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Д.В. Сокольский атындағы «Жанармай,
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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NEWS

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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of 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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**A.Kh. Zhakina¹, O.V. Arnt¹, Ye.P. Vassilets¹, T.S. Zhivotova¹,
Z.M. Muldahmetov¹, A.M. Gazaliev¹, S.A. Semenova²**

¹Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan;

²Federal Research Center of Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences,
Kemerovo, Russia.

E-mail: alzhakina@mail.ru, oxana230590@mail.ru, vassilets88@mail.ru,
zhts2004@mail.ru, semilight@mail.ru

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

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

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

Introduction

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

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

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

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

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

Experimental part

Materials

In preparing the composition, the thiourea formaldehyde resin (TUFR) was used as the cheapest and most technologically advanced synthetic binder. The choice of thiourea-formaldehyde resin is due to its availability and water solubility. Thiourea with a melting point of 180-182°C and a 37% aqueous formaldehyde solution are the feedstock for the synthesis of TUFR. TUFR was obtained by the standard method of polycondensation of thiourea with formaldehyde at a molar ratio of thiourea:formaldehyde = 1:2. Hardener used phosphoric acid (H₃PO₄). The resin yield was 92%. The composition and structure are proved by the data of IR-spectroscopy and conductometry.

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

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

Synthesis of composite material

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

Methods

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

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

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

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

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

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

Results and discussion.

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

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

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

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

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

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

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

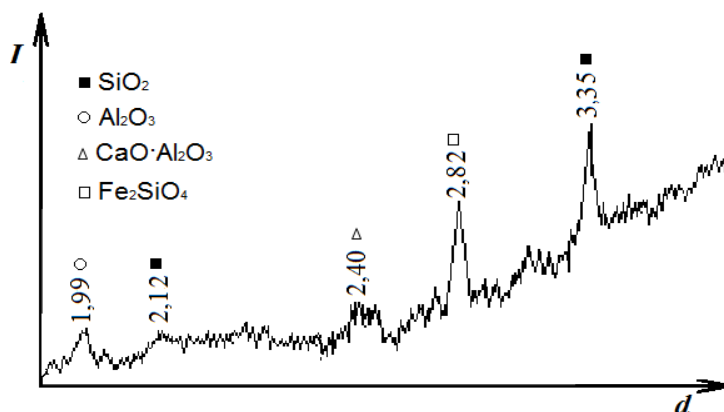


Figure 1 - X-ray diffraction pattern of the obtained composite BR+HNa+TUFR (2:1:1)

As the results of the study showed, heights are indexed in the region of interplanar spacing: $d=1,99 \text{ \AA}$ ($\gamma\text{-Al}_2\text{O}_3$), $d=2,12 \text{ \AA}$ ($\alpha\text{-quartz SiO}_2$), $d=2,40 \text{ \AA}$ ($\text{CaO}\cdot\text{Al}_2\text{O}_3$), $d=2,82 \text{ \AA}$ (Fe_2SiO_4 - fayalite), $d=3,35 \text{ \AA}$ ($\alpha\text{-quartz SiO}_2$).

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

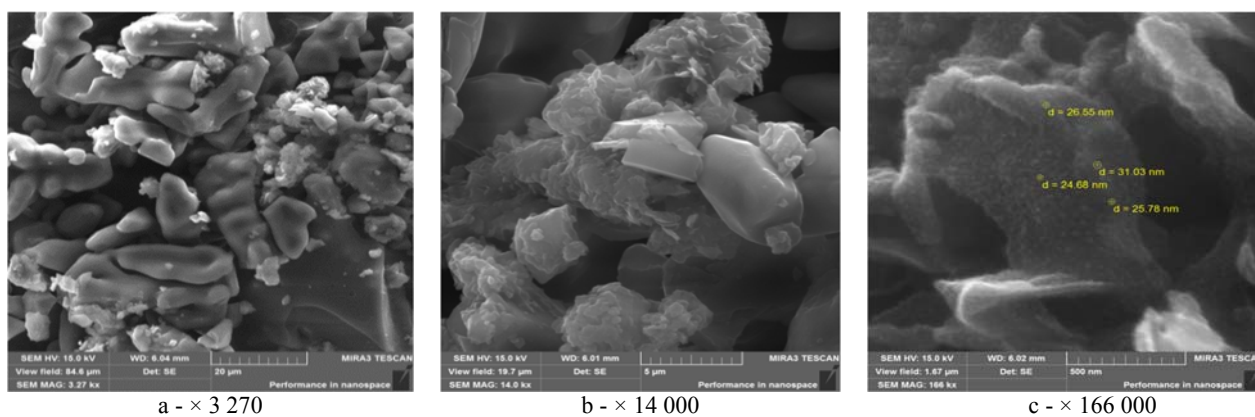


figure 2 - Electron microscopic images of BR+HNa+TUFR (2:1:1)

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

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

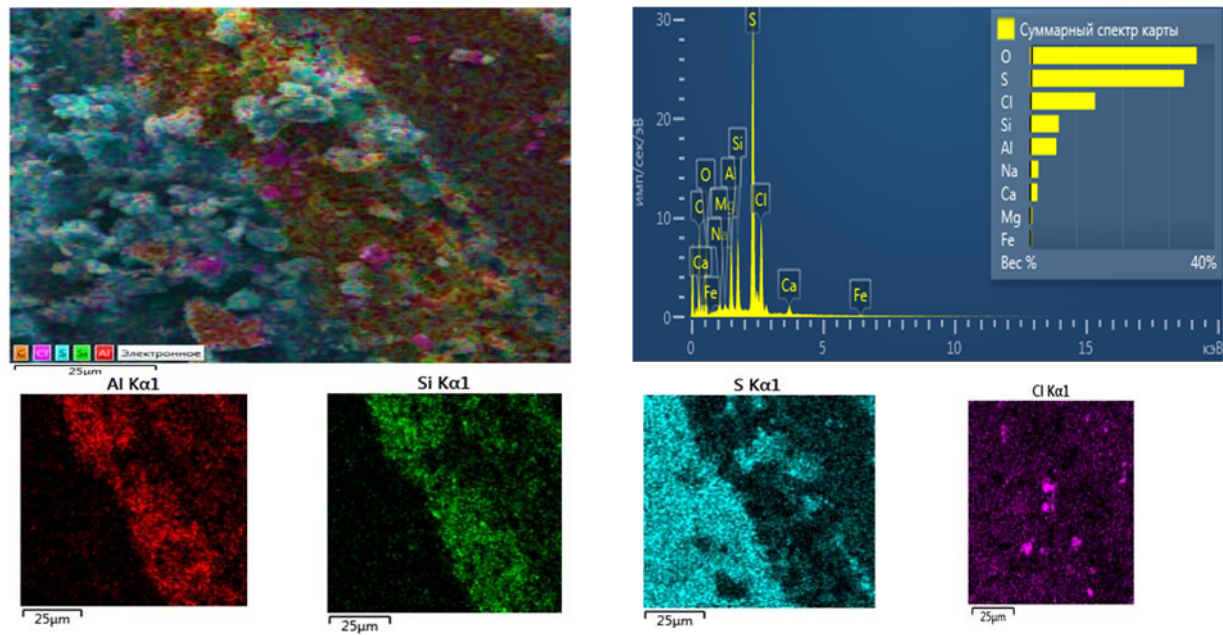


Figure 3 – EDS-map of the composite BR+HNa+TUFR = 2:1:1

Table 2 shows the physicomechanical characteristics of the obtained composites.

Table 2 - Physico-mechanical characteristics of the obtained composites

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

As can be seen from table 2, the curing time for composites based on burned rock with sodium humate in combination with thiourea-formaldehyde resin increases compared with the original resin. However, the addition of filler to the resin leads to a decrease in the formaldehyde content in the composite, thereby reducing its toxicity. The bulk density of thiourea-formaldehyde resin is 0,45 g/cm³, and for composites based on it, the value ranges from 0,92-0,95 g/cm³.

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

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

Conclusion

Thus, a new composite material was developed. By varying the composition of the matrix and filler, the mechanical strength of the composite is increased and toxicity is reduced. The composition of the composite obtained is confirmed by elemental and x-ray phase analysis. A microscopic analysis was performed to study the surface morphology of the synthesized composite. The physicomechanical

characteristics of composites are studied. A decrease in the content of free formaldehyde in the composite indicates a decrease in toxicity. The resulting composite can be used as a building material.

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**А.Х. Жакина¹, О.В. Арнт¹, Е.П. Василец¹, Т.С. Животова¹,
З.М. Мұлдахметов¹, А.М. Газалиев¹, С.А. Семенова²**

¹ҚР ЖШС Органикалық синтез және көмірхимиясы институты, Қарағанды, Қазақстан;

²Ресей ғылым академиясының Сібір бөлімінің көмір және көмір химиясы федералды зерттеу орталығы, Федералдық мемлекеттік бюджеттік ғылыми мекемесі, Кемерово, Ресей

КӨМІР ӨНДІРУ ҚАЛДЫҚТАРЫ НЕГІЗІНДЕГІ КОМПОЗИТТІК МАТЕРИАЛДЫҢ СИНТЕЗІ МЕН ҚАСИЕТТЕРІ

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

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

ұқсас құрам үлгілеріне қарағанда жоғары. Алынған композит құрылыс материалы ретінде пайдаланылуы мүмкін.

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

А.Х. Жакина¹, О.В. Арнт¹, Е.П. Василец¹, Т.С. Животова¹,
З.М. Мулдахметов¹, А.М. Газалиев¹, С.А. Семенова²

¹ ТОО Институт органического синтеза и углехимии РК, Караганда, Казахстан;

² Федеральный научно-исследовательский центр угольной и химической промышленности
Сибирского отделения Российской академии наук, Кемерово, Россия

СИНТЕЗ И СВОЙСТВА КОМПОЗИТНОГО МАТЕРИАЛА НА ОСНОВЕ ОТХОДОВ УГЛЕДОБЫЧИ

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

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

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

Information about authors:

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

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

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

Zhivotova Tatyana Sergeevna – Doctor of Chemical Sciences, professor, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, e-mail: zhits2004@mail.ru, <https://orcid.org/0000-0002-0793-4653>;

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

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

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

REFERENCES

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

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

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

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

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

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

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

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

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

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

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

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

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