Point graphs and curve approximation effect on W silver dissolution:
a - current density on a silver electrode, b - current density on a titanium electrode, c - electrolyte concentration,
d - electrolyte temperature, e– electrolysis duration, f - AC frequency

Thus, we studied the electrochemical behavior of silver during polarization of industrial alternating current in a solution of sulfuric acid by rational mathematical planning. It is shown that all the studied parameters have a significant effect on silver dissolution.

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КҮКІРТ ҚЫШҚЫЛЫ ЕРІТІНДІСІНДЕГІ КҮМІСТІҢ ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТІ

Аннотация. Айнымалы токпен электрохимиялық жүйелердің қасиетін зерттеу – қазіргі электрохимияның ең қолайлы эксперименттік әдістерінің бірі. Бұл әдіс көптеген мәселелерді шешуге мүмкіндік береді. Электрохимияда импеданс әдісін сандық қолданудың басталуын кеңестік электрохимиктер құрды.

Соңғы жылдары айнымалы ток түрлі химиялық және электрохимиялық технология саласында кеңінен қолданылуда. Симметриялы айнымалы токты электрохимиялық ұяшықтан өткізген кезде негізінен ешқандай өзгеріс орын алмауы керек, себебі катодты жартылай периодта тотықсызданған өнім анодты жартылай периодта кері тотығуы тиіс. Алайда электролиз жағдайына, электрод метериалына және т.б. жағдайға байланысты мақсатты электрохимиялық процесс жүруі мүмкін. Жұмыста айнымалы токпен поляризацияланған күміс электродында күкірт қышқылы ерітіндісінде жүретін электрохимиялық үрдістердің ерекшеліктері рациональды жоспарлау әдісі бойынша көрсетілген. Күміс және титан электродтарындағы ток тығыздығының, электролит концентрациясы мен температурасының, электролиз ұзақтығының және айнымалы ток жиілігінің әсерін зерттегенде айнымалы токпен поляризацияланған күмістің еритін оптималды жағдайлары анықталды. Титан электродымен жұптасқанда күміс электродында пассивтену үдерісі жойылып, металдың еру жылдамдығының артатындығы анықталды.

Жұмыстың мақсаты – рационалды математикалық жоспарлау әдісімен күкірт қышқылы ерітіндісіндегі айнымалы токпен поляризация кезіндегі күмістің электрохимиялық қасиетін зерттеу.

Жоспарға сәйкес алты факторға қатысты әрбір фактордың бес деңгейі бар, 25 эксперимент жүргізілді. Статистикалық көпөлшемді тәуелділікті сипаттау үшін жеке функциялар М.М. Протодьяконов теңдеуін талдап қорытты. Осы теңдеу негізінде біз $n = 25$ және $K = 6$ үшін корреляция коэффициентін анықтадық. Оның мәні 0,5338 және $t_r = 3{,}17>2$ тең және бұл жалпыланған теңдеудің сәйкестігін көрсетеді.

Күмістің электрохимиялық еру жағдайының келесідей оңтайлы шаралары анықталды: күміс электродының тығыздығы – 200 А/м^2, титан электродының тығыздығы – 100 кА/м^2, электролит концентрациясы – 1,0 -2,0 моль/л, электролит температурасы – 40-60 °С, электролиз ұзақтығы – 15-45 мин., айнымалы ток жиілігі 50 Гц. Зерттеу нәтижелері көрсеткендей күмісті айнымалы токпен поляризациялағанда күміс иондары және күміс оксиді түзіледі.

Титан электродымен жұптасқанда күміс электродында пассивтену үдерісі жойылып, металдың еру жылдамдығы артатындығы анықталды. Катодты жартылай периодта титан электродында газ тәрізді сутегі бөлінеді және күміс иондарының тотықсыздануы байқалады. Осы сәтте күміс электроды анодты жартылай периодта болады және күміс иондары, дицианоаргентат және күміс оксидінің пайда болуы негізінде ериді. Зерттелген параметрлер күмісті ерітү үдерісіне елеулі әсер ететіні анықталды.

Түйін сөздер: айнымалы ток, күміс, электрод, электролиз, ток тығыздығы, математикалық жоспарлау, ток бойынша шығым.

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ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ СЕРЕБРА В СЕРНОКИСЛОМ РАСТВОРЕ

Аннотация. Изучение поведения электрохимических систем с применением переменного тока является одним из наиболее мощных экспериментальных методов современной электрохимии. Этот метод позволяет решать большое число разнообразных задач. Начало количественному применению импедансного метода в электрохимии было положено советскими электрохимиками.

В последние годы переменный ток находит все более широкое применение в различных областях химической и электрохимической технологии. При пропускании через электрохимическую ячейку симметричного переменного тока в принципе никаких видимых изменений произойти не должно, так как восстановленный в катодный полупериод продукт должен обратно окисляться в анодный полупериод. Однако в зависимости от условий электролиза, материала электрода и т.д. возможно целенаправленное протекание электрохимического процесса. В работе показаны отличительные особенности электрохимических процессов, протекающих на серебряном электроде при электролизе промышленным переменным током в растворе серной кислоты методом рационального математического планирования. Определены оптимальные условия растворения серебра при исследовании влияния плотности тока на электродах, концентрации и температуры электролита, продолжительности электролиза и частоты переменного тока. Показано, что при поляризации переменным током серебра в паре с титановым электродом, устраняется процесс пассивации серебряного электрода, и скорость растворения металла возрастает.

Целью данной работы является исследование электрохимического поведения серебра при поляризации нестационарными токами в растворе серной кислоты методом рационального математического планирования.

В соответствии с планированием для шести факторов, а в каждом факторе пять уровней, было проведено 25 опытов. Для описания статистических многофакторных зависимостей частные функции обобщили уравнение М.М.Протодьяконова. На основании уравнения нашли коэффициент корреляции при N = 25 и K = 6. Он равен 0,5338 и значимость t_R = 3,17> 2, что указывает на адекватность обобщенного уравнения.

Определены оптимальные условия электрохимического растворения серебра: плотность на серебряном электроде – 200 А/м^2, плотность на титановом электроде – 100 кА/м^2, концентрация электролита – 1,0-2,0 моль/л, температура электролита– 40-60 °С, продолжительность электролиза – 15-45 мин., частота переменного тока – 50 Гц. Как показали результаты исследований, при поляризации серебра промышленным переменным током, образуются ионы серебра, оксид серебра.

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

Ключевые слова: переменный ток, серебро, электрод, электролиз, плотность тока, математическое планирование, выход по току.

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THE INFLUENCE OF ASPHALT RESIN PARAFFIN OIL RESIDUE ON ASPHALT CONCRETE TECHNOLOGY

Abstract. Based on scientific research and experimental tests, it has been proved that solid waste from oil fields in the Kyzylorda region based on asphalt resin paraffin sediment (ARPS) is close and binding in its chemical composition to the main component of the asphalt-concrete mixture of the road surface. And the most effective method of disposal and neutralization of oil waste was chosen.

The ARPS formed from the use of oil at the Kumkol field was studied, which includes asphaltenes 3 ... 8%; resins-13 ... 20%; fats-34...65%; mechanical impurities-20...49%; water-1...5%.

In this article, it is proposed to develop an asphalt-concrete technology based on asphalt-resinous paraffin deposits. The issue of increasing the reserves of raw materials for the production of durable asphalt concrete and reducing the amount of oil-containing waste in the fields due to the sale of solid oil-containing waste will be considered. Based on the study, the composition of asphalt-resinous paraffin deposits was analyzed by IR spectroscopy. The infrared (IR) absorption spectrum was captured in the IR-Fourier spectrometer IR Prestige-21.

The absorption spectra of asphalt-tar-paraffin deposits recorded by the IR spectrometer show the structure of hydrocarbons in the methyl (2954-2852 cm-1), methylene (1463-1377 cm-1), and methine (721 cm-1) groups. The analysis shows that the composition of solid oil waste generated at the fields consists mainly of paraffin hydrocarbons.

The results of the study showed the suitability of asphalt-resinous paraffin deposits for use as organic binders to dense asphalt concrete of type" B " grade III for IV-V road climatic zones recommended for applying top layers of coating on roads of technical category IY.

Replacing scarce commercial bitumen with oil waste will significantly reduce the cost of commercial products, as well as simplify the process of preparing the mixture and prevent environmental pollution with harmful substances released from oil.

Key words: oil waste, organic binders, paraffin wax, spectroscopic method, absorption spectrum, paraffinic hydrocarbon, heat resistance, softening temperature.

Introduction. Currently, the topical issue of interest to scientists in the field of construction is the decontamination of waste oil and its use in the production of construction materials as a source of renewable raw materials.

The analysis of the literature has shown that one of the most widely used areas of oil waste is road construction. Oil sludge is used as an additive or as an additive in oil-soil, cement-soil, asphalt-concrete, aerated-concrete, sludge-concrete compositions, which improves the quality of concrete mixes by reducing strength, frost resistance, water resistance, water absorption, swelling and shrinkage.

Parallel use of waste oil in road construction is an expansion of the raw material base of soils, reduction of energy and labor costs, reduction of the road surface cost and simplification of the technological process [1].

Many scientists of the country have done a lot to improve the environmental situation and reduce their negative impact on the environment by using solid oil waste as a raw material. In particular: Academician K.A. Bisenov [2], professors P.A. Tanzharikov [3], A.A. Shomantaev, S.S. Uderbaev [4], R.A. Narmanova [5] and others. Their work is especially valuable not only in the Kyzylorda region, but in the whole territory of Kazakhstan in the development of oil production and industrial waste as a source of renewable raw materials and the production of efficient building materials. It has been proved that the fields of high paraffin oil in Kyzylorda oblast can be used in road construction on the basis of scientific research and experimental tests [6].

The study selected the most efficient type of waste oil for disposal and neutralization. It was found that such wastes include asphalt-resin paraffin sediments. They are formed during the evaporation of pipes using special equipment for cleaning, dewaxing of process equipment (oil storage tanks, bullets, sewage wells) [7].

At present, the issue of disposal of asphalt-resin paraffin sediments and oil wastes remains unresolved. Therefore, one of the study tasks was to solve these problems, and it caused a special scientific research. The research program is based on the directions of this type waste utilization in the world professional practice and the effective implementation of promising technical solutions. The APRS from the Kumkol field was studied, which includes asphaltenes of 3 ... 8%; resins - 13 ... 20%; oil - 34 ... 65%; mechanical additives - 20 ... 49%; water - 1 ... 5%.

Asphalt-resin paraffin sediments are close to bitumen, have a high deformation, soften when heated and completely dissolve in terms of composition and properties. These properties determine the areas of agricultural products use and the possibility of their use as a binder in the production of building materials [6-7]. The use of waste oil as a raw material is widely used in three industries. These are road construction, construction materials and fuel and energy. Table 1 show that the most profitable industry is the production of construction materials.

Table 1 - Efficient use areas of waste oil as a raw material resource

Areas of application	Direction of application	The amount of waste, mass%	Source of waste	Technical result of use
Road construction	Asphalt concrete	5-10	Paraffin sediment	Expansion of raw material construction
	Aerated concrete	1-2	Oil sludge	Increasing mechanical stiffness
	Sludge concrete	80-90	Oil drilling sludge	Increase resistance to water and liquids
	Fuel oil floor	90-95	Techno genic oil sludge	-
Construction materials	Due to the soft roofing water-proofing material	30-40	Oil sludge	Reduce mixing time and temperature
	Roofing and water-proofing mastic	30-50	Waste from spilled oil	Reduction of bitumen consumption
	Waterproofing mixture	100	ARPS (asphalt resin paraffin sediment)	No preparation required
	As a lightening additive	20-50	Oil sludge	Reduction of material density
	Expanded clay	5-15	Oil sludge	Reducing the bulk density of the material and reducing fuel consumption

Materials and methods. The analysis of the asphalt-resin paraffin sediments (ARPS) formation was carried out, the composition and properties of paraffin and resin-asphaltenes were studied in order to discover the meaning of the research topic. Heavy metals in asphalt-resin paraffin sediments were determined by X-ray fluorescence spectroscopy, and their composition was chromatographically analyzed by chromate-mass spectrometer.

A special group of oil wastes is asphalt-resin paraffin sediments, which are considered as the main object of study.

Asphalt-resin paraffin sediments (ARPSs) are formed during the injection of oil through pipelines, as a result of underground and overhaul of wells, cleaning of process equipment, evaporation of pumpcompressor pipes using special dewaxing equipment. Asphalt-resin paraffin sediments are often dark-purple or dark-thick ointment-like masses with high viscosity.

Oil and gas fields as Kumkol, Aryskum, Kyzylkiya and Maibulak, located in the South Turgai depression, were selected as research objects. The oil from the above fields is a type of oil with high paraffin and complex parameters. Based on the characteristics of degassed oil, it was found that the freezing point and the high content of high molecular weight paraffin. The excitation range of these parameters is very large for the objects in the field and it will be very difficult to explain. It was not possible to relate these parameters to the location of the pipe in the hypsometric condition in the selected study material.

The average content of asphalt-resin paraffin sediments in oil recovery systems with wells is paraffin - 12-86%, resin - 0.8-20%, asphalten - 0.3-45%, oils 6.5-50% and inorganic impurities - 0 -37%. Typical composition and physical and chemical properties of asphalt-resin paraffin oil residues from various fields are shown in Table 2.

Table 2 - Composition and physical and chemical properties of asphalt-resin paraffin sediments in oils from various fields

Indicators	ARPS			
	Kumkol	Aryskum	Kyzylkiya	Maibulak
Group hydrocarbon content, mass%				
Hydrocarbons -paraffin-naphthenic (P)	48,60	62,06	43,46	41,80
-aromatic-monocyclic	12,38	10,07	16,03	12,40
-aromatic bicyclic	11,07	10,37	10,04	6,70
- aromatic polycyclic	9,60	7,46	15,86	14,30
Compound of hydrocarbons (M)	81,65	89,96	85,39	75,20
Resin (R)	14,65	8,96	7,74	19,20
Asphalteners (A)	3,70	1,04	6,87	5,60
The ratio of structural elements				
P / (R + A) ratio	2,6	6,2	3,0	1,7
A / (A + R) ratio	0,20	0,10	0,47	0,23
A / (M + R) ratio	0,04	0,01	0,07	0,06
Composition of mechanical impurities, mass%	10,99	1,07	3,26	0,42
Physical and mechanical properties				
Melting point, ^{0}C	72,0	66,5	56,,5	-
Density 20^{0}C, g / cm^3	2,29	1,03	1,05	0,946

The composition and structure of oil from the Kumkol field were analyzed by IR (Infrared) spectroscopy. The absorption spectrum for the infrared (IR) region was recorded on an IR Prestige-21 IR Fourier spectrometer (Shimadzu, Japan) [8].

The composition of asphalt-resin paraffin sediments is determined by the IR spectrum, and the spectra of raw materials from relatively different deposits based on the analysis are shown in figure 1–3.

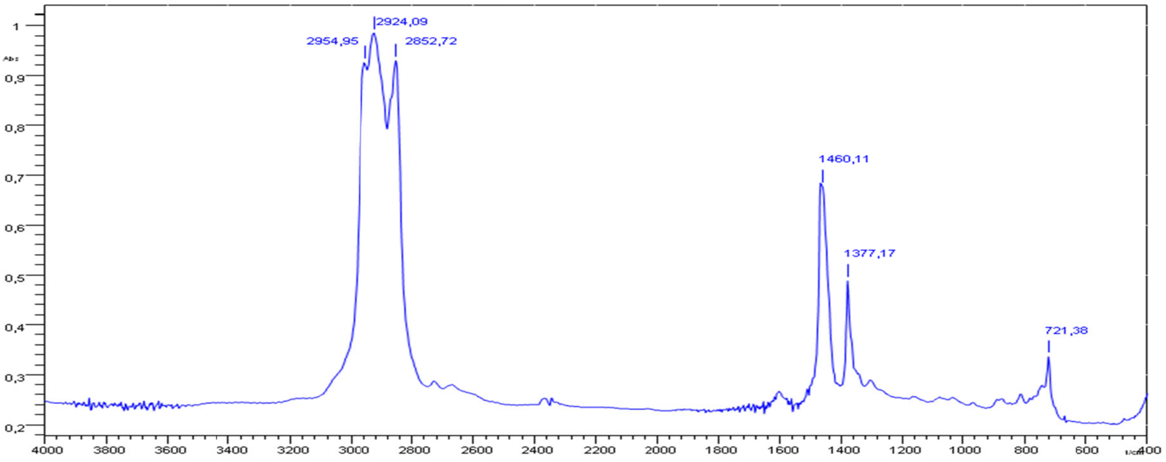

Figure 1 – Infrared spectrum of asphalt-resin paraffin deposits at the Kumkol field

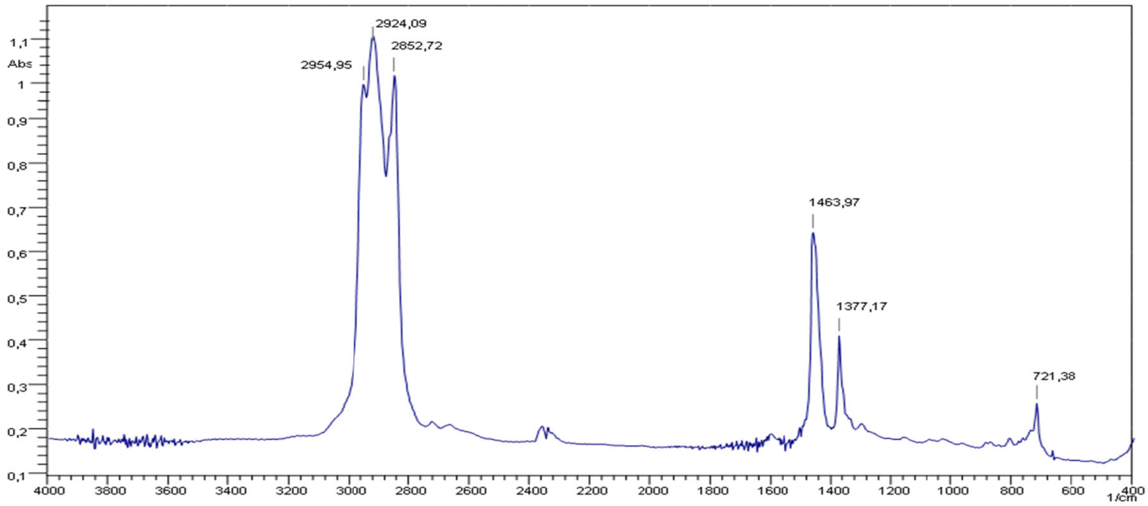

Figure 2 Infrared spectrum of asphalt-resin paraffin deposits at the Aryskum field

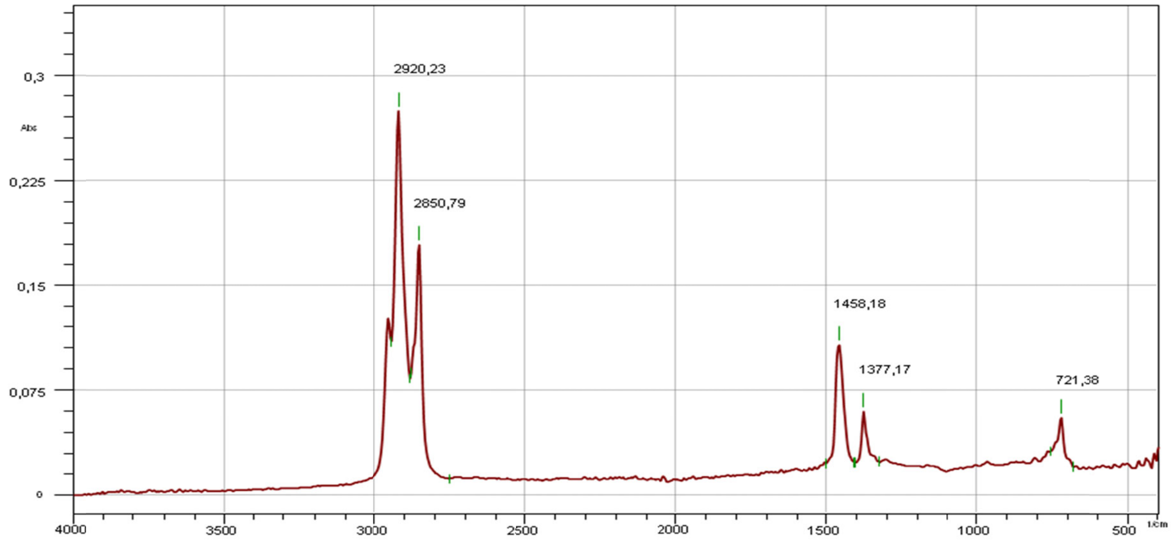

Figure 3 Infrared spectrum of asphalt-resin paraffin deposits at the Maibulak field

Absorption spectra of asphalt-resin-paraffin sediments recorded in the IR spectrum show the structure of hydrocarbons in the methyl (2954-2852 cm^{1}), methylene (1463-1377 cm^{1}), and methyl (721 cm^{1}) groups. The analysis shows that the composition of solid oil residues formed in the fields consists mainly of paraffinic hydrocarbons.

Results and discussion. The purpose of obtaining products in accordance with the standards of physical and mechanical nature, predetermined in the implementation of the ARPS based on the analysis of works on this topic in the literature and summarizing the results of research in this area. Comprehensive experimental and theoretical research to find a technology for the use of asphalt-paraffin resin sediments allows to consider this waste as a source of raw materials for road construction [6, 7]. The study revealed the need to add active substances such as lime and cement to improve the properties of oil waste used in road construction (viscosity of asphalt-resin paraffin sediments and the strength of oily soils). The mineral mixture heated to 140-160 ° C is mixed with asphalt-resin paraffin sediment melted at a temperature of 80-95 ° C, obtained in 10-15% by weight of the mineral component. The addition of agricultural products to the mineral mix in the ratio of 10-15% by weight is sufficient to obtain a quality asphalt concrete mix. It is not enough to get the ARPS below the specified weight ratio, and adding more than the specified limit will lead to a decrease in the quality of the mixture. In addition, the use of ARPS to replace commercial bitumen will significantly reduce the cost of asphalt concrete and improve the environment. The obtained asphalt concrete admixtures were tested by physical and mechanical methods in accordance with ST RK 1225-2003 and ST RK 1218-2003. The results are given in Table 3.

Table 3 - Physical and mechanical properties of asphalt concrete based on asphalt-resin paraffin sediments

Samples #	Weight ratio,%			Compressive strength, megaPascal (MPa)				Long-term water saturation coefficient	Water absorption coefficient	Medium density	Water resistance coefficient
	Mineral admixture (gravel + sand)	ARPS	Bitumen BND 60/90	R_{20}	R_{50}	R_0	R_{cy}				
1	92,0	8,0	-	2,1	1,0	12,7	2,1	0,59	1,2	2,24	0,71
2	90	10,0	-	2,5	1,1	12,5	2,4	0,65	1,5	2,25	0,72
3	88	12,0	-	2,5	1,2	12,1	2,76	0,66	2,4	2,26	0,74
4	86	14	-	2,58	1,2	12,3	2,6	0,66	3,5	2,27	0,73
5	84	16	-	2,63	1,4	12,6	2,5	0,61	3,5	2,25	0,71
6	90	-	10	2,5	1,6	12,8	2,77	0,6	3,8	2,28	0,76
According to the requirements of ST RK 1225-2003, For type B, brand III, IV-V road-climatic zones				Not less than 2.0	Not less than 1.1	Not more than 13.0	Not normalized	Not less than 0.6	1.5 to 4.0	Not normalized	Not normalized

The results of the study showed that asphalt-paraffin resin residues can be used as organic binders for type III "B" type dense asphalt concrete for road climatic zones IV-V, which is recommended for use in the construction of the upper layers of pavement on roads of technical category IV.

Asphalt concrete mix obtained by mixing the mineral component with asphalt-resin paraffin deposits is not inferior to the mixture obtained when using commercial bitumen in terms of technical characteristics. At the same time, the replacement of scarce commercial bitumen with petroleum waste as ARPS, which significantly reduces the cost of commercial products, as well as simplifies the process of preparation of the mixture and prevents pollution of the environment with harmful substances released from oil [9-12].

During the study, the physical and mechanical properties were qualitative, the composition of the resulting mixture was as follows: gravel - 40 ... 50%, sand - 15 ... 20%, limestone - 10 ... 15%, ARPS - 20 ... 25 %. These give new properties to the waterproof mixture.

Strengthening of oil paraffin soil by mixing with gravel showed that it increases the physical and mechanical properties of asphalt concrete mix and accelerates the formation of the mineral surface of the road.

It was observed that the strength of asphalt-concrete mixtures made from oil wastes of oil companies with the addition of active substances (lime and cement) increases to 11%. They are temporary covering of highways; when lying frost-resistant layers in the construction of hard pavements; used in the construction of the lower layers of cement and asphalt pavements.

If the residue consists mainly of pure paraffin sediment, it is very effective to use it instead of bitumen. Its quality is not inferior to bitumen, but it is 10-15 times cheaper [13-15].

It is proposed to use asphalt-resin paraffin sediments as a building material for the asphalt-concrete mixture to be laid on the road surface. Practical tests were carried out at the Asphalt Concrete Plant of Kyran LLP, and on the basis of the proposed technology in Kyzylorda, 100 m long and 5 cm thick asphalt concrete pavement was laid.

The results of laboratory tests of strength and stability of asphalt concrete based on asphalt-resin paraffin sediments are given. Their resistances to moisture and frost, rheological properties, samples were made in the laboratory in special samples in order to test the physical and mechanical properties of asphalt concrete on the basis of asphalt-resin paraffin sediments.

Analysis of the diagram of the composition “mineral powder + amount of ARPS + mineral aggregate” in the system “Mineral aggregate + gravel + sand” led to the following conclusions: mineral aggregate is 80% of the total weight of asphalt concrete components, mineral powder 9.4-10.2% and production in the share of 8.6-10.2% of ARPS leads to high strength [16-21].

Conclusions. The new scientifically based results of research for the development of asphalt concrete mixes, which provide an important environmental solution and expand the stock of road construction materials, and developments in the use of asphalt-resin paraffin sediments, are analyzed in this paper.

The main scientific and practical results are:

1. The analysis of the areas of use of oil wastes as a source of renewable raw materials showed that oil wastes, such as oil sludge and oil soils, are used mainly.
2. In the Laboratory of Methods of Physical and Chemical Analysis of Engineering Profile at Korkyt Ata Kyzylorda University, functional groups of asphalt-resin paraffin oil residues were determined by IR spectrometer method. Heavy metals in ARPS were analyzed by X-ray fluorescence spectroscopy. Chromatographic analysis of oil and asphalt-resin paraffin sediments was performed on Agilent 7890N / 5975 chromate-mass spectrometer.
3. The results of laboratory tests of strength and stability of asphalt concrete on the basis of asphalt-resin paraffin sediments have shown the physical and mechanical properties of asphalt concrete based on ARPS, its resistance to moisture and frost, rheological properties meet current standards.
4. Asphalt-concrete based on asphalt-resin paraffin sediments was introduced into production according to the results of research and experimental tests. This is confirmed by the act of commissioning at the asphalt plant of LLP “Kyran” in Kyzylorda region. The economic efficiency of the developed technology, based on the calculations, the environmental and economic efficiency of the production of asphalt concrete amounted to 1.3 million tenge per 1 km of road surface. In addition, it was recommended for use in the educational process for engineering and environmental specialties and approved by the Act of introduction into the educational process.

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АСФАЛЬТТЫ ШАЙЫРЛЫ ПАРАФИНДІ МҰНАЙ ҚАЛДЫҒЫНЫҢ АСФАЛЬТТЫ БЕТОН ТЕХНОЛОГИЯСЫНА ӘСЕРІ

Аннотация. Жыл сайын автокөлік ағымының артуы автокөліктің тұтастай жол жабынына күш түсіреді. Жол жабынының төменгі қабаттарына қарағанда беткі асфальтты бетон қабаттарының жағдайы нашар. Асфальтты бетон жабынының ерекшелігі жүктеме әсерінің уақытқа, көлемі мен температурасына және төзімділігіне тәуелді болып келеді. Климат жағдайы көлік жүктемесімен қосылып асфальтты бетон жабынының төзімділігіне қаттырақ әсер етеді. Жабынды бастапқы пайдаланудың өзінде-ақ сызаттар пайда болып, пластикалық бұзылыстарды бақылауға болады. Жабындардың мерзімінен бұрын бүлінуінің негізгі себебіне қолданылатын битумның ұзаққа шыдамдылығы мен пайдалану қасиеттері жатады.

Мұнайды қайта өңдеу зауыттары шығаратын жол битумы қасиеттері бойынша жабын іске асатын климат жағдайына сәйкес келмейді. Соның салдарынан энергияны қажет етпейтін әдістер мен технологияларды пайдалану негізінде асфальтты бетон жабынының аязға, ығысуға, сызатқа төзімділігін және беріктігін арттыруға бағытталған тұтқырлы заттар жасау қажеттілігі туындайды.

Ғылыми зерттеулер мен тәжірибелік сынақ барысында Қызылорда облысындағы мұнай кен орындарының асфальтты-шайырлы парафин шөгіндісі (АШПШ) негізіндегі қатты қалдығы жол жабынының асфальтты бетонды қоспасының негізгі құрамына өзінің химиялық құрамы бойынша ұқсастығы және байланыстырушы сипаты дәлелденді. Мұнай қалдықтарын кәдеге асыру және залалсыздандырудың ең тиімді түрі таңдалды.

Басқа қатты мұнай қалдықтарына қарағанда АШПШ айырмашылығы – топырақпен араласпаған және тек қана жоғары молекулалы қатты көмірсутегіден тұратын таза органикалық өнім болып келетіндігі.

Құмкөл кен орнындағы мұнайды пайдаланудан түзілетін АШПШ зерттеліп, құрамында асфальтен 3...8%; шайыр – 13...20%; май – 34...65%; механикалық қоспа – 20...49%; су – 1...5% болатыны анықталды.

Құрамы және қасиеттері жағынан асфальтты-шайырлы парафин шөгінділері битумға жақын, деформациялануы жоғары, қыздырғанда жұмсарып, толық еріп кететін қасиеті бар. Осы қасиеттері АШПШ-ның пайдалану бағыттарын белгілеп, жол құрылысы материалдарын алу барысында байланыстырушы ретінде қолдану мүмкіндігі айқындалды.

Мақалада асфальтты-шайырлы парафин шөгіндісі негізіндегі асфальтты бетон технологиясын жасау жолдары ұсынылады. Қатты мұнай қалдықтарын пайдалану арқылы ұзақ уақытқа шыдамды асфальтты бетон өндірісінің шикізат қорын ұлғайтып, кен орындарындағы мұнай қалдығын азайту мәселесі қарастырылады.

Зерттеу жұмыстарының негізінде асфальтты-шайырлы парафин шөгіндісі құрамына ИҚ спектроскопия әдісі арқылы талдау жасалды. Инфрақызыл (ИҚ) облысы бойынша жұтылу спектрі IR Prestige-21 ИК-фурье спектрометрінде (Shimadzu, Жапония) түсірілді.

ИҚ спектрінде түсірілген асфальт-шайыр-парафин шөгінділерінің жұтылу спектрлері метил (2954-2852 $см^{-1}$), метилен (1463-1377 $см^{-1}$), метинді (721 $см^{-1}$) топтардағы көмірсутек құрылымын көрсетеді. Талдау жұмыстарының нәтижесінде кен орындарында түзілген қатты мұнай қалдықтарының құрамы негізінен парафинді көмірсутектен тұратынын көрсетеді.

Зерттеу нәтижелері асфальтты-шайырлы парафин шөгінділердің IV техникалық санаттағы жол жамылғысының жоғарғы қабатын салу үшін қолдануға ұсынылатын IV-V жол климаттық аймақтар үшін III маркалы «Б» типтегі тығыз асфальтты бетонға органикалық тұтқырлар ретінде пайдалануға жарамдылығын көрсетті.

Минералдық компонентті асфальтты-шайырлы парафин шөгінділерімен араластыру жолымен алынған асфальтты бетон араласпасы техникалық сипаттамалары бойынша тауарлы битумды пайдалану кезінде алынған қоспадан кем түспейді. Сонымен бірге, тапшы тауарлы битумды мұнай қалдығы – АШПШ-мен алмастыру тауарлы өнім құнын едәуір арзандатады, сондай-ақ қоспа дайындау үдерісін жеңілдетеді және мұнайдан бөлініп шыққан зиянды заттармен қоршаған ортаны ластаудың алдын алады.

Түйін сөздер: мұнай қалдықтары, органикалық байланыстырғыштар, қатты парафин, спектроскопиялық әдіс, жұтылу жолағы, парафинді көмірсутек, жылуға төзімділік, жұмсару температурасы.

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ВЛИЯНИЕ АСФАЛЬТО-СМОЛИСТО-ПАРАФИНИСТЫХ НЕФТЯНЫХ ОТХОДОВ НА ТЕХНОЛОГИЮ АСФАЛЬТОБЕТОНА

Ежегодное увеличение потока автомобилей значительно усиливает нагрузку на покрытие автомобильных дорог, и в целом на дороги. Состояние наружных слоев асфальтобетонного покрытия дорог, по сравнению с нижними слоями, неблагоприятное. Особенностью асфальтобетонных покрытий является зависимость воздействия от времени нагрузки, ее объема, температуры и прочности. Климатические условия в сочетании с транспортной нагрузкой оказывают большое воздействие на прочность асфальтобетонных покрытий. Уже на первоначальном этапе эксплуатации покрытия можно заметить трещинообразования и пластические деформации. К основным причинам преждевременного повреждения покрытий относятся недолговечность и низкие эксплутационные свойства применяемых битумов.

Дорожные битумы, производимые на нефтеперерабатывающих заводах, по своим свойствам не соответствуют климатическим условиям, в которых эксплуатируется дорожное покрытие. В связи с этим возникает необходимость разработки вяжущих, ориентированных на повышение морозостойкости, сдвигоустойчивости, трещиностойкости и прочности асфальтобетонных покрытий, с использованием методов и технологий, не требующих энергии.

На основе научных исследований и опытных испытаний доказано, что твердые отходы нефтяных месторождений Кызылординской области на основе асфальто-смолисто-парафиновых отложений (АСПО) являются близкими и связующими по своему химическому составу к основному компоненту асфальтобетонной смеси дорожного покрытия. И был выбран наиболее эффективный метод утилизации и обезвреживания нефтяных отходов.

В отличие от других твердых нефтяных отходов, АСПО является чистым органическим продуктом, не смешанным с почвой и состоящим только из высокомолекулярных твердых углеводородов.

Исследован АСПО, образующийся от использования нефти на месторождении Кумколь, в составе которого асфальтены 3...8%; смолы-13...20%; жиры-34...65%; механических примесей-20...49%; вода-1...5%.

По составу и свойствам асфальто-смолисто-парафинистые отложения близки к битуму, имеют высокую деформацию, обладают мягкими и полностью растворимыми свойствами при нагреве. Эти свойства определены в качестве связующего при получении дорожно-строительных материалов.

В данной статье предлагается разработать асфальтобетонную технологию на основе асфальто-смолисто-парафинистых отложений. Будет рассмотрен вопрос увеличения запасов сырья для производства прочного асфальтобетона и снижения количества нефтесодержащих отходов на месторождениях за счет реализации твердых нефтесодержащих отходов.

На основании исследования был проведен анализ состава асфальто-смолисто-парафинистых отложений методом ИК-спектроскопии. Спектр поглощения по инфракрасной области (ИК) был снят в спектрометре ИК-фурье IR Prestige-21 (Shimadzu, Япония).

Спектры поглощения асфальто-смолисто-парафинистых отложений, записанные ИК-спектрометре, показывают структуру углеводородов в метиловых (2954-2852 см-1), метиленовых (1463-1377 см-1), метиновых (721 см-1) группах. Анализ показывает, что состав твердых нефтяных отходов, образующихся на месторождениях, состоит в основном из парафиновых углеводородов.

Результаты исследования показали пригодность асфальто-смолисто-парафинистых отложений к использованию в качестве органических вяжущих к плотному асфальтобетону типа «Б» марки III для IV–V дорожных климатических зон, рекомендуемых для нанесения верхних слоев покрытия на дорогах IY технической категории.

Асфальтобетонная смесь, полученная путем смешивания минерального компонента с асфальто-смолисто-парафиновыми отложениями, по техническим характеристикам не уступает смеси, полученной при использовании товарного битума.

В то же время замена дефицитного товарного битума нефтяными отходами позволит значительно удешевить товарную продукцию, а также упростить процесс приготовления смеси и предотвратить загрязнение окружающей среды вредными веществами, выделяемыми из нефти.

Ключевые слова: нефтяной отход, органические вяжущие, твердый парафин, метод спектроскопий, спектр поглощения, парафиновый углеводород, теплостойкость, температура размягчения.

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PROPERTIES OF THE STEEL-FIBER-REINFORCEDCONCRETE WITH DISPERSED REINFORCING WIRE FIBER FROM TECHNOGENIC WASTE

Abstract. The article presents the results of theoretical and, most importantly, experimental studies of some properties of steel-fiber-reinforcedconcrete reinforced with dispersed reinforcement from industrial wastes, namely, ITEX steel wire fiber from SPA INNOTECH from spent steel ropes, a large number of which are used as raw materials for fiber production, has accumulated in the region with the mining industry (East Kazakhstan region). The result of the research was indicators of tensile strength of fiber-reinforced concrete during bending of samples, characteristics of crack resistance, and impact strength indicators of fiber-reinforced concrete reinforced with fiber from industrial waste. Knowing and demonstrating these characteristics will make it possible to more effectively ensure the possibility of selling a new product on the building materials market. This publication has been carried out as part of the sub-project Technology for Manufacturing Fiber from Technogenic Wastes, funded by the Government of the Republic of Kazakhstan and the World Bank, Project for Stimulating Productive Innovations.

Key words.steel fiber, industrial waste, fiber concrete, fiber concrete strength, impact strength, crack resistance.

1. Introduction.

The use of steel-fiber-reinforced concrete (SFRC) is increasing as an effective structural material in construction. Steel wire fiber is currently the most widely used. The production amount and use is constantly growing. In world practice, more than 300 thousand tons of steel fiber are used per year. In the Republic of Kazakhstan (RK), unfortunately, the consumptionamount of this promising material is significantly less. The small consumption of steel fiber reinforced concrete (SFRC) are largely explained by the lack of fiber production and the lack of knowledge by Kazakhstan designers and builders of the possibilities and advantages of this material, the absence of normative documentation related to SFRC in Kazakhstan, the lack of advertising and the lack of focused work on its use, especially from organizations project side.

2. Technologies for producing fiber from steel ropes.

Karaganda Promstroyproekt in the 80s of the last century, relying on the development of the Central Research Institute of Industrial Buildings, NIIIZhB and LenZNIIEP, on the basis of the Kazmetallurgstroy in Temirtau, implemented a method for producing wire fiber from used steel ropes using heat treatment. The ropes were preliminarily annealed at a temperature of 400-10000C, then they were cut into segments of a given length, which were split by grinding. Subsequently, steel-fiber-reinforcedconcrete structures for various purposes were made from the obtained fiber [1-3]. The disadvantage of this method was the loss of strength of wires during their heat treatment and the difficulty of washing and drying the finished fiber due to the lack of special equipment for these works. After the collapse of the USSR, research ceased, without having received wide industrial application.

Currently, in the East Kazakhstan region there are a large number of metallurgical and mining enterprises, in which steel ropes are widely used in bridge, overhead, cranes and mine shafts.The Gosgortekhnadzor of the Republic of Kazakhstan (RK) established the service life of ropes used in the industry for no more than 5 years (according to experts, it can be extended for another 3 years), inspection should also be carried out by specialists in the field of flaw detection at least once every 12 months. According to the presence of damage, a decision can be made to reject the rope earlier than the standard period of operation of the rope. Rope culling standards are set out in the requirements of RD ROSEK 012-97.

Nowadays, the disposal of steel ropes is their delivery to scrap points in the Republic of Kazakhstan. Moreover, all spent ropes belong to the same category - 13A, which is determined by GOST 2787-75. This is not advisable, because the material for the manufacture of ropes is a high-strength wire with a large unused resource.

The method for producing wire fiber from used steel ropes was modernized at the D. Serikbayev EKTU, within the framework of the state R&D (agreement with the Ministry of Education and Science of the Republic of Kazakhstan No. 84-210-13 of 04/10/13) [2]. The introduction of this method into production was carried out by INNOTECH Scientific and Production Association LLP in Ust-Kamenogorsk on the basis of the sub-project Technology for Manufacturing Fiber from Technogenic Waste, funded by the World Bank and the Government of the Republic of Kazakhstan project Stimulating Productive Innovations.

Fiber production is as follows (Figure 1). Spent steel ropes are cut into segments of a given length using thermofriction (preliminary) and abrasive (final) disk cutting. The obtained segments of the rope are then subjected to separation into wires, which is carried out due to the complex compressive-abrasive-vibrational impact on the segments in a large extent of the zone, which allows the separation of the rope segments into wires in one pass through the installation.

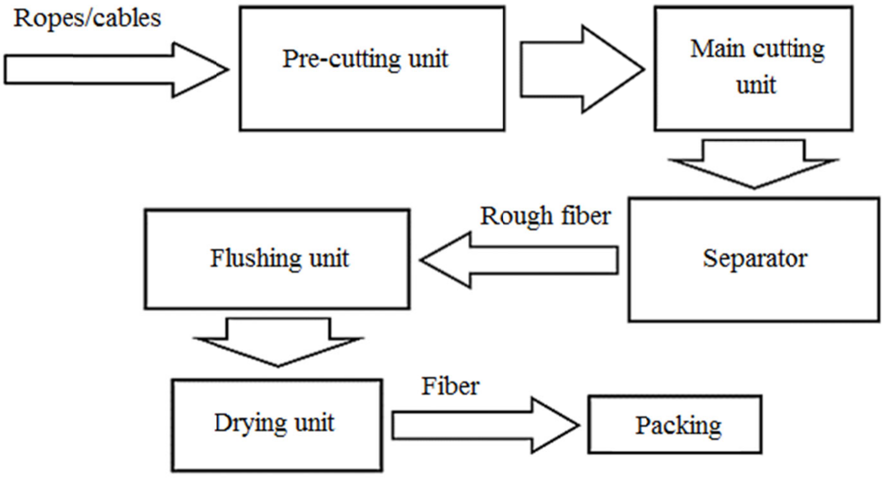

Figure 1 – Line diagram for the manufacture of fiber from waste ropes

Furthermore, dispersed reinforcement in the form of wires obtained as a result of rope separation segments is cleaned of grease and other contaminants by vibration washing in a bath with a special washing liquid with a combination of chemical, mechanical and hydrodynamic effects on pollution. Upon reaching the required quality of fiber cleaning, the washing process stops, the fiber is removed from the bath and sent further for drying or for its intended use. The use of rope cutting with circular knives with an increase in cutting speed and a reduction in cutting forces, splitting of the rope segments into wires due to the complex crushing-abrasive effect on them and their splitting in one pass between the grinding surfaces, and high-quality cleaning of dispersed reinforcement wires in a bath with a washing liquid that vibrates fluctuations [4-7]. It leads to reduce the energy intensity and time of the process of obtaining dispersed reinforcement, to increase the productivity and efficiency of the process, to reduce the costs of its conduct, to increase the surface cleanliness of the wires, to ensure good adhesion of the fiber wires to concrete, and therefore to improve the technological properties of fiber concrete.

3. Experimental research.

To evaluate the strength characteristics of steel fiber reinforced concrete with ITEX wire fiber (trademark registered) from waste ropes produced by Scientific and Production Association INNOTECH LLP, hereinafter referred to as ITEX fiber, an experimental study was conducted. Since dispersed reinforcement of concrete with fiber primarily increases tensile strength, crack resistance, and impact strength, which determines the application field of SFRC, an experimental study was aimed at determining these characteristics. To compare the effectiveness of ITEX fiber with existing analogs, SFRC with an anchor fiber 1/50 Hendix and Dramix 3D 80/60BG was also considered. The amount percentage of reinforcement with wire fiber was adopted as 1%, 1.5% and 2%.The composition of the components for fine-grained concrete matrix was selected in accordance with the recommendations of [3, 8-12] and is shown in table 1.

Technical characteristics of the used fiber Hendix:

Brand - 1/50 Hendix, length - 50 mm, diameter - 1 mm, temporary resistance - 1150 MPa.

Technical characteristics of the used fiber Dramix:

Brand - Dramix 3D 80/60BG, length - 60 mm, diameter - 0.75 mm, temporary resistance - 1225 MPa.

Table 1 – Formulation for concrete matrix per 1 m^3

Component	Quantity (kg / m3)	Ratiocomponents
Cementing agent - Portland cement, grade M450, Bukhtarma cement company (C)	C = 661	
Fine aggregate - quartz sand with a fineness modulus 3.0 (P)	P = 1283	P / C ≈ 1.941
Consolidator - water in accordance with GOST 23732-79 (B)	B = 285	B / C ≈ 0.4312
PlasticizerRheobuild 181A (Pl)	Pl = 4	1% of C

Technical characteristics of ITEX fiber:

Temporary resistance - 1809 MPa.

To analyze the ITEX fiber geometry, 4 samples were taken from different places of the total fiber volume. In the course of measurements, fiber with diameters of 0.5 mm, 1.0 mm and 1.5 mm was detected. The average fiber lengths of the samples are shown in table 2.

Table 2 – Geometrical characteristics of ITEX fiber

Sample number	Fiber length with a diameter of 0.5mm	% contentin the sample	Fiber Length with 1.0mm Diameter	% contentin the sample	Fiber Length with 1.5 mm Diameter	% contentin the sample
№1	6,35 cm	20,5%	6,35 см	72,6%	6,57 cm	6,95%
№2	6,33 cm	23,2%	6,37 см	74,6%	6,57 cm	2,2%
№3	6,34 cm	21,7%	6,38 см	73,6%	6,12 cm	4,7%
№4	6,26 cm	32,8%	6,41 см	59,2%	6,56 cm	8%

Steel fiber was added to the concrete mixture gradually using a tray and was evenly distributed during its preparation in the SBR-132A cyclic gravity concrete mixer. A standard vibrating platform with harmonic vibrations was used to form the samples. The compaction time was 3 s.

The average density of the SFB mixture is 2420 kg/m3.

Delamination coefficient at 2% reinforcement:

- at 3 s of vibration, $k_p = 0.938$;
- at 6 s of vibration, $k_p = 0,882$,which meets the requirements of clause 6.1.40 [3], ($k_p \geq 0.85$).

Coefficient of homogeneity at 2% reinforcement:

1 test, $k_o = 0.87$; 2 samples, $k_o = 1.0$; 3 samples, $k_o = 0.98$, which also meets the requirements of clause 6.1.40 [3, 13-18], ($1.1 \geq k_o \geq 0.9$).

To determine the tensile strength during bending, 10 series of control samples were made in the form of square prisms with dimensions of 100*100*400 mm (three samples in each series). Samples were tested at 28 days of age. The testing equipment used to determine the tensile strength during bending is a 2PG-10 hydraulic press. A sample mounted on two press supports was loaded up to failure at a constant rate of load increase (0.05 ± 0.01) MPa / s. The load was applied in thirds of the span and was evenly distributed over the width of the sample (figure 2).

Figure 2 – Installation diagram for determining the tensile strength and crack resistance in bending

The tensile strength of concrete in bending R_{tb}, MP, was determined according to [4]:

$$R_{tb} = \delta \frac{Fl}{ab^2} \tag{1}$$

where F – breaking load, N; a, b, l – the width, height of the cross section of the prism and the distance between supports, respectively, mm; δ – scale factor to bring concrete strength to concrete strength in samples of basic size and shape.

4. The results of experimental studies.

The results of the experimental determination of concrete tensile strength in bending are shown in figure 3.

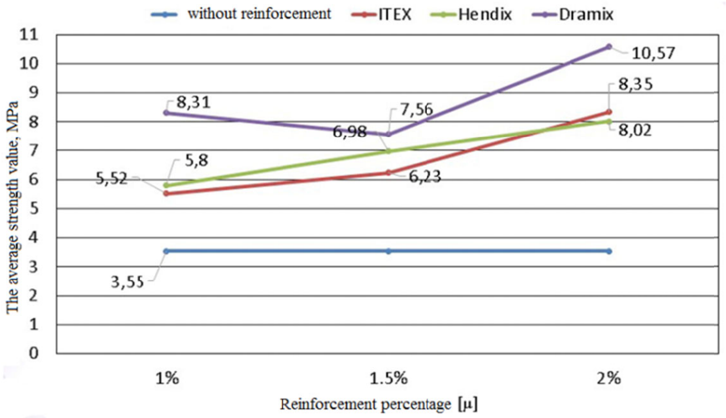

Figure 3 – Graphical comparison of tensile strength in bending

The tensile strength in bending of specimens reinforced with ITEX fiber -1.5% increased by 75% compared with the specimen without reinforcement (that is, 1.8 times), reinforced 2% by 135% (2.3 times). The similar results were shown for the samples reinforced with Hendix fiber: 1.5% - 97% (~ 2 times); reinforcement of 2% fiber - 126% (2.3 times). The samples are reinforced with factory fiber "Dramix", when reinforcing 1%, the strength increased by 134% (2.3 times), while reinforcing 1.5% showed a smaller result - 113% (2 times), which is explained by the uneven distribution of fiber in the samples of this series , 2% reinforcement increased strength by almost 3 times (2.9 times) 198%, which is the best result.

The crack resistance characteristics were determined during nonequilibrium mechanical tests according to [5]. Nonequilibrium tests are characterized by a loss of stability of the sample deformation process at the moment of deformation localization upon reaching the maximum load, with the corresponding development of the main crack.

7 series of control samples of type 1 were manufactured and tested in the form of square prisms with dimensions of 100 * 100 * 400 mm (three samples in each series) for bending tests (figure 2), with initial upper cuts according to [5, 7, 19-21].

Before the test, two loading-unloading cycles were carried out to a value of 10% of the expected maximum load. Then the samples were loaded continuously until they were divided into parts with fixing the value F_c^*.The loading speed was measured by the speed of movement of the loading plate of the press in the range of 0.02-0.20 mm/s.The results of determining the characteristics of crack resistance are shown in figure 4.

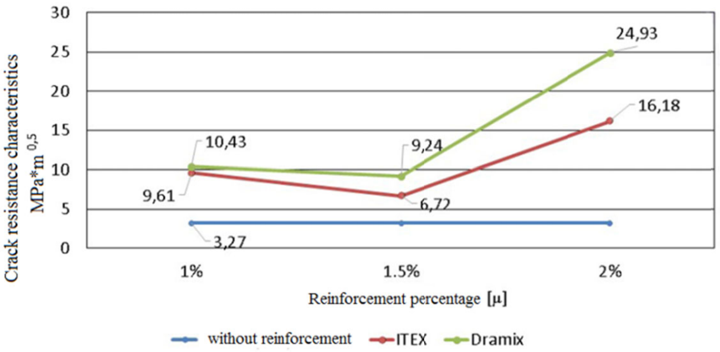

Figure 4 – Graph comparing the performance of crack resistance

Reinforcement of 1% ITEX fiber increased crack resistance by 194% (~ 2.94 times), and Dramix - by 219% (3.19 times), while reinforcing 1.5% fiber in both cases showed a lower result - ITEX106% (2.06 times), Dramix 183% (~ 2.83 times). Reinforcement of 2% fiber - ITEX increased by 395% (4.94 times), Dramix by 662% (~ 7.62 times).

To compare the impact strength, ten series of eight samples were made in the form of a 100*100*100 mm cube: a series of concrete samples without reinforcement, as well as a series of samples reinforced with factory fiber from Hendix and Dramix and fiber from waste ropes ITEX with a volume percentage of reinforcement of 1%, 1.5% and 2%.

The samples were tested on a vertical pile driver after hardening under normal conditions for 28 days. During the tests, the sample was mounted on the metal base of the pile driver, and from above it was hit with a hammer weighing 5 kg, freely falling from a height of 1.07 m (figure 5).

Figure 5 – Installation diagram for determining impact strength (vertical pile driver)

Impact resistance was estimated by the energy spent on the formation of cracks [6, 22-27]:

$$A_{ud} = \frac{PgHn}{L_{tr}}, \tag{2}$$

where P - the hammer mass; g - the acceleration of gravity; H - the hammer height; n - the number of strokes [27-32]; L_{tr}- the length of the cracks formed (average value over all faces of the sample).

In the analysis of impact tests, two indicators were compared: the amount of energy for the formation of the first crack and the amount of energy for the destruction of the sample.The results of determining the resistance of fiber-reinforced concrete to longitudinal impact upon the appearance of the first crack are shown in figure 6.

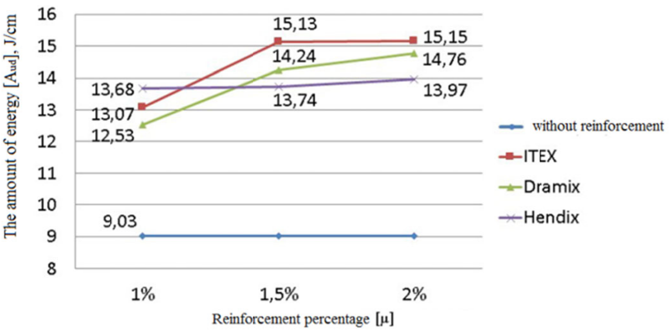

Figure 6 – Comparison of impact strength when the first crack

Figure 6 shows that with percentage reinforcement with steel fiber μ=2% in each series, the impact resistance index increases by an average of 60%, while samples reinforced with fiber of ITEX ropes with a percentage of reinforcement of μ=1.5% and μ=2% show better results than factory fiber samples, respectively.

The results of determining the resistance of fiber-reinforced concrete to longitudinal impact upon fracture of the sample are shown in figure 7.

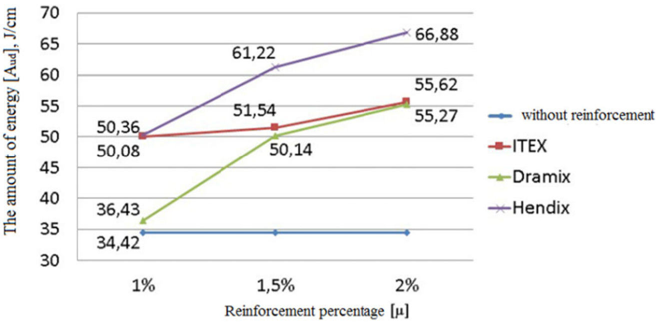

Figure 7 – Comparison of impact strength during fracture of a sample

The comparison of the indices during the destruction of the sample showed that the percentage reinforcement with Hendix fiber μ=2% increases impact resistance by 94%, and ITEX or Dramix fiber - by 60%. At the same time, ITEX fiber shows an average result in comparison with factory fiber. The coefficient of variation according to the calculation results ranged from 13 to 17% for each series.

5. Conclusion.

The results of the tests carried out allow us to justify the prospects of using ITEX steel wire fiber from used ropes as dispersed reinforcement of structures subjected to bending and dynamic stresses. Having close and at certain percentages of reinforcing even better physical and mechanical characteristics compared to the factory options Hendix and Dramix, fiber from spent ropes can be considered a full competitor in the market of dispersed reinforcement in Kazakhstan, whose competitiveness is also increased by its low price (1.3-1.5 times) and a large amount of raw materials in the region (East Kazakhstan region).

The data obtained lead to further commercial prospects for the implementation of the proposed solutions. The presented results served as the basis for the creation of an innovative industrial enterprise for the production of steel fiber from industrial waste.Areas of effective use of steel fiber concrete are given in table 3.

Table 3 – Areas for the effective use of steel fiber reinforced concrete

Typeofconstruction	Reserveofsavings
1 Industrialfloors	1.1 Reducing the thickness of the floor slab 1.2 Reducing the complexity and time of construction due to the lack of the need for the manufacture and installation of reinforcing mesh up to 40% 1.3 Increased wear resistance, impact strength and overall durability 1.4 Cost reduction in business up to 24%, reduced costs up to 32%
2 Pilesdriven	2 High impact resistance, which reduces rejects (pile head destruction) when driving up to 30%
3 Steel-reinforced concrete pressureless pipes	3.1 Reduction by 10-15% of the wall thickness 3.2 Increase in bearing capacity in comparison with standard reinforced concrete up to 2 times
4 Steel-fiber-reinforced concrete thin-walled elements of fixed formwork	4 The use of steel-fiber-reinforced concrete fixed formwork instead of an inventory shield allows reducing labor costs at a construction site by 20–25%, as well as shortening construction time

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ТЕХНОГЕНДІК ҚАЛДЫҚТАРДАН ЖАСАЛҒАН СЫМ ФИБРАСЫМЕН ДИСПЕРСТІ АРМАТУРАЛАНҒАН СТАЛЕФИБРОБЕТОН ҚАСИЕТТЕРІ

Аннотация. Көпірде, аспалы кран және шахта үстіндегі копрларда қолданылатын болат арқанды кәдеге жаратудың жаңартылған тиімді әдісі ұсынылады. Арқанды кәдеге жарату дегеніміз – берік сымнан болат талшығын алу мақсатында қайта өңдеу. Болат арқаннан сым талшығын алу әдісі Дүниежүзілік Банк пен Қазақстан Республикасы Үкіметінің қолдауымен «Өнімдік инновацияларды ынталандыру» жобасы аясында қаржыландырылған «Техногендік қалдықтардан талшық өндірудің технологиясы» шағын жобасы негізінде Өскемен қаласындағы «ИННОТЕХ ғылыми-өндірістік бірлестігі» ЖШС жүзеге асырды.

Талшық дайындау термофрикциялық (алдын ала) және абразивтік (соңғы) дискілі кесу арқылы болат арқанды берілген ұзындыққа кесу арқылы өндіріледі. Арықарай алынған арқанның кесінділері сымдарға бөлінеді, ұзындығы бойынша үлкен аймақтағы кесіндіге күрделі сығу-ысқылау-дірілдік әсер ету есебінен жүзеге асырылады, бұл арқан кесінділерін орнату арқылы бір өту үшін сымға бөлуді жүзеге асыруға мүмкіндік береді. Содан кейін арқан кесінділерін бөлу нәтижесінде алынған сым түріндегі дисперсті арматура ластануға химиялық, механикалық және гидродинамикалық әсерді үйлестіре отырып, ваннада арнайы жуу сұйықтығымен дірілді жуу әдісімен майлаудан және басқа да ластанудан тазартылады. Талшық тазалау сапасына жеткенде жуу процесі тоқтайды, талшық ваннадан шығарылады және одан әрі кептіруге немесе мақсатына қарай пайдалануға жіберіледі.

«ИННОТЕХ ғылыми-өндірістік бірлестігі» ЖШС өндіретін «Itex» талшық деп аталатын пайдаланылған арқаннан жасалған сым талшықтары бар болатфибробетонның беріктік сипаттамасын бағалау үшін эксперименттік зерттеу жүргізілді. Болат фибрабетонның қолдану аймағын анықтайтын бетонның талшықты дисперсті арматурасы ең алдымен, созылу кедергісін, сынуға төзімділігін және соққы беріктігін арттыратындықтан эксперименттік зерттеу осы сипаттамаларды анықтауға бағытталған. «Itex» талшығының тиімділігін қолданыстағы аналогтармен салыстыру үшін «1/50 Hendix» және «Dramix 3D 80/60BG» анкерлік талшығы бар болатфибрабетон қарастырылды. Сым талшықтарын арматуралаудың көлемдік пайызы 1%, 1,5% және 2% болып қабылданды. Үлгілердің иілу кезіндегі созылу беріктігі «Itex» арматураланған талшықта 1,5%, арматураланбаған үлгімен салыстырғанда 75%-ға (яғни 1,8 есе), арматураланған 2%-дан 135%-ға (2,3 есе) өсті. Ұқсас нәтижені «Hendix» талшығымен арматураланған үлгілер көрсетті: 1,5%-97% (~2 есе); 2% талшық арматурасы 126% (2,3 есе). «Dramix» зауыттық талшығымен арматураланған үлгілер 1% арматуралау кезінде беріктігі 134%-ға (2,3 есе) артты, ал 1,5% арматуралау аз нәтиже көрсетті – 113% (2 есе), бұл осы сериядағы үлгілерде талшықтың біркелкі бөлінбеуі негізінде түсіндіріледі, 2% арматуралау беріктігін шамамен 3 есе (2,9 есе) 198% арттырды, бұл жоғары нәтижені көрсетеді.

«Itex»талшығының 1% арматуралау жарыққа төзімділікті 194%-ға (~ 2,94 есе), ал «Dramix» 219%-ға (3,19 есе) арттырды, бұл ретте талшықты 1,5% арматуралау екі жағдайда да аз нәтиже көрсетті: «Itex» 106% (2,06 есе), «Dramix» 183% (~ 2,83 есе). 2% талшықты арматуралау «Itex» 395%-ға (4,94 есе), «Dramix» 662%-ға (~ 7,62 есе) артты.

Үлгінің динамикалық бұзылуындағы көрсеткіштерді салыстыру жұмыстары көрсеткендей, «Hendix» μ = 2% талшықты пайыздық күшейту соққыға төзімділікті 94%-ға, ал «Itex» немесе «Dramix» талшықтары арқылы 60%-ға арттырады. Бұл жағдайда «Itex» талшығы зауыттық талшықпен салыстырғанда орташа нәтижені көрсетеді. Есептеу нәтижелері бойынша вариация коэффициенті әр серия үшін 13-тен 17%-ға дейін жоғарылайды.

Жүргізілген сынақ нәтижелері бүгілуге және динамикалық әсерлерге ұшырайтын конструкциялардың дисперсті арматурасы ретінде істен шыққан арқаннан «Itex» болат сым фибрасын болашақта пайдалануды негіздеуге мүмкіндік береді. «Hendix» және «Dramix» шетелдік нұсқаларымен салыстырғанда арматуралаудың жақын және белгілі бір пайызы кезінде, тіпті жоғары физикалық-механикалық сипаттамаға ие бола отырып, пайдаланылған арқан талшығы Қазақстанның дисперсті арматура нарығында толық құқықты бәсекелес болып саналуы мүмкін, оның бәсекеге қабілеттілігі арзан бағасы (1,3 - 1,5 есе) мен өңірде (Шығыс Қазақстан облысы) шикізат мөлшерін ұлғайтады

Үнемдеу резервін беретін болатфибробетонды тиімді қолданудың келесідей салалары ұсынылады: өнеркәсіптік едендер (еден плитасының қалыңдығын азайту; арматуралық торды дайындау және орнату қажеттілігінің болмауы есебінен құрылыстың еңбек сыйымдылығы мен уақытын 40%-ға төмендету; тозуға төзімділігін, соққыға беріктігін және жалпы төзімділігін арттыру; еңбек құнын 24%-ға, келтірілген шығынды 32%-ға төмендету); қағылған қадалар (жоғары соққыға төзімділік 30%-ға соғылған кезде ақауды (қаданың басын бұзу) сиретеді); болатфибробетонды ағынсыз құбырлар (қабырға қалыңдығының 10-15%-ға азаюы; типтік темірбетон құбырларымен салыстырғанда көтергіш қабілетінің 2 есеге дейін ұлғаюы); алынбайтын қалыптың болатфибробетонды жұқа қабырғалы элементтері (инвентарлық қалқанша орнына болатфибробетонды алынбайтын қалыптарды қолдану құрылыс алаңындағы еңбек шығынын 20-25%-ға төмендетуге, сондай-ақ құрылыс мерзімін қысқартуға мүмкіндік береді).

Түйін сөздер: болат талшығы, техногендік қалдықтар, талшықты темірбетон, талшықты темірбетон беріктігі, соққы беріктігі, жарыққа төзімділік.

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СВОЙСТВА СТАЛЕФИБРОБЕТОНА С ДИСПЕРСНЫМ АРМИРОВАНИЕМ ПРОВОЛОЧНОЙ ФИБРОЙ ИЗ ТЕХНОГЕННЫХ ОТХОДОВ

Аннотация. Предлагается модернизированный эффективный метод утилизации отработанных стальных канатов, используемых в мостовых, подвесных кранах и надшахтных копрах. Утилизация канатов заключается в их переработке с целью получения стальной фибры из высокопрочной проволоки. Метод получения проволочной фибры из стальных канатов внедрён ТОО «Научно-производственное объединение ИННОТЕХ» в г. Усть-Каменогорске на основе подпроекта «Технология изготовления фибры из техногенных отходов», финансируемого в рамках проекта «Стимулирование продуктивных инноваций», поддержи-ваемого Всемирным Банком и Правительством Республики Казахстан.

Изготовление фибры производится посредством разрезания стальных канатов на отрезки заданной длины с помощью термофрикционной (предварительной) и абразивной (окончательной) дисковой резки. Далее полученные отрезки каната подвергаются разделению на проволоки, которое осуществляется за счет сложного сжимающе-истирающе-вибрационного воздействия на отрезки в большой по протяженности зоне, что позволяет осуществлять разделение отрезков каната на проволоки за один проход через установку. Затем дисперсная арматура в виде проволок, полученных в результате разделения отрезков каната, подвергается очистке от смазки и других загрязнений методом вибрационной мойки в ванне со специальной моющей жидкостью при сочетании химического, механического и гидродинамического воздействий на загрязнения. По достижении требуемого качества очистки фибры процесс мойки останавливается, фибра извлекается из ванны и отправляется далее на сушку или для использования по назначению.

Для оценки прочностных характеристик сталефибробетона (СФБ) с проволочной фиброй из отработанных канатов, производимой ТОО «Научно-производственное объединение ИННОТЕХ», далее именуемой фибра «Itex», проведено экспериментальное исследование. Так как дисперсное армирование бетона фиброй в первую очередь повышает сопротивление растяжению, трещиностойкость и ударную прочность, что и определяет область применения СФБ, то экспериментальное исследование было нацелено на определение этих характеристик. Для сравнения эффективности фибры Itexс существующими аналогами рассматривался также СФБ с анкерной фиброй «1/50 Hendix» и «Dramix 3D 80/60BG». Объёмный процент армирования проволочной фиброй был принят 1%, 1,5% и 2%.

Прочность на растяжение при изгибе образцов, армированных фиброй «Itex» 1,5%, повысилась на 75% по сравнению с образцом без армирования (то есть в 1,8 раз), армированные 2% - на 135% (2,3 раза). Схожий результат показали образцы, армированные фиброй «Hendix»: 1,5% - 97% (~ в 2 раза); армирование 2-мя % фибры - 126% (2,3 раза). Образцы же армированные заводской фиброй «Dramix», при армировании 1% прочность повысилась на 134% (2,3раза), при этом армирование 1,5% показало меньший результат – 113% (2раза), что

объясняется неравномерностью распределения фибры в образцах данной серии, 2% армирования повысило прочность почти в 3 раза (2,9 раза) 198%, что является наилучшим результатом.

Армирование 1% фибры «Itex» повысило трещиностойкость на 194% (~ в 2,94 раза), а «Dramix» – на 219% (3,19 раз), при этом армирование 1,5% фибры в обоих случаях показало меньший результат – «Itex» 106% (2,06 раза), «Dramix» 183% (~ в 2,83 раза). Армирование 2% фибры – «Itex» повысило на 395% (4,94 раза), «Dramix» на 662% (~ в 7,62 раза).

Сравнение показателей при динамическом разрушении образца показало, что процентное армирование фиброй “Hendix” μ=2% повышает ударостойкость на 94%, а фиброй “Itex” или “Dramix” – на 60%. При этом фибра “Itex” показывает средний результат в сравнении с заводской фиброй. Коэффициент вариации по результатам расчета составил от 13 до 17% для каждой серии.

Результаты проведенных испытаний позволяют обосновать перспективность использования стальной проволочной фибры “Itex” из отработанных канатов в качестве дисперсной арматуры конструкций, подвергающихся изгибу и динамическим воздействиям. Обладая близкими и при определенных процентах армирования даже лучшими физико-механическими характеристиками по сравнению с зарубежными вариантами “Hendix” и “Dramix”, фибра из отработанных канатов может считаться полноправным конкурентом на рынке дисперсной арматуры Казахстана, чью конкурентноспособность также увеличивает её низкая цена (в 1,3 – 1,5 раз) и большое количество сырья в регионе (Восточно-Казахстанская область).

Рекомендованы области эффективного применения сталефибробетона, дающие резерв экономии:

- промышленные полы (уменьшение толщины плиты пола; снижение трудоёмкости и времени строительства за счёт отсутствия необходимости изготовления и установки арматурных сеток до 40 %; увеличение износостойкости, ударной прочности и в целом долговечности; снижение стоимости в деле до 24%, приведённых затрат до 32%);
- сваи забивные (высокая ударостойкость, что снижает брак (разрушение головы сваи) при забивке до 30 %);
- сталефибробетонные безнапорные трубы (уменьшение на 10–15 % толщины стенок; увеличение несущей способности по сравнению с типовыми железобетонными до 2 раз);
- сталефибробетонные тонкостенные элементы несъемной опалубки (применение сталефибробетонной несъемной опалубки вместо инвентарной щитовой позволяет снизить трудозатраты на строительной площадке на 20–25 %, а также сократить сроки строительства).

Ключевые слова: стальная фибра, техногенные отходы, фибробетон, прочности фибробетона, ударная вязкость, трещиностойкость.

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OBTAINING DERIVATIVES OF HUMIC SUBSTANCES FROM OXIDIZED COAL AND STUDY OF PHYSICO-CHEMICAL AND ADSORPTION PROPERTIES

Abstract. In the work, a chemical analysis of humic substances based on oxidized coal of the Maikuben basin (Kazakhstan) is carried out. Humic acids were obtained on the basis of potassium humates by acidification with a 20% acid solution to pH = 3-4.5. The optimal conditions for obtaining nitrohumic acids from oxidized coals are: the duration of the process is 3 hours, the ratio of S:L = 1:5, the content of nitric acid is 64%, sulfuric acid is 96% and the composition of the nitrating mixture is 1:1 (g/g). Amminohumic derivatives were obtained in the presence of a 3% aqueous solution of ammonia using mechanical activation and ultrasonic treatment. The samples obtained were tested as an adsorbent for water purification from heavy metals. Humic acids and aminohumate showed the highest degrees of purification for zinc (99.0-100.0%) and cadmium (80.0-96.7%), and nitrohumic acid showed a high adsorption capacity for heavy metals like copper - 100.0 % and lead 82.9%. This is due to the fact that when interacting with heavy metals, humic acids and their derivatives (amino and nitro) form chelate complexes due to carboxyl, phenolic, nitro and amino groups. As a result of the study, the possibility of using them as non-toxic available sorbents for the purification of heavy metals in aqueous media has been shown.

Key words: oxidized coal, humic acid, nitrogumic acid, amino humate, adsorbent, heavy metals.

Humic substances (HS) are a macrocomponent of organic matter in soil and water ecosystems, as well as solid fossil fuels. The use of brown and oxidized bituminous coals for the production of humic fertilizers and plant growth stimulants is one of the promising directions in coal chemistry. For humic acids (HA) coals are characterized by a general type of composition and structure. However, depending on the initial composition of coal, the method of extraction and storage, the indicators of their composition and structure may vary. The physiological activity of HA is largely due to the content of quinoid groups and phenolic hydroxides [1].

The presence in the macromolecules of oxidized carbons and humic acids of an aromatic framework, highly substituted by functional groups such as carboxyl, phenolic, quinoid, carbonyl and others, determines their ability to enter into an ion exchange reaction and the possibility of using them as sorbing substances [2].

To increase the efficiency of humic preparations in sorption processes, their directed functionalization seems to be promising, in particular, by introducing nitro-, amino- and other groups into their composition. Interest in such sorbents is caused by the combination of ion-exchange properties with respect to alkali and alkaline earth metals and the possibility of complexation with transition metals. A significant contribution to the complexation is made by nitrogen atoms, which, in contrast to oxygen atoms, have a higher polarizability and are more prone to the formation of donor-acceptor bonds with metal ions [3].

Nitrohumic acids have received considerable attention as potential soil amendments for nitrogen fertilizers and many other applications, such as plant biostimulants and chelating agents for metals [4–7], as they are characterized by high sorption and complexing properties. They are usually produced by basic coal mining that has been oxidized with nitric acid.

Aromatic nitration, discovered by Mitscherlich in 1834, is a typical electrophilic substitution reaction. The electrophile is the nitronium cation NO^{2+}. The nitronium ion has a linear structure, the nitrogen atom is in the sp^{-} state, and oxygen is in the sp^{2-} hybridization state [8].

Humic substances (HS), in addition to being a source of C and N for microorganisms and plants, are important in the chemical and physical properties of the soil, mainly due to their high complexing ability with respect to metal ions, which is a consequence of the presence of oxygen-containing functional groups in their structure associated with their high specific surface [9, 10].

It is known that the coals of humic acids are weakly acidic cation exchangers. When nitrogen atoms are more prone to donor-acceptor bonds with metal ions than oxygen atoms are introduced into these carbons, the latter become more complex and polyampholytic [11].

Methods for introducing nitro and amino groups into the composition of coals or humic acids (HS) are their direct nitration or amination.

The aim of the work is to obtain nitro-, amino-humic substances from oxidized coal of the “Maikuben” basin and to study their physicochemical and adsorption properties.

The raw material used was brown coal from the Maikuben deposit, pre-crushed to a particle size of less than 0.1 mm and having the following characteristics (wt%): A^d - 25.8; W^r - 9.3; V^d - 46.6; S_t^d - 0.71. The yield of free humic acids was (on the analytical state) - 87%.

The moisture, ash content and volatility of the samples were determined on a “Thermoster Eltra” thermogravimetric analyzer (according to ASTM D7582-12). The total pore volume, bulk density, pH of the aqueous extract, adsorption activity for methyl orange and methylene blue were determined in accordance with the procedures [12, 13]. The adsorption characteristics of the sorbents (specific surface area) were studied by the Brunauer-Emmett-Teller (BET) method, measurements were carried out on a KATAKON Sorbtometer M. Chemical analysis and surface morphology were studied by energy dispersive X-ray spectroscopy using an SEM instrument *(Quanta 3D 200i)* with an *EDAX* energy dispersive analysis attachment. The IR spectrum of the samples was recorded on a Nicolet iS 10 FT-IR spectrometer.

Humic substances are obtained from oxidized brown coal, purified and determined in accordance with the recommendations of the International Humic Substances Society (IHSS). Humic acids were obtained on the basis of potassium humates, by acidifying them with a 20% acid solution to pH = 3 - 4.5, as a result of the reaction, humic acids precipitated in the form of amorphous brown sediments.

Nitrohumic acids were obtained according to the method described in [2], where coal was treated with 64% nitric acid and 96% sulfuric acid in a ratio of 1: 1 (g / g) in a cooled flask. The ratio S:L was 1: 5. The coal nitration method using a nitrating mixture is the most effective. Sulfuric acid has a catalytic effect and reduces the oxidative effect of nitric acid. The nitrating mixture was added to the moistened charcoal in small portions with vigorous stirring and cooling. The process was carried out at a temperature not higher than 40-50 ° C to suppress oxidative reactions, the duration of the experiment was 3 hours. The precipitate was separated from the filtrate, washed several times with water, and dried. The nitrocarbon yield was 85%. Nitrohumic acid was obtained from nitrocarbon by alkaline treatment (3% KOH, microwave treatment for 6-7 min, power 1000 W) and subsequent precipitation with 5% acid solution.

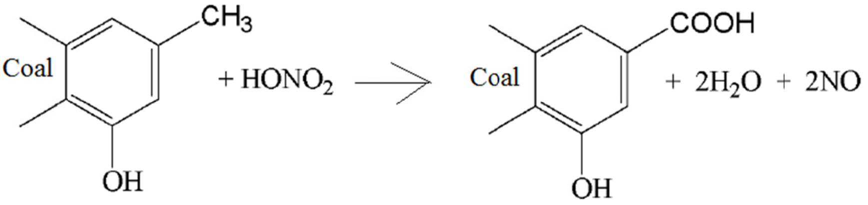
The nitrating agent is nitronium ions, which are formed during the decomposition of concentrated nitric acid:

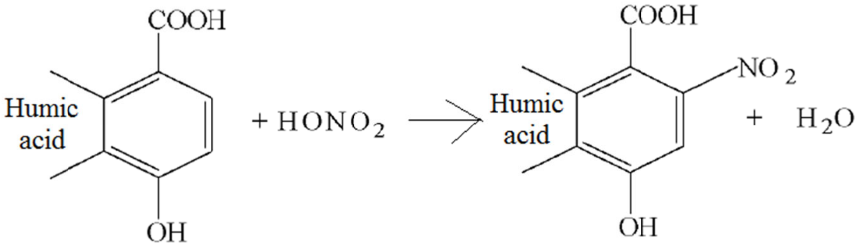
$$2HNO_3 = \overset{+}{NO_2} + \overset{-}{NO_3} + H_2O$$

or in the interaction of sulfuric and nitric acid:

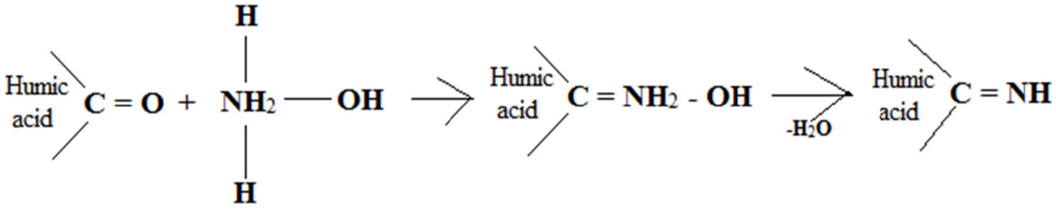
$$HNO_3 + H_2SO_4 = \overset{+}{NO_2} + \overset{+}{H_3O} + 2\overset{-}{HSO_4}$$

Nitration of coals occurs similarly to aromatic hydrocarbons by the mechanism of electrophilic substitution for the aromatic nucleus of carbon macromolecules and leads to the formation of nitrohumic acids [1].





To obtain aminogumic substances, oxidized coal was crushed to 2.95-452 microns. Then, in a rotary-pulsating apparatus (RPA), it was subjected to intensive oxidation and dispersion of coal particles with atmospheric oxygen, the mixture was heated to 50 °C and brought to an ultrafine state and a homogenized mass in the presence of a 3% aqueous ammonia solution for 20 minutes. After RPA, the finished mass was fed into the extraction vessel for holding the solution for 1 hour. The aged solution was fed to the synthesis module for ultrasonic dispersion, where it was subjected to ultrasonic dispersion at a certain frequency. The ultrasonic treatment time was 25 minutes.



To carry out research on the removal of heavy metals using humic substances, a model solution of heavy metals (copper, zinc, lead, cadmium) was prepared from state standard samples (SSS). In a conical flask (250 ml), a weighed portion of the sorbent (0.5 g) was stirred with a model solution (50 ml, pH = 3.26) and stirred in a shaker at room temperature (25^0C) at a stirring speed of 200 rpm for 3 hours. After the process, humic substances with heavy metals were extracted from the solution by filtration. The solution filtered from the adsorbent was analyzed for the content of heavy metals on a Ta-lab voltammetric analyzer.

The chemical composition and physicochemical characteristics of the obtained humic substances are shown in tables 1-3.

Table 1 - Chemical composition of humic substances

№	Denomination	Content of elements, wt.%										
		C	O	Na	Mg	Al	Si	K	Fe	Ca	S	Ti
1	Humic acids	19.47	40.03	-		0.72	0.58	38.06	1.15	-	-	-
2	Nitrohumic acids	50.51	29.19	0.17	0.22	3.45	9.46	0.70	1.69	-	0.19	-
3	Aminohumate	56.09	31.08	0.19	0.30	2.84	7.25	0.65	0.74	0.49	-	0.36

According to the data obtained, it should be noted that the potassium content (38.06%) in comparison with the initial humic acid decreases to 0.70% and 0.65% in the derivatives of nitrogumic and aminohumic acids, respectively, which may be due to the replacement of potassium ions by amino and nitro groups.

Table 2 - Content of functional groups of humic substances

№	Denomination	Carboxyl groups meq / g	Total acidity, meq / g	Phenolic group, meq / g
1	Humic acids	1,18	1,60	0,42
2	Nitrohumic acids	0,60	1,64	1,04
3	Aminohumate	0,12	0,73	0,61

The data in table 2 show a 50 % decrease in carboxyl groups from the original form of humic acid in the derivatives of humic acids. The nitro and amino groups increase the reactivity of other substituents on the aromatic ring. It should be noted that in aromatic acids nitration often occurs the substitution of the carboxyl group for nitro and amino groups.

Table 3 - Physical and chemical characteristics of the obtained humic substances

№	Denomination	W^r_t,%	A^r,%	V^d, %	S_{BET}, m^2/g	ρ_{bulk}, g/cm^3	V_Σ by water, cm^3/g	pH	A_m, mg/g	$A_{m.b.}$, mg/g
1	Humic acids	13.32	25.73	62.25	0.42	0.95	-	4,09	28,0	-
2	Nitrohumic acids	5,52	57,87	67,93	5.637	0,882	0,43	6,60	-	-
3	Aminohumate	3,41	74,13	56,77	3.940	0,857	0,17	10,07	45,5	112,5

Figure 1 shows the IR spectrum of humic acid, peaks were found in the region of 2918 cm^{-1}, which can be associated with CH stretching vibration of alkyl chains, which can also be a broad signal N - H/O - H. Peak at about 1701 cm^{-1} typical for the stretching vibration of C = O carbonyl groups of ketones (including quinones), carboxylic acids and / or amides. The band of deformed stretching vibrations in the region of 1650-1520 cm^{-1} also indicates the presence of a strong N-H group. The peak in the 1100-1000 cm^{-1} range is responsible for the strong elongation of the C-O group.

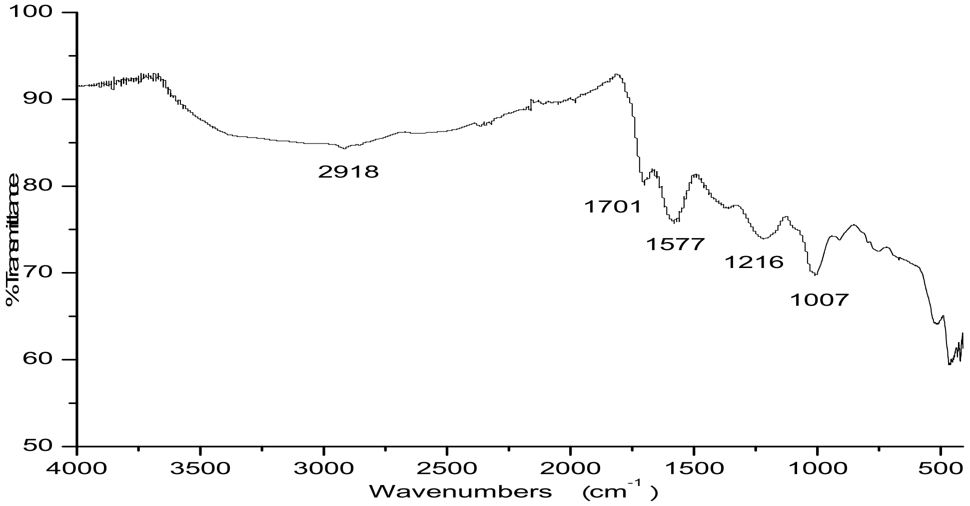


Figure 1 - IR spectrum of humic acid

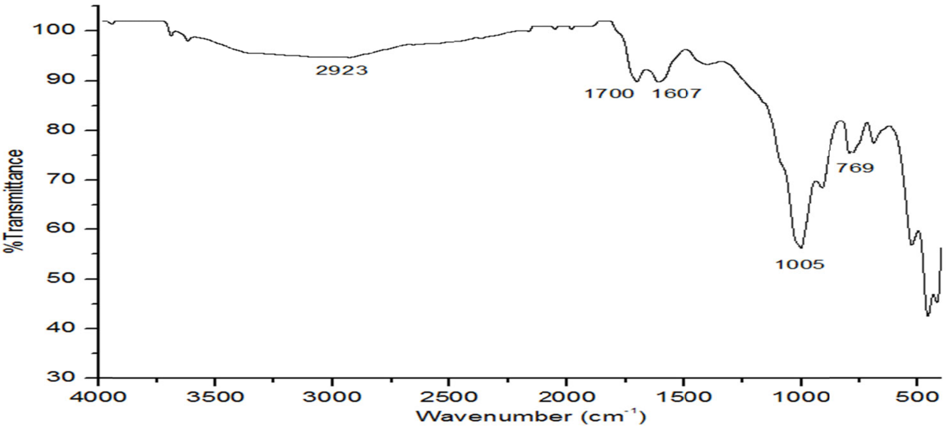


Figure 2 - IR spectrum of nitrohumic acids

In Figure 2, the absorption bands in the range of wavenumbers 3700-3300 cm^{-1} refer to weak stretching vibrations of O – H bonds, probably due to the presence of moisture in this compound. In the region of 2923 cm^{-1} to be associated with C-H stretching vibration of alkyl chains. A peak at about 1700 cm^{-1}, typical of the C = O stretching vibration of carbonyl groups of ketones (including quinones), carboxylic acids and / or amides, confirms that these units are present in humic acid. The peak in the 1100-1000 cm^{-1} range is responsible for the strong elongation of the C-O group. The wide range of peak variation from 800-650 cm^{-1} can be explained by the tensile C-H vibration. Peak 920-830 cm^{-1} for nitroparaffin compounds, 1560-1500 cm^{-1} for aryl groups.

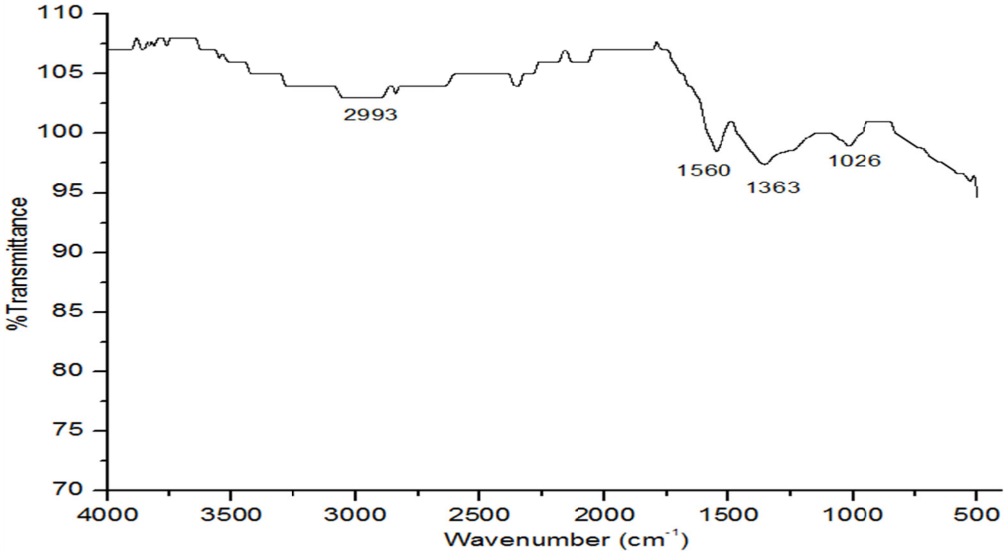


Figure 3 - IR spectrum of amino humate

Figure 3 shows a peak at 2993 cm^{-1}, which is responsible for the presence of aromatic stress assigned to C-H. There is also a slight shift of the band at 1576 cm $^{-1}$, which also indicates the presence of a strong N – H group. The peak at 1560 cm^{-1} is characterized by asymmetric and 1363 cm^{-1} symmetric tensile vibration of aromatic tertiary amines. The peak in the 1100-1000 cm^{-1} range is responsible for the strong elongation of the C-O group.

The particle size of the amino humate was determined using the Mastersizer 3000. The frequency results are shown in Figure 4. The particle size of the amino humate was 10% - 0.687 µm, 50% - 7.21 µm, 90% - 296 µm.

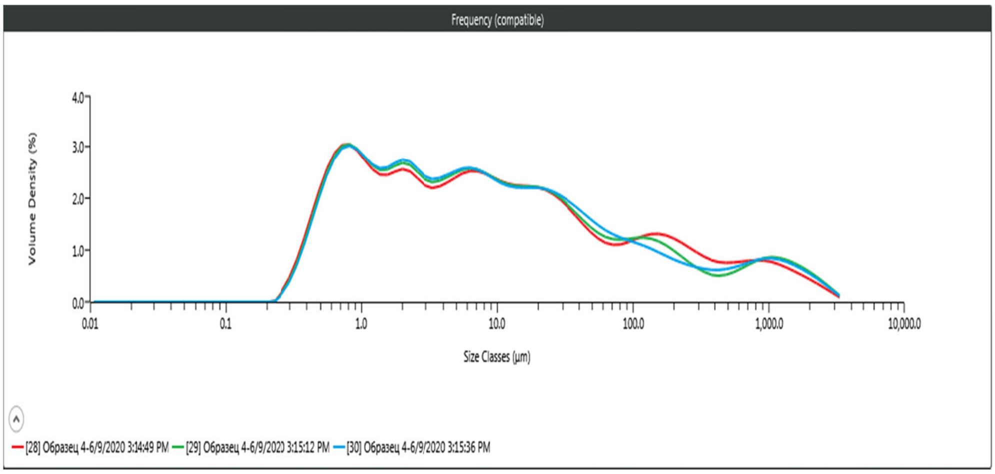


Figure 4 - Particle size of amino humate

The obtained HS were tested for water purification from heavy metals. Analysis of the data obtained showed that after water purification, the values of all heavy metals decrease (table **4**).

Table 4 - Testing of humic substances for water purification from heavy metals

Heavy metals, mg/l	C_0(Me), mg/l	Humic acids		Nitrhumic acids		Aminohumate	
		$C_{residual}$ (Me), mg/l	Purification degree,%	$C_{residual}$ (Me), mg/l	Purification degree, %	$C_{residual}$ (Me), mg/l	Purification degree,%
Zinc	0.10±0.01	0.0010±0.0004	99.00	0.052± 0.009	48,00	Item not found	100,00
Cadmium	0.10±0.01	0.0033±0.0003	96.70	0.10±0.03	-	0.020±0.005	80,00
Lead	0.10±0.01	0.0216±0.0005	78.40	0.015±0.004	85,00	0.036±0.009	64,00
Copper	0.10±0.01	0.0171±0.0003	82.90	Item not found	100,00	0.1±0.01	-

As a result of sorption, the obtained humic substances removed most of the heavy metals from the solution and showed a high degree of purification. Humic acids and aminohumate showed the highest degrees of purification for zinc (99.0-100.0%) and cadmium (80.0-96.7%), and nitrogumic acid showed a high adsorption capacity for heavy metals like copper - 100.0 % and lead 82.9%. This is due to the fact that when interacting with heavy metals, humic acids and their derivatives (amino and nitro) form chelate complexes due to carboxyl, phenolic, nitro and amino groups.

Thus, nitro- and amino-humic substances were obtained from the oxidized coal of the Maikuben deposit by nitration and amination. Their physicochemical and adsorption properties have been studied. As a result of the study, the possibility of using them as non-toxic available sorbents for the purification of heavy metals in aqueous media has been shown.

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ТОТЫҚҚАН КӨМІРДЕН ГУМИНДІ ЗАТ ТУЫНДЫСЫН АЛУ ЖӘНЕ ФИЗИКА-ХИМИЯЛЫҚ, АДСОРБЦИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

Аннотация. Жұмыста Майкөбе бассейні (Қазақстан) тотыққан көмір негізінде алынған гуминді заттарға химиялық талдау жүргізілді. Гумин қышқылдары калий гуматынан 20% қышқыл ерітіндісімен pH = 3-4,5 дейін қышқылдандыру арқылы алынды. Тотыққан көмірден нитрогумин қышқылдарын алудың оңтайлы шарттары: үдерістің ұзақтығы – 3 сағат, қатынасы қ:с=1:5, азот қышқылының концентрациясы 64%, күкірт қышқылы 96% және нитратқа арналған қоспаның құрамы 1:1 (г/г). Нитрат қоспасын қолдану арқылы көмірді нитраттау әдісі тиімді болып саналады. Күкірт қышқылы каталитикалық әсерге ие және азот қышқылының тотығу әсерін азайтады. Көмірдің нитрленуі ароматикалық көмірсутектер сияқты көмірдің макромолекула-сының ароматикалық ядросы бойынша электрофильді алмастыру механизміне сәйкес жүреді және нитрогумин қышқылдары пайда болады. Нитрат қоспасы қарқынды араластыру және салқындату кезінде ылғалданған көмірге қосылды. Процесс тотығу реакцияларын басу үшін 40-50 ^{0}С аспайтын температурада жүргізілді, тәжірибенің ұзақтығы 3 сағатты құрады. Тұнба фильтраттан бөлініп, бірнеше рет сумен жуылды және кептірілді. Нитрокөмір шығымы 85% құрады. Нитрогумин қышқылын нитрокөмірден сілтілік өңдеу арқылы (3% КОН, микротолқынды пеште 6-7 мин бойы өңдеу, қуаты 1000 Вт) және одан кейін 5% қышқыл ерітіндісімен тұндыру арқылы алды.

Амминогумин туындылары механоактивация және ультрадыбыстық тұрғыда өңдей отырып, аммиактың 3% сулы ерітіндісінің қатысуы негізінде алынды. Амминогуминді заттарды алу үшін тотыққан көмір 2,95-452 мкм дейін ұсақталды. Одан әрі роторлы-пульсациялық аппаратта (РПА) көмір бөлшектері ауа оттегі қатысында қарқынды тотығуға және диспергирлеуге ұшырады, қоспа 50°С дейін қыздырылды және 20 минут ішінде аммиактың 3% сулы ерітіндісінің қатысуы арқылы ультрадисперсті күйге және гомогенделген массаға дейін жеткізілді. РПА-дан кейін дайын масса ерітіндіні 1 сағат ұстау үшін экстракция ыдысына берілді. Ұсталған ерітінді ультрадыбыстық диспергацияға арналған синтез модуліне жіберілді, онда ол белгілі бір жиілікте ультрадыбыстық диспергирлеуге ұшырады. Ультрадыбыстық өңдеу уақыты 25 минутты көрсетті. Гуминді заттарды қолдана отырып, ауыр металдан тазарту бойынша зерттеулер жүргізу үшін мемлекеттік стандартты үлгілерден (ГСО) ауыр металдардың модельдік ерітіндісі (мыс, мырыш, қорғасын, кадмий) дайындалды. Конустық колбада (250 мл) сорбент (0,5 г) модельдік ерітіндімен (50 мл, pH=3.26) араластырылды және шейкерде бөлме температурасында (25^{0}С), араластыру жылдамдығы 200 айн/мин, 3 сағат бойы араластырылды. Процесті жүргізгеннен кейін ерітіндіден ауыр металдармен гуминді заттар сүзу арқылы алынды. Адсорбенттен сүзілген ерітінді Ta-lab вольтамперометрлік анализаторындағы ауыр металдардың құрамында талданды.

Сорбция нәтижесінде алынған гуминді заттар ерітіндіден ауыр металдардың көп бөлігін алып тастап, тазартудың жоғары дәрежесін көрсетті. Гумин қышқылдары мен аминогумат мырыштан (99,0-100,0 %) және кадмийден (80,0-96,7%) тазартудың ең жоғары дәрежесін көрсетті, ал нитрогумин қышқылы мыс – 100,0% және қорғасын 82,9% сияқты ауыр металдарға жоғары адсорбциялық қабілетін көрсетті. Ауыр металдармен әрекеттескен кезде гумин қышқылдары және олардың туынды формалары (амин және нитро) карбоксил, фенол, нитро және амин топтарының әсерінен хелат кешенін құратындығы түсіндіріледі. Зерттеу нәтижесінде оларды сулы ортаның ауыр металдарын тазарту кезінде уытты емес қолжетімді сорбенттер ретінде пайдалану мүмкіндігі көрсетілген.

Түйін сөздер: тотыққан көмір, гумин қышқылы, нитрогумин қышқылы, аминогумат, адсорбент, ауыр металдар.

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ПОЛУЧЕНИЕ ПРОИЗВОДНЫХ ГУМИНОВЫХ ВЕЩЕСТВ ИЗ ОКИСЛЕННОГО УГЛЯ И ИЗУЧЕНИЕ ФИЗИКО-ХИМИЧЕСКИХ И АДСОРБЦИОННЫХ СВОЙСТВ

Аннотация. В работе представлены результаты химического анализа гуминовых веществ на основе окисленного угля Майкубенского бассейна (Казахстан). Гуминовые кислоты были получены на основе гуматов калия путем подкисления 20%-ным раствором кислоты до pH = 3-4,5. Оптимальными условиями для получения нитрогуминовых кислот из окисленных углей являются: продолжительность процесса 3 часа, соотношение Т:Ж=1:5, концентрация азотной кислоты 64%, серной кислоты 96% и состав нитрующей смеси 1:1 (г/г). Метод нитрования угля с использованием нитрующей смеси является наиболее эффективной. Серная кислота оказывает каталитическое влияние и уменьшает окислительное действие азотной кислоты. Нитрование углей происходит подобно ароматическим углеводородам по механизму электрофильного замещения по ароматическому ядру макромолекул угля и приводит к образованию нитрогуминовых кислот. Нитрующую смесь прибавляли к увлажненному углю небольшими порциями при интенсивном перемешиваний и охлаждении. Процесс проводился при температуре не выше 40-50 ^{0}С для подавления окислительных реакций, продолжительность опыта составил 3 часа. Осадок отделяли от фильтрата, промывали многократно водой и сушили. Выход нитроугля составил 85%.

Нитрогуминовую кислоту получали из нитроугля щелочной обработкой (3 % КОН, обработка в микроволновой печи течение 6-7 мин, мощность 1000 Вт) и последующим осаждением 5 % раствором кислоты.

Амминогуминовые производные были получены в присутствии 3 % водного раствора аммиака с применением механоактивации и ультразвуковой обработки. Для получения амминогуминовых веществ окисленный уголь был измельчен до 2,95-452 мкм. Далее в роторно-пульсационном аппарате (РПА) подвергался интенсивному окислению и диспергированию частиц угля кислородом воздуха, смесь нагре-вался до 50°С и доводился до ультрадисперсного состояния и гомогенизированной массы в присутствии 3 % водного раствора аммиака в течение 20 минут. После РПА готовая масса подавался в емкости экстракции для выдержки раствора в течение 1 часа. Выдержанный раствор подавался в модуль синтеза для ультразву-ковой диспергации, где подвергался воздействию ультразвуковому диспергированию, определенной частотой. Время ультразвуковой обработки составил 25 минут. Для проведения исследований по очистке от тяжелых металлов с применением гуминовых веществ, готовился модельный раствор тяжелых металлов (медь, цинк, свинец, кадмий) из государственных стандартых образцов (ГСО). В конической колбе (250 мл) размешивали навеску сорбента (0,5 гр) с модельным раствором (50 мл, pH=3.26) и перемешивали в шейкере при комнатной температуре (25^0С), при скорости перемешивания 200 об/мин в течение 3 часов. После проведения процесса, из раствора гуминовые вещества с тяжелыми металлами извлекали путем фильтрации. Отфильтрованный от адсорбента раствор анализировали на содержание тяжелых металлов на вольтамперо-метрическом анализаторе Ta-lab.

В результате сорбции, полученные гуминовые вещества вывели из раствора большую часть тяжелых металлов и показали высокую степень очистки. Гуминовые кислоты и аминогумат показали наиболее высокие степени очистки по цинку (99,0-100,0 %) и кадмия (80,0-96,7 %), а нитрогуминовая кислота показала высокую адсорбционную способность к тяжелым металлам как медь – 100,0 % и свинец 82,9 %. Это объясняется тем, что при взаимодействии с тяжелыми металлами гуминовые кислоты и их производные формы (амино- и нитро-) образуют хелатные комплексы за счет карбоксильных, фенольных, нитро- и амино- групп. В результате исследования показана возможность использовать их в качестве нетоксичных доступных сорбентов при очистки тяжеллых металлов водных сред.

Ключевые слова: окисленный уголь, гуминовая кислота, нитрогуминовая кислота, аминогумат, адсорбент, тяжелые металлы.

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DETOXICATION OF BY-PRODUCTS OF OIL AND GAS INDUSTRY ACCOMPANIIED BY OBTAINING IRON AND SULFUR-CONTAINING BINDERS FOR STRUCTURAL BUILDING MATERIALS

Abstract. In this paper, the authors considered the issues related to reducing negative impact of large-tonnage toxic industrial wastes on environment by means of their detoxication and application as effective binders for building materials. For implementation of scientific researches, the standard methods of analysis of physical and mechanical properties have been used for the stone based on iron and sulfur containing binders; the contemporary methods of differential and thermal, X-ray diffraction analysis, microscopic analysis and testing apparatuses have been used. While carrying out experimental research, the authors have realized a scientific hypothesis stating that for increasing the effect of additional activation for eact particles of iron- and sulfur containing additives, their co-milling has been applied. As the result, there took place mutual neutralization and detoxication of solid industrial by-products with opposite chemical properties. In the course of experimental work aimed at preliminary determination of composition and activation of sulfur-contating additives, wet grinding was done on the pebble mill by applying abrasive and impact forces. In the course of combined action of mechano-chemical activation of industrial by-products, in the presence of water, accompanied by sulfur-containing raw mixtures for manufacturing of building materials, there was used the method of mutual neutralizion of chemically hazardous substances forming a part of industrial wastes. These methods enable to reduce the consumption of a binder due to its partial replacement by toxic by-products of oil and gas industry and metallurgy. The characteristics and properties of the specimens of iron and sulfur-containing binder have been studied at the age of 7, 14 and 28 days of air hardening. The specimens were exposed to thermal and steam curing. It was stated that air hardened iron and sulfur-containing binders at the age of 14 days have reached the ultimate compressive strength of 62.0 MPa, at the age of 28 days – 66.5 MPa, correspondingly. The same composition exposed to steam curing at the age of 28 days has compression strength of 74.5 MPa that attests to the fact that steam curing has a positive impact on gain in strength of iron and sulfur-containing binder. The obtained research results could be apllied as an effective substance for manufacturing mortars and concrets in construction industry.

Key words: Activation, mechanical and chemical treatment, detoxication of industrial wastes, neutralization of hazardous substances, thermodynamic calculations, iron and sulfur containing binders, ferric iron, oxidation, deoxidization, compression strength, pyrite cinder, sulfur.

Introduction. In the southern regions of the Russian Federation as well as in the western regions of Kazakhstan, there accumulated vast raw materials in the form of large-tonnage by-products of oil and gas industry. Thus, their utilization in the composition of building materials is of paramount importance for national economies of these countries. It is well known from the literature sources that addition of technical sulfur in the powder form has an impact of physical and mechanical properties of concrete [1-20]. Along with that, the mechanism of the influence of sulfur containing additive on the structure and properties of cement composites has not identified, the optimum compositions and the methods of manufacturing sulfur containing concretes have not been determined. This proves the relevance of researching the necessity of obtaining effective building materials on the base of sulfur by-products of oil and gas industry, and the development of technologies for their production.

For the solution of this issue, the authors have conducted the research of the influence of the additives on the base of sulfur wastes of oil and gas industry on the structure formation and physical-chemical properties of composite iron- and sulfur containing binders. The processes of mechanochemical activation of binders, as shown in the studies [11-20], lead to enhancement of physical amd mechanical properties of the obtained building materials. In the course of mechanochemical activation of iron- and sulfur containing by-products, at the presence of water, with obtaining raw mixtures for manufacturing building materials, the principle of mutual neturalization of chemically hazardous substances that are present in industrial by-products has been applied. In the works [1-20], the possibility of obtaining effective concretes with enhanced physical and mechanical properties has been shown for various methods of additional activation of a binder. These methods enable to reduce concrete consumption due to its partial replacement by the wastes of oil and gas industry as well as metallurgy by-products.

Materials: the following raw materials and binders have been tested for the research purposes:

1. For the research purpose, Portalnd cement of the grade 400 produced by Novotrotsk cement plant has been used. Its chemical composition is presented in the table 1 below.

Table 1 - Chemical composition of cement produced by Novotroitsk cement plant

Content, %									
Basic oxides						Basic minerals			
CaO	$Si0_2$	$A1_2O_3$	Fe_20_3	R_2O	SO_3	C_3S	C_2S	C_3A	C_4AF
61.39	23.39	6.39	6.07	0.38	0.60	57.61	17.39	7.91	13.11

2. As an additive, pyrite cinder manufactured by Plc Phosphorchim of Aktobe region has been used. The addtivie consists of the iron oxide mixture (II, III) Fe_3O_4 (Fe_2O_3**)**, recalculating for the content of iron 42-63% and sulfur admixtures 1-2%. The reminder are oxides of non-ferrous metals. The chemical composition of pyrite cinder, % wt. is given in the table 2.

Table 2 – Chemical composition of pyrite cinder, % wt.

CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	SO_3	R_2O	п.п.п
10.6	19.6	66.2	2.2	1.2	-	-	0.2

3. As a modifier, sulfur by-products, being secondary products of processing high-sufur oil of Aktobe region deposits, Kazakhstan, have been used. Technical sulfur represents a granulated product complying with the requirements of the All-Union Standard GOST 127.1-03. The chemical composition of technical sulfur applied in the experiment is enclosed in the table 3.

Table 3 – Chemical composition of sulfur

Gost	Sulfur % wt.	Cinder, % wt.	Organic substances, % wt.	Water, % wt.
127.1-93	99.060	0.400%;	0.053%;	0.010%.

For binder's preparation, tap potable water corresponding to the GOST 23732 requirements "Water for concrete and mortars. Specifications" has been used.

Methods. Characteristics of original and activated binder have been determined in compliance with the GOST 30515-97, GOST 31108-2003 and GOST 7473-2010.

Determining ultimate tensile and bending strength of iron- and sulfur containing binders have been carried out on the test-beams with the dimensions 40x40x160mm on the apparatus IP 2710.

Differential thermal analysis of iron- and sulfur containing powders have been done by the photo derivatograph under the standard method. By means of X-ray diffraction analysis, there has been determined the phase composition of activated iron- and sulfur-contatining binder.

Thermodynamic evaluation of chemical reactions probability has been done for the given components of industrial by-products in raw sludges by means of the standard thermodynamic values and electrochemical potentials.

In order to get effective iron- and sulfur containing binders, there has been applied the principle of mutual neutralization and detoxication of hazardous industrial wastes by means of their mechanochemical treatment at low temperature.

While carrying out experiments, the amount of sulfur wastes and pyrite cinders have been taken by weight in proportion to stoichiometric reactions constants; correspondingly, the raw materials mixture has been moistured to reach the consistency of “wet sand”.

Having worked out the plan of the research, there has been realized the scientific hypothesis that in order to exercize additional activation of each particle of additives, their co-milling had been used. In the result, there took place mutual detoxication of solid wastes with specific contrasting chemical properties. Having impelemented experiments aimed at preliminary analysis of composition and activation of sulfur containing additives, wet grinding was done by pebble mills creating abrasive and impact action. As said above, the addition of technical sulfur and its derivatives to concrete mixture enhances the characteristics of concrete stone.

In the paper, the authors also researched the influence of sulfur addition on the strength properties of sulfur contatining binders. The following proportions of the mortar mixture components have been taken: (cement: pyrite cinder: technical sulfur, % wt.): 74:18:8, 70:18:12, 67:20:13. Water-solid ratio of sulfur containing binders has been taken provided casting into molds of mortar mixtures with the cone flow diameter ensuring the optimum formation of porous structure and the maximum mortar strength. In order to carry out research for determining the impact of technical sulfur addition on the strength properties of sulfur containing cement stone, the specimens with dimensions 100x100x100 mm have been prepared, with water-solid ratio equal to 0.385, when cone flow of 200 mm on the flow table was provided. For comparison, there have been prepared the specimens of cement mortars with equal fluidity and water-solid ratio of 0.385, no-additive composition. Technical sulfur was introduced in the composition in the amount of 8-13% combined with pyrite cinder (18% pyrite cinder + 8% tehcnical sulfur), (18% pyrite cinder + 12% technical sulfur), (20% pyrite cinder + 13% technical sulfur) from the dry components weight.

Results. The obtained estimates related to the binding reactions of technical sulfur (IV) and iron (III) by means of elecromotive forces (e.m.f.) of electrochemical couples are given in the table 4.

Table 4. - Evaluation of reaction capacity by means of electomotive forces of electrochemical couples

Systems and reactons	e.m.f. of electrochemical couples
$Fe (III) + S^{o} \rightarrow Fe(II) + S (VI)$;	$E = 0.771 – (- 0.13) = + 0.784$ (в)> 0

As seen from the table 4, the analysis of estimated values (e.m.f.) of electrochemical systems under standard electrode potentials shows, that the reactions are possible as the value of e.m.f. ›0 (positive), whereas recovery of pyrite cinder by technical sulfur is more energy-efficient than the one by carbon. Ferric iron can oxidize sulfur transforming into ferrous form. It is worth noting that sulfur containing sludges have $pH > 3$ (alkaline reaction of aqueous migrate) [18], they have undergone the thermal treatments similar to cement clinker and demonstrate binding properties. The standard values of enthalpy ΔH^{o} and enthropy ΔS^{o} at the temperature of 298° K, taken form the literature sources [19-20], are enclosed in the table 5.

Calculations of thermodynamic values change for chemical reactions have been done under the well-known formula:

$$\Delta H^{o}298xp = \Delta H^{o}298(finite) - \sum \Delta H^{o}298(transitional) \qquad (1)$$

Table 5 – The values of standard enthalpy and enthropy for the reacting substances

Substance	$\Delta H^{o}298$ kkal/mole	$\Delta S^{o}298$ kkal/degrees·mole
SO_2	-71.0	59.2
Fe_3O_4	-266.5	35.0
FeS	-22.8	16.1
Fe_2O_3	-145.2	21.5
FeS_2	-38.8	12.7
FeO	-64.5	13.4

At mechanical abrasion and mixing of sulfur and iron in the presence of water in base condition, there have been estimated enthalpies for oxidation-reduction reactions (the calculations for values of the change of standard thermodynamic potentials have been done at standard temperature T = 298°). The obtained values of ΔH – enthalpies and thermal effect of oxidation-reduction reactions are presented in the table 6 (the alphabetical references of oxidation-reduction reactions are given in the alphabetical order).

Table 6 – Thermal effects of oxidation-reduction reactions

Alphabetical references of the reactions	Systems and reactions	Thermal effect of the reaction, ΔH° kkal
A	$3Fe_3O_4 + S \rightarrow FeS + 4Fe_2O_3$	195.9
B	$FeS + S \rightarrow FeS_2$	-16.0
C	$4Fe_2O_3 + S^o \rightarrow SO_2 + 4FeO$	-38.6
D	$2FeO + 3S^o \rightarrow 2FeS + SO_2$	12.4
E	$FeO + S \rightarrow FeOS$	20.8

Comparing the estimated values and their references, one can draw a conclusion that reactions A, D and E are impossible from the point of thermodynamics, the values of enthalpy are higher than 0 C^0, i.e. positive (ΔH)> 0, whereas other reactions could be executed at ordinary temperature. The most probable are reactions B and C as they are characterized by the highest value of ΔH. It should be noted that it worth conducting the reaction in the presence of sufficient amount of water, thus, hydrogen ions in the reaction C will bond and form neutral water molecules in alcaline medium, and sulfur dioxide - into the molecule of salt

$CaSO_3$. For the experiment, the amount of by-products on the base of pyrite cinder and technical sulfur have been taken in the weight ratio, proportional to stoichiometric constants of reactons, and raw materials mixture was slightly humidified to reach the consistency of "wet sand". The products of reaction visually differed by colour from the primary raw mixture. In the process of mechanochemical treatment, significant rise in temperature of reactive atmosphere was observed (about 40^0C). Mostly likely, raw mixture [1, 18-20] was heated at the account of chemical exothermal reactions and energy transfer from mechanical to thermal one.

Apparently, at mechanochemical grinding the temperature factor plays a crucial role for the instant heating of reacting chemicals at the moment of mechanical impact. Defects of extrinsic and non-stoichiometric origin have a noticeable impact on crystal grid of iron oxide [18-20].

For example, the sintering rate usually increases with the growth of derivation from stoichiometry, and activation energy of creeping of crystal gird of non-stoichiometric oxide is reduced by 20-25 kkal/mol if compared with normal oxide.

It should be added that thermodynamically impossible reaction realized under the scheme C in the presence of metallic iron (Fe^o) becomes possible (ΔH< 0):

$$3Fe^o + Fe_3O_4 + 2S \rightarrow 2FeS + 4FeO, \Delta H = -37.1 kkal \quad (2)$$

The results given above have proven that sulfur is bonded with iron oxides when exposed to mechanical impact at the temperatures close to the standard ones.

Having carried out the experimental work aimed at detoxication and activation of sulfur containing wastes, the authors came to conclusion that ferric iron is able to oxidate sulfur while transforming into its ferrous form, as the color of the treated mixture has changed from yellowish to grayly-green. Joint grinding of sulfur containing components and cement has a positive impact on mechanical properties of the researched specimens. Strength of sulfur containing specimens at the age of 28 days has reached 37.7MPa. Along with that, pyrite cinder apparently acted as an initiating agent of physical and chemical coagulation process of binder's mixture. During coagulation process, polarization of dispersed particles and their mutual attraction takes place that facilitates the process of structure formation. Addition of iron dust and iron nanoparticles with the purpose of sulfur binding could be considered a quite interesting variant of mutual wastes utilization [20]. However, iron compounds are characterized by high density that results in gain in weight. The reactions D and E are of paramount importance. The fact of the matter is they demonstrate the principle possibility, hish sustainability and cost effectiveness of rational utilization of toxic sulfur containing sludge. When treated by pyrite cinder, hazardous sulfur oxide in the slugde composition is transformed into low-toxic sulfur oxide, i.e. could be fully utilized in the composition of chipcrete concrete. It is rational to utilize these raw mixtures by adding vegetation residues, such as stems of cotton plant or other organic components used for manufacturing of lightweight chipcrete concretes. In the course of the research, physical and mechanical properties of sulfur contatining specimens have been also determined. The results of findings are given in the table 7.

Table 7 – Characterisitcs of sulfur contating binders with addition of sulfur

N	Binder's composition,%				Dry density, kg/m^3	Ultimate strength, MPa	
	Sulfur серы, %	Pyrite cinder	Cement	Water Влажность		compressive	bending
1	8	18	64	9.89	1590	64.7	8.53
2	12	18	70	9.12	1570	66.5	9.14
3	13	20	67	9.27	1590	74.5	10.9

It was stated that insertion of technical sulfur additive in the amount of 8-13% increases ultimate compressive strength of the specimens made from the mortars with water-solid ration equal to 0.385 in a wet and dry state. The furthre increase in the amount of technical sulfur additive leads to lowering strength properties of the mortar, along with that, regularity of strength change for all the specimens are similar.

Discussions. It is known [1-20] that increase in capacity of reaction of the binder's components at wet milling is achieved not only due enhancement of dispersive capacity in liquid phase but also by the change of crystal structure, particles shape that preconditioned intensifying the coagulation process of sulfur containing mixture. Along with that, chemical and mineralogical composition of an initial binder remain stable. The activation mechanism involves interaction of newly exposed surfaces of binder's particles at wet milling, i.e. adding mechanical and chemical-energetic momentum to each particle. It could be mentioned that activation mechanism includes increase in forces of interionic mutual attractions and appearance of surface valence forces when nanoparticles of colloid system attract to each other. The obtained research results provide basis for a conclusion that by activation and detoxication of industrial by-products it is possible to obtain sulfur containing binders with advanced physical and technical characteristics.

Conclusions. It was stated that technical sulfir, pyrite cinders, by-products of oil and gas industry and metallurgy are effective additive in iron and sulfur containing compositions providing increase in strength properties, lowering sorption humidity and water absorption of lightweight concretes.

The obtained results of thermodynamic analysis give evidence of the possible binding of sulfur and iron oxides when exposed to mechanical impact at the temperatures proximal to standard ones. It was also confirmed that the essence of activation mechanism of sulfur containing compositions is in interaction of newly etched surfaces of binder particles at wet re-grinding. Along with that, the process of binding mixture coagulation is intensified and rapid development of crystal grid occurs due to crystallohydrate formation.

In the course of experiments it was also stated that additives on the base of technical sulfur, a by-product of oil and gas industry, enhance physical and mechanical properties of iron- and sulfur containing cement stone. Thus, introduction of iron- and sulfur containing addtivies in the amount of 8-13% ensures the increase in strength up to 74.5 MPa, whereas binding components (cement 67%+pyrite cinder 20%+sulfur 13%) in the mixture composition by weight.

Thus, proposed binding compositions increase their strength by a factor of 1.5-2.5 over time when compared with initial strength. This is explained by the optimum composition of iron- and sulfur containing binding compounds and the conditions of their hardening. The developed iron- and sulfur containing composites can be applied in the production of effective concretes, walling materials as well as industrial and civil engineering structures.

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МҰНАЙ-ГАЗ ӨНЕРКӘСІБІ ҚАЛДЫҒЫН ДЕТОКИКАЦИЯЛАУ АРҚЫЛЫ КОНСТРУКЦИЯЛЫҚ ҚҰРЫЛЫС МАТЕРИАЛДАРЫНА ТЕМІРЛІ-КҮКІРТТІ БАЙЛАНЫСТЫРҒЫШТАРДЫ АЛУ

Аннотация. Жұмысымызда көп тонналы уытты өнеркәсіп қалдықтарының қоршаған ортаға теріс әсерін детоксикациялау жолымен азайту және оларды құрылыс материалдарына тиімді тұтқыр байластырғыш материалдар ретінде пайдалану мәселелері қарастырылды. Ғылыми зерттеулер жүргізу үшін дифферанциялды-термиялық, рентген-фазалық, микроскопиялық талдау және сынау жабдықтарының заманауи әдістерін пайдалану негізінде алынған темірлі-күкіртті байланыстырғыштардан даярланған үлгі тасының физикалық-механикалық қасиеттерін талдаудың стандартты әдістері пайдаланылды.

Эксперименттік зерттеулер жүргізу кезінде темірлі-күкіртті қоспалардың әрбір бөлшегінің қосымша белсенділігінің әсерін арттыру үшін олар бірге ұсақталып қолданылды және соның нәтижесінде химиялық қасиеттері бойынша қарама-қарсы сипаттамалары бар қатты уытты қалдықтарды өзара бейтараптандыру және детоксикациялау жүргізілді. Құрамында күкірт бар қоспалардың құрамын алдын ала анықтау және белсендендіру бойынша тәжірибелік-эксперименталдық жұмыстарды жүргізу ұнтақтау шар диірмені конструкцияларында ұсақтау және соққы беру әдістері арқалы іске асырылады. Өнеркәсіптік қалдықтардың механикалық-химиялық белсенділігін біріктіру жұмысы үдерісінде құрылыс материалдарын өндіру үшін құрамында күкірт бар шикізат қоспалары арқылы су қосып, өнеркәсіптік қалдық құрамындағы химиялық зиянды заттарды өзара бейтараптандыру әдісі пайдаланылды. Бұл әдістер тұтқыр заттың бір бөлігін мұнай-газ және мелаллургия өнеркәсібінің уытты қалдықтарымен ауыстыру есебінен шығынын азайтуға мүмкіндік береді. Құрамында темір-күкірт бар тұтқыр үлгілерінің сипаттамалары мен қасиеттерін 7, 14 және 28 тәуліктік мезгілде табиғи жағдайда, жылу және жылу ылғалдылығын өңдеуден кейін зерттеді.

Табиғи жағдайда 14 тәулік мерзіміне қарай құрамында қатты темір-күкірт бар тұтқырлар 62,0 МПа қысылған кезде беріктік шегіне жетті, 28 тәулік мезгілінде 66,5 МПа берік бола түсетінін анықтадық. Жылу ылғалдылығын өңдеуден өткен осы құрам 28 тәулік уақытында 74,5 МПа сығуда берік болады әрі бұл жылу ылғалдылығын өңдеу құрамында темір-күкірт бар тұтқыр беріктігінің жиынтығына қолайлы әсер ететінін көрсетеді. Алынған зерттеу нәтижелерін құрылыс саласына ерітінділер мен бетондарды дайындау кезінде тиімді тұтқыр зат ретінде пайдалануға болады.

Түйін сөздер: активтендіру, механохимиялық өңдеу, өнеркәсіптік қалдықтарды детоксикациялау, зиянды заттарды бейтараптандыру, термодинамикалық есептеулер, құрамында темірлі-күкіртті байланыстырғыштар, үшвалентті темір, тотығу, қалпына келтіру, сығу кезіндегі беріктігі, пириттік қышқыл, күкірт.

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ДЕТОКСИКАЦИЯ ОТХОДОВ НЕФТЕГАЗОВОЙ ПРОМЫШЛЕННОСТИ С ПОЛУЧЕНИЕМ ЖЕЛЕЗО-СЕРОСОДЕРЖАЩИХ ВЯЖУЩИХ ДЛЯ КОНСТРУКЦИОННЫХ СТРОИТЕЛЬНЫХ МАТЕРИАЛОВ

Аннотация. В работе рассматириваются вопросы по уменьшению отрицательного влияния многотоннажных токсичных промышленных отходов на окружающую среду путем детоксикации и использование их в качестве эффективного вяжушего для строительных материалов. Для проведения научных исследований использовались стандартные методы анализа физико-механических свойств камня железо-серосодержащего вяжущего, полученных с использованием современных методов дифферациально-термического, рентгенофазового, микроскопического анализа и испытательного оборудования. При проведении экспериментальных исследований была реализована научная гипотеза, что для повышения эффекта дополнительной активации каждой частицы железо-серосодержащих добавок применялось их совместное измельчение, в результате чего происходила взаимная нейтрализация и детоксикация твердых токсичных отходов, имеющих особые противоположные характеристики по химическим свойствам. При проведении опытно-экспериментальных работ по предварительному определению состава и активации серосодержащих добавок влажное измельчение происходило на конструкциях шаровой мельницы, за счет истирающих и ударных воздействий. В процессе работы совмещенной механохимической активации промышленных отходов, в присутствии воды, с получением серосодержащих сырьевых смесей для производства строительных материалов использован метод взаимной нейтрализации химически вредных веществ, находящихся в составе промышленных отходах. Эти методы позволяют сократить расход вяжущего вещества за счет замены его части токсичными отходами нефтегазовой и мелаллургической промышленности. Характеристики и свойства образцов железо-серосодержащего вяжущего изучали в 7, 14, и 28 суточном возрасте в естественных условиях твердении и после тепловой и тепловлажностной обработки. Нами установлено, что железо-серосодержащие вяжущие, твердевших в естественных условиях к 14-суточному возрасту имеют предел прочности при сжатии 62,0 МПа, в 28-суточном возрасте достигается прочность 66,5 МПа. Этот же состав, прошедший тепловлажностную обработку, в 28-суточном возрасте имеет прочность при сжатии 74,5 МПа, что свидетельствует о том, что тепловлажностная обработка благоприятно влияет на набор прочности железо-серосодержащего вяжущего. Полученные результаты исследований можно использовать в качестве эффективного вяжущего вещества при изготовлении растворов и бетонов для строительной отрасли.

Ключевые слова: активация, механохимическая обработка, детоксикация промышленных отходов, нейтрализация вредных веществ, термодинамические расчеты, железо-серосодержащие вяжущие, трехвалентное железо, окисление, восстановление, прочность при сжатии, пиритный огарок, сера.

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PHOSPHORUM SLAG AND PHOSPHOGYPSUM AS MAN-MADE INDUSTRIAL WASTE FOR CREATION OF MODIFIED FIRE AND EXPLOSION-SUPPRESSING POWDER COMPOSITIONS

Abstract. One of the priority areas of life safety and environmental protection is the creation of modified fire and explosion-suppressing powder compositions using man-made waste from various industries. Their use makes it possible to reuse substandard (expired) fire extinguishing compositions, possibly as substances that slow down the processes of explosion and combustion of materials. Fire and explosion-suppressing powders at the end of the shelf life must be regenerated or disposed of. For the regeneration procedure, i.e. restoration of the fire-extinguishing properties of the powder, it is sent to the manufacturing plant to restore its properties and characteristics. This allows you to modify the properties of the powder and produce an improved product. At the same time, a significant contribution is made to the development of a system for the rational use of natural resources, disposal of production waste, preservation of the ecological situation in the area, as well as prevention of emergencies and emergencies at industrial dumps. Comprehensive and rational use of secondary material and raw materials and wastes of various industries should take a certain place in the raw material balance of industry and in the prevention of emergencies.

Keywords: fire and explosion-suppression powder compositions, waste from various industries, disposal of production waste, secondary and raw materials.

Introduction. This research work presents the classification of different types of reuse of raw materials used for explosion and fire. The focus is on recovery issues and different reuse ways where the used powder (or its components) at least restores the original level of performance. The thesis describes the implementation of a life cycle assessment method. In addition, various numerical and analytical software tools are used, which model the processes of creation and testing of the obtained mixtures, as MATLAB. In the future, the potential environmental benefits of the recovery of fire and explosion-suppressing powders will be investigated. The mentioned method includes several new aspects: it allows the analysis of possible trade-offs between potential impacts and energy efficiency; independently simulate some parameters that affect the reuse of the product; the method is applicable even on the early stages of the modernization process, when some technical characteristics not defined yet. The environmental impact parameters of the product life cycle stages is used as input to the assessment.

The issues of environmental protection and prevention of pollution leads to the need for the use of alternative raw materials from industrial waste for the prevention of emergencies. At the same time, millions of tons of industrial waste in the form of electrothermophosphoric slags, phosphogypsum and internal overburden have accumulated at the enterprises of the phosphorus and coal mining industry. Meanwhile such kind of industrial waste allow to solve the problem of rational use of material resources and the environmental situation in industrial regions.

Problem statement. By investigation of the composition of fire-extinguishing powders, two main tasks are solved, as consisting in the selection of the chemical and granulometric composition of the powder and providing the highest possible fire-extinguishing ability for a class of fire. The system of fire safety of the object is established as a set of organizational measures and technical means aimed at preventing fire and reducing damage from it at the object, i.e. it is necessary to minimize the possibility of occurrence and development of fire, as well as the impact on people and property of fire hazards. In this regard, both flame retardants (including flame retardants and paints) and building materials are used to increase the fire resistance of building structures, i.e. the use of primary fire extinguishing agents, such as fire-extinguishing powders. Among other things, such powders are included in the composition for extinguishing fires of various classes in the compositions of powder extinguishers, which must have the appropriate charges: for class A-powder ABC (E); for classes B, C and (E) - BC (E) or ABC (E) and class D – D [1-4].

For effective fire extinguishing it is necessary to determine the temperature limits of flame propagation – (ignition). The ignition temperature is the temperature of the substance at which its saturated vapor forms in the oxidizing medium concentrations equal respectively to the lower (lower temperature limit) and upper (upper temperature limit) concentration limits of flame propagation. During extinguishing the flame, strong heating of the powder composition leads to its melting and transition of the solid into a liquid state, and then, when evaporating, into a gas. Melting of solids and boiling of liquids occurs at different temperatures, due to different energies of bonds between atoms and molecules of substances. These physical properties of substances are considered in the development, selection and evaluation of the effectiveness of fire extinguishing agents and materials. [5-7]

The complex task of developing the composition of fire extinguishing powders is solved with the help of optimally selected qualitative and mathematically calculated quantitative composition of components made from waste fine dusts and substandard fire extinguishing powder based on ammophos.

An active base for fire-extinguishing powders for multi purposes is known [8], containing monoammonium phosphate, ammonium sulfate and a mixture of organosilicon substances. The disadvantage of this invention is the multi-componence of the active base and the high cost of preparing.

A powder composition for extinguishing fires of various combustible materials is also known [9]. This composition includes a hydrophobic organosilicon liquid, an additive of highly dispersed silicon dioxide and the main component, which is used as silvinite, ammophos, and as a highly dispersed silicon dioxide – white soot with a specific surface area of 100 sq.m. / h, as well as an additional aluminosilicate. The disadvantages of this powder include multi-component active base, high cost and complex technology of its production.

It is technically and economically efficient to use phosphogypsum and electrothermophosphoric slag in fire extinguishing compositions. These dusts are mainly composed of particles up to 1.0 mm in size, i.e. do not require the cost of electricity for their additional grinding. Dust-like fractions are captured by dust-gas-cleaning devices and accumulate in storage bins.

To date, there is a wide range of fire-extinguishing powders. But the intensive work continues to create new fire-extinguishing and explosion-suppressing compositions. The standard formulations used are very expensive; unused batches of expired or post-fire powder are only partially used as fertilizers. Substandard powder is mostly stored and does not find application.

According to the results of the study, we have identified the preservation of the fire-extinguishing ability of the expired powder of the P-2AP and the possibility of its use as a fire-extinguishing agent.

Based on further research, we offer fire-extinguishing powder compositions based on expired powder P-2AP and waste slag phosphorus production, located 1) in the dump DPO-Khimprom and Novo-Dzhambul Phosphorus Plant and 2) phosphogypsum of LLP "Kazphosphate". These compounds can be used to extinguish fires of smoldering materials, flammable liquids and gases. The production of the proposed compositions is possible from the waste of non-scarce domestic raw materials.

The main component of expired powder grade P-2AP is ammophos, the mass fraction of which is more than 90%. Additives in the composition of this powder are: chamotte-kaolin powder Al_2O_3 • SiO_2 • H_2O with impurities of iron oxide and titanium, and Aerosil AM-1-300 or AM-1-175 (mass fraction in powders up to 2.5%).

Three samples of each type of waste were collected, averaged and dried to a constant humidity at 50 degrees Celsius in a drying cabinet. Table 1 presents the results of determining the chemical composition of fine dust waste, and Table 2 shows their granulometric composition.

Table 1 – Chemical composition of the investigated raw medium, %

Components mm	Electrochemistry slag	Phosphogypsum
SiO_2	40	13,33
CaO	44,5	26,59
Al_2O_3	3,96	0,45
MgO	2,65	
Fe_2O_3	0,33	0,80
Na_2O	-	0,12
K_2O	-	0,10
P_2O_5	0,89	1.15
others	0,39	16,4

Research of granulometric composition of the slag of the waste phosphorus production was carried out using a sieve and microscopic analysis. Sieve analysis of fire extinguishing powders was carried out on two grids: No. 02 (200 microns) and No. 005 (50 microns). A significant part of the powder particles has a size of less than 50 microns. A similar pattern was observed in phosphogypsum during fractional sieve analysis by standard technique (ROTAP); in electrothermophosphoric slag the predominance of fraction less than 50 microns was not detected. Microscopic analysis of the samples was performed on a scanning electron microscope JEOL with the possibility of energy-dispersive analysis.

Table 2 – Granulometric composition of the investigated raw medium, %

Dispersion, mm	Phosphogypsum	Electrothermophosphoric slag
> 2,5	-	19,7
1,6-2,5	-	13,5
1,0-1,6	0,8	12,4
0,63-1,0	2,9	8,6
0,1-0,63	18,2	32,7
0,63-0,1	4,8	13,5
0,05-0,0063	41,3	15,6
< 0,05	52,1	6,2

In order to determine the optimal compositions of mixtures based on expired powder P-2AP with industrial waste, the mathematical model MATLAB was used [10,11].

CONCLUSION. We applied statistical analysis methods to identify the dependence of fire extinguishing capacity on the percentage of expired powder and industrial waste in the mixture. Using the Least Squares Method, we considered the ranges of powder-to-industrial waste ratios:

- the first option (phosphogypsum) from 20: 80 to 30: 70
- the second option (Electrothermophosphoric slag) from 50:50 to 35:65

Combining the calculated data for the first and second variants, the dependence of the extinguishing capacity on the percentage of the mixture components was obtained.

Thus, the suitability of waste phosphorus production and fire-extinguishing powders with expired shelf life as fire and explosion suppressants was investigated; the mathematical and computer model (MATLAB) was used to obtain fire-and-explosion-suppressing powder using fire-extinguishing compositions (as the main component, the expired powder P-2AP was selected) and non-demanded pulverized waste of phosphogypsum and electrothermophosphoric slag, which provide sufficiently high operational properties of the compositions at a very low cost; the composition of fire and explosion-suppressing powder from a mixture with the following ratios was developed:

composition No. 1 - fire-extinguishing powder based on expired powder P-2AP (73-74,5%) + phosphogypsum (27-25,5%) and

composition No. 2 - fire-extinguishing powder based on expired powder P-2AP (54-57%) + electrothermophosphoric slag (46-43%).

For these compositions requires grinding 10-15% fineness of grinding raw powder.

The mathematical analysis of the MATLAB model is confirmed by the results of the compositions of the studied raw medium: expired fire-explosion powder composition + phosphogypsum and expired fire-explosion powder composition +electrothermophosphoric slag.

Analyzing the results obtained, we came to the conclusion that the use in the proposed fire extinguishing compositions as the main component of expired powder P-2AP (which retained the main operational properties – fire extinguishing ability) and non-demanded waste phosphogypsum and electrothermophosphoric slag provide sufficiently high operational properties of the compositions at a very low cost. [11]

Thus, the efficiency of the proposed fire and explosion-suppressing compositions is achieved, while making a significant contribution to the development of the system of rational use of natural resources, waste disposal, preservation of the ecological situation of the area, as well as the prevention of emergencies and emergencies at industrial dumps.

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ФОСФОРЛЫ ҚОЖ ЖӘНЕ ФОСФОРЛЫ ГИПС: ТҮРЛЕНДІРІЛГЕН ӨРТ ЖӘНЕ ЖАРЫЛЫС СІҢІРГІШ ҰНТАҚТЫ КОМПОЗИЦИЯ ЖАСАУҒА АРНАЛҒАН ТЕХНОГЕНДІК ӨНЕРКӘСІПТІК ҚАЛДЫҚТАР

Аннотация. Тіршілік қауіпсіздігі мен қоршаған ортаны қорғаудың басым бағыттарының бірі – түрлі өндірістің техногендік қалдығын қолдану негізінде түрлендірілген өрт-жарылыс сөндіргіш ұнтақ құрамын жарату. Оларды жарамсыз (мерзімі өткен) өрт сөндіру құрамын материалдардың жарылуы мен жану үдерісін баяулататын зат ретінде қайта пайдалануға мүмкіндік беретіндіктен қолданған тиімді.

Өрт-жарылыс сөндіргіш ұнтақтар жарамдылық мерзімі аяқталғаннан кейін қалпына келтіріліп немесе жойылады. Қалпына келтіру шарасы, яғни ұнтақтың өрт сөндіру қасиеттері мен сипаттамаларын қалпына келтіру үшін өндіруші зауытқа жіберіледі. Бұл ұнтақ қасиеттерін өзгертуге және жетілдірілген өнімді шығаруға мүмкіндік береді. Бұл ретте табиғи қорды ұтымды пайдалану, өндіріс қалдықтарын жою, жергілікті жердің экологиялық жағдайын сақтау, сондай-ақ өнеркәсіптік үйінділерде төтенше және апаттық жағдайлардың алдын алу жүйесін дамытуға елеулі үлес қосылады.

Қайталама материалдық-шикізат қорлары мен түрлі өндіріс қалдықтарын кешенді және ұтымды пайдалану өнеркәсіптің шикізат теңгерімінде және төтенше жағдайды болдырмау барысында белгілі бір орын алуы тиіс. Қазіргі уақытта оларды пайдалану үлесі шикізат көлемінің 25-30% есептік көрсеткішінің шамамен 3-5% құрайды. Сол себепті индустриялық-инновациялық даму кезеңінде техногендік қалдықтарды ұтымды және кешенді пайдалану мәселелерінің практикалық маңызы зор.

Өнімді қайта пайдаланудың маңыздылығы заңнамада да, ғылыми ортада да бірнеше рет атап көрсетілгенімен, қазіргі уақытта экологиялық тұрғыдан өрт сөндіру ұнтағын бағалау мен қайта пайдаланудың кешенді және жүйелі әдістері жоқ. Сонымен қатар, ғылыми әдебиетте және заңнамада қолданылатын қайта пайдалану анықтамасы әрдайым бірдей бола бермейді. Аталған жұмыста бірнеше ұсынылған анықтамалармен қоса қайта пайдаланудың алуан түрлерін жіктеу ұсынылған. Пайдаланылған ұнтақ (немесе оның бөліктері) қалай болғанда да бастапқы өнімділік деңгейін қалпына келтіру үшін қайта пайдалану түрлері мәселесіне баса назар аударылады. Жұмыста өмірлік циклді бағалау әдісін зерттеу жолдары сипатталады. Сонымен қатар, алынған қоспаларды жасау және сынау үдерістерін модельдейтін түрлі сандық-талдамалы бағдарламалық құралдар, атап айтқанда, МАТЛАБ сияқты бағдарламалық өнімдер қолданылады. Болашақта өрт-жарылыс сөндіргіш ұнтақты қалпына келтірудің әлеуетті экологиялық пайдасы зерттеледі. Аталған әдіс бірнеше жаңа аспектілерді қамтиды. Ол ықтимал әсер мен энергия тиімділігі арасындағы ықтимал мәмілеге талдау жасауға; өнімді қайта пайдалануға әсер ететін кейбір көрсеткіштерді дербес модельдеуге мүмкіндік береді; әдіс кейбір техникалық сипаттамалар анықталмаған кезде жетілдіру үдерісінің алғашқы кезеңдерінде пайдаланылады. Өнімнің өмірлік цикл кезеңдерінің қоршаған ортаға әсері бағалаудағы кіріс көрсеткіштері ретінде қолданылады.

Түйін сөздер: өрт және жарылыс қауіпсіздігіне арналған ұнтақты құрам, түрлі өндіріс қалдығы, өндіріс қалдығын жою, қайталама материалдық-шикізат қоры.

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ФОСФОРНЫЙ ШЛАК И ФОСФОГИПС: ТЕХНОГЕННЫЕ ПРОМЫШЛЕННЫЕ ОТХОДЫ ДЛЯ СОЗДАНИЯ МОДИФИЦИРОВАННЫХ ПОЖАРО- И ВЗРЫВОПОГЛОЩАЮЩИХ ПОРОШКОВЫХ КОМПОЗИЦИЙ

Аннотация. Одним из приоритетных направлений безопасности жизнедеятельности и защиты окружающей среды является создание модифицированных пожаро-взрывоподавляющих порошковых составов с применением техногенных отходов различных производств. Их применение делает возможным повторное использование некондиционных (просроченных) огнетушащих составов возможно в качестве веществ, замедляющих процессы взрыва и горения материалов.

Пожаро-взрывоподавляющие порошки по окончании срока годности подлежат регенерации или утилизации. Для процедуры регенерации, т.е. возобновления пожаротушащих свойств порошка он отправляется на завод-производитель для восстановления его свойств и характеристик. Это позволяет модифицировать свойства порошка и выпускать усовершенствованный продукт. При этом вносится весомый вклад в развитие системы рационального использования природных ресурсов, утилизации отходов производства, сохранения экологической обстановки местности, а также предотвращения чрезвычайных и аварийных ситуаций на промышленных отвалах.

Комплексное и рациональное использование вторичных материально-сырьевых ресурсов и отходов различных производств должно занимать определенное место в сырьевом балансе промышленности и предупреждении чрезвычайных ситуаций. К настоящему времени доля их использования составляет около 3-5%, вместо расчетных показателей 25-30% от объема сырья. Поэтому в период индустриально-инновационного развития вопросы рационального и комплексного использования техногенных отходов имеют важное практическое значение.

Несмотря на то, что важность повторного использования продуктов неоднократно отмечалась как в законодательстве, так и в научных кругах, на данный момент нет комплексных и систематических методов оценки и повторного использования огнетушащих порошков с экологической точки зрения. Более того, определения повторного использования, применяемые в научной литературе и законодательстве, не всегда совпадают. В данной работе представлена классификация различных видов повторного использования, включая некоторые предлагаемые определения. Основное внимание уделяется вопросам восстановления и типам повторного использования, при которых использованный порошок (или его компоненты), по крайней мере, восстанавливает первоначальный уровень производительности. В работе описывается разработка метода оценки жизненного цикла. Помимо этого, используются различные численно-аналитические программные средства, которые помогают моделировать процессы создания и апробации полученных смесей, в частности, такие программные продукты, как МАТЛАБ. В перспективе будут исследованы потенциальные экологические выгоды восстановления пожаро-взрывоподавляющих порошков. Упомянутый метод включает в себя несколько новых аспектов: он позволяет проводить анализ возможных компромиссов между потенциальными воздействиями и энергоэффективностью; независимо моделировать некоторые параметры, которые влияют на повторное использование продукта; метод применим даже на ранних этапах процесса модернизации, когда некоторые технические характеристики, возможно, еще не были определены. Воздействие на окружающую среду этапов жизненного цикла продукта используется в качестве входных параметров для оценки.

Ключевые слова: порошковые составы для пожаро- и взрывобезопасности, отходы различных производств, утилизация отходов производства, вторичные материально-сырьевые ресурсы.

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METHOD FOR ADSORPTION PURIFICATION OF ASSOCIATED OIL GASES FROM MERCAPTANS

Abstract. The paper examines methods of utilization of zeolite regeneration gases to assess the possibility of using them in an industrial adsorption unit for drying and purifying gases from hydrogen sulfide and mercaptans. The most promising is the method of decomposition of mercaptans to hydrogen sulfide and hydrogen on solid catalysts, which is carried out at a pressure and temperature of 200-350 °C, as well as the method of direct gas-phase catalytic oxidation of mercaptans with atmospheric oxygen. We carried out experiments on the purification of zeolite regeneration gases of the Orenburg GPP by oxidation with atmospheric oxygen using an iron oxide catalyst at a temperature of 180-250 °C. They showed that the gas purified from mercaptans contained elemental sulfur and disulfides as the main oxidation products, and 0.2% vol. of sulfur dioxide was present as a by-product. The method of purification from mercaptans and heavy hydrocarbon gases regeneration of composite adsorbent by thermocatalytic oxidation is also proposed. To reduce the yield of undesirable sulfur dioxide in the regeneration gas purified from mercaptans, it is proposed to divide the regeneration gas stream into two streams, while the larger part, comprising about 80-90% vol., is sent to oxidation on a zinc-iron catalyst at 200 °C, the second stream is mixed with oxidation products in a volume ratio in terms of mercaptans and sulfur dioxide equal to 1.5-2.2÷1, respectively, then the resulting mixture is passed at 160-200 °C through a titanium oxide catalyst with a gas volumetric velocity of 4000-6000 h^{-1}. The proposed scheme for gas purification from mercaptans and heavy hydrocarbons on a composite adsorbent with oxidative regeneration makes it possible to carry out the subsequent process of amine purification of gas from hydrogen sulfide without the complications associated with foaming of the working solution. Furthermore, it becomes possible to transport gas purified from mercaptans and hydrogen sulfide through the pipeline without precipitation of condensate.

Keywords: adsorption; gas purification; associated gas; mercaptans; hydrogen sulfide; regeneration gases; thermocatalytic decomposition; oxidation; sulfur; disulfides; recirculation gases.

The relevance of the topic. Adsorption treatment using aluminosilicates is widely used in the gas and petrochemical industry for drying and purifying natural gases from mercaptans. The process of drying and purification of natural gas from sulfur compounds is carried out in an adsorber system, which is filled with zeolites and work alternately at the stages of adsorption of impurities from raw materials, regeneration, and cooling of zeolites. During the adsorption treatment of gas, impurities such as water, hydrogen sulfide, mercaptans pass into the primary porous structure of the adsorbent. When the adsorbent is saturated with extracted impurities, its high-temperature regeneration is performed by a gas stream, into which previously extracted impurities pass [1]. The degree of gas adsorption treatment and its economic efficiency largely depends on the technology of adsorbent regeneration, the choice of regeneration gases (i.e. desorbing gas), and the method of their utilization (i.e. gases of desorption or regeneration) of adsorbents. In addition to mercaptans, hydrogen sulfide and water vapors, carbon dioxide, and sulfur compounds from the source gas are concentrated there.

Thus, current research projects are aimed at developing methods for adsorption purification of associated petroleum gases from mercaptans.

Discussion of problems. Regeneration of the adsorbent of the drying process and purification of natural gas from sulfur compounds is carried out by heating the layer by purging the gas heated up to 320-380 °C through it. Moreover, as the regeneration gas, one can use 17-23% of raw gas that is delivered for drying and purification [2]. In industry as regeneration gas and cooler for zeolite, a natural gas adsorption drying unit usually uses 5-15% of gas (in terms of crude gas), which is supplied for drying and purification, and drained and purified from sulfur compounds [3]. It is possible to achieve deep regeneration of zeolite when the adsorbent is purged with a methane fraction extracted from a part of the natural gas, which is drained and purified from sulfur compounds and mixed with the nitrogen-methane fraction. This fraction is a waste of the helium concentrate production that ensures the calorific value of the fraction mixture to be no lower than 7600 kcal/m3 at the corresponding ratio [4]. Also, there is a well-known method of zeolite regeneration, which is applied for the drying and purifying of natural gas, where a methane fraction is used to purge the regenerated CaA zeolite [5].

A common disadvantage of the above-mentioned methods of zeolite regeneration at units of drying and purification of hydrocarbon gases is that adsorbent regeneration gases are obtained when using as a desorbing agent of hydrocarbon gases (methane fraction or part of the purified source hydrocarbon gas). Later, those adsorbent regeneration gases are used as fuel that is contaminated with the same sulfur-containing substances as the initial purified hydrocarbon gas. The purpose of the adsorption process is to concentrate sulfur-containing and other undesirable impurities of the source gas (then used as fuel) in its part, which is then also used as fuel for the needs of the enterprise. It pollutes the industrial zone instead of distribution in the environment by numerous consumers in the absence of purification of the hydrocarbon fuel gas. The process of adsorption treatment without the utilization of regeneration gases does not reduce the amount of sulfur oxide release into the atmosphere. Furthermore, the burning of valuable sulfur-containing substances leads to their irretrievable loss to the economy. The validity of extracting and processing of sulfur-containing substances present in zeolite regeneration gases is of ecological and economic importance.

Materials and methods of research. The production conditions where the adsorption installation operates, the composition of the purified gas, nature, and concentration of sulfur compounds, which are present in it, largely influence the choice of a rational method of utilization of zeolite regeneration gases or other adsorbents used in the drying processes and purification of the gas from sulfur compounds. The following three thermocatalytic methods are the most promising for gas processing plants (GPP). The first of them is based on the reaction of decomposition of mercaptans to hydrogen sulfide and hydrogen on solid catalysts, which is carried out at a pressure and temperature (200-350 °C) of the adsorbent regeneration [6-12]. The practical implementation of this method at GPP is facilitated by the availability of energy at the plant for further purification of regeneration gas from hydrogen sulfide formed during the decomposition of mercaptans, and its utilization by the Claus process. In addition to hydrogen sulfide, thermocatalytic decomposition of mercaptans is accompanied by the production of saturated and unsaturated hydrocarbons, and parallel reactions of the destruction of amines, methanol, and other impurities contained in the zeolite desorption gas [13-15].

The third method is more attractive, and that is direct thermocatalytic gas-phase oxidation of mercaptans to sulfur by atmospheric oxygen. We carried out experiments on the purification of zeolite regeneration gases of the Orenburg GPP by oxidation with atmospheric oxygen using an iron oxide catalyst at a temperature of 180-250 °C. They showed that the gas purified from mercaptans contained elemental sulfur and disulfides as the main oxidation products, and 0.2% vol. of sulfur dioxide was present as a by-product [16-17]. In these experiments, it was found that hydrogen sulfide and other sulfur-containing compounds (carbonyl sulfide, carbon disulfide, sulfides), which are contained in small amounts in zeolite regeneration gases, are also subjected to oxidation, and the product of their oxidation is elemental sulfur. Most of the sulfur-containing oxidation products can be separated from the reaction gas by condensation when cooled to ambient temperature, which greatly simplifies the process.

One of the crucial processes for purification of zeolite regeneration gases is alkaline-free direct oxidation of mercaptans based on the conversion of H_2S and mercaptans to non-toxic forms (di-and polysulfides) by atmospheric oxygen directly in hydrocarbon media [18]. Oxidation reactions occurring in hydrocarbon raw materials are significantly accelerated in the presence of metal-complex catalysts based on transition metals [19-22]. This technology eliminates the stage of alkaline extraction and, consequently, the need for disposal of toxic sulfur-alkaline effluents. The effectiveness of such catalytic systems was established in the laboratory conditions on model mixtures of thiols and hydrocarbons, for example, which is shown in [18].

Most of the works of Kazakh scientists are devoted to the purification of oil gases.

The authors of the following work conducted research on the use of liquefied petroleum gas as a raw material for the production of liquid oxygen-containing organic compounds [23].

Research results. This article describes a method for purification of composite adsorbent regeneration gas, which, in contrast to aluminosilicate sorbents, can absorb not only mercaptans but heavy hydrocarbons contained in associated petroleum gas or processing gases of light hydrocarbon raw materials. The composite adsorbent is porous coal or natural sorbent impregnated with a moisture-absorbing substance, which has a high dynamic capacity for water [24]. During the development of the technology of gas regeneration of composite adsorbent by direct oxidation, a few new technical solutions were found that ensured the achievement of the following positive result [25]:

1) simplification of the catalytic stage by conducting the process in a single stage and lack of need for precise control of the ratio of components in the catalytic oxidation of mercaptans;

2) increase of purification degree of hydrocarbon gases by removing, along with mercaptans, both heavy hydrocarbons, and volatile oxidation products and sulfur vapors when gas purification on composite adsorbents is applied;

3) reduction of the energy consumption of the process due to the use of pre-concentration of mercaptans on composite adsorbents;

4) reduced material consumption by decreasing the volume of the catalytic oxidation reactor and loading the catalyst while decreasing the volume flow of the purified gas.

Figure 1 illustrates the scheme of a hydrocarbon gas treatment installation on a composite adsorbent with the utilization of regeneration gases by direct oxidation and recirculation into the stream of purified gas.

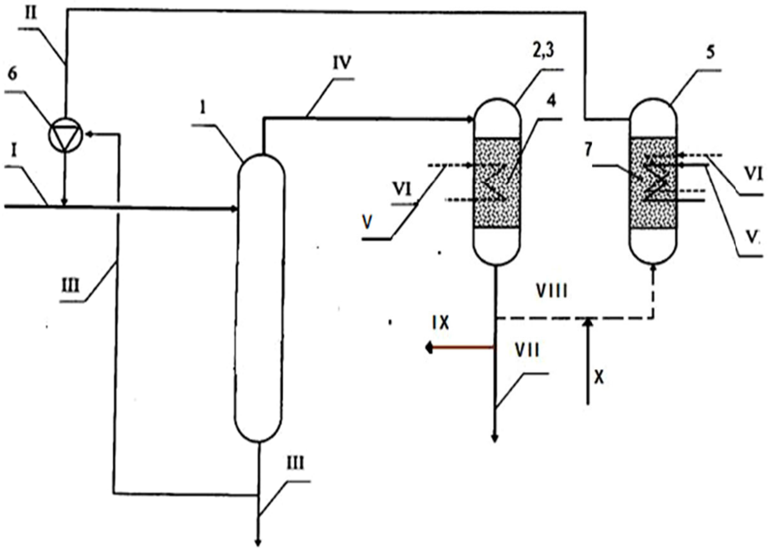

Figure 1 - The scheme of a hydrocarbon gas treatment installation on a composite adsorbent with the utilization of regeneration gases:
Flows: I – purified gas; II – oxidation products; III – liquid oxidation products; IV – separation gas; V – air-coolant; VI – air-refrigerant; VII – gas purified from mercaptans; VIII – regeneration gas; IX – purge gas; X – process air.
Devices: 1 - gas separator; 2,3 - adsorbers; 4 - composite adsorbent; 5 – oxidation reactor; 6 – liquid-ring pump; 7 – catalyst

According to this technology, the hydrocarbon gas is pre-mixed with the oxidation products, and the mixture is separated with the release of liquid oxidation products and separation gas. This gas is subjected to adsorption treatment on a composite adsorbent, using as porous coal, for example, the Sibunit brand, while indirectly cooling the adsorbent to the adsorption temperature, which should not be lower than the freezing point of water or hydrate formation. The adsorbent regeneration is carried out by blowing off the purified gas at low pressure and indirect heating the adsorbent with coolant to the regeneration temperature, and the regenerated adsorbent is cooled indirectly with a refrigerant to the adsorption temperature.

After that, the regeneration gas is mixed with air at a mass ratio of mercaptans to atmospheric oxygen equal to 2.2÷3:1, which is higher than the stoichiometric ratio equal to 2:1, and it is passed through the oxidation catalyst at the volume rate and oxidation temperature. The oxidation products are recirculated into the purified gas stream, compressed to the pressure of the hydrocarbon gas utilizing a liquid-ring pump using the liquid oxidation products as the working fluid. In this case, for example, atmospheric air can be used as a refrigerant, and the coolant can be atmospheric air heated with a catalytic air heater by direct mixing of the oxidation products of hydrocarbon condensate or dry gas with atmospheric air.

Pre-mixing of hydrocarbon gas with oxidation products and separation of the mixture with the release of liquid oxidation products and separation gas allows to remove the liquid products of the oxidative conversion of mercaptans from the process, to obtain a working fluid for a liquid-ring pump that recirculates the regeneration gas, as well as to recirculate the non-reacting mercaptans for re-oxidation. This prevents contamination of the adsorbent and increases its lifetime.

The purification of hydrocarbon gas from mercaptans, heavy hydrocarbons, volatile oxidation products, and sulfur fumes is possible thanks to adsorption treatment of separation gas using carbonaceous adsorbent at simultaneous indirect cooling of the adsorbent to the adsorption temperature, but not below the freezing point of water or hydrate formation. It is achieved through making the most favorable conditions for adsorption with a maximum dynamic capacity of the adsorbent, preventing its heating because of the heat release of adsorption. This reduces the adsorbent load and the metal content of the equipment.

Regeneration of the adsorbent by blowing off the purified gas at low pressure and simultaneous indirect heating the adsorbent with coolant to the regeneration temperature (200 °C) allows for deep regeneration of the adsorbent with minimal purge gas consumption. The optimal regeneration temperature depends on the chemical composition of purified gas and the type of adsorbent, the desired degree of purification of hydrocarbon gas from mercaptans, and heavy hydrocarbons (desired dew point by hydrocarbons), energy costs, etc.

The optimal flow rate of the purified gas for the regeneration of the adsorbent depends on the chemical composition of the gas being treated, the type of adsorbent, as well as the condition of the thermal balance of the mercaptan oxidation stage. When the concentration of mercaptans in the regeneration gas is high, the purified gas consumption for regeneration is increased to keep the temperature during the oxidation stage below the permissible level and to ensure the selectivity of the oxidation of mercaptans to disulfides and sulfur without the formation of sulfur dioxide. As the concentration of mercaptans in the regeneration gas decreases, the consumption of the purified gas for regeneration is reduced, and, if necessary, indirect heating of the catalyst with coolant is additionally performed to maintain the oxidation temperature.

The usage of indirect heating of the adsorbent by coolant to regeneration temperature in the regeneration stage and the indirect cooling of the regenerated adsorbent by the refrigerant to the adsorption temperature allows to control the temperature of the adsorbent and reduce the total duration of the regeneration stage and adsorption cycle, as well as to reduce the load of the adsorbent and metal content of equipment.

Oxidation of mercaptans present in the regeneration gas in a mixture with air has a mass ratio of mercaptans to atmospheric oxygen equal to 2.2÷3:1, which is higher than the stoichiometric ratio for the oxidation reaction to sulfur and disulfides, and it prevents the formation of sulfur dioxide, which can potentially contaminate the purified gas during a slip in the adsorber. A raise in the mass ratio of mercaptans to atmospheric oxygen higher than 3:1 leads to an increase in the recirculation of non-reacted mercaptans and an overload of the adsorbent. When the mass ratio of mercaptans to atmospheric oxygen becomes lower than 2.2:1, it leads to the formation of sulfur dioxide in the oxidation products, which pollutes the purified gas. The experiments have shown that the optimal temperature and volume rate of oxidation depend on the type of catalyst.

The loss of hydrocarbon gas with the regeneration gas is prevented by recirculation of the oxidation products into the purified gas stream compressing it to the pressure of hydrocarbon gas. This is achieved by utilizing a liquid-ring pump that uses liquid oxidation products as the working fluid. Besides, it becomes possible to conduct regeneration at a reduced pressure of up to 5-15 kPa, which is determined by the characteristics of the pump and the initial pressure of the gas being treated. During compression, the oxidation products are cooled due to the contact of the gas with the working fluid, the liquid oxidation products are condensed, and most of the mercaptans contained in the hydrocarbon gas are absorbed. These processes take place without the use of additional cooling and separation equipment. As a result, the load of the adsorbent and the material consumption of the process can be reduced, whereas the degree of purification of hydrocarbon gas can be increased.

For example, the use of atmospheric air as a refrigerant and, as a coolant, atmospheric air heated with a catalytic air heater by direct mixing of the oxidation products of a hydrocarbon fuel with atmospheric air, allows providing effective heating and cooling of the adsorbent with the minimal technological difficulties.

The use of a catalytic air heater instead of a conventional fire furnace reduces the cost of equipment, the fire and explosion hazard of the installation and increases the reliability of its operation, as well as reduces the release of nitrogen oxides and carbon monoxide into the atmosphere due to controlled flameless combustion (oxidation) of gaseous or liquid distillate fuel at temperatures below 900 °C.

The efficiency of the described purification method of associated petroleum gas and regeneration gas is shown by the data of the following experiment at the pilot installation. The composition of the gas supplied for treatment, vol.% is oxygen 0.03, nitrogen 10.90, carbon dioxide 0.28, methane 70.10, ethane 5.61, propane 4.02, n-butane 2.65, isobutane 1.14, isopentane 1.35, pentane and higher 2.06, hydrogen sulfide 1.64, mercaptans 0.24. Chromatographic analysis reveals the absence of mercaptans in the purified gas, the content of other components is oxygen 0.13, nitrogen 11.66, carbon dioxide 0.29, methane 71.7, ethane 5.73, propane 4.10, n-butane 2.40, isobutane 1.12, isopentane 1.18, and pentane and higher hydrocarbons are absent.

Conclusions. Thus, the lack of heavy hydrocarbons in gas purified from mercaptans on composite adsorbent enables a subsequent process of its amine purification from hydrogen sulfide without the complications associated with the foaming of the working solution. Furthermore, it becomes possible to transport gas purified from mercaptans and hydrogen sulfide through the pipeline without precipitation of condensate.

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ІЛЕСПЕ МҰНАЙ ГАЗЫН МЕРКАПТАННАН АДСОРБЦИЯЛЫҚ ТАЗАРТУДЫҢ ТӘСІЛІ

Аннотация. Цеолиттер регенерация газын кәдеге жарату әдістеріне оларды кептіру және газды күкіртті сутегі мен меркаптаннан тазартудың өнеркәсіптік адсорбциялық қондырғысында пайда-лану мүмкіндігін бағалау үшін талдау жүргізілді.

Жұмыста композитті адсорбент регенерация газын тазарту әдісі сипатталған, оның алюмосиликатты сорбенттерден негізгі айырмашылығы – меркаптандармен қатар жеңіл көмірсутекті шикізатты қайта өңдеу газында немесе ілеспе мұнай газының құрамында кездесетін ауыр көмірсутектерді де сіңіру мүмкіндігі бар.

Тікелей тотығу әдісімен композиттік адсорбентті регенерациялау газын алу технологиясын әзірлеудің негізінде бірнеше оң нәтижеге қол жеткізуді қамтамасыз ететін бірқатар жаңа техникалық шешімдер ұсынылды, атап айтқанда:

– процесті жүргізуді бір саты шеңберінде өткізу және және меркаптандардың каталитикалық тотығуы кезінде компоненттердің арақатынасын дәл реттеу қажеттілігінің болмауы есебінен каталитикалық кезеңді анағұрлым қарапайым түрге айналдыру;

– меркаптандармен қатар, ауыр көмірсутектерді де және сонымен қатар тотығудың ұшпа өнімі мен күкірт буын өшіру және композиттік адсорбенттерде газ тазартуды қолдану арқылы газ тазарту деңгейін арттыру;

– композиттік адсорбенттерге меркаптанды алдын ала шоғырландыруды қолдану есебінен процестің энергия сыйымдылығын азайту;

– тотығу каталитикалық реакторының көлемін және тазартылатын газдың көлемдік шығынын азайту кезінде катализаторды қолдану есебінен материалдық сыйымдылықты төмендету.

Неғұрлым перспективті деп қысым мен 200-350 °С температура аралығында жүргізілетін меркаптанды күкіртті сутегі мен сутегіне дейінгі қатты катализаторда ыдырату әдісін, сондай-ақ, меркаптанның ауа оттегімен тікелей газофазды каталитикалық тотығу әдісін айтуға болады. 180-250°С температурада темiроксидтi катализаторда ауаны оттегімен тотықтыру арқылы Орынбор ГӨЗ цеолиттерін регенерациялау газын тазарту бойынша жүргізген тәжірибеміз меркаптандардан тазартылған газда негізгі тотығу өнімдері ретінде қарапайым күкірт пен дисульфидтердің болатын-дығын, ал күкірттің қос тотығы жанама өнімінің мөлшері 0,2% деңгейде екендігін көрсетті. Сонымен қатар, меркаптан мен ауыр көмірсутектерден композиттік адсорбент регенерациясын меркаптандарды термокаталитикалық тотығу әдісімен күкіртке дейін ауа оттегімен тазарту әдісі ұсынылды.

Меркаптаннан тазартылған регенерация газында күкірттің қос тотығының шығымын азайту үшін регенерация газының ағынын екі ағынға бөлу ұсынылды, осыған орай көлемнің шамамен 80-90% құрайтын үлкен бөлігі 200°С кезінде темірхромцинк катализаторына тотығуға жіберіледі, ал екінші ағын тотығу өнімдерімен меркаптан мен күкірттің қос тотығына шаққанда 1,5-2,2÷1 тең сәйкес көлемдік қатынаста араластырылады және алынған қоспаны газдың көлемдік жылдамдығы 4000-6000 сағ$^{-1}$ құрайтын титан-тотықты катализатор арқылы 160-200°С кезінде өткізеді.

Тотығу регенерациясы бар композиттік адсорбентте меркаптан мен ауыр көмірсутектен газ тазартудың ұсынылған схемасы газды аминді күкіртті сутегіден тазартудың келесі процесін жұмыс ерітіндісінің көбіктенуіне байланысты туындайтын қиындықтың алдын ала жүргізуге және меркаптан мен күкіртсутектен тазартылған регенерация газын конденсат түспестен құбыр арқылы тасымалдауды жүзеге асыруға мүмкіндік береді.

Суытқыш агент ретінде, мысалы, атмосфералық ауаны, ал жылу тасығыш ретінде ауаның каталитикалық жылытқышы арқылы көмірсутекті отынның атмосфералық ауамен тотығу өнімін тікелей араластыру негізінде қыздырылған атмосфералық ауаны пайдалану, адсорбентті тиімді жылыту мен салқындату үрдісінің технологиялық күрделілігін жеңілдетуге мүмкіндік береді.

Әдетте қолданылатын отпен қыздыру пешінің орнына ауаның каталитикалық қыздырғышын пайдалану қолданылатын жабдық құнын азайтуға, қондырғының өрт пен жарылыс қауіптілігін азайтуға және жұмысының сенімділігін арттыруға, сондай-ақ 900°С төмен температурада газ тәрізді немесе сұйық дистиллятты отынның бақыланатын жалынсыз жағу (тотығу) есебінен атмосфераға азот және көміртегі тотығының шығарындысын қысқартуға мүмкіндік береді.

Түйін сөздер: адсорбция, газ тазарту, ілеспе газ, меркаптан, күкіртсутек, регенерация газы, термокаталитикалық ыдырау, тотығу, күкірт, дисульфидтер, рециркуляция гадары.

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СПОСОБ АДСОРБЦИОННОЙ ОЧИСТКИ ПОПУТНЫХ НЕФТЯНЫХ ГАЗОВ ОТ МЕРКАПТАНОВ

Аннотация. Проведен анализ методов утилизации газов регенерации цеолитов для оценки возможности использования их на промышленной адсорбционной установке осушки и очистки газа от сероводорода и меркаптанов.

В работе описан метод очистки газов регенерации композитного адсорбента, который, в отличии от алюмосиликатных сорбентов обладает возможностью поглощения наряду с меркаптанами и тяжелых углеводородов, содержащихся в попутном нефтяном газе или в газах переработки легкого углеводородного сырья.

Разработкой технологии получения газов регенерации композитного адсорбента методом прямого окисления найдены ряд новых технических решений, обеспечивающих достижение нескольких положительных результатов, а именно:

- упрощение каталитической стадии за счет проведения процесса в одну стадию и отсутствия необходимости точного регулирования соотношения компонентов при каталитическом окислении меркаптанов;

- повышение степени очистки углеводородных газов за счет удаления наряду с меркаптанами, как тяжелых углеводородов, так и летучих продуктов окисления и паров серы, путем применения очистки газов на композитных адсорбентах;

- уменьшение энергоемкости процесса за счет применения предварительного концентрирования меркаптанов на композитных адсорбентах;

- снижение материалоемкости за счет уменьшения объема каталитического реактора окисления и загрузки катализатора при уменьшении объемного расхода очищаемого газа.

Наиболее перспективными являются метод разложения меркаптанов до сероводорода и водорода на твердых катализаторах, который проводится при давлении и температуре 200–350 °С, а также метод прямого газофазного каталитического окисления меркаптанов кислородом воздуха. Опыты, проведенные нами по очистке газов регенерации цеолитов Оренбургского ГПЗ путем окисления кислородом воздуха на железооксидном катализаторе при температуре 180-250°С показали, что в очищенном от меркаптанов газе в качестве основных продуктов окисления присутствуют элементарная сера и дисульфиды, а содержание побочного продукта двуокиси серы находится на уровне 0,2% об. Предложен также метод очистки от меркаптанов и тяжелых углеводородов газов регенерации композитного адсорбента методом термокаталитического окисления меркаптанов до серы кислородом воздуха.

Для снижения выхода нежелательной двуокиси серы в очищенном от меркаптанов газа регенерации предложено поток газа регенерации делить на два потока, при этом большая по объему часть, составляющая примерно 80-90 % об., направляют на окисление на железохромцинковом катализаторе при 200°С, а второй поток смешивают с продуктами окисления в объемном соотношении в пересчете на меркаптаны и двуокись серы, равном 1,5-2,2÷1, соответственно, и полученную смесь пропускают при 160-200°С через титаноксидный катализатор при объемной скорости газа 4000-6000 ч$^{-1}$.

Предложенная схема очистки газов от меркаптанов и тяжелых углеводородов на композитном адсорбента с окислительной регенерацией дает возможность вести последующий процесс аминовой очистки газа от сероводорода без осложнения, связанного с вспениванием рабочего раствора, и осуществлять транспортировку очищенного от меркаптанов и сероводорода газа регенерации по трубопроводу без выпадения конденсата.

Использование в качестве хладагента, например, атмосферного воздуха, а в качестве теплоносителя - атмосферного воздуха, нагретого с помощью каталитического нагревателя воздуха прямым смешением продуктов окисления углеводородного топлива с атмосферным воздухом, позволяет с наименьшими технологическими сложностями обеспечить эффективный нагрев и охлаждение адсорбента.

Использование каталитического нагревателя воздуха вместо обычно применяемой печи огневого нагрева позволяет снизить стоимость оборудования, уменьшить пожаро- и взрывоопасность установки и повысить надежность его работы, а также сократить выбросы окислов азота и окиси углерода в атмосферу за счет контролируемого беспламенного сжигания (окисления) газообразного или жидкого дистиллятного топлива при температуре ниже 900°С.

Ключевые слова: адсорбция; очистка газов; попутный газ; меркаптаны; сероводород; газы регенерации; термокаталитическое разложение; окисление; сера; дисульфиды; газы рециркуляции.

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MECHANISM OF FILTRATION DRYING OF ORGANIC MATERIALS OF FIBROUS STRUCTURE AND RESULTS OF RESEARCH OF EXTERNAL HEAT EXCHANGE

Abstract. One of the high-intensity methods for removing both free and bound moisture is filtration drying. This is due to the fact that during filtration drying, the heat agent is filtered through the porous structure of the wet material, which is placed on the perforated partition in the direction "wet material–perforated partition". The velocity of the heat agent in the pores and channels of a stationary layer of wet material determines the thickness of the boundary layer (hydrodynamic, thermal, and diffusion) and, accordingly, the values of the heat and mass transfer coefficients. In addition, the surface of heat and mass transfer is the total surface of the pores and channels through which the heat agent is filtered. The filtration rate of the heat agent is determined based on technical and economic considerations, given that its increase affects the growth of pressure loss. Moreover, the actual speed of the heat agent relative to the layer elements is much higher than in the case of drying by any other methods (in a fluidized bed, during drying in pneumatic transport dryers, etc.). Large heat and mass transfer surfaces and the speed of the heat agent in the pores and channels of the stationary layer of wet material provide high heat and mass transfer coefficients and, accordingly, the intensity of filtration drying. This article presents the results of the study of external heat exchange between the heat agent and dry particles of organic materials of fibrous structure, in particular raw cotton and its stems, and the mechanism of filtration drying.

Ключевые слова: cotton fiber, heat transfer, mass transfer, hydrodynamics, filtration drying, porosity, organic materials of fibrous structure.

Introduction. Organic materials of a fibrous structure are characterized by an irregular shape of the fibers, roughness of the external surface, the presence of protrusions, depressions, and a network of pores of different sizes. During processing or other technological processes, moisture gets into the pores of these materials, and also wetting the outer surface [1-2]. As a result, the properties of fibrous materials deteriorate and the layer structure is formed unevenly. The surfaces of some particles can be screened by the surfaces of others, while forming non-flowing or partially flowing zones for the thermal agent, which will certainly affect the kinetics of filtration drying [3-7]. Moisture from non-flowing zones will evaporate only due to molecular diffusion, which will lead to an increase in the total drying time[8]. For the study of filtration drying, organic materials of a fibrous structure were selected: raw cotton and its stems, which differ in shape and internal structure. According to the method given in [8], the influence of the temperature and filtration rate of the heat agent on the kinetics of filtration drying was studied.

The intensity of filtration drying of organic materials of a fibrous structure largely depends on the amount of heat that is transferred from the heat agent to the wet particle and is determined by the filtration rate of the heat agent, the temperature difference between the surface of the solid particle and the heat agent, as well as the surface of the interfacial contact [9,10].

Moisture in organic materials of a fibrous structure is located mainly inside and partially on the surface. During drying, moisture evaporates due to heat input, and the driving force of the process is the temperature difference between the heat agent and the material particles.

Based on the analysis of the kinetic curves of drying of crushed and granular materials, it can be concluded that filtration drying is characterized by three main stages of moisture removal: mechanical displacement, mass transfer at a constant rate of moisture removal, and intra-difusion moisture removal at a rate that decreases [8-11].

The presence or absence of mechanical displacement is determined by the presence of free moisture, which is contained by the surface tension forces between the particles that form the layer and the processing technology of organic materials of a fibrous structure. The intensity of mechanical displacement is determined by the pressure drop and the amount of free moisture. The greater the pressure drop, the smaller the channels formed by the layer particles, free moisture will be removed. Of course, the maximum amount of moisture that can be removed is determined by the free volume and structural structure of organic materials of a fibrous structure, which determine the amount of moisture that can be contained[8-11].

Experimental part. To implement the process of drying raw cotton, as noted in [12,13], the industry uses drum-type dryers and fluidized bed dryers, which are energy-consuming and expensive. Therefore, we were faced with the task of developing a new type of dryer that would reduce the energy costs of the drying process.

Generalization of results of experimental and theoretical research of hydrodynamics and heat and mass transfer during filtration drying of organic materials of a fibrous structure in particular, we explored the drying of seed cotton and stalks, are allowed to offer the design of the dryer, which takes into account the physico-mechanical properties of raw cotton and its stems, to improve the methodology of calculation of the main dimensions of this installation and calculate the optimal process parameters of the heat agent.

We suggest using a schematic diagram of a drum-type filtration drying unit for drying raw cotton, the design of which is described in [14-17].

The essence of filtration drying is to filter the heat agent through the porous structure of the dispersed material in the direction "material layer-perforated partition" due to the pressure drop[9-16].

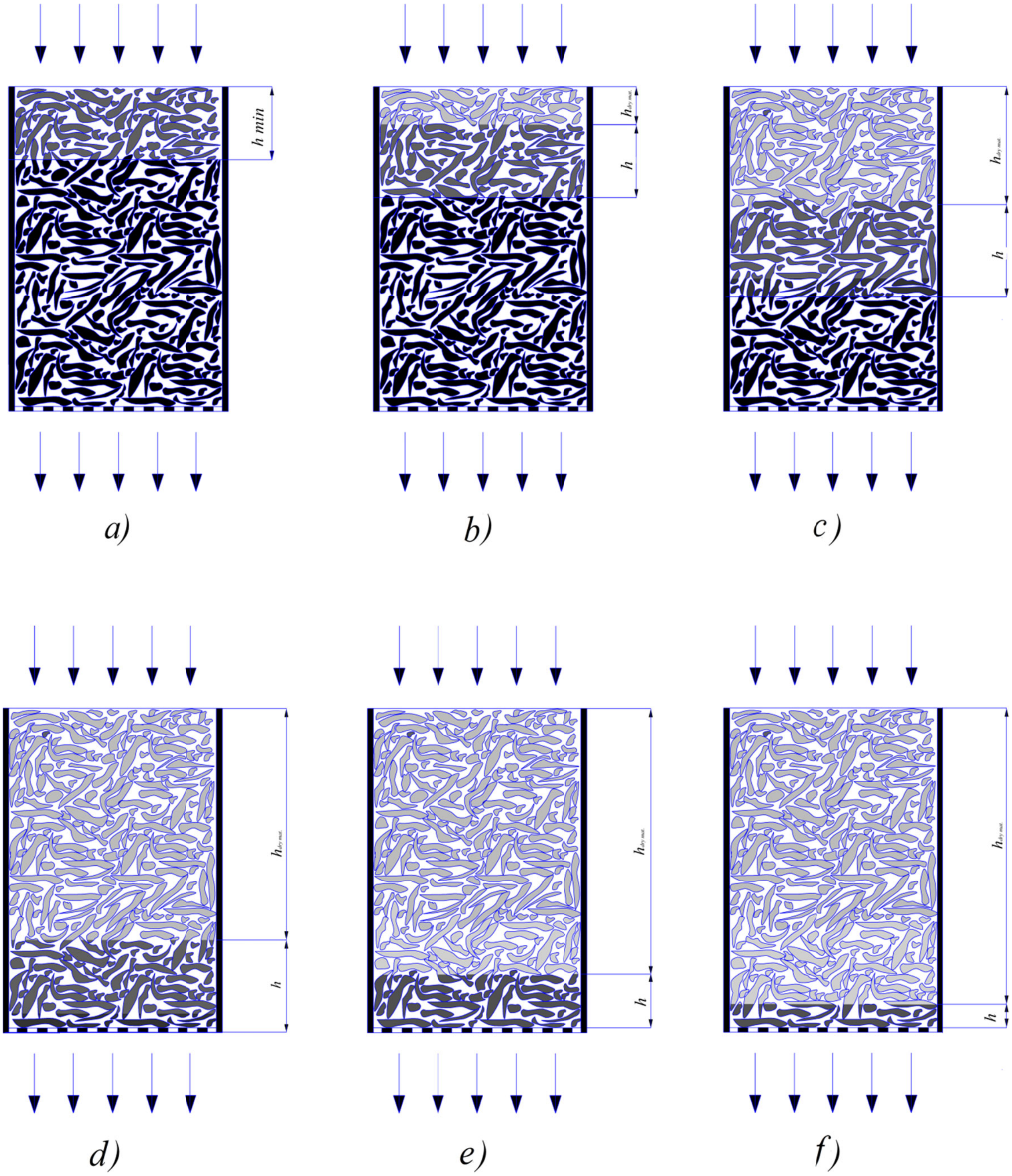
It is known that during filtration drying, in the same way as in the processes of ion exchange, extraction from the solid phase, mass transfer, etc.does not occur over the entire height of the layer [9], but only at a certain height, which is called the mass transfer front. During filtration drying in the beginning is formed by the front height (figure 1 a), at this altitude, thermal agent, filtrating through the porous structure of the wet layer of raw cotton and its stems, gives up its heat to the material and is saturated with moisture, if the layer height is significant, but moisture is sufficient, then after some time the moisture content of the heat agent reaches saturation, as a consequence, its temperature decreases to the temperature of the wet thermometer. In the future, the heat agent under the influence of a pressure drop continues to filter through the porous structure of the layer, but it no longer takes part in mass transfer.

The filtration drying mechanism is schematically shown in figure 1.

After removing external moisture from the upper layers of raw cotton and its stems, the mass transfer front expands in the direction of the heat agent movement. This is because exterior moisture material, which is first in contact with fresh thermal agent is removed faster than the material of the lower layers, where the thermal agent is saturated with moisture and its drying capacity is less, so after some time in the upper layers does not remain external moisture begin to evaporate moisture from the upper layers of the material, while the evaporation rate depends on the coefficient of internal diffusion of moisture from the raw cotton and its stems[18,19]. This causes the formation of a moisture transfer front with height h (figure 1b). After some time, the evaporation of internal moisture in the upper layers is completed and there is an equilibrium between the dispersed material and the heat agent, a layer of dry material $h_{dry\ material}$ appears, which does not take part in mass transfer (figure 1 c), and the mass transfer zone moves to the perforated partition. After the frontal part of the mass transfer front reaches the perforated partition (figure 1 d), its height h begins to decrease, the heat agent is only partially saturated with moisture vapor, and its temperature at the exit from the layer begins to increase (figure 1 e,f).

It is known that in many works devoted to filtration drying [10-12], the concept of drying in the first and second conditional periods was used to describe kinetics by analogy with convective drying.

Analyzing the filtration drying mechanism shown in figure 1, we conclude that the entire process can be divided into the period of full saturation of the heat agent (figure 1 a-d) and the period of partial saturation of the heat agent (figure 1 e,f), which actually corresponds to the physical essence of the process.



a) formation of a mass transfer front with a height of h_{min}; b) simultaneous existence of a layer of dry and wet material $h_{dry\ material}$; c) moving the mass transfer zone in the direction of the perforated partition; d) reaching the frontal part of the mass transfer front of the perforated partition; e, f) reducing the mass transfer zone and completing the drying process.
Figure 1 - the Mechanism of the filtration drying of raw cotton and its stems

Theoretical part and discussion of the results. Taking into account that during filtration drying, the layer contains both dry and wet materials that take part in heat exchange (the dry material is heated to a temperature close to the temperature of the heat agent), it is necessary to study the process of heat exchange between dry and wet particles of raw cotton and its stems.

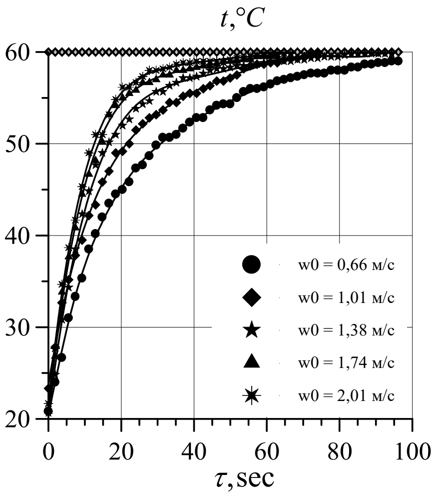


Figure 2 – temperature Change of the heat agent at the exit from the layer of dry raw cotton and its stems, at different speeds of the heat agent movement (the height of the material layer is 26 mm)

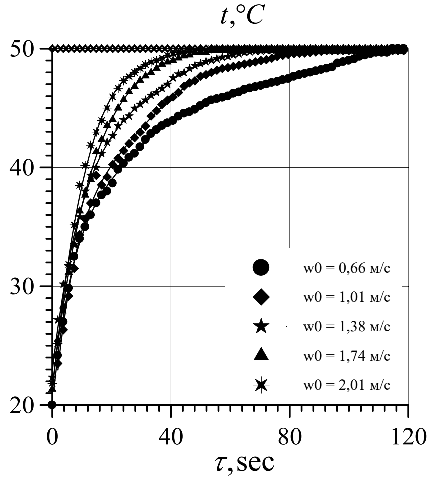


Figure 3 - Change in the temperature of the heat agent at the exit of the layer of dry raw cotton and its stems at different speeds of the heat agent and (the height of the material layer is 26 mm)

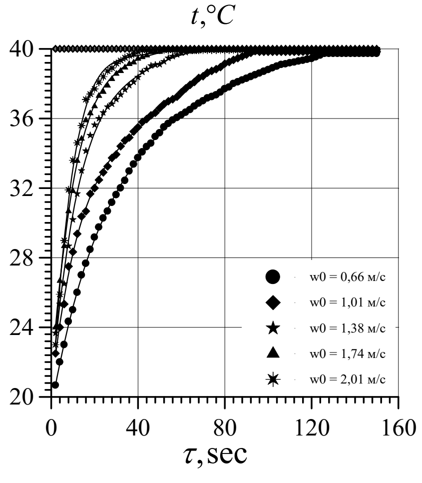


Figure 4 – temperature Change of the heat agent at the exit from the layer of dry raw cotton and its stems at different speeds of the heat agent movement (the height of the material layer is 26 mm)

The average values of the temperature of the heat agent at the exit from the layer of dry raw cotton and its stems are experimentally determined in figures 2-4, at different temperatures of the heat agent, which varied in the range: 40-60 ^{0}C, and at different speeds of the heat agent from 0.66 to 2.01 m/s. The temperature value of the heat agent was chosen due to the transience of the heating process of raw cotton particles and their stems, the average size of which does not exceed 2 mm.

The presented graphic dependences of the temperature change of the heat agent at the exit from the material layer allow us to determine the coefficient of heat transfer from the heat agent to dry particles of raw cotton and its stems.

Given that the heat agent is filtered through a layer of dry raw cotton and its stems and the porosity of the layer is high ($\varepsilon_{layer\ of\ material}$=0.900÷0.960 m^3/m^3), it is assumed that the temperature of the heat agent is the same on all sides of the particle. It is impossible to experimentally measure the surface temperature ($\overline{T_n}$) of raw cotton and its stems, so it was estimated based on the analytical dependences for the average layer temperature and the temperature on the surface of a solid particle, given in [8] for cylindrical particles. Due to the fact that the material particles were washed by the heat agent from all sides, it was assumed that the distribution of the temperature field over the particle diameter is parabolic. The average temperature of the surface of solid particles ($\overline{T_n}$) it was determined as follows: the average temperature of the particles ($\bar{T}$) was determined from the heat balance equation:

$$V_c \cdot \rho \cdot c \cdot (t_n - t_л) = \Delta Q = m \cdot c_s \cdot \left(\bar{T} - T_0\right), \tag{1}$$

where: *m* – weight of raw cotton and its stems, kg; c_s – heat capacity of raw cotton particles and their stems, kJ/(kg*K); $\bar{T}$– the average temperature of the layer,°C; T_0 – the initial temperature of the particle, °C.

$$\bar{T} = \bar{t} - \left(\bar{t} - T_0 \cdot e^{-\mu_n^2 \cdot Fo}\right) \cdot \left(1 - \frac{r}{R}\right) \cdot e^{-\mu_n^2 \cdot Fo}, \tag{2}$$

where: $\bar{t}$ – average temperature of the heat agent,°C; R и r– particle radius and current radius, respectively ($0 < r < R$), м; μ_n– root of the characteristic equation; F_0 – the criterion Fourier.

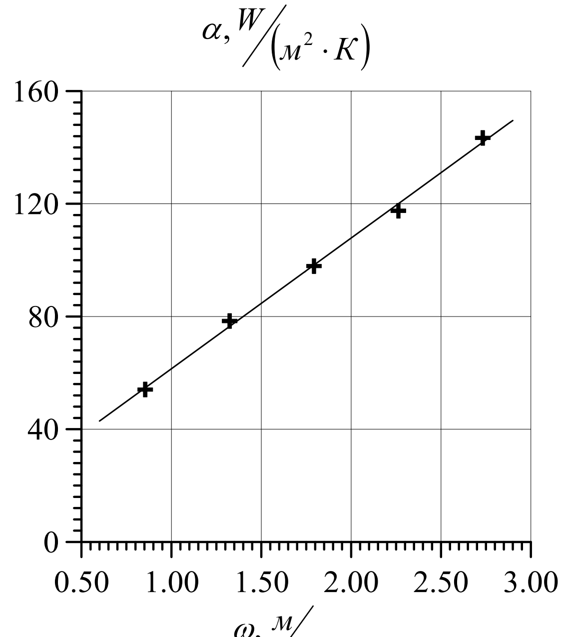


Figure 5-Dependence of the heat transfer coefficient α on the actual filtration rate ω of the heat agent at a temperature of 60 ^{0}C

Based on the experimental values shown in figures 2-4, the value of the heat transfer coefficients α was calculated according to the heat transfer equation [20]:

$$\alpha = \frac{\Delta Q}{F \cdot \left(\bar{t} - \bar{T}_{n.}\right) \cdot \Delta \tau}, \tag{3}$$

where: ΔQ - calculated according to the heat balance equation for the heat agent, J; $\bar{t}$ - the average temperature of the heat agent at the exit from the layer according to the experimental data shown in figures 2-5, °C; F– effective heat and mass transfer surface,$м^2$; Δt – change in the time, in seconds.

The values of the heat transfer coefficient obtained by us are averaged over the layer, due to the fact that the heat agent moves along a complex trajectory of channels between the particles that form the material layer, its speed changes many times with respect to the particle surface, so the local heat transfer coefficient changes. Figure 5 shows the calculated values of the heat transfer coefficient α from the actual speed of the heat agent.

Conclusions. The mechanism of filtration drying of a layer of raw cotton and its stems and the existence of a period of full and partial saturation of the heat agent is revealed. Criteria dependences are proposed for determining the heat transfer coefficients from the heat agent to the layer of dry particles of raw cotton and its stems. As we can see from the obtained graphic dependences, the experimental values of the heat transfer coefficient from the heat agent to dry particles of raw cotton and its stems, depending on the actual filtration rate, are approximated by a straight line. An increase in the speed leads to an intensification of the heat exchange process. This is due to the fact that at a higher filtration rate, a greater amount of heat agent is filtered through the channels between the particles and a greater amount of heat enters the material layer. The error between the theoretically calculated values and the experimental data does not exceed 14.2%, which is quite acceptable for design calculations of new drying equipment.

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ҚҰРЫЛЫМЫ ТАЛШЫҚТЫ ОРГАНИКАЛЫҚ МАТЕРИАЛДАРДЫ СҮЗГІЛЕП КЕПТІРУ МЕХАНИЗМІ ЖӘНЕ СЫРТҚЫ ЖЫЛУ АЛМАСУДЫ ЗЕРТТЕУ НӘТИЖЕЛЕРІ

Аннотация. Еркін және байланысты ылғалды жоюдың жоғары қарқынды әдісінің бірі – сүзгілеп кептіру. Сүзгілеп кептіру барысында жылу агенті ылғалды материалдың кеуекті құрылымы арқылы сүзіледі, ол перфорацияланған бөлікке орналастырылған «ылғал материал – перфорацияланған оқшау» бағытында қозғалады. Ылғал материалдың стационарлық қабатының кеуектері мен арналарындағы жылу агентінің қозғалыс жылдамдығы шекара қабатының қалыңдығын (гидродинамикалық, жылу және диффузиялық) және тиісінше жылу және масса беру коэффициенттерінің мәнін анықтайды. Сонымен қатар, жылу және масса алмасу беті жылу агенті сүзілетін кеуек пен арналардың жалпы беті болып саналады. Жылу агентінің сүзу жылдамдығының ұлғаюы қысымның жоғалуына әсер ететіні негізге алынып, техникалық-экономикалық тұрғыдан анықталады. Сонымен қатар, қабат элементтеріне қатысты жылу агентінің нақты жылдамдығы кез-келген басқа әдістермен (қайнаған қабатта, пневматикалық кептіргіште кептіру барысында және т.б.) кептіргенге қарағанда әлдеқайда жоғары. Ылғал материалдың стационарлық қабатының кеуегі мен арналарындағы жылу және масса алмасудың үлкен беті және жылу агентінің жылдамдығы жылу мен массаның жоғары коэффициенттерін және сәйкесінше сүзгілеу кептіру қарқындылығын қамтамасыз етеді. Мақалада жылу агенті мен талшықты құрылымның органикалық материалдарының құрғақ бөлшектері, атап айтқанда, мақта шикізаты мен сабағын сүзгілеп кептіру механизмі арасындағы сыртқы жылу алмасуды зерттеу нәтижелері келтірілген. Зерттеу нәтижелері бойынша шитті мақта қабатын және сабағын сүзгілеп кептіру механизмі және жылу агентінің толық әрі ішінара қанығу кезеңі анықталды. Құрғақ мақта шикізатының қабатынан және оның сабақтарынан шыққан жылу агенті температурасының орташа мәні эксперименталды түрде анықталды, 40 – 60^{0}С және жылу агентінің жылдамдығы бойынша 0,66-дан 2,01 м / с дейін түрлі температурада жылу агенті өзгереді. Жылу агентінің температуралық мәні шитті мақта бөлшектері мен сабағын қыздыру үдерісінің жылдамдығына байланысты таңдалады, олардың орташа мөлшері 2 мм аспайды. Ұсынылған материал қабатынан шыққан жылу агентінің температура өзгерісінің графикалық тәуелділігі жылу агентінен шикі мақта мен сабағының құрғақ бөлшегіне жылу беру коэффициентін анықтауға мүмкіндік береді.

Жылу агентінен шитті мақтаның құрғақ бөлшек қабатына және сабағына жылу беру коэффициенттерін анықтау үшін критериалды тәуелділік ұсынылады. Графикалық тәуелділіктен жылу агентінен алынған мақта шикізатының құрғақ бөлшектеріне және сабағына жылу беру коэффициентінің тәжірибелік мәні нақты сүзу жылдамдығына байланысты түзу сызықпен жақындағанын анықтауға болады. Жылу алмасу үдерісінің қарқындылығы жылу агенті жылдамдығының артуына байланысты екендігі анықталды, бұл бөлшектердің арасындағы арналар арқылы сүзу жылдамдығы жоғары болғанда жылу агентінің мөлшері көбірек сүзіліп, материал қабатына көбірек жылу өтеді. Теориялық есептелген мән мен эксперименттік мәліметтердің арасындағы сәйкессіздік 14,2% аспайды әрі бұл жаңа кептіру жабдықтарының жобалық есебіне өте қолайлы.

Түйін сөздер: мақта талшығы, жылу алмасу, масса алмасу, гидродинамика, фильтрациялық кептіру, кеуек, талшықты құрылымның органикалық материалдары.

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МЕХАНИЗМ ФИЛЬТРАЦИОННОЙ СУШКИ ОРГАНИЧЕСКИХ МАТЕРИАЛОВ ВОЛОКНИСТОЙ СТРУКТУРЫ И РЕЗУЛЬТАТЫ ИССЛЕДОВАНИЯ ВНЕШНЕГО ТЕПЛООБМЕНА

Аннотация. Одним из высокоинтенсивных методов удаления как свободной, так и связанной влаги является фильтрационная сушка. Это обусловлено тем, что во время фильтрационной сушки тепловой агент фильтруется сквозь пористую структуру влажного материала, который размещен на перфорированной перегородке в направлении «влажный материал–перфорированная перегородка». Скорость движения теплового агента в порах и каналах стационарного слоя влажного материала определяет толщину пограничного слоя (гидродинамического, теплового и диффузионного) и соответственно значения коэффициентов тепло- и массоотдачи. Кроме этого поверхностью тепло- и массообмена является суммарная поверхность пор и каналов, сквозь которые фильтруется тепловой агент. Скорость фильтрации теплового агента определяют исходя из технико-экономических соображений, учитывая то, что ее увеличение влияет на рост потери давления. Причем, действительная скорость движения теплового агента относительно элементов слоя значительно выше, чем в случае сушки любыми другими методами (в кипящем слое, во время сушки в пневмотранспортных сушилках и др.). Большие поверхности тепло- и массообмена и скорость теплового агента в порах и каналах стационарного слоя влажного материала обеспечивают высокие коэффициенты тепло- и массоотдачи и соответственно интенсивность фильтрационной сушки. В этой статье приведены результаты исследования внешнего теплообмена между тепловым агентом и сухими частицами органических материалов волокнистой структуры, в частности хлопка сырца и его стеблей и механизм фильтрационной сушки. По результатам исследований установлен механизм фильтрационной сушки слоя хлопка-сырца и его стеблей и существование периода полного и частичного насыщения теплового агента. Экспериментально определены усредненные значения температуры теплового агента на выходе из слоя сухого хлопка-сырца и его стеблей, при разных температурах теплового агента, которая изменялась в пределах: 40 – 60 ^{0}C, и при различных скоростях движения теплового агента от 0,66 до 2,01 м/с. Значение температур теплового агента выбрано ввиду быстротечности процесса нагрева частиц хлопка сырца и его стеблей, усредненный размер которых не превышает 2 мм. Представленные графические зависимости изменения температуры теплового агента на выходе из слоя материала позволяют определить коэффициент теплоотдачи от теплового агента в сухие частицы хлопка сырца и его стеблей.

Для определения коэффициентов теплоотдачи от теплового агента к слою сухих частиц хлопка-сырца и его стеблей предложены критериальные зависимости. Из графических зависимостей можно установить, что полученные экспериментальные значения коэффициента теплоотдачи от теплового агента в сухие частицы хлопка-сырца и его стеблей в зависимости от действительной скорости фильтрования аппроксимируются прямой линией. Установлено, что интенсификация процесса теплообмена зависит от роста скорости теплового агента, это объясняется тем, что при большей скорости фильтрования через каналы между частицами профильтровывается большее количество теплового агента и в слой материала поступает большее количество тепла. Расхождение теоретически рассчитанных значений от и экспериментальных данных не превышает 14,2%, что вполне приемлемо для проектных расчетов нового сушильного оборудования.

Ключевые слова: волокно хлопка, теплообмен, массообмен, гидродинамика, фильтрационная сушка, пористость, органические материалы волокнистой структуры.

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ИЗУЧЕНИЕ ВЕЩЕСТВЕННОГО СОСТАВА ПРОБЫ МАРГАНЕЦСОДЕРЖАЩЕЙ РУДЫ МЕСТОРОЖДЕНИЯ «КАРАМОЛА»

Аннотация. В данной работе изучены вещественный состав руды месторождения «Карамола». На исследования по изучению вещественного состава поступила проба марганцевой руды месторождения «Карамола» крупностью 0-120 мм.

Марганцевая минерализация пробы представлена минеральными рядами полианита-пиролюзита и вада-псиломелана. Минеральные выделения представляют собой кристаллические землистой структуры и смешанные образования.

Оксиды марганца распространены практически по всей массе породы. Представлены раскристаллизованными гелевыми образованиями, сажистыми, скелетными структурами.

Рудные гели пропитывают породу по трещинам, просечкам, пустотам выщелачивания, по порам, плоскостям спайности и проникают между чешуйками слоистых минералов и образуют в массе породы самые разнообразные формы: отдельные штрихи, нитевидные просечки, прожилки, каемки, прослойки, гнезда.

Замещающие растворы носят кремнистый или марганцово-кремнистый характер и окрашивают породу в соответствующий цвет минеральными микрочастицами: черными – марганец, красными и рыжими – железо. Породообразующие минералы представлены в основном кварцем.

Определен гранулометрический состав пробы руды, дробленной до класса минус 2,0+0 мм.

Ключевые слова: руда, марганец, минералогия, вещественный состав, гранулометрический состав.

Основным потребителем – до 95% производимого товарного марганца – является черная металлургия [1].

Прежде всего, марганец служит десульфуризатором, способным переводить в шлак серу. Другое важное свойство марганца – способствовать образованию жидких шлаков, что позволяет отделять металл в конце плавки. Не менее важное свойство марганца – способность восстанавливать окислы железа и связывать почти весь находящийся в расплаве кислород, тем самым значительно повышая физические свойства стали. Кроме того, марганец обладает легирующими свойствами - незначительная (1-2%) его присадка к стали заметно повышает ее физические свойства (ковкость, твердость, износостойкость). Марганец применяется также при производстве сплавов с другими металлами. Так сплав манганин, содержащий 83% меди, 4% никеля и 8-13% марганца обладает большим электрическим сопротивлением и применяется в электротехнике. Медно-марганцевые сплавы с содержанием 4-5% марганца применяются для изготовления лопастей турбин. Ряд марганцевых сплавов применяется при изготовлении оборудования для химической и пищевой промышленности [2-5].

В черной металлургии марганец применяется преимущественно в виде ферромарганца. Другой марганцевый сплав – силикомарганец – используется как комплексный раскислитель при плавке малоуглеродистого и среднеуглеродистого ферромарганца [6-10]. Металлический марганец (95-99% марганца) используют в основном при выплавке нержавеющей и других специальных сталей. Значительно реже для легирования чугуна и стали используются концентраты и товарная марганцевая руда [11-15]. Около 10% марганца используется для изготовления сухих электрических батарей, в стекольном деле для обесцвечивания стекла, в медицинских препаратах, в пищевой промышленности [16-20].

Проба руды месторождения «Карамола» представляет зону выветривания по толще метаморфизованных силикатных черноцветных марганецсодержащих пород. Проба представлена кусковым материалом черного цвета размером кусков 70-120 мм.

С поверхности руды представлены марганцевыми шляпами. Минералы первичных руд - браунит, гаусманит, менее развиты манганит и псиломелан, встречаются родонит, бустамит, гематит, манганокальцит, тефроит. Широко развит кварц. Присутствуют также пирит, в незначительном количестве – халькопирит.

На рисунке 1 - приведен образец, составляющий пробу руды.

Рисунок 1 – Минералы марганца

Среднее содержание марганца 26,0%, железа 0,90-1,71%, фосфора 0,60%, серы 0,41%, кварца 53,20%, глинозема 0,44-7,66%, окиси титана 0,04-0,16%, извести 1,0-5,72%, свинца и цинка до 0,04%.

В марганцевых прожилках наблюдаются вкрапления зерен пирита размером от 0,1 мм и 1,5 мм (преобладают 0,25-0,6 мм) и гнезда марганцевых минералов величиной 2,0-5,0 мм, приуроченные к областям раздувов и растрескиваний. Оксиды марганца распространены практически по всей массе породы, представлены раскристаллизованными гелевыми образованиями, сажистыми, скелетными структурами.

Непосредственно в массе рудовмещающей толщи присутствуют отдельные аморфные вкрапления марганцевых минералов и сульфидов железа (пирит). Величина вкрапленников от 1,0-2,0 мм до 0,01 мм, преобладают 0,05-0,13 мм.

Около 9,0% от оксидов марганца в пробе приходится на кристаллически-зернистые соединения, 15,0% – на землистые структуры, а 12,0% составляют примазки и налеты.

В выделениях величиной 0,001-0,002 мм по границам оксидов наблюдались единичные точечные выделения куприта.

Из таблицы 1 следует, что при дроблении исходной руды крупностью 120 мм до минус 2,0+0 мм 73,03% представлен классом минус 2,0+0,2 мм, 26,97% - классом минус 0,2+0 мм.

Основные капитальные и эксплуатационные затраты на обогатительных фабриках связаны с процессами дробления и измельчения. Главными характеристиками, на основании которых рассчитываются параметры (размеры, мощность) промышленных дробилок являются пределы прочности руды, а также индексы дробимости, определяемые по методике Бонда.

Таблица 1 – Результаты гранулометрического состава пробы руды

Крупность класса, мм	Выход, %
-2+1	27,04
-1+0,5	20,27
-0,5+0,2	25,72
-0,2+0,1	5,97
-0,1+0,071	3,81
-0,071+0,044	5,23
-0,044+0,030	2,22
-0,030+0	9,74
Итого	100,0

По методике Бонда дробимость и измельчаемость характеризуется «индексом чистой работы» Wi (кВт·ч/т), то есть количеством электроэнергии необходимой для дробления одной тонны руды до определенной крупности.

С учетом полученных значений «индексов чистой работы» определяется схема рудоподготовки и производится выбор дробильно-измельчительного оборудования.

Для определения коэффициента «чистой работы» при дроблении (индекс Бонда) проведен ситовой анализ пробы исходной руды в количестве 81,6 кг. По ширине разгрузочной щели выделен класс 25 мм.

Индекс «чистой работы» определялся по формуле Бонда:

$$\frac{(\mathrm{Nз} - \mathrm{Nxx})}{\mathrm{Q}} = \frac{10 \times \mathrm{Wi} \times \left(\sqrt{\frac{\mathrm{F}_{80}}{\mathrm{P}_{80}}} - 1\right)}{\sqrt{F_{80}}},$$

где N_3 – мощность, потребляемая дробилкой при дроблении, кВт; $N_{х\text{-}х}$ – мощность холостого хода дробилки, кВт; Q – производительность дробилки, т/ч; W_i – индекс «чистой работы» дробления, кВт·ч·мкм^{0,5}/т; F_{80}, P_{80} – размеры квадратных отверстий сит, через которые проходит 80% соответственно исходного питания и разгрузки дробилки, мкм.

Опыт по определению коэффициента «чистой работы» проводился на дробилке ЩДС – 2,5х4, на которой установлен двигатель АОП 2 – 72 с техническими характеристиками:

– мощностью - 22 кВт;

– cos α - 0,77;

– U - 380 V.

Для определения мощности холостого хода произведен замер тока холостого хода прибором Ц 4505М, $I_{х\text{-}х}$ = 28,7А.

В таблице 2 и 3 приведены гранулометрическая характеристика исходной и дробленой руды.

Таблица 2 - Гранулометрическая характеристика исходной руды

Размер сита, мм	Выход классов, оставшихся на сите, %		Суммарный выход классов, прошедших через сито, %
	частный	суммарный	
120	-	-	100,0
80	67,15	67,15	32,85
45	22,55	89,70	10,30
30	6,13	95,83	4,17
25	4,17	100,0	-
Итого	100,0	-	-

Таблица 3 - Гранулометрическая характеристика дробленой руды

Размер сита, мм	Выход классов, оставшихся на сите, %		Суммарный выход классов, прошедших через сито, %
	частный	суммарный	
25	-	-	100,0
20	7,05	7,05	92,95
12	24,94	31,99	68,01
6	28,98	60,97	39,03
3	15,38	76,35	23,65
0,5	15,63	91,98	8,02
-0,5	8,02	100,0	-
Итого	100,0	-	-

Таблица 4 - Показатели дробления пробы руды

Наименование показателей	Единица измерения	Значения
Производительность, Q	т/ч	3,58
Мощность, потребляемая при дроблении, N	кВт	16,81
Мощность холостого хода, $N_{х-х}$	кВт	14,53
F_{80} – размеры отверстий сита, через которые проходит 80 % исходного продукта	мкм	108000
P_{80} – размеры отверстий сита, через которые проходит 80 % дробленого продукта	мкм	15500
Индекс Бонда	кВт·ч/т мкм^{0,5}	12,76

В таблице 4 приведены показатели дробления, определенные по методу Бонда. Тест на измельчаемость руды по методике Бонда служит для определения в лабораторных условиях показателей, на основании которых можно рассчитать параметры (размеры, мощность) промышленной шаровой мельницы для измельчения данной руды на обогатительной фабрике. По методике Бонда измельчаемость характеризуется «индексом чистой работы» BWi. Индекс чистой работы по Бонду определялся по результатам мокрого измельчения исследуемой руды в лабораторной шаровой мельнице.

На средней пробе были определены плотность пробы и ее гранулометрическая характеристика.

Исследования измельчаемости проводили на пробе руды, дробленной до крупности минус 2,0+0 мм в шаровой мельнице типа МЛ-40 объемом 9,0 дм^3, общий вес шаровой загрузки составляет 9,83 кг, диаметры шаров от 16 до 40 мм.

Отсев измельченного продукта проводили на сите с ячейками 0,071 × 0,071 мм, затем продукт + 0,071 мм сушили, взвешивали и по разности с первоначальной навеской определяли выход класса минус 0,071 мм.

Продолжительность измельчения измерялась количеством оборотов вращения барабана мельницы. Частота вращения барабана 70 мин$^{-1}$. После стабилизации показателей измельчения определяли гранулометрическую характеристику исходного и готового продуктов (таблица 5).

Таблица 5 - Гранулометрическая характеристика исходного и готового продуктов измельчения

Размер сита, мм	Исходный продукт			Готовый продукт		
	выход классов, оставшихся на сите, %		суммарный выход классов, прошедших через сито, %	выход классов, оставшихся на сите, %		суммарный выход классов, прошедших через сито, %
	частный	суммарный		частный	суммарный	
2,0	-	-	100,0			
1,0	27,04	27,04	72,96			
0,50	20,27	47,31	52,69			
0,20	25,72	73,03	26,97			
0,10	5,97	79,00	21,00			
0,071	3,81	82,81	17,19	-	-	100,0
0,040	5,23	88,24	11,96	45,05	45,05	54,95
0,030	2,22	90,26	9,74	13,91	58,96	41,04
- 0,030	9,74	100,0	-	41,04	100,0	-
Итого	100,0	-	-	100,0	-	-

Индекс чистой работы измельчения в шаровой мельнице по Бонду определялся по формуле:

$$Wiш.изм. = \frac{E \times \sqrt{F_{80}}}{10 \times \left(\sqrt{\frac{F_{80}}{P_{80}}} - 1 \right)}, \frac{кВт\ ч}{т} мкм^{0,5}$$

В таблице 6 приведены показатели измельчения пробы руды в шаровой мельнице в периодически замкнутом цикле с циркулирующей нагрузкой 255%.

Таблица 6 - Показатели измельчения пробы руды

Наименование показателей	Единица измерения	Значения
Производительность, Q	т/ч	0,00215
Мощность, потребляемая при измельчении, N	кВт	0,320
Мощность холостого хода мельницы без измельчающей среды, $N_{х\text{-}х}$	кВт	0,266
Удельный расход электроэнергии, E	кВтч/т	25,12
Циркуляционная нагрузка, C	%	255
F_{80} – размеры отверстий сит, через которые проходит 80 % исходного продукта	мкм	1250
P_{80} – размеры отверстий сит, через которые проходит 80 % готового продукта измельчения	мкм	57
Индекс Бонда	кВт·ч/т·мкм^{0,5}	24,11

На основании проведенной работы получены результаты минералогической характеристики марганцевой руды месторождения «Карамола».

Марганцевая минерализация пробы представлена минеральными рядами полианита-пиролюзита и вада-псиломелана. Минеральные выделения представляют собой кристаллические землистой структуры и смешанные образования.

Замещающие растворы носят кремнистый или марганцово-кремнистый характер и окрашивают породу в соответствующий цвет минеральными микрочастицами: черными – марганец, красными и рыжими – железо. Породообразующие минералы представлены в основном кварцем.

- индекс Бонда при дроблении - 12,76 кВт·ч/т мкм^{0,5};
- индекс Бонда шарового измельчения - 24,11 кВт·ч/т мкм^{0,5}.

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«ҚАРАМОЛА» КЕН ОРНЫНЫҢ МАРГАНЕЦ ҚҰРАМДЫ КЕН ҮЛГІЛЕРІНІҢ ЗАТТЫҚ ҚҰРАМЫН ЗЕРТТЕУ

Аннотация. Жұмыста «Қарамола» кен орны марганец кенінің материалдық құрамы зерттелді. Кеннің материалдық құрамын анықтау үшін «Қарамола» кен орны марганец кенінің 0-120 мм ірі үлгісі алынды. Үлгінің марганецті минералдануы полианитті-пиролюзитті және вада-псиломеланды минералдық қатар бойынша таралған. Минералды бөлініс кристалды жер құрылымды және аралас түзілімді көрсетеді. Марганец оксидтері жыныстың бүкіл массасына таралған. Олар кристалданған гельдік түзілім, қопсытқыш, қаңқалық құрылымдар арқылы ұсынылған.

Кенді гель тау жынысын жарық, ойық, шаймалау қуысы, кеуек, адгезия жазықтығы бойымен сіңдіреді және қабатты минералдарды қабыршақтар арасына еніп, тау жынысы массасында жеке соққы, жіп тәрізді ойық, тамыр, жиек, қабат, ұя сынды түрлі формаларды құрайды.

Ауыстыру ерітінділері табиғатта кремнийлі немесе марганец-кремнийлі және минералды микробөлшектермен сәйкес түске, атап айтқанда, қара-марганец, қызыл және қызыл-темірге боялған. Тау жыныстарын құрайтын минералдар негізінен кварц негізінде ұсынылған.

Минус 2,0+0 мм класқа дейін ұнтақталған кен сынамасының гранулометриялық құрамы анықталды.

Түйін сөздер: кен, марганец, минералдану, материалдық құрам, грануламетриялық құрам.

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STUDY OF THE MATERIAL COMPOSITION OF THE SAMPLE MANGANESE-CONTAINING ORE DEPOSITS “KARAMOLA”

Abstract. In this work, the material composition of the ore of the Karamola Deposit is studied. A sample of manganese ore from the Karamola Deposit with a size of 0-120 mm was received for research on the material composition.

The manganese mineralization of the sample is represented by the mineral series polyanite-pyrolusite and WADA-psilomelane. Mineral secretions are crystalline earthy structures and mixed formations.

Manganese oxides are distributed almost throughout the entire mass of the rock. They are represented by crystallized gel formations, soot, and skeletal structures.

Ore gels permeate the rock through cracks, cleavages, leaching voids, pores, cleavage planes and penetrate between the scales of layered minerals and form a variety of forms in the mass of the rock: individual strokes, thread-like cuts, veins, edges, layers, nests.

Replacement solutions are siliceous or manganese-siliceous in nature and color the rock in the corresponding color with mineral microparticles: black – manganese, red and red – iron. Rock-forming minerals are mainly represented by quartz.

The granulometric composition of an ore sample crushed to the minus 2.0+0 mm class was determined.

Key words. Ore, manganese, mineralogy, material composition, granulometric composition.

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SELECTIVE EXTRACTION OF GOLD (III) BY INERT ORGANIC SOLVENTS AND DETERMINATION OF ITS METHYLENE BLUE (MB) DIRECTLY IN THE ORGANIC PHASE

Abstract. A new highly selective, accelerated and simple extraction photometric method for determining gold with MB directly in the organic phase has been elaborated. The developed method is tested on the analysis of production solutions of hydrometallurgical plants, concentrates and rocks without separation of accompanying elements. The developed method of extraction-photometric determination of gold with MB is recommended for the analysis of industrial solutions, waste water, ores, concentrates, rocks and other materials complex in terms of chemical composition without separation of the accompanying elements directly in the organic phase.

Key words: photometric method, gold, complex compounds, chloroform, gold extraction.

Introduction. Existing photometric and extraction-photometric methods for the determination of gold (III) for the use of organic dyes [1,2,3,4] are not very selective. Only a few works we can see investigates about minerals and receiving concentrates for extraction chloride of metal ions [5]. The results of the leaching of the tailings from the heap leaching section with the aim of extracting gold associated with sulfides are presented [6,7].Since the complexation of gold (III) with organic reagents happens during the water phase, the resulting ions often form complex colored compounds and conflict with the definition of gold. In the work [8] given general information on the chemical composition of ash and slag wastes and the content of valuable components of the most developed and used deposits in Kazakhstan and attractive from the point of view of extracting valuable materials from them.

Recently for increase of selectivity of methods for determination of elements a new method is applied - selective extraction of colorless complexes of elements by inert organic solvents, with the subsequent addition to the extract of organic dyes and their complexation directly in the organic phase [9,10].

This paper discusses a new selective, simple method based on selective extraction of gold chloride complex (III) with inert organic solvents and its complexation with MB directly in the organic phase.

Source solution of gold (III) with a concentration of 1MB/ml was prepared from the salt of chloride gold. Titer of solution was set by potentiometric titration with Mora salt [11]. Aqueous solution of MB was used.

The spectra of extracts of gold (III) and reagent complexes were shot on SP-26 spectrophotometer, ℓ=1 see. Optical density of the solution was measured on the photoelectric colorimeter KPC-2.

Experiments have shown that gold (III) from highly acidic solutions in the presence of chloride ions and dimethylformamide (DMFA) is well extracted by chloroform. In the absence of DMFA, gold (III) is not extracted. The study of gold extraction (III) by chloroform depending on the concentration of hydrogen ions, chloride ions and DMFA showed that the optimal conditions for gold extraction (III) are: 0.50 - 6.0 g ion/l for hydrogen ions; 0.06 - 2.5 g ion/l for chloride ions and 13 - 26 % (by volume) for DMFA, shaking duration of phases 5 - 10 s. At equal volumes of aqueous and organic phases extraction of gold (III) at a single extraction is 99.9 % and does not change to a ratio of 20:1 phase volume [12].

In these optimum conditions, the composition of the extractable gold chloride complex (III) by the equilibrium shift method has been determined [13]. For this purpose, the dependence of gold extraction (III) on concentration was studied: 1) hydrogen ions (0.030 - 0.96 g ion/l) at constant concentrations of chloride ions (1.0 g ion/l), DMFA (20%) and ionic force (μ = 1) created by adding NaCl solution; 2) chloride ions (0.01 - 0.34 g ion/l), at constant concentrations of hydrogen ions (1.0 g ion/l), DMFA (20%) and ionic strength (μ=1); 3) DMFA (5 - 13%), at constant concentrations of hydrogen ions (1.0 g ion/l), chloride ions (1.0 g ion/l) and ionic strength (μ=1).

The concentration of gold (III) in the extract was determined by the photometric method with the MB reagent. For this purpose, an aqueous solution of MB was added to the extract and the phases in the organic phase were shaken. The resulting colored gold complex (III) with MB was photometrically photometrical relative to the blank experience extract prepared in a similar way. The data obtained are given in tables 1 - 3 and Figures 1 - 3, shows that in bilogorithmic coordinates $\ell gD_{Au} - \ell gC_{H+}$, $\ell gD_{Au} - \ell gC_{Cl-}$, $\ell gD_{Au} - \ell gC_{DMFA}$ DMFA (where D is the distribution coefficient, C is the equilibrium concentration, moths) there is a straight-line dependence with tangent angles of straight lines equal to 1,4,3 respectively. Consequently, gold (III) is extracted by chloroform in the form of $HAuCl_4$; the solvate number $HAuCl_4$ in the extract is 3 [14].

Table 1 - Determination of the number of H^+-ions involved in the extraction of gold by chloroform. $A_{пр}$=0,57; C_{Au}=0,91·10^{-5} m

C_{H+}, mol	A	D	ℓgD	-ℓgC_{H+}
0.015	0,340	1,100	0,040	1,820
0,030	0,400	2,350	0,372	1,580
0,60	0,470	4,700	0,671	1,320
0,119	0,510	8,500	0,930	0,919
0,340	0,540	18,000	1,360	0,630
0,260	0,550	27,500	1,440	0,440

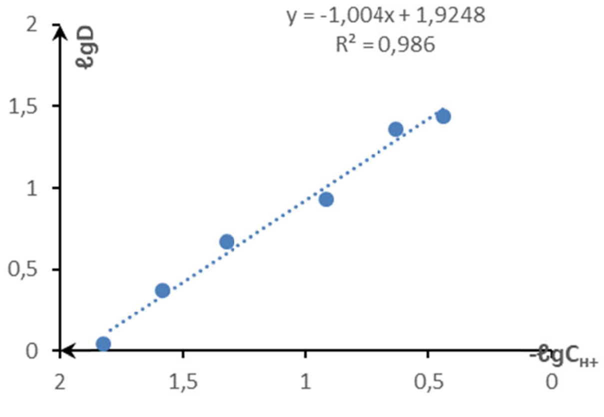

Figure 1 - Determination of molar ratios of Au: H^+ - ions by the equilibrium shift method during chloroform extraction, V_0=10 ml ℓ = 1 cm

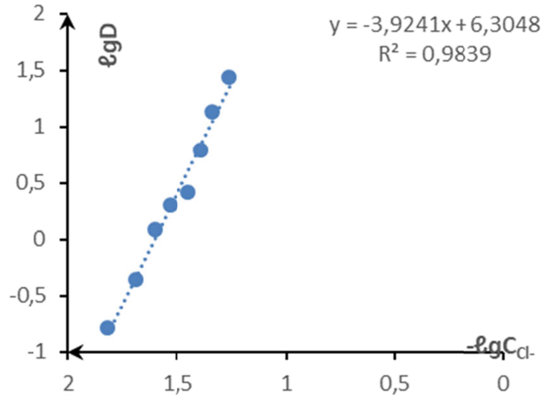

Figure 2 - Determination of molar Au: Cl^- ratios by the equilibrium shift method during chloroform extraction, V_0 =10 ml ℓ = 1 cm

Table 2 - Determination of the number of chloride ions involved in the extraction of gold by chloroform. $A_{пр}=0,57$; $C_{Au}=0,91\cdot10^{-5}$ m

C_{Cl^-}, mol	A	D	ℓgD	$-\ell g C_{Cl-}$
0,015	0,080	0,160	0,790	1,819
0,019	0,180	0,450	0,350	1,690
0,035	0,260	0,810	0,090	1,600
0,030	0,360	1,630	0,310	1,530
0,035	0,419	2,630	0,419	1,450
0,040	0,500	6,250	0,790	1,390
0,045	0,540	13,500	1,130	1,340
0,050	0,560	38,000	1,440	1,260

Таблица 3 - Determination of the number of DMFA molecules involved in the extraction of gold by chloroform. $A_{пр}=0,57$; $C_{Au}=0,91\cdot10^{-5}$ m

C_{DMFA}^-, mol	A	D	ℓgD	$-\ell g C_{DMFA}$
0,519	0,135	0,310	- 0,508	0,285
0,789	0,280	0,960	-0,0177	0,103
0,909	0,340	1,480	0,170	0,040
1,039	0,390	3,160	0,499	-0,016
1,169	0,440	3,380	0,530	-0,067
1,300	0,480	5,300	0,724	-0,113

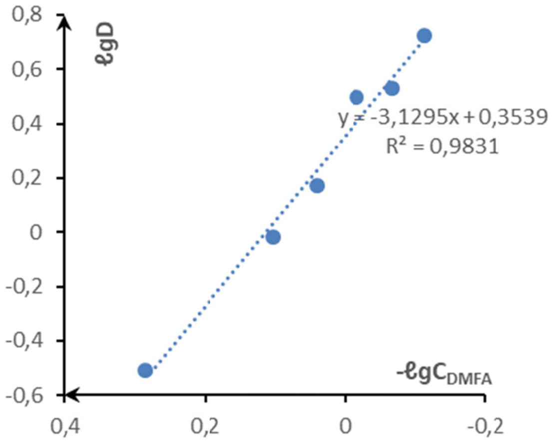

Figure 3 - Determination of Au: DMFA molar ratios by the equilibrium shift method during chloroform extraction

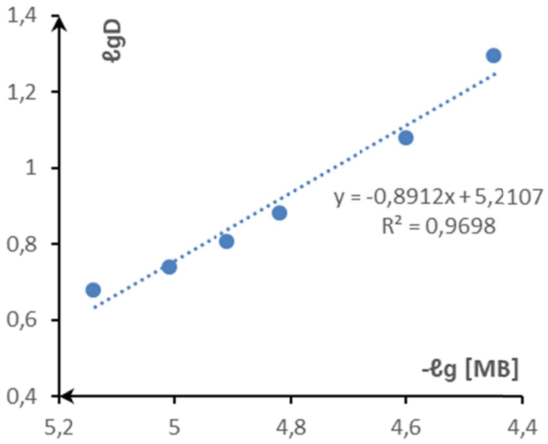

Figure 4 - Determination of the composition of the gold complex with MB method of balance shift

To fully identify the mechanism of extraction of gold (III) studied the number of hydrated water molecules in the extract. For this purpose, 10 ml of a mixture containing 1 M HCl and 20% DMFA, 10 ml of chloroform and shaking for 5 - 10 seconds was added to 5 MB of gold (III). A blank solution without gold was prepared in a similar way (III). After complete separation of the aqueous phase extract, the extracts were poured into dry cylinders with grated plugs. Determination of water was carried out by the Fisher method [15] by amperometry titration. For this purpose, Fischer reagent from micro burette was poured to 1 ml of the test extract taken by the dispenser, the titer of which was determined in advance by water suspension. Under the action of the Fisher reagent the arrow of the galvanometer was shifted towards the current increase and set constant at the end of titration. Knowing the Fisher reagent titer (T=0.0018 g/ml), the water content was determined by formula: $g_{H2o}= T\cdot V$, (where V - is the volume of Fisher's reagent that went on hydrated water titration (V=0.101 ml), T - is the Fisher's reagent titer). The amount of hydrated water in chloroform extraction: $g_{H2o} = 0,0018 \cdot 0,101 = 0,0001818$ gr/ml = 0,1818 gr/l.

Given that the titration of the taken 5 MB of gold (III) and the volume of chloroform 10 ml we calculate the number of hydrated water molecules: $n_{H2o}=\frac{g_{H2o}}{M_{H2o}}:\frac{g_{Au}}{A_{Au}}=\frac{0,1818}{18}:\frac{0,5}{196,9}=\frac{35,7964}{9}=3,9777\approx 4.$

Consequently, during the extraction of gold (III) chloroform hydrate 4 water molecules. Considering this, the mechanism of extraction of gold (III) can be represented by an equation: $AuCl_4{}^-{}_{(в)} + H(H_2O)_4{}^+ + 3\ DMFA(в) \leftrightarrows [H(H_2O)_4(DMFA)_3]^+[AuCl_4]^{--}{}_{(0)}$.

Therefore, the gold chloride complex (III) in the presence of DMFA is extracted by the chloroform for the hydro-solvate mechanism [16].

After extraction of gold (III) chloroform in optimal conditions, separation of the aqueous phase of the addition to the extract of aqueous solution of MB and shaking phases for 10-15 seconds is complexing gold (III) with MB in the organic phase. The study showed that almost complete complex formation of gold (III) with MB in the chloroform occurs in the pH = 6-10 range. The stability of the gold (III) extract has been studied depending on the volume of MB aqueous solution. It is found that the chloroform extract of gold (III) is stable to the ratio of water and organic phases of 1.5:1.0. Gold complex (III) with MB in the organic phase is stable for more than 3 days.

The influence of MB concentration on the completeness of gold complexation has been studied (III). For this purpose, to a constant amount of gold (III), after extraction in optimal conditions, added an increasing amount of MB and photometric. Experimental data showed that the full complex formation of gold (III) is achieved at 18-fold molar excess of MB (table 4 and figure 4).

Table 4 - Determination of the equilibrium composition
of the gold complex with MB method of balance shift. C_{Au} =7,65 · 10^{-6} m, $A_{пр}$=0,52

C_{MB}, M·10^{-5}	A	D	ℓgD	[kompl]M·10^6	[MB] M·10^6	-ℓg [MB]
1,357	0,430	4,777	0,679	6,319	7,255	5,140
1,630	0,440	5,500	0,740	6,470	9,819	5,010
1,900	0,450	6,419	0,808	6,619	13,385	4,910
2,172	0,460	7,619	0,880	6,760	14,950	4,819
3,358	0,480	12,000	1,079	7,060	25,530	4,600
4,344	0,500	25,000	1,297	7,360	36,085	4,450

The absorption spectra of gold (III) complexes with MB and reagent MB are shown in figure 5.

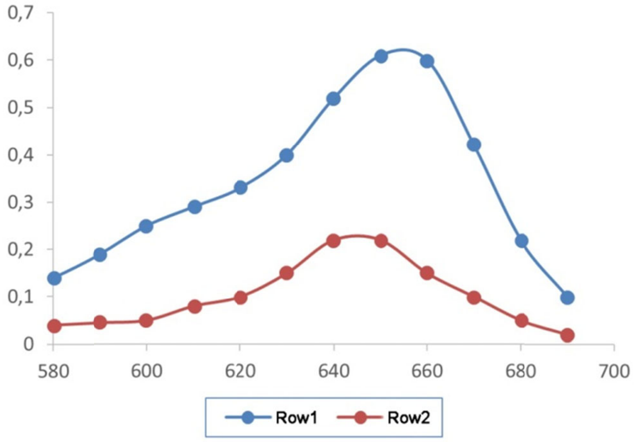

Figure 5 - Absorption spectra of gold complexes (III) with MB (Row1)
and MB reagent (Row2) in chloroform (C_{Au} =0,51 · 10^{-5} M; V_0=10 ml; ℓ =1см)

As can be seen from figure 5, the maximum light absorption of the complex with MB (Row1) is at 650 nm. The molar repayment ratio of the complex is 1.22·105. The Ber law is observed in the interval of 1-120 µg of gold (III) in 10 ml of the extract. Reproducibility of definitions is in the range of 2-5%. There are three graded charts in the intervals of 10 - 10, 10 - 60, 60 - 120 µg of gold. Optical density of complexes was measured in cuvettes with thickness of 20, 10, 3 mm.

The determination of molar ratios of the components in the resulting gold (III) and MB complexes was carried out by the equilibrium shift method [8]. To determine the composition of the gold (III) complex with MB to chloroform extract containing a constant amount of gold (III) (1,326 · 10-5 M, $A_{пр}$ = 0,7) were added 10 ml from 1,359 · 10-5 to 24,403 · 10-5 M aqueous solution of MB in the chloroform and shaken the phases 10-15 sec. The resulting painted gold complex (III) with MB was photometrically photometrical relative to the blank solution prepared in a similar way with the same amounts of reagent. From the tabular data (Table 4) we made a graph of dependence of ℓgD on -ℓg[MB] (figure 4).

The tangent angle of the straight line on the graph shows that gold (III) in the chloroform interacts in a molar ratio of 1:1. Considering the mechanism of extraction of gold chloride complex (III) and the composition of complex compounds with MB, the reaction of complexation of gold (III) with the MB reagent in the organic phase can be presented in the following scheme: $[H\,(H_2O)_4\,(DMFA)_3]^+\,[AuCl_4]^-_{(o)} + PCl_{(B)} \rightleftarrows PAuCl_4 + 3DMFA + HCl + H_2O$. Where the P - is the MB cation.

Methods for determining gold in pure solutions. The dividing funnel is filled with the analyzed solution containing 1.0-120 µg of gold (III), 1 ml of concentrated hydrochloric acid is added to the dividing funnel and the volume of the solution is brought to 8 ml with water, 2 ml of DMFA, 10 ml of chloroform is added and 5-10 s are shaken. The extract is washed with 10 ml of solution containing 1 M HCl and 20% DMFA, and 5-10 s are shaken. Then add 10 ml of 0.010% aqueous solution of MB to the extract and shake 10-15 sec. The resulting colored complex is filtered through filter paper into a cuvette and measured the optical density relative to the blank extract.

In industrial samples and minerals, gold is found in mixtures with many elements. In order to identify the possibility of determining gold from complex chemical samples was studied the influence of foreign ions in determining gold with MB. The method for determining gold in the presence of foreign ions is the same as for determining it in pure solutions, with the only difference being that certain amounts of foreign ions or compounds are preliminarily added to the determined solution and in some cases, if necessary, masking agents are added and the extract is washed once with a washing solution containing HCl and DMFA.

Under conditions of extraction of gold (III) partially extracted thallium ions (III) and antimony (V) and interfered with the definition. However, thallium (III) in chloroform extract with MB in the medium of 0.05 - 0.5 M of borax does not form a colored complex compound and its 5000-fold amount does not interfere with the definition of gold. In the presence of tungsten to prevent the deposition of tungsten acid and to eliminate the interfering effects of antimony (V) previously added 0.01 - 0.5 g tartaric acid. Data on the definition of gold in the presence of foreign ions are given in table 5 with a relative error within 2-5%.

Table 5 - Determination of gold (III) with MB in the presence
of foreign ions (10 µg gold was taken)

M	M/Au	M	M/Au	M	M/Au	M	M/Au
Ag (I)	2000	Mn (II)	100000	Cr (III)	20000	W (VI)	2000[2]
Ag (I)	15000	Cd (II)	80000	Ti (IV)	15000	Mo (VI)	15000
Pb (II)	2000	Hg (II)	10000	Sn (IV)	50000	Te (VI)	30000
Pb (II)	20000[3]	Bi (III)	20000	Th (IV)	22000	Mn (VII)	1000
Zn (II)	50000	Fe (III)	30000	Pt (IV)	2000	Os (VIII)	200
Ca (II)	20000	Iu (III)	15000	Se (IV)	3000	NaF	5000
Ba (II)	20000	Al (III)	15000	Zr (IV)	15000	NO_3^-	6000
Cu (II)	20000	Ga (III)	10000	Sb (V)	150	PO_4^{-3}	2000
Ni (II)	30000	La (III)	20000	Sb (V)	3000[2]	tartaric acid	100000
Co (II)	35000	Tl (III)	1000[1]	As (V)	20000	citric acid	100000
Pd (II)	2000	Tl (III)	5000[4]	U (VI)	10000		
Be (II)	2000	Tl (III)	10000[1]	W (VI)	150	thionalide	10000

Where M - ion or compound; M/Au - allowable ratio to gold by weight; 1 - in the presence of 100 MB thionalide; 2 - in the presence of 0.5 g of tartaric acid; 3 - after heating the solution with sludge in a water bath for 2 - 3 minutes; 4 - when shaking the extract with aqueous solution of MB, containing 0.05 - 0.5 borax.

In order to find out the possibility of determining gold in various objects, we carried out the analysis of production solutions, (Table 6) concentrates and rocks (table 7).

In determining the gold (III) in the production solutions are taken 1 - 2 ml of aliquot part of the solution and further analysis is carried out as in the analysis of gold from pure solutions. The gold content is determined from the calibration chart.

Table 6 - Determination of gold in production solutions (n = 4; p = 0.95)

Content of gold in the production solution, MB/l	Found ($\bar{x}$) gold, MB/l	Sr	$\Delta_{\bar{x}}$	$\pm\frac{\Delta x}{x}\cdot 100$
1,60	1,55	0,0160	± 0,039	± 2,50
15,20	15,30	0,0094	± 0,220	± 1,50
45,00	45,50	0,0056	± 0,410	± 0,990
101,00	101,60	0,0075	± 1,220	± 1,20
142,50	142,30	0,0094	± 2,134	± 1,50

To determine the gold (III) in the concentrates and rocks calcined at 600–650^0 C for 1.5 hours a canopy (10 - 20 g) is placed in a conical flask for 250 ml, 30-60 ml of a mixture of hydrochloric (p 1.19) and nitric (p 1.4) acids (3:1) and evaporated to wet salts. Then add 10 - 20 ml of the same mixture of acids and again evaporate to wet salts, then pour 30 - 40 ml of 1 M HCl and boil for 5 - 10 minutes. Cool the solution and filter it into a measuring flask for 50 or 100 ml, then dilute the filtrate 1 M HCl to the mark and determine the gold content from the aliquot of the solution.

Table 7 - Results of gold (III) determination in concentrates and rocks at chloroform extraction (n = 4; p = 0.95)

Sample	Contents, Au gr/t	Found Au ($\bar{x}$), gr/t	Sr	$\Delta_{\bar{x}}$	$\pm\frac{\Delta x}{x}\cdot 100$
Concentrate	50,00	51,20	0,034	± 2,780	± 5,42
Concentrate	37,50	96,50	0,022	± 1,277	± 3,50
Concentrate	22,00	21,60	0,028	± 0,972	± 4,50
Breed	8,30	7,60	0,036	± 0,441	± 4,80
Breed	5,60	5,15	0,041	± 0,334	± 6,50

Discussion of results. Therefore, our research allows us to conclude that the low selectivity of metalloids definitions using basic dyes, as well as the use of other organic reagents in the complex formation in the aqueous phase is the main disadvantage of existing methods.

Our research has focused on ways to increase the selectivity and sensitivity of photometric definitions, as these analytical characteristics play an important role in the practice of analytical chemistry. We have investigated the conditions of selective extraction of the gold chloride complex in the presence of DMFA inert organic solvents and its determination directly in the organic phase without separation of the accompanying elements.

Researches have shown that gold (III) from a highly acidic environment is selectively extracted by chloroform in the presence of chloride ions and DMFA. At 5 - 10 second phase shaking gold (III) is extracted by 99.9% without changes to the ratio of phase volumes 20:1.

Under these optimal conditions, thallium (III), antimony (V) and tungsten (VI) are partially extracted together with gold and interfere with the definition. However, thallium, antimony, and tungsten interfere with the extraction by adding masking agents to the extraction mixture.

The research of substance of extracting gold chloride complex (III) in the extract has shown that the gold chloride complex (III) is extracted by the hydro-solvate mechanism. Gold chloride complexes (III) in the extract are stable for a long time and subject to the Beer`s law in a wide concentration range. The method is valuable also by the fact that after the extraction of gold in the organic phase there is a possibility of forming complexes with more sensitive organic reagents, which due to low selectivity have not received wide application.

Conclusions. The research resulted in the development of a new highly selective, accelerated and quick spectrophotometric extraction method for the determination of gold directly in the organic phase. It has been established that gold (III) is extracted by chloroform from a highly acidic medium in the presence of chloride ions and DMFA by the hydro-solvate mechanism. The influence of foreign ions that do not interfere with the definition of gold in large multiples has been studied. The developed method was tested on the analysis of production solutions, concentrates and rocks without separation of accompanying elements. The method is easy to perform, highly selective and rapid.

The developed method of extraction-spectrophotometric determination of gold is therefore suggested for the analysis of industrial solutions, wastewater, concentrates, ores, rocks and other materials with complex chemical composition without the separation of the corresponding elements directly in the organic phase.

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АЛТЫНДЫ (III) ИНЕРТТІ ОРГАНИКАЛЫҚ ЕРІТКІШТЕРМЕН ІРІКТЕУ ЭКСТРАКЦИЯСЫ ЖӘНЕ ТІКЕЛЕЙ ОРГАНИКАЛЫҚ ФАЗАДА МЕТИЛЕНДІ КӨКПЕН (МГ) АНЫҚТАУ

Аннотация. Органикалық бояғыш қолдану арқылы алтын (III) анықтаудың фотометриялық және экстракциялық-фотометриялық әдістері аз іріктелген. Органикалық реагенттермен алтынның (III) кешенді түзілуі су фазасында жүреді, жанама иондар боялған кешенді қосылыс түзеді және алтынды анықтауға бөгет жасайды.

Соңғы уақытта элемент анықтау әдістерінің селективтілігін арттыру үшін жаңа тәсіл – инертті органикалық еріткіштермен элементтердің түссіз кешенін таңдап алу экстракциясы қолданылады, онда кезектегі органикалық бояғыштарды тұндырғышқа қосу және оларды тікелей органикалық фазада кешенді түзілісі жүреді.

Жұмыста инертті органикалық еріткіштері бар және тікелей органикалық фазада МГ кешенді түзу арқылы алтынның (III) хлоридті кешенінің таңдаулы тұндырмасына негізделген жаңа селективті, қарапайым әдіс талқыланады.

Алтынның (III) бастапқы ерітіндісінің 1мг/мл концентрациясы алтын хлориді тұзынан дайындалады. Ерітіндінің титрі Мор тұзымен потенциометриялық титрлеу арқылы орнатылады. МГ су ерітіндісі қолданылады. Алтын (III) кешені және реагенттер тұндырмасының спектрін СФ-26 спектрофотометрде түсіреді, ℓ=1 см тең. Ерітіндінің оптикалық тығыздығы КФК-2 фотоэлектроколориметрінде өлшенеді. Тәжірибе нәтижесі көрсеткендей, хлорид-иондар және диметилформамидтің (ДМФА) қатысуы негізінде күшті қышқылды ерітінділерден алтын (III) хлороформмен жақсы тұндырылады. ДМФА болмаған жағдайда алтын (III) тұнбаға түспейді. Сутегі иондары, хлорид иондар және ДМФА концентрациясына байланысты алтынды (III) хлороформмен тұнбаға түсіруді зерттеу жұмыстары көрсеткендей, алтын (III) тұндырудың оңтайлы шарттары: сутегі иондары бойынша 0,50-6,0 г-ион/л; хлорид иондары бойынша 0,06-2,5 г-ион/л және ДМФА бойынша 13 -26 % (көлемі негізінде), фазаларды сілку ұзақтығы – 5-10 с. Су және органикалық фазалардың бірдей көлемінде алтын (III) бөлу бірреттік тұндыруда 99,9% құрайды және 20:1 фаза көлемінің арақатынасына дейін өзгермейді.

Көрсетілген оңтайлы жағдайда тепе-теңдікті жылжыту әдісімен тұндырылатын алтын (III) хлоридті кешен құрамы анықталады. Бұл үшін алтын (III) тұндырмасының концентрацияға тәуелділігі зерттеледі: 1) хлорид-иондары (1,0 г - ион/л), ДМФА (20%) тұрақты концентрациясы және $NaCl$ ерітіндісін қосу арқылы жасалатын ион күші барысында сутегі иондары (1,0 г-ион/л); 2) сутегі иондары (1,0 г-ион/л), ДМФА (20%) тұрақты концентрациясы және ион күші барысында хлорид-иондар (0,01-0,34 г-ион/л); 3) сутегі иондары (1,0 г-ион/л), хлорид-иондарының (1,0 г-ион/л) тұрақты концентрациясы және ион күші кезіндегі ДМФА (5-13%).

Зерттеу нәтижесінде тікелей органикалық фазада алтын анықтаудың жаңа жоғары селективті, жылдамдатылған және қарапайым тұндырмалы-спектрофотометриялық әдісі әзірленеді. Тәжірибе барысында анықталғандай, алтын (III) хлорид-ионы және гидрат-сольватты механизм бойынша ДМФА қатысуымен күшті қышқылды ортадан хлороформмен тұнбаға түседі. Көпеселік мөлшерде алтын анықтауға бөгет болмайтын басқа иондар әсері зерттеледі. Жасалған әдіс өндірістік ерітінді, концентрат және жынысты қосалқы элементтерді бөлмей талдауда тексеріледі. Әдіс қарапайым орындау арқылы, жоғары талдау бойынша экспрессиямен ерекшеленеді.

Осылайша алтынды тұндыру-спектрофотометриялық анықтау негізінде жасалған әдіс өндірістік ерітінді, ағынды су, концентрат, кен, тікелей органикалық фазада жанама элементтерді бөлмей материалдардың химиялық құрамы бойынша жыныс және басқа күрделі талдау жасауға ұсынылады.

Түйін сөздер: фотометриялық әдіс, алтын, кешенді қосылыстар, хлороформ, тұндыру.

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ИЗБИРАТЕЛЬНАЯ ЭКСТРАКЦИЯ ЗОЛОТА (III) ИНЕРТНЫМИ ОРГАНИЧЕСКИМИ РАСТВОРИТЕЛЯМИ И ОПРЕДЕЛЕНИЕ ЕГО МЕТИЛЕНОВЫМ ГОЛУБЫМ (МГ) НЕПОСРЕДСТВЕННО В ОРГАНИЧЕСКОЙ ФАЗЕ

Аннотация. Существующие фотометрические и экстракционно-фотометрические методы определения золота (III) с применением органических красителей малоизбирательны. Так как комплексообразование золота (III) с органическими реагентами происходит в водной фазе, в которой сопутствующие ионы также образуют окрашенные комплексные соединения и мешают определению золота.

В последнее время для повышения селективности методов определения элементов применяют новый приём – избирательная экстракция бесцветных комплексов элементов инертными органическими растворителями, с последующим добавлением к экстракту органических красителей и комплексообразования их непосредственно в органической фазе**.**

В настоящей работе обсуждается новый селективный, простой метод, основанный на избирательной экстракции хлоридного комплекса золота (III) с инертными органическими растворителями и комплексообразование его с МГ непосредственно в органической фазе.

Исходный раствор золота (III) концентрацией 1мг/мл готовили из соли хлоридного золота. Титр раствора устанавливали потенциометрически титрованием с солью Мора. Использовали водный раствор МГ.

Спектры экстрактов комплексов золота (III) и реагента снимали на спектрофотометре СФ-26, ℓ=1 см. Оптическую плотность раствора измеряли на фотоэлектроколориметре КФК-2. Опыты показали, что золото (III) из сильнокислых растворов в присутствии хлорид-ионов и диметилформамида (ДМФА) хорошо экстрагируется хлороформом. В отсутствии ДМФА золото (III) не экстрагируется. Исследование экстракции золота (III) хлороформом в зависимости от концентрации водород-ионов, хлорид-ионов и ДМФА показало, что оптимальными условиями экстракции золота (III) являются: 0,50 – 6,0 г-ион/л по водород-ионов; 0,06 – 2,5 г-ион/л по хлорид-ионов и 13 – 26 % (по объёму) по ДМФА, продолжительность встряхивания фаз 5–10 с. При равных объёмах водной и органической фаз извлечение золота (III) при однократной экстракции составляет 99,9 % и не изменяется до соотношения объёмов фаз 20:1.

В указанных оптимальных условиях определён состав экстрагирующегося хлоридного комплекса золота (III) методом сдвига равновесия. Для этого изучена зависимость экстракции золота (III) от концентрации: 1) водород-ионов (0,030 - 0,96 г-ион/л) при постоянных концентрациях хлорид-ионов (1,0 г-ион/л), ДМФА (20%) и ионной силе ($\mu = 1$), создаваемой добавлением раствора NaCl; 2) хлорид-ионов (0,01 - 0,34 г-ион/л), при постоянных концентрациях водород-ионов (1,0 г-ион/л), ДМФА (20%) и ионной силе ($\mu = 1$); 3) ДМФА (5 – 13%), при постоянных концентрациях водород-ионов (1,0 г-ион/л), хлорид-ионов (1,0 г-ион/л) и ионной силе ($\mu = 1$).

В результате исследования разработан новый высокоизбирательный, ускоренный и простой экстракционно-спектрофотометрический метод определения золота непосредственно в органической фазе. Установлено, что золото (III) экстрагируется хлороформом из сильнокислой среды в присутствии хлорид-ионов и ДМФА по гидратно-сольватному механизму. Изучено влияние посторонних ионов, которые не мешают определению золота в больших кратных количествах. Разработанный метод проверен на анализе производственных растворов, концентратов и пород без отделения сопутствующих элементов. Метод отличается простотой выполнения, высокой избирательностью и экспрессностью.

Таким образом, разработанный метод экстракционно-спектрофотометрического определения золота рекомендуется для анализа производственных растворов, сточных вод, концентратов, руд, пород и других, сложных по химическому составу материалов без отделения сопутствующих элементов непосредственно в органической фазе.

Ключевые слова: фотометрический метод, золото, комплексное соединение, хлороформ, экстракция.

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PROSPECTS FOR THE INTEGRATED USE OF SLAG WASTES FROM FERROCHROME PRODUCTION FOR HEAT-RESISTANT MATERIALS

Abstract. The research results of physicochemical and physicotechnical properties of slag wastes from ferrochrome production as raw materials for heat-resistant materials are presented. Chemical and mineralogical composition of slag from high-carbon ferrochrome production and slag from low-carbon ferrochrome production, as well as their constituent main crystalline phases, represented by magnesium and calcium aluminosilicates of complex composition, have been determined by physicochemical research methods. According to X-ray phase analysis, the slag from the high-carbon ferrochrome production is represented mainly by forsterite Mg_2SiO_4, spinel $MgAl_2O_4$, partially amorphous glass phase and admixture of calcium orthosilicate Ca_2SiO_4. In the slag from the low-carbon ferrochrome production, the main crystalline phase is calcium orthosilicate γ-Ca_2SiO_4, as well as magnesium orthosilicate forsterite Mg_2SiO_4. The research results of specific surface area, average particle size determination and sieve analysis have shown that the slag from the low-carbon ferrochrome production is a finely dispersed gray powder with the following characteristics: the specific surface area – 295 m^2/kg, the average particle size – 6.8 μm, the true density – 3.01 g/cm^3, the bulk density – 739 kg/m^3. The research of the physicochemical and physicotechnical properties has established that in terms of chemical, mineralogical composition and refractoriness indices, the slags from the high-carbon ferrochrome and low-carbon ferrochrome productions can be valuable raw materials for heat-resistant materials.

Key words: slag wastes from high-carbon and low-carbon ferrochrome production, refractoriness, specific surface area, calcium and magnesium orthosilicates, heat-resistant materials.

Introduction. There is no domestic production of fireclay refractory materials and products in mass demand in Kazakhstan [1]. The need for heat-resistant materials and products is fully covered only by imports from the CIS countries, primarily from Russia and Ukraine.

At the same time, there are various types of technogenic mineral raw materials in the republic, which, with appropriate processing using special technologies and component compositions, can serve as components for production of high-grade heat-resistant materials that are not inferior in their basic properties to traditional fireclay heat-resistant materials.

In Kazakhstan, slag dumps of Aktobe Ferroalloy Plant of TNC Kazchrome JSC have accumulated more than 15 million tons of slag wastes, of which 5 million tons are slags from production of high-carbon ferrochrome, and about 8-9 million tons are dusty dispersed slag from production of low-carbon ferrochrome.

Costs for disposal of slag wastes and maintenance of slag dumps are a big economic and environmental problem facing the enterprise. In the processing of slags from the production of ferrochrome, the problem of ecological safety is no less important, since chromium is recognized as a dangerous carcinogen [2, 3].

A distinctive feature of the slags from the production of ferrochrome is their refractory and heat-resistant properties [4, 5].

The research of the physicochemical properties and mineralogical composition of slag wastes from ferroalloy production made it possible to draw a conclusion about the possibility and expediency of their use as components of heat-resistant binders and composite heat-resistant materials.

Considering refractory properties, in [6] it is proposed to use high-carbon ferrochrome slag as a component of refractory materials. At the same time, it is proposed to use finely ground slag from production of high-carbon ferrochrome and bag dust of gas cleaning from furnaces for high-carbon ferrochrome production as raw materials for refractory brick manufacture.

At present, the slag of the current output high-carbon ferrochrome production is processed in the slag processing shop, where the slag is crushed and residual metallic ferrochrome is extracted from it, and the crushed slag is sold as crushed stone for road construction [7].

The low-carbon ferrochrome production annually produces over 200,000 tons of slag, which is sent to the dumps of the enterprise.

According to the chemical and mineralogical characteristics, slags from the production of low-carbon ferrochrome [8, 9, 10], characterized by a tendency to self-decomposition and transformation into fine powder [11], are among the wastes of ferroalloy production.

Analysis of published works showed a small amount of research and proposed directions for the use of the slag from the low-carbon ferrochrome production in foundries for self-hardening mixture manufacture, as a raw material for cement production, in road construction as a mineral filler for asphalt concrete preparation [12, 13].

Currently, development of effective types of composite binders from natural and technogenic mineral raw materials is one of the urgent scientific, technical, economic and environmental problems [14-17].

Methods. *The chemical analysis* of the studied samples of the slags from the high-carbon ferrochrome and low-carbon ferrochrome production was carried out according to the procedure adopted for inorganic materials [18].

The X-ray phase analysis (XRA) of the slags was carried out using DRON-3 diffractometer with CuK_α radiation with a nickel filter. The speed of movement of the goniometer counter was 8 deg/min. The tube voltage – 40 kV, the tube current – 20 mA.

The surface morphology research of the slag samples was carried out using JSM-6490LV scanning electron microscope (JEOL, Japan), with which the elemental chemical composition was also determined by the energy dispersive method.

The granulometric composition and the bulk density of the crushed and dispersed slags were determined according to the method used in industry [19].

The specific surface area and the average particle size of the slags were determined by the method of air permeability of dispersed materials using PSKh-K computer multifunctional device manufactured by Ruspribor LLC (Russia).

The sieve analysis of the slag was carried out using “Analysette 3” vibrating sieving device from FRITSCH (Germany).

The refractoriness of the slags was determined according to the standard procedure for refractory raw materials [20].

Results and discussion. The results of determining the granulometric composition and the bulk weight of the slags from the ferrochrome production according to the standard method are presented in table 1.

Table 1 – The granulometric composition and the bulk weight of the slags from the ferrochrome production

Indicators	Content of fractions in the ferrochrome slag, wt. %	
	high-carbon	low-carbon
Granulometric composition:	31.9	4.1
fraction of more than 5 mm	31.1	23.4
fraction of 3-5 mm	4.5	18.5
fraction of 2-3 mm	2.5	17.5
fraction of 1-3 mm	4.5	17.5
fraction of 0.5-1 mm	25.5	19.0
fraction of less than 0.5 mm	12.7	9.5
including fraction of 0.088-0.5 mm		
fraction of less than 0.088 mm	12.7	9.5
Bulk weight, g/cm^3	1.92	1.58

The average chemical composition and refractoriness indices of the slags from the high-carbon ferrochrome and low-carbon ferrochrome production are presented in Table 2.

Table 2 – The chemical composition and refractoriness of the slags from the ferrochrome production

Type of slag from the ferrochrome production	Content of oxides, %						Refractoriness, ºC
	Cr_2O_3	MgO	Al_2O_3	SiO_2	CaO	FeO	
Slag from the high-carbon ferrochrome production	5.1	43.1	17.8	31.2	2.4	1.1	1630
Slag from the low-carbon ferrochrome production	5.2	13.4	7.1	29.3	45.2	1.1	1360

The results of determining the mineralogical composition of the slags from the ferrochrome production by the method of X-ray phase analysis are presented in Table 3.

Table 3 – The mineralogical composition of the slags from the ferrochrome production

Type of slag from the ferrochrome production	Phase composition of minerals according to the X-ray phase analysis
Slag from the high-carbon ferrochrome production	Mg_2SiO_4 (main phase) (Mg, Fe) (Al, Cr)$_2$O$_4$ Ca_2SiO_4 – admixture
Slag from the low-carbon ferrochrome production	Ca_2SiO_4 (main phase) Mg_2SiO_4 (Mg, Fe) (Al, Cr)$_2$O$_4$

According to the X-ray phase analysis, presented in figure 1, the mineralogical composition of the slag from the high-carbon ferrochrome production is represented by the following main minerals: forsterite Mg_2SiO_4 (d=3.89, 3.48, 2.77, 2.27, 2.16, 1.75, 1.49 Å), spinel $MgAl_2O_4$ (d=4.81, 4.25, 2.47, 1.58 Å), partially amorphous glass phase and impurity of calcium orthosilicate Ca_2SiO_4.

In this case, in the system MgO – Al_2O_3 – SiO_2, the formation of spinel – forsterite solid solutions is possible [21].

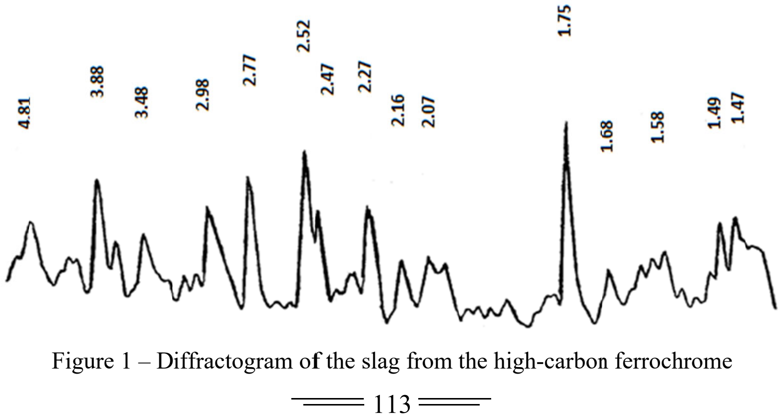

Figure 1 – Diffractogram of the slag from the high-carbon ferrochrome

The diffractogram of the slag from the low-carbon ferrochrome production, shown in figure 2, confirms the phases of calcium orthosilicate Ca_2SiO_4 (basic phase) and forsterite Mg_2SiO_4.

The X-ray research of the slag from the low-carbon ferrochrome production showed that the main crystalline phase in it is calcium orthosilicate γ-Ca_2SiO_4, and there is also α-Ca_2SiO_4 phase, and magnesia silicates in the form of magnesium orthosilicate – forsterite Mg_2SiO_4.

The diffractogram of the slag (figure 2) shows the most intensive diffraction reflections with d = 3.81; 2.79; 2.74; 1.88; 1.62 Å correspond to γ-Ca_2SiO_4 phase.

The diffraction maxima with d = 2.71; 2.66, 1.72 Å, obviously, are due to the presence of α-Ca_2SiO_4 in the slag. The presence of this crystalline phase in the slag indicates that the modification transformations $\alpha \rightarrow \alpha'_H \rightarrow \alpha'_L \rightarrow \beta \rightarrow \gamma$ did not occur completely, and a small amount of α-Ca_2SiO_4 is present in the system.

The presence of forsterite Mg_2SiO_4 is indicated by the reflections with d = 3.81; 2.74; 2.66 Å.

The research results of specific surface area, average particle size determination and sieve analysis have shown that the slag from the low-carbon ferrochrome production is a finely dispersed gray powder with the following characteristics: the specific surface area – 2955 cm^2/g, the average particle size – 6.8 μm, the true density – 3.01 g/cm^3, the bulk density – 739 kg/m^3.

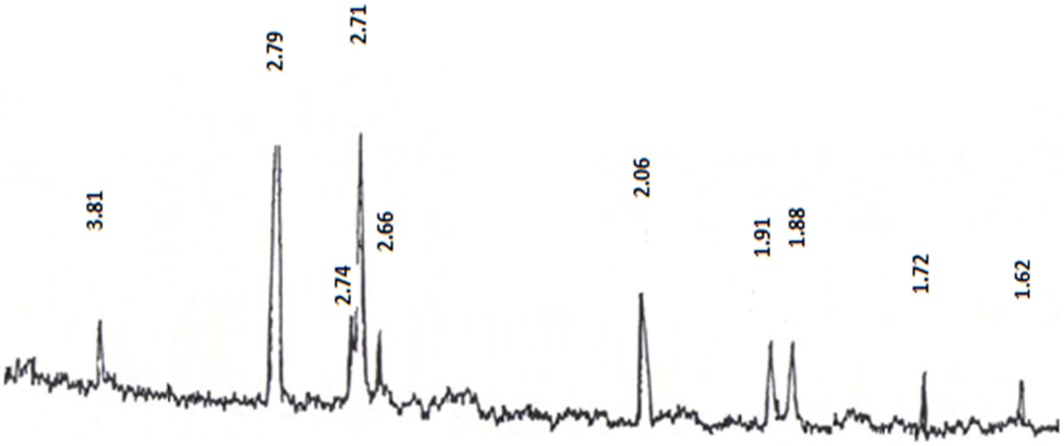

Figure 2 – Diffractogram of the slag from the low-carbon ferrochrome

The results of studying the surface morphology of the slag sample are shown in figure 3.3. The surface of the studied slag sample has a polydisperse character, with both dusty particles and larger particles in the form of detrital and fragmentary material present.

The research of the elemental chemical composition by the spectral analysis showed that the slag composition is characterized by the content of Ca, Si, Mg, Cr, Al elements, which corresponds to the mineralogical composition of the slag.

By the chemical composition, the slag can be referred to the main slags with the lime factor $M_O = 2.16$, determined by the percentage ratio (%CaO+% MgO) / (%SiO_2+%Al_2O_3), with the low modulus of activity Ma = 0.18, determined by the percentage ratio of the content of Al_2O_3 and SiO_2 in the slag.

The results of the physicochemical research have shown that minerals of the slags from the high-carbon and low-carbon ferrochrome production, such as spinel $MgAl_2O_4$, as well as calcium orthosilicate Ca_2SiO_4, and magnesium orthosilicate forsterite Mg_2SiO_4 have high refractoriness. So, the mineral larnite Ca_2SiO_4 is the most refractory slag mineral, it melts congruently at 2130°C, the mineral spinel $MgAl_2O_4$ melts at 2105°C, and refractoriness of the mineral forsterite Mg_2SiO_4 reaches 1900°C [22, 23].

Due to these specific properties, the slag from the low-carbon ferrochrome production can also be used as a raw component of heat-resistant binders used in heat-resistant materials' production.

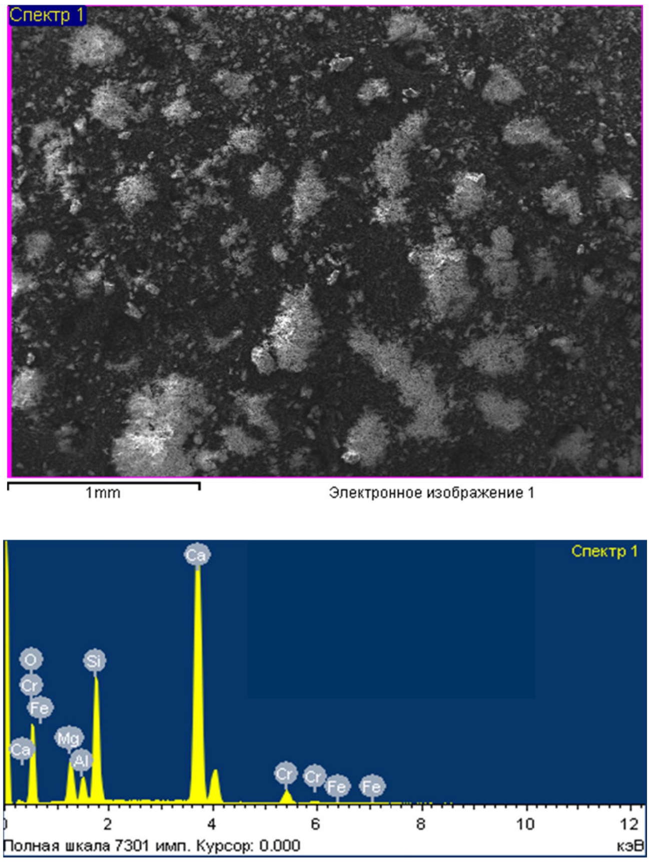

Figure 3 – The surface morphology and the elemental composition when scanning the slag sample of low-carbon ferrochrome production

Conclusion. As a result of the research carried out on the physicochemical and physicotechnical properties, it has been established that, in terms of chemical, mineralogical composition and refractoriness indices, the slags from the high-carbon ferrochrome and low-carbon ferrochrome production can be valuable raw materials for heat-resistant materials.

At the same time, the crushed slag from the high-carbon ferrochrome production, due to its chemical-mineralogical composition and refractoriness, is recommended as a filler for heat-resistant materials.

The dusty self-disintegrating dispersed slag from the low-carbon ferrochrome production is a ready-made component for heat-resistant binders, since when using this slag, the stage of its fine grinding can be excluded.

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ФЕРРОХРОМ ӨНДІРІСІНІҢ ШЛАК ҚАЛДЫҒЫН ЫСТЫҚҚА ТӨЗІМДІ МАТЕРИАЛДАРҒА КЕШЕНДІ ҚОЛДАНУ МҮМКІНДІГІ

Аннотация. Қазақстанда жаппай сұранысқа ие шамотты ыстыққа төзімді материалдар мен өнім өндірісі дамымаған. Ыстыққа төзімді материалдар мен бұйымдарға қажеттілік ТМД елдерінен, ең алдымен Ресей мен Украинадан импортпен толықтай қамтамасыз етіледі.

Сонымен бірге, республикада техногендік минералды шикізаттың алуан түрлері бар, олар арнайы технологиялар мен компоненттік құрамды қолдану барысында өңдеу арқылы негізгі қасиеттері жағынан дәстүрлі шамотты ыстыққа төзімді материалдардан кем түспейтін жоғары сапалы ыстыққа төзімді материал өндіруге қызмет етеді.

Қазақстанда «ТҰК Қазхром» АҚ Ақтөбе ферроқорытпа зауытының шлак үйіндісінде 15 миллион тоннадан астам шлак қалдықтары жинаалған, оның 5 миллион тоннадан астамы – жоғары көміртекті феррохром өндіріс шлагы, ал шамамен 8-9 миллион тоннасы – аз көміртекті феррохром өндірісінің шаң тәрізді ұнтақ шлагы. Шлак қалдығын орналастыруға және сақтауға байланысты шығын кәсіпорынның маңызды экономикалық және экологиялық мәселесі болып есептеледі.

Ферроқорытпа өндірісіндегі шлак қалдығының физико-химиялық қасиеттері мен минералогиялық құрамын зерттеу оның ыстыққа төзімді байланыстырғыш мен композитті ыстыққа төзімді материал компоненттері ретінде қолдану мүмкіндігі мен тиімділігі туралы қорытынды жасауға мүмкіндік берді.

Қазіргі кезде жоғары көміртекті феррохром өндіріс шлактары қайта өңдеу цехында өңделеді, онда шлакты ұсақтап, одан феррохром металының қалдықтары алынады, ал ұсақталған шлак жол құрылысы үшін қиыршық тас ретінде сатылады. Нашар көміртекті феррохром өндіріс шлактары пайдаланылмайды, ал төмен көміртекті феррохром өндірісі жыл сайын кәсіпорын үйіндісіне жіберілетін 200 000 тоннадан астам шлак шығарады.

Қазіргі уақытта техногендік минералды шикізаттан ыстыққа төзімді құрама байланыстырғыштардың тиімді түрін жасау – маңызды ғылыми-техникалық, экономикалық және экологиялық мәселелердің бірі.

Мақалада феррохром өндіріс шлак қалдықтарының ыстыққа төзімді материалдардың шикі заттар ретінде физика-химиялық және физика-техникалық зерттеулердің нәтижелері келтірілген. Физика-химиялық зерттеу әдістерімен көміртегі жоғары және көміртегі төмен феррохром өндіріс шлагының химия-минералогиялық құрамы және күрделі құрамды магний және кальций алюмосиликатынан тұратын негізгі кристалды фазалар анықталған. Рентгенофазалық талдау бойынша көміртегі жоғары феррохром өндіріс шлагын форстерит Mg_2SiO_4, шпинель $MgAl_2O_4$, жартылай аморфты шыны фаза және қоспалы кальций ортосиликаты Ca_2SiO_4 құрайды. Көміртегі төмен феррохром өндірісінің шлак құрамында негізгі кристалды фазалар кальций ортосиликаты Ca_2SiO_4 және магний ортосиликаты – форстерит Mg_2SiO_4. Үлестік бетін, бөлшектің орташа мөлшерінің анықтау, електі талдау зерттеу нәтижелері көміртегі аз феррохром өндірісінің шлак қалдығынына мынадай сипаттама беруге болады: үлестік беті 295 $см^2$/кг, орташа бөлшек мөлшері 6,8 мкм, шынайы тығыздығы 3,01 г/$см^3$, үйілген тығыздығы 739 кг/$м^3$, сұр түсті ұнтақ болып саналатынын көрсетті.

Химиялық құрамы бойынша шлактың (% CaO +% MgO) / (% SiO_2 +% Al_2O_3) пайыздық арақатынасы негізінде анықталатын негізді модулі M_O = 2.16 негізгі шлак ретінде, ал құрамындағы Al_2O_3 және SiO_2 мөлшерінің қатынасы бойынша анықталатын модулі Ма = 0,18 арқылы белсенділігі әлсіз шлактарға жіктеуге болады. Жүргізілген физика-химиялық және физика-техникалық қасиетін зерттеу бойынша көміртегі жоғары және көміртегі төмен феррохром өндіріс шлактары химиялық және минералогиялық құрамы әрі отқа төзімділік көрсеткіштері бойынша ыстыққа төзімді материалдардың толыққанды шикі заттар ретінде қолдануы мүмкін.

Түйін сөздер: көміртегі жоғары және көміртегі төмен феррохром өндірісінің шлак қалдықтары, отқа төзімділік, үлестік бет, кальций және магний ортосиликаты, ыстыққа төзімді материалдар.

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ПЕРСПЕКТИВЫ КОМПЛЕКСНОГО ИСПОЛЬЗОВАНИЯ ШЛАКОВЫХ ОТХОДОВ ФЕРРОХРОМОВОГО ПРОИЗВОДСТВА ДЛЯ ЖАРОСТОЙКИХ МАТЕРИАЛОВ

Аннотация. В Казахстане отсутствует отечественное производство имеющих массовый спрос шамотных жаростойких материалов и изделий. Потребность в жаростойких материалах и изделиях полностью покрывается за счет импорта из стран СНГ, в первую очередь из России и Украины.

В то же время в республике имеются различные виды техногенного минерального сырья, которые при соответствующей переработке по специальным технологиям и компонентным составам, могут послужить компонентами для производства полноценных жаростойких материалов, не уступающих по своим основным свойствам традиционным шамотным жаростойким материалам.

В Казахстане в шлаковых отвалах Актюбинского завода ферросплавов АО ТНК «Казхром» накоплено более 15 млн тонн шлаковых отходов, из них более 5 млн тонн составляют шлаки производства высокоуглеродистого феррохрома, а около 8-9 млн тонн составляет пылевидный дисперсный шлак производства низкоуглеродистого феррохрома.

Затраты на размещение шлаковых отходов и содержание шлаковых отвалов являются большой экономической и экологической проблемой, стоящей перед предприятием.

Изучение физико-химических свойств и минералогического состава шлаковых отходов ферросплавного производства позволило сделать вывод о возможности и целесообразности их использования в качестве компонентов жаростойких вяжущих и композиционных жаростойких материалов.

В настоящее время шлак производства высокоуглеродистого феррохрома текущего выхода перерабатывается в цехе по переработке шлаков, где шлак дробится и из него извлекается остаточный металлический феррохром, а дробленый шлак продается как щебень для строительства автодорог [3].

Шлак производства низкоуглеродистого феррохрома практически не используется, при производстве низкоуглеродистого феррохрома ежегодно образуется более 200 000 тонн шлака, направляемого в отвалы предприятия.

В настоящее время разработка эффективных видов композиционных жаростойких вяжущих материалов из техногенного минерального сырья является одной актуальных научно-технических, экономических и экологических проблем.

В статье приведены результаты исследований физико-химических и физико-технических свойств шлаковых отходов феррохромового производства как сырьевых компонентов для жаростойких материалов. Методами физико-химических исследований определены химико-минералогический состав шлака производства высокоуглеродистого феррохрома и шлака производства низкоуглеродистого феррохрома, а также составляющие их основные кристаллические фазы, представленные магниевыми и кальциевыми алюмосиликатами сложного состава. По данным рентгенофазового анализа, шлак производства высокоуглеродистого феррохрома представлен, в основном, форстеритом Mg_2SiO_4, шпинелью $MgAl_2O_4$, частично аморфной стеклофазой и примесью ортосиликата кальция Ca_2SiO_4. В шлаке производства низкоуглеродистого феррохрома основной кристаллической фазой является ортосиликат кальция γ-Ca_2SiO_4, а также ортосиликат магния форстерит Mg_2SiO_4. Результаты исследований удельной поверхности, определения среднего размера частиц и результаты ситового анализа показали, что шлак производства низкоуглеродистого феррохрома представляет собой тонкодисперсный порошок серого цвета со следующими характеристиками: удельная поверхность 295 м^2/kг, средний размер частиц 6,8 мкм, истинная плотность - 3,01 г/см^3, насыпная плотность - 739 кг/м^3.

По химическому составу шлак можно отнести к основным шлакам с модулем основности M_O = 2,16, определяемым по процентному соотношению (%CaO + %MgO) / (%SiO_2+%Al_2O_3), с низким модулем активности Ма = 0,18, определяемым по процентному соотношению содержания в шлаке Al_2O_3 и SiO_2.

В результате проведенных исследований физико-химических и физико-технических свойств установлено, что по химическому, минералогическому составу и показателям огнеупорности шлаки производства высокоуглеродистого феррохрома и низкоуглеродистого феррохрома могут быть полноценными сырьевыми ресурсами для жаростойких материалов.

Ключевые слова: шлаковые отходы производства высокоуглеродистого и низкоуглеродистого феррохрома, огнеупорность,удельная поврхность, ортосиликаты кальция и магния, жаростойкие материалы.

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RAW MATERIALS IDENTIFICATION AND MANUFACTURED PRODUCTS AUTHENTICATION TECHNOLOGIES

Abstract. DNA technologies for the raw grapes identification and the authentication of wine products made from them are popular scientific and practical direction with the prospect of introducing developments into the quality management system. The molecular genetic approaches development to the technical grape varieties' genetic identification and wines DNA authentication produced from them was the aim of this work. Sample preparation of experimental wines was carried out by exposure in a mixture with a precipitant and a co-precipitant, followed by wine debris precipitation. The nucleic acids extraction from wine debris was carried out with the same commercial kit as from the pulp of a mature grape fruit, but with an additional lysis solution modification. The obtained results indicated the selected conditions effectiveness for sample preparation, DNA isolation and PCR for amplification of the analyzed *Vitis vinifera* L. *UFGT*-gene loci. The described strategy for the raw materials geno-identification and the manufactured products authentication is based on the polymorphic positions of diagnostically significant *UFGT*-gene-associated groups analysis, interpreted by sequencing the corresponding PCR product.

Key words: grapes, wine, variety, *Vitis vinifera* L, sample preparation, extraction, DNA, identification, authentication, gene, *UFGT*, SNP, PCR, sequencing.

Introduction. The development of DNA technologies for the raw grapes identification and the wine products made from them authentication is a popular area of molecular genetic research methods, whose promising developments can be introduced into the quality management system to ensure traceability of the entire product life cycle and counterfeit products monitoring [1-6].

Wines DNA authentication is a technological process of verifying their authenticity by geno-identification of the main plant component (technical grape varieties) through molecular genetic analysis of the extracted of *Vitis vinifera* L. nucleic acids. At the same time, the yield of isolated from wine debris DNA is significantly reduced in the vinification process up to its complete absence by wine aging [7-11].

Among genetic markers multitude, SNP-markers have a high identification potential, which are suitable for the raw materials genetic identification [12-14] and wines DNA authentication [8, 15, 16] due to discrimination of individual genotypes of *Vitis vinifera* L. and identification of combined genotypes groups, including single-varietal and blended wines in the analysis of fragmented nucleic acid of low quality and yield.

The research purpose is the molecular genetic approaches development to the genetic identification of technical grape varieties and DNA authentication of wines produced from them.

Material and research methods. The work was carried out on the basis of the Intersectoral Scientific and Technical Center for Monitoring the Quality of Food Products of the All-Russian Scientific Research Institute of Brewing, Beverage and Wine Industry – Branch of V.M. Gorbatov Federal Research Center for Food Systems of RAS.

Research objects: technical grape varieties and experimental young wines produced from them.

Sample preparation of technical grape varieties was carried out by extracting 50 mg of the ripe fruit pulp and placing the selected sample in an Eppendorf test tube.

Sample preparation of experimental wines was carried out by exposure in a mixture with a precipitant (isopropanol) and a co-precipitant (polyvinylpyrrolidone), followed by centrifugal wine debris precipitation.

When using only a precipitant [17], they were poured into 15 ml Falcon tubes, each 8 ml of the test wine samples. Then 6 ml of cold isopropanol was added, smoothly stirring the mixture until homogeneous state by manually test tube shaking the. The tubes were kept with tightly closed lids at a temperature of -20 °C for 1-14 days in a freezer. After the exposure, the tubes were centrifuged in a CM-6M centrifuge (Elmi, Latvia) at 3000 rpm for 1 hour. The supernatant was decanted off, and the precipitate was dried by keeping the tubes upside down under a filter paper layer.

When using a precipitant and a co-precipitant, it was poured into 1.5 ml Eppendorf tubes with 10 mg of polyvinylpyrrolidone K30, 900 µl of isopropanol, previously poured into them, the mixture was stirred until homogeneous state on a Microspin FV-2400 vortex centrifuge (Biosan, Latvia). Then, 100 µl of the test red wines samples were added, stirring the mixture until homogeneous state by smooth manual shaking of the test tube. The tubes with tightly closed lids were kept at room temperature for 10 minutes to 14 days. After exposure, the tubes were centrifuged in a CM-50 microcentrifuge (Elmi, Latvia) at 15,000 rpm for 10 min. The supernatant was disposed of using an FTA-1 aspirator with a trapping flask (Biosan, Latvia).

The extraction of nucleic acids from the grape fruit pulp was carried out with the commercial set "DNA-sorb-S-M" (Central Research Institute of Epidemiology, Russia), and from the precipitated young wine debris - with the same set, but with an additional modification of the lysis solution by adding 4 µl of mercaptoethanol and 100 µl of proteinase K of initial concentration 10 mg/ml.

PCR with isolated DNA samples was performed with a commercial Encyclo Plus PCR kit ("Evrogen ZAO" (Close Joint-stock Company), Russia), which included the necessary components of the reaction mixture (sterile water, buffer system, a mixture of dNTP and Encyclo polymerases).

The list of oligonucleotide primers [14, 15] and thermocycling modes on the Tertsik amplifier (DNA-technology, Russia) are presented in table 1.

Table 1 – Primer kits and thermal cycling modes

Name and sequence of oligonucleotide primers	Thermal cycling modes	PCR-product
Vv1-Fwd: 5′-GCAATGTAATATCAAGTCC-3′ Vv1-Rev: 5′-TTTCTTTCTTTGAGCCATT-3′	×1: 95 °C – 300 s. ×40: 95 °C – 30 s, 58 °C – 30 s, 72 °C – 30 s. ×1: 72 °C – 300 s	705 bp
Vv3-Fwd: 5′-AGCAGAGATGGGGGTGGCTT-3′ Vv3-Rev: 5′-AGCAGGTAAAACCACCTGAA-3′	×1: 95 °C – 300 s. ×40: 95 °C – 30 s, 58 °C – 30 s, 72 °C – 30 s. ×1: 72 °C – 300 s	119 bp
UFGT-F1: 5′-CTTGGCTGCCGTTTTGGA-3′ UFGT-R1: 5′-AGGTAAAACCACCTGAAACT-3′	×1: 95 °C – 300 s. ×40: 95 °C – 10 s, 58 °C – 10 s, 72 °C – 10 s. ×1: 72 °C – 300 s	99 bp

Electrophoretic detection of PCR products in a SE2 horizontal electrophoresis chamber (Helikon, Russia) was carried out in 2.5% agarose gel with 1×TAE buffer stained with ethidium bromide, followed by result visualization in a UV-transilluminator (Vilber Lourmat, France).

Amplicons of the analyzed *UFGT*-gene locus were sequenced on an ABI PRISM 3100 genetic analyzer (Applied Biosystems, USA) with their subsequent alignment in BLAST with the corresponding partial nucleotide sequences of *Vitis vinifera* L.

Results and discussion. The initial stage of technical grape varieties sample preparation, which consisted in extracting and transferring the ripe fruits pulp into test tubes for further DNA extraction procedure, was a balanced approach to the selection of biomaterial from studied raw material.

At the same time, the *Vitis vinifera* L. nucleic acids samples isolated from the raw grapes sample-prepared material by the commercial kit "DNA-sorb-S-M" ensured the achievement of positive PCR results, expressed in the amplification of specific amplicons of the analyzed gene loci.

The electrophoretic results pattern of the *Vitis vinifera* L. *UFGT*-gene loci PCR amplification initiated with sets of well-known primers is shown in figure 1.

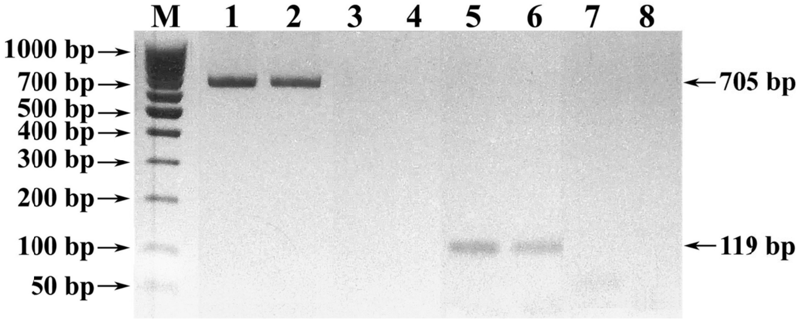

Figure 1 – Electropherogram of the PCR amplification results of the *Vitis vinifera* L. *UFGT*-gene loci

Notations: M) DNA markers 100 bp + 50 bp (SibEnzyme). 1-4) Amplified with Vv1-Fwd and Vv1-Rev primers PCR tests of DNA samples extracted from the ripe grape pulp and precipitated debris of wine material: 1) the ripe grape pulp of Cabernet Sauvignon veriety; 2) the ripe grape pulp of Chardonnay veriety; 3) the precipitated debris of Cabernet Sauvignon wine material; 4) the precipitated debris of Chardonnay wine material; 5-8) Amplified with Vv3-Fwd and Vv3-Rev primers PCR tests of DNA samples extracted from the ripe grape pulp and precipitated debris of wine material: 5) the ripe grape pulp of Cabernet Sauvignon veriety; 6) the ripe grape pulp of Chardonnay variety; 7) the precipitated debris of Cabernet Sauvignon wine material; 8) the precipitated debris of Chardonnay wine material.

Thus, in PCR tests of DNA samples extracted from the industrial grape varieties pulp using a set of DNA-sorb-S-M, specific amplicons were generated, initiated with Vv1-Fwd and Vv1-Rev (705 bp) [14] and Vv3-Fwd and Vv3-Rev (119 bp) [15] primers, respectively. At the same time, in PCR tests of DNA samples isolated from precipitated wine debris, by a similar extraction method, specific PCR products were not amplified (figure 1).

Thus, the obtained results indicated the effectiveness of the selected conditions for sample preparation, DNA isolation and PCR for amplification of the analyzed *Vitis vinifera* L. *UFGT*-gene loci in relation to the studied raw grape samples, but not to the wine materials produced from them.

Subsequent extraction of nucleic acids from sample-prepared wine materials using the DNA-sorb-S-M kit modified with supplemental application of mercaptoethanol and proteinase K to the lysis solution led to a satisfactory PCR result in conjunction with the UFGT-F1 and UFGT-R1 primers that we designed (figure 2).

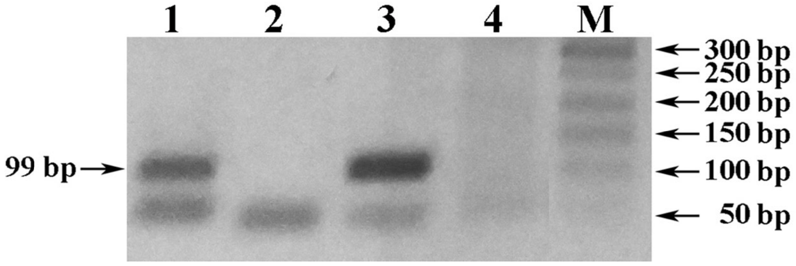

Figure 2 – Electropherogram of the PCR amplification result
of the *Vitis vinifera* L. *UFGT*-gene locus with UFGT-F1 and UFGT-R1 primers

Notations: 1-3) PCR tests of DNA sample extracted from the precipitated Cabernet Sauvignon wine material debris: 1) 3 μl of DNA; 2) 4 μl of DNA; 3) 5 μl of DNA added to the PCR reaction mixture; 4) Negative control of DNA extraction. M) DNA length marker 50+ bp DNA Ladder (Evrogen).

This primers set for PCR amplification of the *Vitis vinifera* L. *UFGT*-gene locus by PCR differs from the prototype [15] in that other oligonucleotide sequences are used that initiate the production of specific PCR product with a length of 99 bp with localization in the flanked region (404-502 nt, GenBank A/N: DQ513314) 5 polymorphic positions interpreted by sequencing or HRM analysis during geno-identification of grape varieties and DNA authentication of the wine materials produced from them.

In this case, the PCR sensitivity and reproducibility with the designed primers set (UFGT-F1 and UFGT-R1) turned out to be higher than the prototype (Vv3-Fwd and Vv3-Rev) (figure 3).

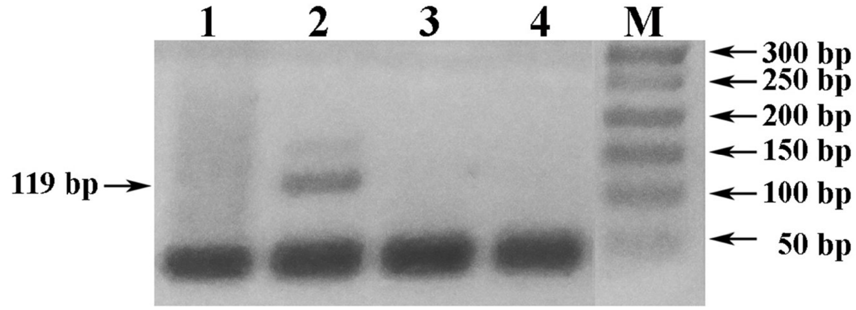

Figure 3 – Electropherogram of the PCR amplification result of the *Vitis vinifera* L. *UFGT*-gene locus with Vv3-Fwd and Vv3-Rev primers

Notations: 1-3) PCR tests of DNA sample extracted from the precipitated Cabernet Sauvignon wine material debris; 1) 3 μl of DNA; 2) 4 μl of DNA; 3) 5 μl of DNA added to the PCR reaction mixture. 4) Negative control of DNA extraction. M) DNA length marker 50+ bp DNA Ladder (Evrogen).

However, it should be noted that the efficiency of the well-known Vv3-Fwd and Vv3-Rev primers, initiating the PCR product amplification with a length of 119 bp, was previously shown in DNA extraction by the Pereira method [17], which is characterized by a relatively high nucleic acids yield isolated from precipitated wine debris, in comparison with other methods [18-21].

The technical grape varieties grouping and breakdown according to the analyzed polymorphic positions profile of the *UFGT*-gene locus is one of the ways of their gene identification and DNA authentication of wines produced from them.

Bioinformatic analysis of nucleotide sequences of the *Vitis vinifera* L. *UFGT*-gene locus allows to distribute technical grape varieties by breaking down into gene-associated groups (table 2).

Table 2 – Polymorphic positions of the *UFGT*-gene locus of *Vitis vinifera* L.

Technical grape variety	Polymorphic positions (INDEL*/SNPs)																
	205	207	220	238	240	257	264	265	272	309	366	375	424*	425	442	459	483
Chardonnay	R	S	S	G	C	A	G	C	T	G	T	Y	-	G	C	C	G
Touriga Brasileira	G	G	G	G	C	A	G	C	T	G	T	T	-	G	C	C	G
Gouveio	G	G	S	G	M	A	G	C	T	G	T	Y	-	G	C	C	G
Donzelinho Tinto	G	G	C	R	M	R	K	C	T	G	T	Y	-	G	C	C	G
Tinta Francisca	G	G	S	R	C	R	K	C	T	R	T	Y	-	G	C	C	S
Alicante Bouschet	G	G	S	R	C	R	K	C	T	R	T	Y	-	G	C	C	S
Tinta Amarela	G	G	S	R	C	R	K	C	T	R	T	Y	-	G	C	C	S
Côdega do Larinho	G	G	S	R	C	R	K	C	T	R	T	Y	-	G	C	C	S
Fernão Pires	A	C	C	G	C	A	G	M	C	A	T	C	-	G	C	T	G
Tinta Roriz	A	C	C	G	C	A	G	M	C	A	T	C	-	G	C	T	G
Malvasia Fina	A	C	C	G	C	A	G	A	C	A	T	C	-	G	C	T	G
Tinto Cão	R	S	C	R	C	R	K	C	Y	R	T	Y	-	G	C	Y	G
Pinot Noir	G	G	S	S	C	R	K	C	T	G	T	T	-	G	C	Y	G
Moscatel Galego	R	S	S	G	C	A	G	C	Y	R	T	Y	-	G	C	Y	G
Merlot	G	G	G	G	C	A	G	C	T	W	W	C	-	K	C	C	C
Tinta Barroca	G	G	G	G	C	A	G	C	T	A	T	C	-	K	C	C	C
Touriga Nacional	G	G	G	G	C	A	G	C	T	R	T	Y	-	K	C	C	S
Touriga Franca	G	G	S	R	C	R	K	C	T	R	T	Y	-	K	C	C	S

Viosinho	R	S	S	G	C	A	G	C	Y	A	T	C	-	G	C	Y	S
Rufete	R	S	C	R	C	A	G	M	C	A	T	C	-	G	M	Y	G
Cabernet Sauvignon	R	S	S	G	C	A	G	C	Y	A	T	C	T	G	C	Y	S
Sousão	R	S	S	G	C	A	G	C	Y	A	T	C	T	G	C	T	S
Cannonao	G	G	S	G	C	A	G	C	T	R	T	C	-	G	C	C	C
Parda	G	G	C	A	C	R	K	C	Y	R	T	Y	-	G	M	C	G
Technical grape variety	Polymorphic positions (INDEL*/SNPs)																
	525	555	560	562	598	600	617	619	636	663	685	762	789	816	841	843	850
Chardonnay	A	M	A	G	A	T	C	A	C	C	A	C	C	T	R	A	A
Touriga Brasileira	A	A	A	G	A	T	C	A	C	C	A	C	C	T	A	A	A
Gouveio	A	M	R	G	A	Y	M	R	Y	Y	A	C	C	T	R	A	A
Donzelinho Tinto	A	C	G	R	A	Y	A	G	T	T	A	Y	M	Y	G	A	W
Tinta Francisca	A	C	R	R	A	T	M	R	Y	Y	A	Y	M	Y	G	W	W
Alicante Bouschet	A	C	R	R	A	T	M	R	Y	Y	A	Y	M	Y	G	W	W
Tinta Amarela	A	C	R	R	A	T	M	R	Y	Y	A	Y	M	Y	G	W	W
Côdega do Larinho	A	C	R	R	A	T	M	R	Y	Y	A	Y	M	Y	G	W	W
Fernão Pires	T	C	A	G	T	T	C	A	C	C	A	C	C	Y	G	A	A
Tinta Roriz	T	C	A	G	W	T	C	A	C	C	A	C	C	Y	G	A	A
Malvasia Fina	T	C	A	G	W	T	C	A	C	C	A	C	C	Y	G	A	A
Tinto Cão	W	C	R	R	A	T	M	R	Y	Y	A	Y	M	C	G	A	W
Pinot Noir	W	M	A	G	A	T	C	A	C	C	W	C	C	T	S	W	A
Moscatel Galego	W	M	A	G	A	T	C	A	C	C	A	C	C	T	R	A	A
Merlot	A	C	A	G	A	T	C	A	C	C	A	C	C	T	G	T	A
Tinta Barroca	A	C	A	G	A	T	C	A	C	C	A	C	C	T	G	T	A
Touriga Nacional	A	M	A	G	A	T	C	A	C	C	A	C	C	T	R	W	A
Touriga Franca	A	C	R	R	A	T	M	R	Y	Y	A	Y	M	Y	G	W	W
Viosinho	W	C	A	G	A	T	C	A	C	C	A	C	C	Y	G	W	A
Rufete	W	C	A	G	W	T	C	A	C	C	A	C	C	T	G	A	A
Cabernet Sauvignon	W	C	A	G	A	T	C	A	C	C	A	C	C	Y	G	W	A
Sousão	W	C	A	G	A	T	C	A	C	C	A	C	C	Y	G	W	A
Cannonao	A	C	R	R	A	T	M	R	Y	Y	A	C	C	T	G	W	A
Parda	A	C	R	G	A	T	M	R	Y	Y	A	C	M	Y	G	A	A

The table below shows 34 polymorphic positions of the *Vitis vinifera* L. *UFGT*-gene locus (33 SNP and 1 INDEL), flanked by the Vv1-Fwd and Vv1-Rev primers, the interpretation of which allows the geno-identification of technical grape varieties by establishing their belonging to a certain gene-associated group by sequencing or HRM analysis of the amplified PCR product with a length of 705 bp.

The generated table is based mainly on the previously presented information [14], which allowed the authors to discriminate 18 different grapes genotypes from 22 studied technical varieties, supplemented by us with two more genotypes (varieties Cannonao and Parda) as reference.

In total, this identification strategy is characterized by the presence of 21 diagnostically significant *UFGT*-gene-associated groups.

With regard to DNA authentication of wine material, the most valuable is the analysis of 5 polymorphic positions of the *Vitis vinifera* L. *UFGT*-gene locus (1 INDEL - 424 nt, 4 SNPs - 425, 442, 459, and 483 nt), flanked as well-known (Vv3-Fwd and Vv3-Rev) [15], and a set of primers designed by us (UFGT-F1 and UFGT-R1).

In total, this DNA authentication strategy is already characterized by the presence of 12 diagnostically significant *UFGT*-gene-associated groups, which are also identified by sequencing or HRM analysis of the corresponding PCR product.

Conclusion. The described strategy of raw grapes geno-identification and DNA-authentication of wine material, based on the detection and interpretation of polymorphic positions (SNP/INDEL) of diagnostically significant UFGT-gene-associated groups by sequencing or HRM analysis, is achieved in a complex of selected conditions for sample preparation, nucleic acid isolation and PCR for amplification of the corresponding gene loci. The practical significance of the work is aimed at introducing developments into the quality management system of raw materials and products based on the standards being developed for the wine industry.

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ШИКІЗАТТЫ ИДЕНТИФИКАЦИЯЛАУ ЖӘНЕ ӨНДІРІЛЕТІН ӨНІМДІ АУТЕНТИФИКАЦИЯЛАУ ТЕХНОЛОГИЯСЫ

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ТЕХНОЛОГИИ ИДЕНТИФИКАЦИИ СЫРЬЯ И АУТЕНТИФИКАЦИИ ПРОИЗВОДИМОЙ ПРОДУКЦИИ

Аннотация. Развитие ДНК-технологий идентификации винограда-сырья и аутентификации произведенной из нее винодельческой продукции является востребованным направлением молекулярно-генетических методов исследования, чьи перспективные разработки могут быть внедрены в систему менеджмента качества с обеспечением прослеживаемости всего жизненного цикла продукта и мониторинга фальсифицированной продукции. ДНК-аутентификация вин – технологический процесс проверки их подлинности геноидентификацией основного растительного компонента (технических сортов винограда) посредством молекулярно-генетического анализа экстрагируемых нуклеиновых кислот Vitis vinifera L. При этом выход выделенной из винного дебриса ДНК значительного сокращается в процессе винификации вплоть до полного ее отсутствия по мере старения вина. Цель исследований – разработка молекулярно-генетических подходов к геноидентификации технических сортов винограда и ДНК-аутентификации производимых из них вин. Работа выполнена на базе Межотраслевого научно-технического центра мониторинга качества пищевых продуктов Всероссийского научно-исследовательского института пивоваренной, безалкогольной и ивнодельческой промышленности – филиала Федерального научного центра пищевых систем им. В.М. Горбатова РАН. Объекты исследований: технические сорта винограда и произведенные из них экспериментальные молодые вина. Пробоподготовку технических сортов винограда проводили извлечением 50 мг мякоти зрелого плода и помещением отобранного образца в пробирку типа Эппендорф. Пробоподготовку экспериментальных вин осуществляли экспозицией в смеси с осадителем (изопропанол) и соосадителем (поливинилпирролидон) с последующим центробежным осаждением винного дебриса. Экстракцию нуклеиновых кислот из мякоти плода винограда осуществляли коммерческим набором «ДНК-сорб-С-М» (ЦНИИ Эпидемиологии, Россия), а из осажденного дебриса молодого вина – этим же набором, но с дополнительной модификацией лизирующего раствора добавлением 4 мкл меркаптоэтанола и 100 мкл протеиназы К исходной концентрации 10 мг/мл. Постановку ПЦР с образцами выделенной ДНК выполняли коммерческим набором реактивов «Encyclo Plus PCR kit» (ЗАО «Евроген», Россия), включающего необходимые компоненты реакционной смеси (стерильная вода, буферная система, смесь dNTP и полимераз Encyclo). Образцы нуклеиновых кислот *Vitis vinifera* L, выделенные из пробоподготовленного материала винограда-сырья коммерческим набором «ДНК-сорб-С-М», обеспечивали достижение положительных результатов ПЦР, выраженных в амплификации специфичных ампликонов анализируемых локусов гена. Последующая экстракция нуклеиновых кислот из пробоподготовленных виноматериалов набором «ДНК-сорб-С-М» в модификации с дополнительным внесением в лизирующий раствор меркаптоэтанола и протеиназы К, приводила к удовлетворительному результату ПЦР в связке со сконструированными нами праймерами UFGT-F1 и UFGT-R1. Данный набор праймеров для амплификации локуса *UFGT*-гена *Vitis vinifera* L. методом ПЦР, отличается от прототипа тем, что используются другие последовательности олигонуклеотидов, инициирующих наработку специфичного ПЦР-продукта длиной 99 bp с локализацией во фланкируемом регионе (404-502 nt, GenBank A/N: DQ513314) 5 полиморфных позиций, интерпретируемых секвенированием или HRM-анализом при геноидентификации сортов винограда и ДНК-аутентификации производимых из них виноматериалов. Группирование и разбивка технических сортов винограда по профилю анализируемых полиморфных позиций локуса *UFGT*-гена является одним из способов их геноидентификации и ДНК-аутентификации производимых из них вин. Биоинформационный анализ нуклеотидных последовательностей локуса *UFGT*-гена *Vitis vinifera* L. позволяет распределить технические сорта винограда разбивкой на ген-ассоциированные группы. Описанная стратегия геноидентификации винограда-сырья и ДНК-аутентификации виноматериала, базирующаяся на детекции и интерпретации полиморфных позиций (SNP/INDEL) диагностически значимых *UFGT*-ген-ассоциированных групп секвенированием или HRM-анализом, достигается в комплексе подобранных условий пробоподготовки, выделения нуклеиновых кислот и постановки ПЦР для амплификации соответствующих локусов гена. Практическая значимость работы направлена на внедрение разработок в систему менеджмента качества сырья и продукции на основе разрабатываемых стандартов для винодельческой промышленности.

Ключевые слова: виноград, вино, сорт, *Vitis vinifera* L, пробоподготовка, экстракция, ДНК, идентификация, аутентификация, ген, *UFGT*, SNP, ПЦР, секвенирование.

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CHEMICAL RESEARCH AND BIOLOGICAL ACTIVITY OF PLANTS OF THE GENUS *ATRAPHAXIS* (*A. SPINOSA*)

Abstract. In this article identifies new sources of obtaining biological substances from plants of the genus *Atraphaxis* (*A. spinosa*) prepared in the Almaty region.

According to well - known methods, the analysis of indicators and standards of raw material quality-humidity, total ash, sulphate ash, insoluble ash in 10% hydrochloric acid-was developed and carried out.

Micro- and macroelements determined by atomic absorption spectroscopy. Analysis of the elemental composition shows that iron predominates from microelements, and sodium, potassium and calcium from macronutrients.

Conditions for obtaining a biologically active complex from the aboveground part of Atraphaxis spinosa developed for the first time. The optimal conditions for obtaining the complex are extractant – 50% ethanol, the ratio of extractant and raw materials – 1:8, double extraction time – 48 hours, temperature – 22 - 26 °C.

The lipophilic composition identified by chromatography-mass spectroscopy. Since lipophilic fractions of plant samples include such classes of compounds as fatty acids; mono-; di-; triglycerides, phospholipids, sterols, Sterol esters, glycolipids, fat-soluble vitamins, they can considered not only as nutritional products, but also as possible pharmacological agents. The content of lipophilic components – 26 organic compounds-was determined. It found that A. spinosa contains a large amount of di - (2-ethylhexyl) phthalate (54.66%) and β-sitosterol (13.11%).

A complex study of plant resources as medicinal raw materials provides for the chemical study of biologically active substances and biological screening of extracts and individual compounds obtained from plants. In most cases, the extract showed a wide range of antibacterial activity against the used strains of microorganisms.

Key words: *Atraphaxis spinosa*, mineral composition, plant quality, lipophilic composition, biological activity, Polygonaceae family.

Introduction. The family *Polygonaceae* includes about 27 genera and 800 species. Kazakhstan species of plants of the genus *Atraphaxis* have not systematically studied; therefore, the study of the chemical composition, the development of methods for the isolation of potentially biologically active substances, the study of biological activity, and the development of new drugs and herbal remedies are relevant [1].

The object of the study was *Atraphaxis spinosa* of the *Polygonaceae* family germinating in the Almaty region of the Republic of Kazakhstan [2-4].

Biologically active substances contained in the plant *Atraphaxis spinosa*. The roots of the plant contain flavonoids. In the aerial part - alkaloids. The leaves of the plant contain tannins. The flavonoids compounds - spinoside. 3,8,3', 4'-tetrahydroxyflavon, luteolin 7-methyl ester, 3-β-L-rhamnopyranoside 3,8,3', 4'-tetrahydroxyflavone, 4'-α-D-glucofuranoside 7-luteolin 7-methyl ester, 4'-β-D-glucofuranosyl-6-β-D-glucopyranoside 7-O-luteolin methyl ester.

Materials and methods. The aerial part of *Atraphaxis spinosa*, which grows in the Almaty region, used as the object of study. In the studied object, the quantitative content of macro- and microelements was determined. The elemental composition determined by atomic absorption spectroscopy on an ASSIN instrument from Karl Zeiss [5].

For determination of the lipophilic composition of the plant, *Atraphaxis spinose* use Soxhlet apparatus. The resulting extract was concentrated under mild conditions (water bath temperature 40-45 ℃) after them, sample concentrate and analyzed on Agilent Technologies 7000 GS / MS system. Component identification carried out automatically by analogy with the known mass spectra of samples stored in the Wiley database [8-18].

Determination of the biological activity of a plant. The plant extracts used in this study coded as AS-1. The following eight strains used in this study, which included two-Gram positive strains; *Staphylococcus aureus* ATCC 6533 and *Staphylococcus epidermidis* ATCC 12228. Four-Gram negative strains, which included;

Escherichia coli ATCC 10536, *Pseudomonas aeruginosa* ATCC 15442, *Klebsiella pneumoniae* ATCC 700603, *Stenotrophomonas maltophilia* ATCC 13637, *Candida albicans* ATCC 10231. In addition to fungi strains, *Aspergillus fumigatus* ATCC 36607. All strains obtained from ATCC, Medical Microbiology Laboratory, Gazi University, and Ankara, Turkey.

As briefly, all strains cultured on tryptic soy agar (OXOID, Turkey) and aerobically incubated at 35 °C for 24 hours. Then the bacterial cultures were suspended into steril saline (0.85% NaCl) and adjusted to 0.5 McFarland turbity (10^{8} cfu/mL). We used 96-well, round-bottom microtiter included negative controls (medium with plant extract only) and positive controls (medium with bacteria only) and 10 serial twofold dilutions of each eight plant extracts ranging from 0,0075-5 mg/mL with a final concentration of the bacterial cell suspension equal to 1×10^{5} colony forming units per milliliter (CFU/ml). All inoculated plates incubated as mentioned above. MICs evaluated after 24 hours. MBC/MFCs performed by subculturing of 10 µl from all wells, which exhibited no visible growth (concentration equal or higher than of MICs) on Mueller Hinton agar-free plant extract and incubated as mentioned above. MBC/MFCs evaluated after 24 hours. Tests repeated twice or more and mean values reported.

Results and ıts dıscussıon. Medicinal vegetable raw materials must not contain moisture above acceptable standards, so as increased humidity, it is not necessary to store food. For the majority of species of medicinal, healthy raw materials, the acceptable moisture limit is usually 12–15%. The data presented in tables 1.

Table 1 - Benign indicators of the aerial part of *Atraphaxis spinose*

Index	Content, %
Humidity	5,7
Total ash	7,32
Ash insoluble in 10% hydrochloric acid	0,36
Sulfate ash	6,9

It was found that humidity corresponds to "not more than 10%", total ash - "not more than 11%", ash insoluble in 10% hydrochloric acid "not more than 1%", sulfate ash - "not more than 10%".

The study of the content of macro- and microelements in the studied sample of the aerial part of *Atraphaxis spinosa* is of interest in connection with the high biological role of individual chemical elements. In the etiology of many diseases, a significant role-played by a violation of the exchange of elements in the human body at the subcellular, tissue and organism levels. So, correlations between their imbalance and various pathologies are noted. In many diseases, the level of micro and macro elements decreases, so the search for new types of plant materials as valuable additional sources of micro and macro elements is an urgent task [3,5].

Data on the mineral composition obtained by atomic absorption analysis carried out on the material and technical basis of the center of physicochemical methods of analysis.

The results are presented in tables 2 and 3.

Table 2 - The quantitative content of trace elements in the aerial part of *Atraphaxis spinosa*

Element	Cu	Cd	Pb	Fe	Ni	Mn
Mass in sample, mg/ml	0.9827	0.5031	2.8704	92.0683	2.2263	14.2490
The content in the sample, %	0.00009	0.00005	0.00023	0.00915	0.00022	0.00138

Table 3 - The quantitative content of macronutrients in the aerial part of *Atraphaxis spinosa*

Element	Zn	K	Na	Mg	Ca
Mass in sample, mg/ml	343.2117	2600.0997	1161.3053	210.0357	4790.358
The content in the sample, %	0.0339	0.260	1.161	0.021	0.479

From these tables it follows that the content of Na, K exceeds the concentration of Na +, K + in the *Atraphaxis spinosa* plant under saline conditions, and they quickly diffuse inward and easily saturate the cell sap. For halophytes, ion pumps operate in the opposite direction, pumping out excess Na +, K + cations in exchange for H + ions. The highest Ca content is also noted.

It known that a number of trace elements that accumulate by plants play a positive role in the biosynthesis of biologically active substances. It established that plants producing polyphenolic compounds, coumarins, vitamins, selectively absorb copper, zinc, manganese. By the quantitative content of trace elements, iron dominates in the aerial part of *Atraphaxis spinosa*. In addition, a large amount contains manganese.

The specific need of halophytes for a certain concentration and composition of ash elements serves as the scientific basis for developing methods for introducing halophytes in botanical gardens. The content of macro- and micronutrients in raw materials meets the MPC standards.

Biologically active substances from *A. spinosa* extracted with 50% ethyl alcohol in the ratio of raw solvent 1:8, at room temperature for 48 hours. The resulting extract was concentrated in the vacuum of a water-structural pump. For preliminary separation of BAS, fractional hexane extraction performed. Hexane extract was analyzed by chromatography - mass spectrometry. The data presented in table 4.

Table 4 - Lipophilic composition of the plant

№	Name of compound	Formula	RT	Share,%
1	Tridecan	$C_{13}H_{28}$	6,79	1,20
2	Gibylphthalate	$C_{16}H_{22}O_4$	20,53	1,15
3	Palmitic acid	$C_{16}H_{32}O_2$	20,63	1,22
4	9.17 - Octadecandianal	$C_{18}H_{32}O$	23,98	3,95
5	2 -Nadonecanone	$C_{19}H_{38}O$	26,70	1,44
6	1.21- Docosadien	$C_{22}H_{42}$	28,64	0,56
7	Di (2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	30,65	54,66
8	Tricosan	$C_{23}H_{48}$	32,72	0,68
9	α - Toxopyro B	$C_{29}H_{50}O_4$	34,92	1,92
10	Eicosan	$C_{20}H_{42}$	35,50	1,10
11	4,5-Dimethyl benzenediol-1,3	$C_8H_{10}O_2$	37,65	0,48
12	1-Chlorheptacosan	$C_{27}H_{55}CI$	38,10	0,76
13	Vitamin E	$C_{29}H_{50}O_2$	38,60	0,75
14	P- (3-methoxy-2-methyl) propanamide	$C_5H_{11}NO_2$	38,70	0,50
15	1,3-Benzenediol 5-pentadecyl	$C_6H_6O_2$	39,65	4,70

16	Campester	$C_{28}H_{48}O$	39,79	0,74
17	Stigmaster	$C_{29}H_{48}O$	40,20	1,50
18	2-Methyl-5- (methyl ethyl) cyclohex sen	$C_{10}H_{16}O$	40,29	2,57
19	β-Systerol	$C_{29}H_{50}O$	41,03	13,11
20	α-Amirin	$C_{30}H_{50}O$	41,73	1,89
21	lanosterol	$C_{30}H_{50}O$	42,02	0,50
22	lupeol	$C_{30}H_{50}O$	42,10	2,40
23	Stigmast-4-en- 3-one	$C_{29}H_{48}O$	42,90	0,86

Various derivatives of hydrocarbons of lipophilic substances of a plant of the genus *A.spinosa* were found: tridecane (1.20%), dibylphthalate (1.15%), palmitic acid (1.22%), 9.17 - octadecandianal (3.95%), 2 -nadonecanone (1.44%), 1.21-backed (0.56%), di (2-ethylhexyl) phthalate (54.66%), tricosan (1.02%), α - toxopyro B (0.90%), α - toxocipro B (1.10%), eicosan (10.48%), 4,5-dimethyl benzenediol-1,3 (0.76%), 1-chlorheptacosan (0.75%), vitamin E (0.64%), P- (3-methoxy-2-methyl) propanamide (4.70%), 1,3-benzenediol 5-pentadecyl (4.70%), campester (1.50%), stigmaster (1.89%), 2-methyl-5- (methyl ethyl) cyclohexsen (2.57%), β-systerol (13.11%), α-amirin (1.89%), lanosterol (0.50%), lupeol (2.40%), stigmast-4-en- 3-one (0.86%).

It found that a large amount of *A. spinosa* contains Di - (2-ethylhexyl) phthalate (54.66%) and β-sitosterol (13.11%).

The MIC and MBC/MFC values shown in table 5 and 6.

Table 5 - Minimum Inhibitory Concentration (MIC) of various plant extracts against different strains

Microbial strains	MIC mg/mL
	AS-1
S. aureus	0.075
S. epidermidis	0.0075
E. coli	0.625
P. aeruginosa	0.156
K. pneumonia	0.078
S. maltophilia	0.156
C. albicans	0.312
A. fumigatus	2.5

Table 6 - Minimum Bactercidal Concentration (MBC/MFC) of various plant extracts against different strains.

Microbial strains	MBC/MFC mg/mL
	AS-1
S. aureus	0.03
S. epidermidis	0.03
E. coli	1.25
P. aeruginosa	0.625
K. pneumonia	0.312
S. maltophilia	0.625
C. albicans	1.25
A. fumigatus	>5 >5

In most cases, extracts exhibited a broad spectrum of antibacterial activity against used microbial strains. AS-1 showed the lowest MIC values (0.0075 mg/mL) with respect to *S. aureus* and *S. epidermidis*. MBC values of 0.03 mg/mL for AS-1.

Conclusion. Thus, the elemental composition and benignity of the aerial parts of the plant *Atraphaxis spinosa* studied. It established that the benignity of the plant does not exceed acceptable values.

As a result, the plant can considered medicinal raw materials. An analysis of the elemental composition showed that Fe prevails from microelements, and Na, K and Ca from macroelements.

The lipophilic composition and biological activity of the plant was also established. It found that a large amount of *A. spinosa* contains di - (2-ethylhexyl) phthalate (54.66%) and β-sitosterol (13.11%).

These plant extracts could be new antimicrobial agents with significant potential. This matter may be due to the materials extracted from various solvents

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ATRAPHAXIS (*A.SPINOSA*) ТЕКТЕС ӨСІМДІГІН ХИМИЯЛЫҚ ЗЕРТТЕУ ЖӘНЕ БИОЛОГИЯЛЫҚ БЕЛСЕНДІЛІГІ

Аннотация. Мақалада Алматы облысында дайындалған *Atraphaxis* (*A. spinosa*) тектес өсімдіктен биологиялық зат алудың жаңа көзі айқындалды. Белгілі әдістер бойынша шикізат сапасының көрсеткіші мен нормалары – ылғалдылық, жалпы күл, сульфатты күл әрі 10% тұз қышқылында ерімейтін күл анықтау сараптамалары жүргізілді. Атомдық-абсорбциялық спектроскопия әдісімен микро және макроэлементтік құрамы анықталды. Элемент құрамын талдау микроэлементтерден темір басым, ал макроэлементтерден натрий, калий және кальций басым екенін көрсетеді.

Алғаш рет *Atraphaxis spinosa* жерүсті бөлігінен биологиялық белсенді кешенді алу жағдайы жасалды. Кешен алу үшін анықталған оңтайлы жағдайлар: экстрагент – 50% этанол, экстрагент пен шикізаттың арақатынасы – 1:8, екіреттік экстракция уақыты – 48 сағат, температура – 22-26 °С.

Хромато-масс-спектроскопия әдісімен липофильді құрам анықталды. Өсімдік үлгілерінің липофильді фракциясында май қышқылы сияқты қосылыс кластары, яғни моно-; ди-; триглицерид, фосфолипид, стерол, стерол эфирі, гликолипид, майда еритін витаминдер кіретіндіктен оларды тек қоректік зат ретінде ғана емес, фармакологиялық агенттер ретінде де қарастыруға болады. Липофильді компоненттер құрамы анықталды, яғни ол – 26 органикалық қосылыс. *A. spinosa* құрамында көп мөлшерде ди- (2-этилгексил) фталат (54,66%) және β-ситостерол (13,11%) бар екені анықталды.

Дәрілік шикізат ретінде өсімдік ресурстарын кешенді зерттеу биологиялық белсенді заттарды химиялық зерттеуді, сондай-ақ өсімдіктерден алынған экстрактілер мен жеке қосылыстардың биологиялық скринингін жүргізуді көздейді. Көп жағдайда экстракт қолданылған микроорганизмдер штамына қарсы антибактерилды белсенділіктің кең спектрін көрсетті.

Түйін сөздер: *Atraphaxis spinosa*, минералды құрам, өсімдік сапасы, липофильді құрам, биологиялық белсенділік, Polygonaceae тұқымдасы

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ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ И БИОЛОГИЧЕСКАЯ АКТИВНОСТЬ РАСТЕНИЙ РОДА *ATRAPHAXIS* (*A.SPINOSA*)

Аннотация. В данной статье определены новые источники получения биологических веществ из растений рода *Atraphaxis (A. spinosa),* заготовленных в Алматинской области.

По известным методикам отработаны и проведены анализы показателей и норм качества сырья: влажность, общая зола, сульфатная зола, зола нерастворимая в 10% -ной соляной кислоте.

Методом атомно-абсорбционной спектроскопии установлены микро- и макроэлементы. Анализ элементного состава показывает, что из микроэлементов преобладает железо, а из макроэлементов – натрий, калий и кальций.

Впервые разработаны условия получения биологически активного комплекса из надземной части *Atraphaxis spinosa*. Оптимальными условиями для получения комплекса являются: экстрагент – 50% этанол, соотношение экстрагента и сырья – 1:8, время двукратной экстракции – 48 часа, температура – 22 - 26 °C.

Методом хромато-масс-спектроскапией идентифицирован липофильный состав. Поскольку липофильные фракции растительных образцов включают такие классы соединений, как жирные кислоты; моно-; ди-; триглицериды, фосфолипиды, стерины, эфиры стеринов, гликолипиды, жирорастворимые витамины, можно рассматривать их не только в качестве питательных продуктов, но и как возможные фармакологические средства. Установлено содержание липофильных компонентов – 26 органических соединений. Выявлено, что в составе *A.spinosa* большое количество содержится ди - (2-этилгексил) фталата (54,66%) и β-ситостерола (13,11%).

Комплексное исследование растительных ресурсов как лекарственного сырья предусматривает и химическое изучение биологически активных веществ, и проведение биологического скрининга экстрактов и индивидуальных соединений, полученных из растений. В большинстве случаев экстракт проявлял широкий спектр антибактериальной активности в отношении использованных штаммов микроорганизмов.

Ключевые слова: *Atraphaxis spinosa*, минеральный состав, доброкачественность растения, липофильный состав, биологическая активность, семейство *Polygonaceae*.

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THE INHIBITING EFFECT OF FS-1 DRUG ON THE ANTIOXIDANT PROTECTION SYSTEM OF MYCOBACTERIA TUBERCULOSIS

Abstract. Results of inhibitory action of FS-1 drug on antioxidant system of pathogenic mycobacteria tuberculosis, including resistant MDR strain, are presented. The study of the effect of FS-1 drug on the activity of the antioxidant system was carried out on the reference strain *Mycobacterium tuberculosis* H37Rv and MDR (rifampicin, isoniazid, streptomycin, ethambutol, ethionamide, kanamycin, cycloserine and pyrazinamide resistant) strain *Mycobacterium tuberculosis* 320. FS-1 drug under experimental conditions *in vitro* showed a new mechanism of action on mycobacteria tuberculosis - suppression of functional activity of the enzyme superoxide dismutase, which protects the microorganism from oxidative stress. The loss of resistance to oxidative stress by a bacterial cell, i.e. the ability to neutralize highly toxic oxygen radicals, leads to the destruction of cellular structures, metabolic and energy processes, disruption of the respiratory system and, as a result, its death. Antioxidant activity of *Mycobacterium tuberculosis* H37Rv after exposure with FS-1 preparation at concentrations of 4μg/ml is inhibited by 90.64 %, while at concentration of 2 μg/ml on bacterial culture of this strain - by 89.07 %. The obtained results show significant suppression of functional activity of superoxide dismutase enzyme in bacterial culture of *Mycobacterium tuberculosis* H37Rv under the influence of FS-1 in these concentrations, showing pronounced inhibitory effect. Similar studies of the effect of iodine-containing FS-1 drug on the antioxidant system were carried out on the bacterial culture of *M. tuberculosis* multidrug resistant strain 320. It was found that antioxidant activity of FS-1 preparation in concentration 4 μg/ml is inhibited by 99 %, while in concentrations 2 μg/ml FS-1preparation suppresses antioxidant activity of strain 320 by 98 %.

Thus, the studies showed that the FS-1 preparation at the test concentrations of 4 μg/ml and 2 μg/ml has a mechanism for pronounced inhibition of the functional activity of the enzyme superoxide dismutase in *Mycobacterium tuberculosis* of both the reference sensitive strain H37Rv and the multidrug resistant strain 320. This leads to disruption of the redox transformations of various chemical compounds that form the respiratory process in the bacterial culture, providing the energy demand of the microorganism.

Key Words. Iodine-containing FS-1 drug, mycobacterium tuberculosis, enzymes of the antioxidant system of bacterial cells, superoxide dismutase (SOD), UV spectrometry.

Introduction. Tuberculosis is one of the most common infectious diseases that occurs in all countries of the world. The causative agent of tuberculosis is the bacterium of a closely related complex (MTBC) *Mycobacterium tuberculosis*, which most often affects the lungs and is prone to genetic changes with the development of new forms. One of the reasons for the decrease in the effectiveness of treatment is the increased level of spread of the multidrug-resistant (MDR) infectious agent to anti-tuberculosis drugs.

Currently, an important role in the spread of tuberculosis is played not only by the pathogen drug resistance, but also by defense mechanisms factors of both immune system of macroorganism and of the bacterial cell itself [1-3]. Over recent years, according to the literature, the search for intracellular targets has expanded to create new anti-infective drugs [4-8]. Thus, there is evidence that antibiotics can cause an increase in the production of ROS (reactive oxygen species), which leads to oxidative stress. In the works of Kohanski M.A. et. al.; Kohanski M. A., Dwyer et. al.; Belenky, P. et al. [5,6,9] oxidative stress in the bacterial cell itself, as exemplified in *E. coli*, is considered to be one of the components of the antimicrobial activity of antibiotics leading to their death. Oxidative stress is a condition of cells characterized by an excess content of free oxygen radicals. Kurbanov A.I., Zenkov N.K. et al. [7,8] in their works state that the course of disease and the nature of treatment of many infections are influenced by free radical oxidation processes. Free radicals are produced as a result of respiratory function and the use of oxygen received by cells for energy production. Molecular oxygen is the main source of free radicals in the body. Oxygen is not an essential component of metabolic processes in the body.

Superoxide is the active form of oxygen is. Its change is catalyzed by the antioxidant enzyme superoxide dismutase (SOD), which is produced during aerobic respiration, a chemical reaction, and transfers energy to cells. SOD catalyzes dismutation of O_2 - radicals and prevents transformation of the superoxide radical anion into the OH hydroxyl radical, which is highly toxic. Hence, SOD is a key enzyme that directly ensures termination of free radical reactions chains in the cells of aerobic organisms [10-12]. This enzyme accelerates biochemical process in the cell from constantly generated highly toxic oxygen radicals and always "works" in tandem with catalase, which quickly and efficiently breaks down hydrogen peroxide into neutral compounds.

Thus, enzyme superoxide dismutase, which is considered to be a universal mechanism of pathogenesis in infections, plays an important part in the antioxidase defense system of the microbe organism against oxidative stress. This prompted us to study the effect of FS-1 drug developed at our Scientific Center for Anti-Infectious Drugs JSC [13,18] on the activity of SOD in mycobacterium tuberculosis.

Initial research carried out by us in experiments on *M. smegmatis* saprophyte culture selected a method for measuring SOD activity and established the ability of FS-1 drug to suppress SOD activity [14]. This work presents the results of studying the effect of FS-1 drug on the activity of antioxidant system of mycobacterium tuberculosis as a reference sensitive strain and a highly pathogenic multidrug-resistant strain of this pathogen type.

Materials and Methods. The study of the effect of the FS-1 drug on the activity of antioxidant system was carried out on the reference strain *Mycobacterium tuberculosis* $H_{37}Rv$, as well as MDR strain *Mycobacterium tuberculosis 320*, resistant to rifampicin, isoniazid, streptomycin, ethambutol and pyrazinamide [15].

The investigated concentrations of the FS-1 drug of 2 µg/ml and 4 µg/ml proceeded from the MBC of the taken mycobacterium tuberculosis cultures. The suspension of the studied *M. tuberculosis* cultures was prepared at a concentration of 1.5x108 CFU/ml in sterile saline. Tests of samples of different mycobacterium tuberculosis strains were carried out simultaneously on the same day under the same settings.

Determination of the effect of the test substance on the antioxidant system of bacteria was carried out by adrenaline autooxidation method *in vitro* [16]. We used 0,1% solution of adrenaline hydrochloride; 0.2 M bicarbonate buffer solution (pH = 10.65).

For the research, 2 ml of bicarbonate buffer was poured into test tubes, a 2 ml suspension of the test culture of Mycobacterium tuberculosis at a concentration of 1.5x108 CFU/ml prepared in physiological saline was added, the investigated concentrations of the FS-1 drug were also added, then 0.2 ml 0, 1% solution of adrenaline hydrochloride. The test tubes were incubated for 15 min at room temperature, then the supernatant was separated by centrifugal settling at 5000 rpm for 5 min.

The control was a sample without the addition of test substances, i.e. containing 2 ml of bicarbonate buffer, 2 ml of saline and 0.2 ml of 0.1% adrenaline hydrochloride solution.

The optical density of the test samples of the supernatant was measured every minute for 30 min (30 cycles) in the spectral range from 200 to 500nm on a Lambda 35 double-beam spectrophotometer (Perkin-Elmer, USA). The operation principle of this device is based on measuring the ratio of two light fluxes that had passed through the reference channel (blank - 2ml bicarbotate buffer, 2ml saline solution) and the sample channel in the cell holder, which allows cutting off baseline values.

The degree of impact of the test substance on the antioxidant system of bacteria was calculated using the formula described in the method [16]:

inhibition % (units) = $[1 - (OD_{control}/OD_{experiment})] \times 100\%$ (1) where $OD_{control}$ is the mean value (n = 30) of control sample optical density; $OD_{experiment}$ is the mean value (n = 30) of the optical density of the test sample.

The results of measuring the kinetics of adrenaline autooxidation process in an alkaline medium and in the presence of the investigated concentrations of the FS-1 drug are presented as mean values (n=30) from 2 independent experiments.

According to the method, values above 30% were taken as a significant suppression of activity of the bacterial antioxidant system exposed to the test substance.

Processing and visualization of experimental data was carried out using the Origin package. URSS [17].

Obtained Results. The effect of iodine-containing FS-1 drug on the antioxidant system of *M. tuberculosis* bacterial cell of the $H_{37}Rv$ reference strain and multidrug resistant strain 320 was studied by adrenaline autooxidation method *in vitro*. Figure 1 shows the results of a spectral study of a control sample (0.1% adrenaline solution) in the range from 200 to 500 nm. Three absorption maxima were found at 242, 292, and 347 nm.

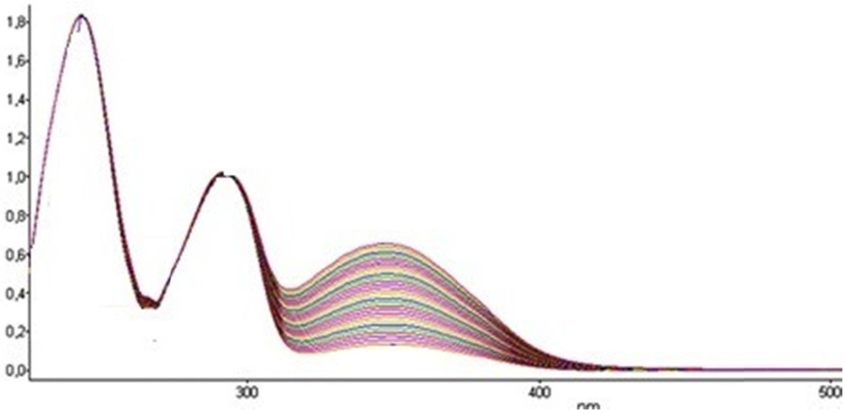

Figure 1 - UV absorption spectrum of the control sample

It should be noted that when measuring an aqueous adrenaline solution with pH=7.0, its maximum absorption at a wavelength of 280 nm was established. When measuring the kinetics of the autooxidation of adrenaline in a bicarbonate buffer pH=10.65, the maximum absorption in the UV region was determined at a wavelength of 292 nm. Observation of the entire spectrum at a length of 347 nm for 30 min showed the dynamics of spectral changes increasing in direct proportion to the measurement time. The increase in the optical density of the primary adrenaline oxidation product accumulation was 0.52 op. units/min. When measured immediately, optical density was 0.139A, and after 30 minutes, optical density was 0.658A. However, the optical density in the spectrum typical of adrenaline in an alkaline medium - 292 nm decreased only by 0.01A within 30 minutes (from 1.03A to 1.02A).

Figure 2 shows the results of UV spectroscopy of an experimental sample of *M. tuberculosis* $H_{37}Rv$ supernatant after exposure to FS-1 at a concentration of 2 µg/ml. Three absorption maxima were found at the spectra of 242 nm, 292 nm, and 347 nm.

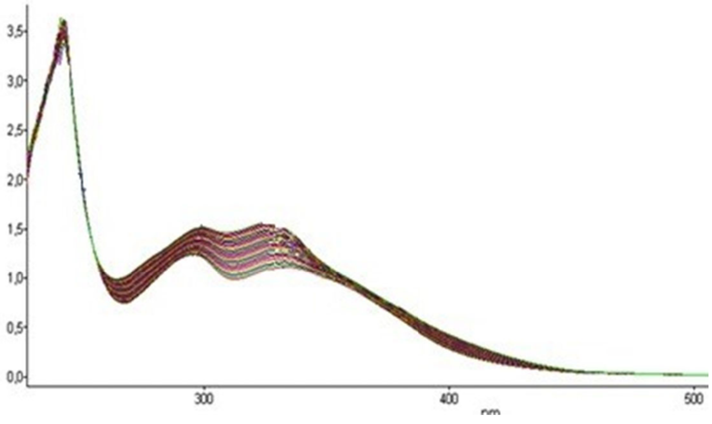

Figure 2 - UV absorption spectrum of a test specimen
of *M. tuberculosis* $H_{37}Rv$ supernatanta after exposure to FS-1 at a concentration of 2 µg/ml

The increase in the optical density of the adrenaline autooxidation primary product accumulation at a spectrum of 292 nm exposed to FS-1 drug at a concentration of 2 µg/ml on *M. tuberculosis* $H_{37}Rv$ culture was 0.28 op.u/min. In immediate measurement, the optical density was 1.24A, and after 30 minutes it was 1.52A.

In immediate measurement in the spectrum of 347 nm, the optical density of the test sample after exposure to FS-1 drug on the cell culture of *M. tuberculosis* $H_{37}Rv$ was 1.03A, and after 30 minutes it increased by 0.16A and amounted to 1.19A.

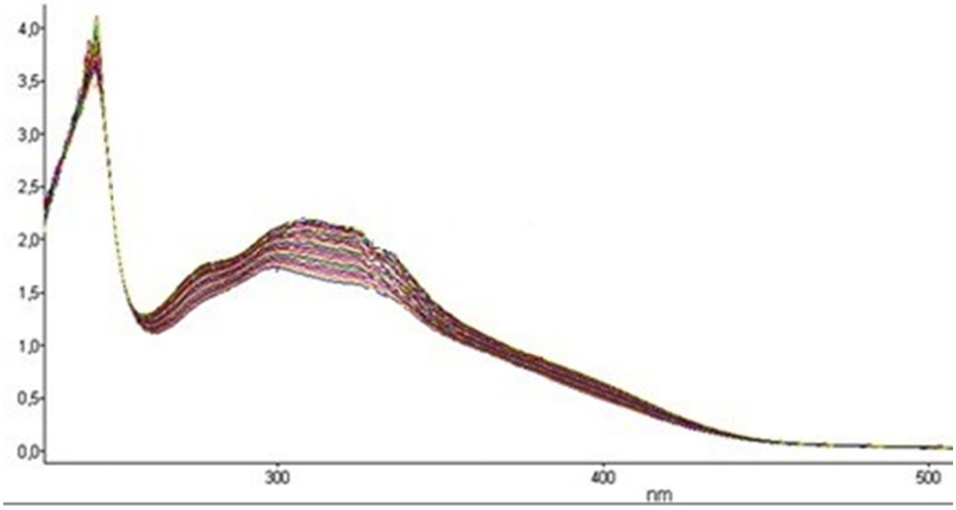

Figure 3 - UV absorption spectrum of a test specimen of M. tuberculosis $H_{37}Rv$ supernatanta after exposure to FS-1 in concentration of 4 µg/ml

Figure 3 shows the UV absorption spectrum of a test sample of *M. tuberculosis* $H_{37}Rv$ supernatant after exposure to FS-1 at a concentration of 4 µg/ml.

Increase in the optical density of adrenaline autooxidation primary product accumulation at a spectrum of 292 nm when exposed to FS-1 drug at a concentration of 4 µg/ml on *M. tuberculosis* $H_{37}Rv$ cell culture averaged 0.46 op.u/min. When measured immediately, the optical density was 1.74A, and after 30 minutes it was 2.20A.

The optical density of the test sample after exposure to FS-1 drug at a concentration of 4 µg/ml on *M. tuberculosis* $H_{37}Rv$ cell culture with immediate measurement in the spectrum of 347 nm was 1.18A, and after 30 minutes it increased by 0.28A and amounted to 1.46A.

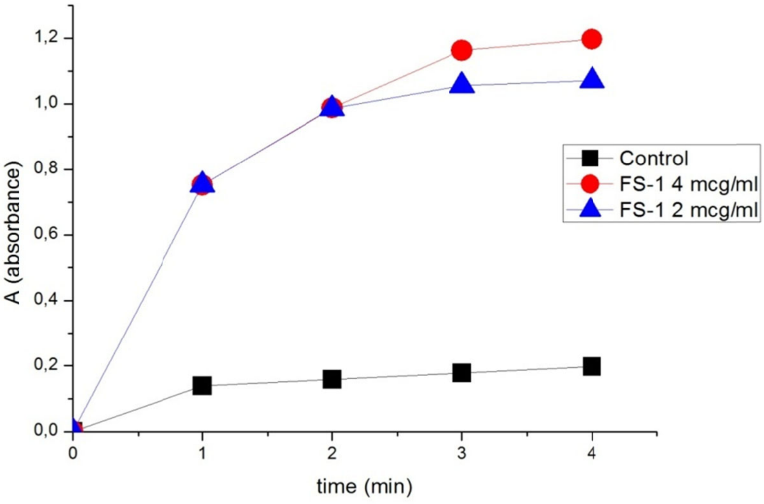

Figure 4 - Dynamics of changes in the optical density of the control and experimental samples supernatanta of *M. tuberculosis* $H_{37}Rv$ at a wavelength of 347 nm

Figure 4 shows the summary data of UV spectroscopy with the dynamics of changes in the optical density of the supernatant of experimental samples of *M. tuberculosis* $H_{37}Rv$ after exposure to FS-1 at concentrations of 2 µg/ml and 4 µg/ml at a wavelength of 347 nm for 30 minutes versus control sample without adding the test substance. Observation of the entire spectrum at a length of 347 nm for 30 min showed spectral changes dynamics in the optical density of the culture liquid of *M. tuberculosis* $H_{37}Rv$ exposed to FS-1 drug in the tested doses. Figure 4 shows a graph constructed using the OriginPro software (17). As can be seen from Figure 4, the addition of FS-1 drug to the test samples at concentrations of 4 and 2 µg/ml with *M. tuberculosis* $H_{37}Rv$ culture versus control sample (without the FS-1 drug) 10.7 ($p<0.0001$) and 9.1 ($p<0.0001$) times, increase accumulation of the toxic product of adrenaline autooxidation in the supernatant.

The degree of impact of FS-1 drug at concentrations of 2 µg/ml and 4 µg/ml on the antioxidant system of bacteria, calculated according to the selected research methodology, showed an inhibitory antioxidant activity of the effect on pathogenic mycobacterium tuberculosis. It was found that the antioxidant activity of mycobacterium tuberculosis $H_{37}Rv$ strain after exposure to FS-1 at a concentration of 4 µg/ml is inhibited by 90.64%. This indicates a significant suppression of the functional activity of the superoxide dismutase enzyme in the Mycobacterium tuberculosis bacterial culture exposed to FS-1 drug at a given concentration. The degree of impact of FS-1 drug at a concentration of 2 µg/ml on the bacterial culture of this strain was also determined. It was found that the drug inhibits antioxidant activity by 89.07%. The obtained results indicate a significant suppression of the functional activity of the superoxide dismutase enzyme in the bacterial culture of Mycobacterium tuberculosis $H_{37}Rv$ strain exposed to FS-1 at these concentrations, demonstrating a pronounced inhibitory effect.

We have also simultaneously carried out similar studies of the effect of iodine-containing FS-1 drug on the antioxidant system of *M. tuberculosis* bacterial cell of multidrug-resistant strain 320 by adrenaline autooxidation method *in vitro*.

Figures 5-7 show the spectral studies data of the supernatant of the test samples after exposure to FS-1 drug on MDR *M. tuberculosis* strain No. 320 in the range from 200 to 500 nm. There is also a shift in wavelength observed from 242 nm to 292 nm and up to 347 nm.

In the studied ranges, the time-dependent dynamics of spectral changes are also shown. Figure 5 shows the data of spectral absorption of the experimental sample of the supernatant of *M. tuberculosis* strain No. 320 after exposure to FS-1 drug at a concentration of 4 µg/ml. Three absorption maxima were revealed at the spectra of 242 nm, 292 nm, and 347 nm.

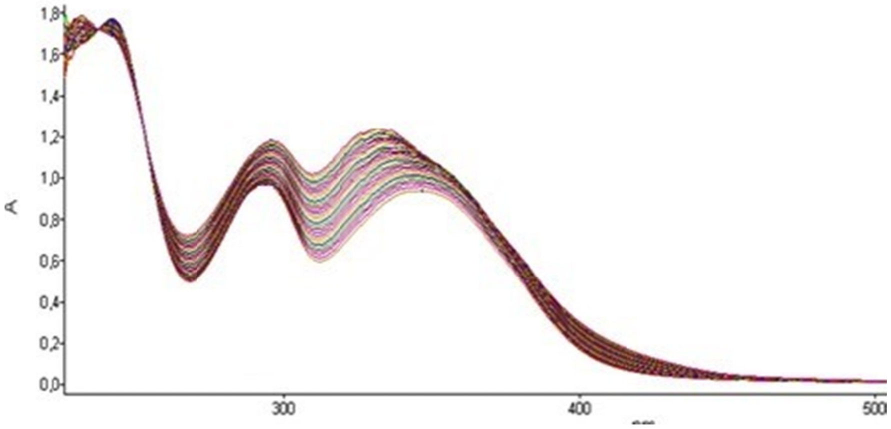

Figure 5 – UV absorption spectrum of a test specimen of supernatant of *M. tuberculosis* strain 320 after exposure to FS-1 in concentration of 4 µg/ml

The increase in the optical density of adrenaline autooxidation primary product accumulation (292 nm) under the impact of FS-1 drug at a concentration of 4 µg/ml in the culture of MDR *M. tuberculosis* strain 320 was 0.11 op.u/min, with immediate measurement the optical density was 1,70A and after 30 minutes it amounted to 1.81A. The optical density of the supernatant of the test sample after exposure to FS-1 drug with immediate measurement in the spectrum of 347 nm was 0.84A, and after 30 minutes - 1.02A increased by 0.18A.

Figure 6 shows the data of spectral absorption of the experimental sample supernatant of the test culture of MDR *Mycobacterium tuberculosis* strain 320 after exposure to FS-1 drug at a concentration of 2 µg/ml. Three absorption maxima were revealed at the spectra of 242 nm, 292 nm, and 347 nm.

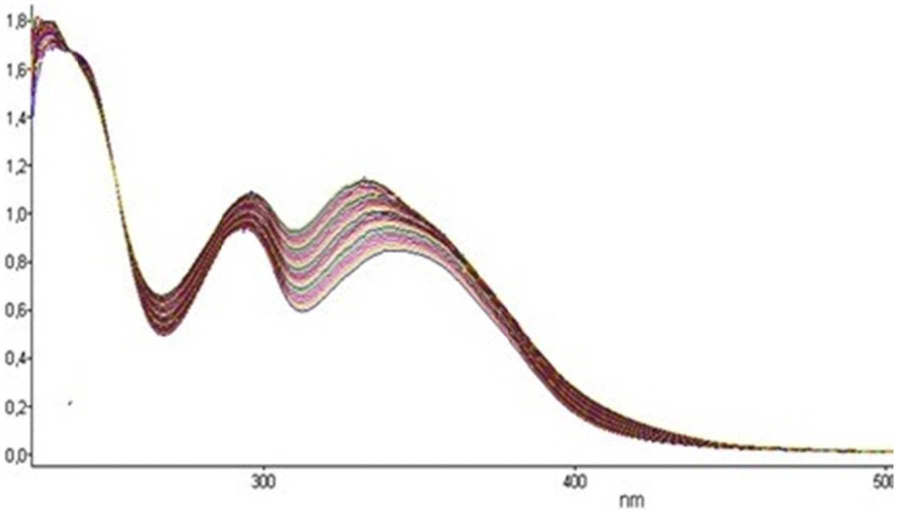

Figure 6 – UV absorption spectrum of a test specimen of supernatant of the MDR *M. tuberculosis* after exposure to FS-1 in concentration of 2 µg/ml

The increase in optical density with the accumulation of the primary adrenaline autooxidation product in the spectrum of 292 nm when exposed to FS-1 drug at a concentration of 2 µg/ml in the MDR *M. tuberculosis* strain 320 of was 0.21 op.u/min, with immediate measurement the optical density was 0.97A, and after 30 minutes it amounted to 1.18A. The optical density of the supernatant after exposure with immediate measurement in the spectrum of 347 nm was 0.94A, and after 30 minutes - 1.11A, which shows an increase of 0.17A.

Figure 7 shows the summary data of UV spectroscopy with the dynamics of changes in the optical density of the control and experimental samples of the supernatant of the MDR of strain 320 of *M. tuberculosis* after exposure to FS-1 on bacterial cells at concentrations of 4 µg/ml and 2 µg/ml at a wavelength of 347 nm within 30 minutes.

As can be seen from Figure 7, the addition of FS-1 drug at concentrations of 4 and 2 µg/ml into experimental samples of the culture liquid of the MDR of strain 320 *M. tuberculosis* in comparison with the control sample without the drug, by 9.3 times ($p<0.0001$) and 8.5 times ($p<0.0001$), respectively, increases accumulation of the adrenaline autooxidation toxic product in the studied culture liquid.

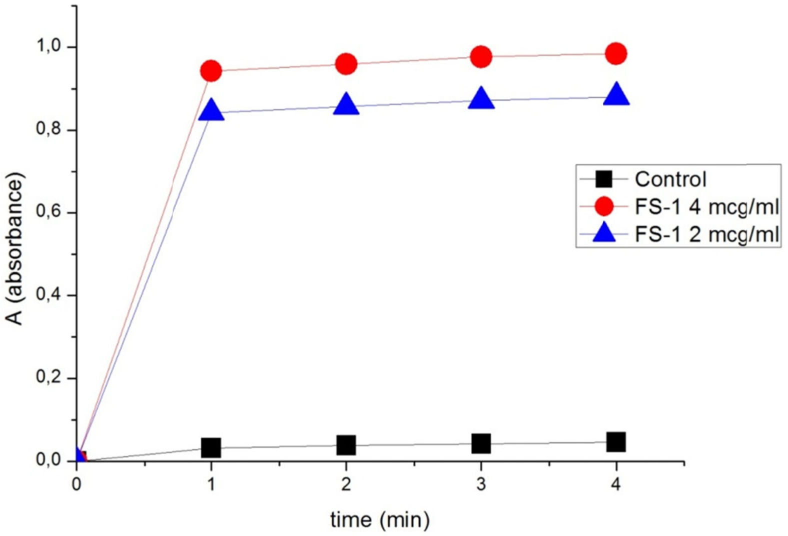

Figure 7 - Dynamics of changes in the optical density of the control and Experimental samples supernatanta of the MDR *M. tuberculosis* at a wavelength of 347 nm

The degree of impact of FS-1 drug on the antioxidant system of bacteria in the studied concentrations was calculated using formula (1) according to the procedure. It was found that the antioxidant activity of FS-1 at a concentration of 4 µg/ml is inhibited by 99%. This indicates a significant suppression of the functional activity of the superoxide dismutase enzyme in the bacterial culture of mycobacterium tuberculosis MDR strain 320 when exposed to FS-1 drug at a given concentration.

FS-1 drug at a concentration of 2 µg/ml inhibits antioxidant activity of the bacterial culture of strain 320 by 98%.

Thus, the conducted studies have shown that FS-1 drug in the studied concentrations has a mechanism for suppressing functional activity of the superoxide dismutase enzyme in bacterial cultures of Mycobacterium tuberculosis, both the reference sensitive strain and the multidrug-resistant strain 320.

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«Инфекцияға қарсы препараттар ғылыми орталығы» АҚ

ФС- 1 ДӘРІЛІК ЗАТЫ МИКОБАКТЕРИЯ ТУБЕРКУЛЕЗІНІҢ АНТИОКСИДАТТЫ ҚОРҒАНЫС ЖҮЙЕСІНЕ ИНГИБИРЛЕУШІ ӘСЕРІ

Аннотация. ФС-1 дәрілік затының туберкулездің патогенді микобактерияларының антиоксидантты жүйесіне, оның ішінде көптеген резистентті дәрінің төзімділік штамына тежеуші әсерінің нәтижелері ұсынылған. *Mycobacterium tuberculosis* $H_{37}Rv$ эталондық штамында және *Mycobacterium tuberculosis* 320 штамында(рифампицинге, изониазидке, стрептомицинге, этамбутолға, пиразинамидке, этионамидке, ПАСК, канамицинге және циклосеринге) жүргізілетін антиоксидантты жүйенің белсенділігіне ФС-1 дәрілік затының ену жолдарын зерттеу. ФС-1 дәрілік заты in vitro эксперименттік жағдайында туберкулез микобактерияларына әсер етудің жаңа механизмін, яғни микроағзаны тотығу күйзелісінен қорғайтын супероксиддисмутаза ферментінің функционалдық белсенділігін басуды көрсетті. Бактериялық жасушаның тотығу стресіне төзімділігін жоғалтуы, яғни жоғары уытты оттегі радикалын бейтараптандыру қабілеті жасушалық құрылымды, метаболикалық және энергетикалық процестер мен тыныс алу жүйесін бұзады және нәтижесінде өлім тудырады. ФС-1 препаратымен 4 мкг/мл концентрациясында әсер еткеннен кейін $H_{37}Rv$ штамы туберкулез микобактерияларының антиоксидантты белсенділігі 90,64%-ға, ал осы штамның бактериялық культурасына 2 мкг/мл концентрациясында 89,07%-ға тежелетіні анықталды. Алынған нәтижелер айқын ингибиторлық әсерін байқатып, концентрацияда ФС-1 әсерінен $H_{37}Rv$ штамы туберкулез микобактерияларының бактериялық культурасындағы супероксиддисмутаза ферментінің функционалдық белсенділігінің айтарлықтай басылғанын көрсетеді. Құрамында иоды бар ФС-1 дәрілік затының антиоксидантты жүйеге әсерін ұқсас зерттеулер *M.tuberculosis* көп дәріге төзімді штамм 320 бактериялық культурасына жүргізілді. Бұл ретте 4 мкг/мл концентрациядағы ФС-1 препаратының антиоксиданттық белсенділігі 99%-ға тежелетіні анықталды, ал 2 мкг/мл концентрациясында ФС-1 препараты 320 штамының антиоксиданттық белсенділігін 98%-ға бәсеңдетеді.

Осылайша жүргізілген зерттеулер 4 мкг/мл және 2 мкг/мл зерттелетін концентрациядағы ФС-1 препаратының н37rv референттік сезімтал штамының да, көп дәріге төзімді 320 штамының да туберкулез микобактериясында супероксиддисмутаза ферментінің функционалдық белсенділігін айқын тежеу тетігіне ие екендігін көрсетті. Бұл микроорганизмнің энергетикалық қажеттілігін қамтамасыз ететін бактериялық культурада тыныс алу процесін құрайтын түрлі химиялық қосылыстардың тотығу-тотықсыздану өзгерістерін бұзады.

Түйін сөздер: құрамында йод бар ФС-1 препараты, туберкулез микобактериялары, бактерия жасушасының антиоксидантты жүйе ферменттері, супероксиддисмутаза (СОД), УК-спектрометрия

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АО «Научный центр противоинфекционных препаратов»

ИНГИБИРУЮЩЕЕ ДЕЙСТВИЕ ЛЕКАРСТВЕННОГО СРЕДСТВА ФС-1 НА СИСТЕМУ АНТИОКСИДАНТНОЙ ЗАЩИТЫ МИКОБАКТЕРИЙ ТУБЕРКУЛЕЗА

Аннотация. Представлены результаты ингибирующего действия лекарственного средства ФС-1 на антиоксидантную систему патогенных микобактерий туберкулеза, в т.ч. резистентного МЛУ- штамма. Изучение влияния лекарственного средства ФС-1 на активность антиоксидантной системы проведены на референтном штамме *Mycobacterium tuberculosis* $H_{37}Rv$ и МЛУ (к рифампицину, изониазиду, стрептомицину, этамбутолу, пиразинамиду, этионамиду, ПАСК, канамицину и циклосерину) штамме *Mycobacterium tuberculosis* 320. Лекарственное средство ФС-1 в экспериментальных условиях *in vitro* показал новый механизм действия на микобактерии туберкулеза – подавление функциональной активности фермента супероксиддисмутазы, защищающего микроорганизм от окислительного стресса. Потеря бактериальной клеткой устойчивости к окислительному стрессу, т.е. способности нейтрализовать высокотоксичные кислородные радикалы ведет к разрушению клеточных структур, метаболических и энергетических процессов, нарушению дыхательной системы и , как следствие, к ее гибели. Установлено, что антиоксидантная активность микобактерий туберкулеза штамма $H_{37}Rv$ после воздействия препаратом ФС-1 в концентрациях 4 мкг/мл ингибируется на 90,64 %, тогда как в концентрации 2 мкг/мл на бактериальную культуру данного штамма – на 89,07 %. Полученные результаты свидетельствуют о существенном подавлении функциональной активности фермента супероксиддисмутазы у бактериальной культуры микобактерий туберкулеза штамма $H_{37}Rv$ под воздействием ФС-1 в данных концентрациях, проявляя выраженное ингибирующее действие. Аналогичные исследования влияния иодсодержащего лекарственного средства ФС-1 на антиоксидантную систему проведены на бактериальную культуру *M.tuberculosis* множественно лекарственно устойчивого штамма 320. При этом установлено, что антиоксидантная активность препарата ФС-1 в концентрации 4 мкг/мл ингибируется на 99 %, тогда как в концентрациях 2 мкг/мл препарат ФС-1 подавляет антиоксидантную активность штамма 320 на 98%.

Таким образом, проведенные исследования показали, что препарат ФС-1 в исследуемых концентрациях 4 мкг/мл и 2 мкг/мл обладает механизмом выраженного ингибирования функциональной активности фермента супероксиддисмутазы у микобактерий туберкулеза как референтного чувствительного штамма $H_{37}Rv$, так и множественно лекарственно устойчивого штамма 320. Это приводит к нарушению окислительно-восстановительных преобразований различных химических соединений, образующих дыхательный процесс у бактериальной культуры, обеспечивающих энергетическую потребность микроорганизма.

Ключевые слова: иодсодержащий препарат ФС-1, микобактерии туберкулеза, ферменты антиоксидантной системы бактериальной клетки, супероксиддисмутаза (СОД), УФ-спектрометрия.

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Жаңа материалдар технологиясы

Органикалық заттар технологиясы

Бейорганикалық заттар технологиясы

Химиялық тыңайтқыштар технологиясы

Полимерлік және құрылыс материалдары мен силикаттар технологиясы

Тамақ өнімдері технологиясы

Фармацевтикалық химия

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