ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

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

ХАБАРЛАРЫ

ИЗВЕСТИЯ

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

NEWS

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

SERIES CHEMISTRY AND TECHNOLOGY

6 (444)

NOVEMBER - DECEMBER 2020

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR



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

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

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«ҚР ҰҒА Хабарлары. Химия және технология сериясы».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.).

Қазақстан Республикасының Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 29.07.2020 ж. берілген № **KZ66VPY00025419** мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Тақырыптық бағыты: химия және жаңа материалдар технологиясы саласындағы басым ғылыми зерттеулерді жариялау.

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

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

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

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

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«Известия НАН РК. Серия химии и технологий».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы).

Свидетельство о постановке на учет периодического печатного издания в Комитете информации Министерства информации и общественного развития Республики Казахстан № **KZ66VPY00025419**, выданное 29.07.2020 г.

Тематическая направленность: публикация приоритетных научных исследований в области химии и технологий новых материалов.

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

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28; ком. 219, 220; тел. 272-13-19; 272-13-18,

http://chemistry-technology.kz/index.php/en/arhiv

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

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News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.

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

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty).

The certificate of registration of a periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan **No. KZ66VPY00025419**, issued 29.07.2020.

Thematic scope: publication of priority research in the field of chemistry and technology of new materials

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

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19; 272-13-18,

http://chemistry-technology.kz/index.php/en/arhiv

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

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

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

https://doi.org/10.32014/2020.2518-1491.99

Volume 6, Number 444 (2020), 65 – 72

UBC 691 MRNTI 67.09.55

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DETOXICATION OF BY-PRODUCTS OF OIL AND GAS INDUSTRY ACCOMPANIED 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 comilling has been applied. As the result, there took place mutual neutralization and detoxication of solid industrial byproducts 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 byproducts, 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 sulfurcontaining 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.

Content, %									
Basic oxides					Basic minerals				
CaO Si0 ₂ A1 ₂ O ₃ Fe ₂ O ₃ R ₂ O SO ₃				C ₃ S	C_2S	C_3A	C ₄ AF		
61 30	23 30	6.30	6.07	0.38	0.60	57.61	17 30	7 01	13 11

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

2. As an additive, pyrite cinder manufactured by Plc Phosphorchim of Aktobe region has been used. The additive consists of the iron oxide mixture (II, III) Fe₃O₄ (Fe₂O₃), 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	AI_2O_3	MgO	SO_3	R_2O	п.п.п
10.6	19.6	66.2	2.2	1.2	-	ı	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-containing 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% technical 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 electromotive forces (e.m.f.) of electrochemical couples are given in the table 4.

Table 4. - Evaluation of reaction capacity by means of electromotive 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 (B) > 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:

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

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

Substance	ΔH°298 kkal/mole	ΔS°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
Fe_2O_3 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 $T = 298^{\circ}$). 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).

Alphabetical references of the reactions	Systems and reactions	Thermal effect of the reaction, ΔH° kkal
A	$3\text{Fe}_3\text{O}_4 + \text{S} \rightarrow \text{FeS} + 4\text{Fe}_2\text{O}_3$	195.9
В	$FeS + S \rightarrow FeS_2$	-16.0
C	$4\text{Fe}_2\text{O}_3 + \text{S}^\circ \rightarrow \text{SO}_2 + 4\text{FeO}$	-38.6
D	$2\text{FeO} + 3\text{S}^{\circ} \rightarrow 2\text{FeS} + \text{SO}_2$	12.4
Е	$FeO + S \rightarrow FeOS$	20.8

Table 6 – Thermal effects of oxidation-reduction reactions

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 $0 \, \text{C}^0$, 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

CaSO₃. 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°C). 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):

$$3Fe^{o} + Fe_{3}O_{4} + 2S \rightarrow 2FeS + 4FeO, \Delta H = -37.1kkal$$
 (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.

N		Binder's co	mposition,%		_	Ultimate strength, MPa		
	Sulfur серы, %	Pyrite cinder	Cement	Water Влажность	Dry density, kg/m ³	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	

Table 7 - Characterisites of sulfur contating binders with addition of sulfur

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 additives 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 дифферанциялдытермиялық, рентген-фазалық, микроскопиялық талдау және сынау жабдықтарының заманауи әдістерін пайдалану негізінде алынған темірлі-күкіртті байланыстырғыштардан даярланған үлгі тасының физикалықмеханикалық 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 мұнайгаз 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 железосеросодержащего 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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REFERENCES

- [1] Abdrakhimov V., Abdrakhimova E., Kairakbaev A. Waste utilization gold deposit, petrochemistryand energy in the production of ceramic materials a promising direction for the "green" economy" // Ecology and industry of Russia. 2015. N 19(5), P. 37-41.
- [2] Assakunova B.T., Jussupova M.A., Baimenova G.R., Kulshikova S.T. Utilization of heat power industry waste in the form of binding composite materials in Kyrgyzstan // N e w s of the national academy of sciences of the Republic of Kazakhstan series of geology and technical sciences. Volume 3, Number 435 (2019), P. 67 72. https://doi.org/10.32014/2019.2518-170X.69
- [3] Akulova M.V., Isakulov B.R., Dzhumabaev M.D. Reception of a light arbolit concrete on the basis of cement ash slurry binder and organic filler from walnut shell // Internet-journal "Naukovedenie" ISSN 2223-5167. Vol. 8, N 4. P.1-8. Access mode: Internet: http://naukovedenie/ru/Moscow. 2016 (date of circulation: August 25, 2016).
- [4] Akulova M.V., Isakulov B.R. Dzhumabaev MD Complex electromechanical activation of ash-slurry-binding for light production arbolit concrete // Scientific and Technical Herald of the Volga Region. 2014. N 1. P. 49-52.
- [5] Akchabaev A.A., Bisenov K.A., Uderbaev S. S. Activation of bidning polarization as a way to increase the strength of the arbolite // Reports of the Ministry of Science and higher education. Almaty: NAS RK, 1999. N 4. P. 57-60.
- [6] Akulova M.V., Isakulov B.R. Mechanochemical activation and detoxification of industrial waste to obtain binding lightweight concretes // Bulletin VolGASU. Series: construction and architecture. N 31(50). Part 2. Building sciences. Volgograd, 2013. P. 75-80.
- [7] Akulova M.B., Isakulov B.R., Fedosov S.B., Shchepochkina YU.A. Wood concrete mix contains portland cement, rush cane stems, technical sulphur, chrome-containing sludge, pyrite stubs and water. Patent RU2535578-C1, 20 Dec 2014, C04B-028/04, Russia.

- [8] Akulova M.B., Isakulov B.R., Fedosov S.B., Shchepochkina YU.A. Method to produce wood concrete products with making base for plastering on their surface. Patent RU2517308-C1, 08 JuI 2013, Russia.
- [9] Beysenbayev O.K., Umirzakov S.I., Tleuov A.S., Smaylov B.M., Issa A.B., Dzhamantikov Kh., Zakirov B.S. Obtaining and research of physical and chemical properties of chelated polymer-containing microfertilizers on the basis of technogenic waste for rice seed biofortification / N e w s of the national academy of sciences of the Republic of Kazakhstan series of geology and technical sciences. Volume 1, Number 433 (2019), P. 80 89 https://doi.org/10.32014/2019.2518-170X.10
- [10] Bazhirov N.S., Dauletiyarov M.S., Bazhirov T.S., Serikbayev B.E., Bazhirova K.N. Research of waste of aluminum production as the raw components in technology of composite cementing materials // News of the national academy of sciences of the Republic of Kazakhstan. Series of geology and technical sciences. ISSN 2224-5278. 2018. Vol. 1, N 427. P. 93-98.
- [11] Sokolova, Y., Akulova, M., Isakulov, B.R., Sokolova, A., Isakulov, A.B. The study of structure formation and mechanical strength properties of sulfur-containing woodcrete composites exposed to permanently acting loads. IOP Conference Series: Materials Science and Engineering, 2020, 869 (3), 032005.
- [12] Sadieva Kh. R., Massalimova B. K., Abisheva R. D., Tsoy I. G., Nurlybayeva A. N., Darmenbayeva A. S., Ybraimzhanova L. K., Bakibaev A. A., Sapi A. K. Preparation of carbon nanocomposites on the basis of silicon-tin containing substances / N e w s of the national academy of sciences of the Republic of Kazakhstan series of geology and technical sciences. Volume 4, Number 436 (2019), P. 158 166. https://doi.org/10.32014/2019.2518-170X.110
- [13] Zhiv A.S., Galibuy S., Isakulov B.R. Resource-saving technologies Arbolite production based on industrial waste and local raw materials of Asia and Africa // Mechanization of construction. 2013. N 3(825). P. 14-17.
- [14] Dzhumabaev M.D. Lightweight arbolitic concrete based on compositementitious slurry binding and solid organic waste (for example by-products of agriculture of the Republic of Kazakhstan): dissertation on competition of the scientific degree of the candidate tehn. sciences. Ivanovo, 2016. 59 p.
- [15] Tulaganow A.A. HochfesteLeichtbetoneauf der Basis modifizierter Alkalis chlachen Bindemittel I Wissehschaftliche Zeitschrift der Bauha «s-ttn Weimar / BRD Heft 1/2, 1998 44. Jahragang. P. 222-225.
- [16] Suleimenov S.T. Physico-chemical processes of structure formation in building materials from mineral waste industry. M.: Manuscript, 1996. 138 p.
- [17] Zhiv A.S., Isakulov B.R. Resource-saving technologies for the production and research of the properties of wood concrete based on a sulfur-containing binder. Scientific Herald of the Voronezh State University of Architecture and Civil Engineering. Construction and Architecture. 2014. V. (23). P. 61-74.
- [18] Issakulov B.R., Zhiv A.S., Zhiv Yu.A., Strelnikova A.S. Light concrete on the base of industrial and agricultural waste. In: Proc. 2nd International Conference on Sustainable Construction Materials and Technologies, 2010.
- [19] Isakulov, B.R., Akulova, M.V., Kulsharov, B.B., Sartova, A.M., Isakulov, A.B. Formation of strength and phases of sequence of destruction of arbolite composites at various long loads. News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences, 2020, 4(442), c. 28-34.
- [20] Isakulov, B.R., Jumabayev, M.D., Abdullaev, H.T., Akishev, U.K., Aymaganbetov, M.N. Properties of slag-alkali binders based on industrial waste. 2019. Periodico Tche Quimica, 16 (32), P. 375-387.

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

Редакторы: М. С. Ахметова, Д. С. Аленов, А. Ахметова Верстка на компьютере А.М. Кульгинбаевой

Подписано в печать 03.12. 2020. Формат 60х881/8. Бумага офсетная. Печать – ризограф. 9,1 п.л. Тираж 300. Заказ 6.