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ТЕХНИКАЛЫҚ ҒЫЛЫМДАР ЖӘНЕ ТЕХНОЛОГИЯЛАР СЕРИЯСЫ / TECHNICAL SCIENCES AND TECHNOLOGY SERIES/ СЕРИЯ ТЕХНИЧЕСКИЕ НАУКИ И ТЕХНОЛОГИИ

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Investigations of the influence of organic aggregate on physical mechanical and adhesion properties of sulfur-containing arbolite

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Abstract. The main issue of this study is to investigate the effect of the porous structure of organic aggregate on cement stone and on the nature of the contact zone. As it is known, porous aggregate draws away some of the moisture from the adjacent cement stone layers, which promotes their compaction. In turn, the contact layers of the sulfur-containing binder also undergo changes. Also in the work, sulfur and its derivatives are used as an additive for chemical treatment. It is known that sulfur itself is a strong reducing agent, so it can affect the morphology and chemical composition of the surface of the organic aggregate of sulfur-containing arbolites. It was found that the highest index of efficiency coefficient equal to 1.02 and 1.01 have samples of sulfur-containing arbolite based on shredded cane and cotton stalks. The study of the structure of contact zones of sulfur-containing binder with shredded mercerized cane on samples from the binder dough with inclusion of shredded cane fiber showed that it has a dense and strong binder shell with a width of 35-60 µm. The results confirm that mercerization of cellulosic organic aggregates of sulfur-containing arbolites increases its adhesion ability. The obtained results of the study can be used for the manufacture of wall materials for low-rise construction.

Keywords: Sulfur-containing arbolite, contact zone, efficiency factor, sulfur, microhardness of organic aggregate, mercerization, compressive strength.

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Introduction

In recent years, the attention of many scientists of the Central Asian republics has been attracted to the issues of obtaining structural materials based on organomineral compositions, as components of which are used combined mineral binder and cellulose organic aggregate [1-15]. From the basic provisions of the theory of artificial conglomerates [1-7], which establishes the relationship between the components in concretes of optimal structure, it follows that the binder, organic aggregate and the contact zone between them should have a decisive influence on the strength of sulfur-containing concretes. At the same time, optimization of the structure of sulfur-containing arbolite can be achieved through a more complete use of the properties of organic aggregates and their involvement in the "work" of the whole arbolite concrete. The role of aggregates of different mineralogical composition in the formation of concrete structure has been studied in [3-10]. To study the adhesion of different types of organic aggregates with the mortar part of sulfur-containing arbolite and their influence on its strength properties, we used stalks of cane, rice straw and cotton, which were crushed to the same fraction and introduced into the composition of sulfur-containing binder. Evaluation of the processes occurring in the contact zone of the mortar part of sulfur-containing arbolite with organic aggregate was the cohesive force [1-15]. It is known that sulfur itself is a strong reducing agent, so it can affect the morphology and chemical composition of the surface of the organic aggregate of sulfur-containing arbolites. Thus, Japanese researchers applied sulfur in the presence of sulfur-containing bacteria for the reduction of hexavalent chromium [6, 7]. The bacteria oxidized elemental sulfur to SO2. H2SO3 was formed as an intermediate compound. Treatment with alkaline sulfur-containing solution (mercerization) of cellulose consists in treating it with alkali solutions, as a result of which it acquires additional (OH-) groups, which in turn gives it increased sorption capacity to ions of multivalent elements.

The methodology

Cellulose organic aggregates from vegetation and agro-industrial wastes according to GOST 19222 were used as initial porous aggregates for obtaining sulfur-containing arbolites. The physical and chemical properties of reed, its chemical and fractional composition (Tables 1, 2) were established experimentally in accordance with the requirements of GOST 19222, GOST 25820-2000, as well as on the basis of reference and literature data [1-10].

Cellulose $C_6H_{10}O_5$	Lignin $C_{41}H_{40}O_{15}$	Pentosan $C_5H_8O_4$	Resins and soluble components
46,17	29,76	22,00	2,07

Bulk density of reed stalks with natural moisture content is 70 kg/m3, and dried to constant weight - 58 kg/m3. The fractional composition of reed stalks is given in Table 2.

Table 2. Fractional composition of reed stalks in % by weight

Residuals	Sieve mesh size, mm						Passed a sieve with a 1.25 mm opening
	40	20	10	5	2.5	1.25	
Private	10	15	47	17	9,5	1,5	1,5
Full	10	25	72	86	95,6	98,5	100

As fillers and additives for the manufacture of arbolite were used industrial waste from enterprises of Kazakhstan in the form of sludge and solids [3-12]. As a modifying additive was considered technical sulfur - a secondary product of processing of high-sulfur oil from the fields of the Republic of Kazakhstan and pyrite cinders of the enterprise JSC "Phosphorhim", consisting mainly of a mixture of iron oxides, with a recalculation of the iron content of 40 - 63%, and sulfur impurities 1-2%. The rest are oxides of non-ferrous metals. Sulfur is a granulated product that meets the requirements of GOST 127.1-93. Portland cement of 400 grade of Chimkent cement plant in accordance with GOST 10178-85 and GOST 30744-2001 were also used for the study. The compositions of the studied samples are given in Table 3.

Table 3. Compositions of investigated sulfur-containing arbolites

20	Material consumption 1m^3 of arbolite				Density, kg/m^3
№ Compositions	Shredded cane stalks, kg	Technical sulphur, kg	Pyrite cinders, kg	Cement, kg	
1	255	25	80	270	450
2	260	23	82	260	420
3	250	25	80	280	550
4	240	27	78	300	500
5	230	30	75	320	600
6	200	35	70	350	650

Sulfur-containing arbolite samples were produced in the following technological sequence. Shredded cane stalks were subjected to the process of mercerization from 15 min to 24 h or more in contact with sulfur-containing solutions of 5 -15 % alkali, then performed:

– preparation of mercerized cane stalks and sulfur-containing additives by particle size distribution;

– preparation and dosing of each component of sulfur-containing binder separately;

– preparation and mixing of sulfur-containing components with the addition of a certain amount of water;

– loading of crushed cane stalks together with sulphur-containing binder into the drum mill;

– stopping the mill and unloading finished sulphur-containing arbolite mixtures;

– molding of products with compaction of the mixture by press method;

– natural hardening or heat treatment;

– demolding of products.

Optimization of composition, properties and technology of sulfur-containing arbolite was carried out experimentally. The study of properties of organic aggregates was carried out using standard methods according to GOST 19222. Physical and mechanical characteristics of sulfur-containing arbolite were determined in accordance with GOST 19222, 25820-2000, 7076-99, 7473-94, 10060.0-95 and 3476. When studying the bond strength of organic aggregate with the mortar part of sulfur-containing arbolite, we used a set of independent methods that allow us to obtain sufficiently complete and reliable data on the processes occurring at the contact boundary between binder and aggregate. The study of strength and deformation properties of sulfur-containing arbolite was carried out in climatic conditions of Central Asia and after normal curing chambers. Shrinkage strains were measured 28 days after curing in natural conditions. Creep of sulfur-containing arbolite was investigated during long-term loading under different loads on samples – prisms, sizes 150x150x600mm and samples cubes, sizes 100x100x100mm. The study was carried out in 28 days after curing in natural conditions and after heat treatment. Arbolite loading was carried out at loads of 0.3, 0.45, and 0.75 of the prism strength of sulfur-containing arbolite. The properties of thermal conductivity, fire resistance and biostability of sulfur-containing arbolite were studied under a wide variation of factors. The study of thermal conductivity was carried out at the Department of Physics of Aktobe Regional State University together with the Department of Building Materials Science, Special Technologies and Technological Complexes of Ivanovo State Polytechnic University in the natural and dry state or after heat treatment. To study the adhesion of different types of organic aggregates with the mortar part of sulfur-containing arbolite and their influence on its strength properties, we used cane stalks, rice straw and cotton stalks chopped to the same fraction, which were introduced into the composition of sulfur-containing binder. Evaluation of the processes occurring in the contact zone of the mortar part of sulfur-containing arbolite with organic aggregate was the cohesive force. To characterize the magnitude of the cohesive force of organic aggregates with sulfur-containing mortar part, as well as its influence on the strength of sulfur-containing arbolite concrete, the coefficient of efficiency of the aggregate in arbolite (α) was chosen, which was calculated from the results of determining the tensile strength. It is known [5-7] that the bonding force is determined by the chemical interaction processes occurring in the contact zones, so it is obvious that the efficiency factor α will change when the aggregate surface is isolated from the mortar part of the concrete. The coefficient φ is taken as a value characterizing the influence of chemical interaction on the bonding force in the investigated concretes, indicating how many times the efficiency factor of the aggregate in concrete will decrease when the chemical interaction in the contact is eliminated:

$$\varphi = \frac{\alpha_{uninsulated}}{\alpha_{isolated}},$$

where, $\alpha_{uninsulated}$, $\alpha_{isolated}$ – efficiency coefficients of uninsulated and insulated organic aggregates in arbolite concrete.

To evaluate the micromechanical properties of the contact layers of sulfur-containing cement stone and organic aggregate, the method of microhardness determination was used. The tests were carried out on polished slits of 30x30x30 mm cube specimens made of sulfur-containing cement dough, in the middle of which a fiber of crushed reed was placed. Since the main changes in the structure of contact layers of sulfur-containing cement stone are related to moisture migration in the organic aggregate, the dependence of microhardness change of sulfur-containing cement stone on the initial mortar with different ratio of components at 3 and 28 days of age was established. Together with measurements of microhardness, tests of compressive strength of specimens were carried out.

To investigate the change in the properties of cellulose fibers of organic aggregates, the crushed fibers of cotton stalks were subjected to chemical treatment with sulfur alkali solutions and its derivatives. The concentration of alkali in the sulfur solution ranged from 5 to 7%. The effect of mercerized cellulose on the strength properties of sulfur-containing arbolite was evaluated on 10x10x10cm arbolite cubes of density 550-600 kg/m3. Cane stalks and rice husk were used to determine the effect of different mercerization on the properties of organic aggregates.

It was found that the porous aggregate draws some moisture from the adjacent layers of cement stone, which promotes their compaction. In turn, the contact layers of sulfur-containing binder also undergo changes. The studies have shown that the use of all organic aggregates under study is effective - in all cases $\alpha > 1$. The samples with organic aggregate based on rice straw have a lower coefficient (Table 4). It was found that the highest coefficient of efficiency equal to 1.02 and 1.01 have samples of sulfur-containing arbolite based on shredded cane and cotton stalks (Table 4). Intensive chemical interaction with the mortar part of sulfur-containing arbolite is observed on organic aggregates from shredded cane and cotton stalks, for which the efficiency coefficient φ is in the range of 2.1-2.3. When excluding the chemical interaction with the mortar part of rice straw arbolite, the efficiency coefficient decreases 2 times, which can be explained by their structural features.

Table 4. Efficiency coefficient of different organic aggregates in sulfur-containing arbolite

Type aggregate	Tensile strength tensile strength, MPa			Coefficient efficiency of aggregate in arbolite	φ
	Arbolite	Organic aggregate	Sulphur stone binder		
Shredded cane stalks 18 mm fraction	3,34	1,24	4,7	1,02	2,6
Chopped rice straw stalks 18 mm fraction	1,27	0,89	4,7	0,85	2,1
Shredded cotton stalks 18 mm fraction	2,73	1,22	4,7	1,01	2,3

It is established that high microhardness in the contact layer of the binder stone and aggregate decreases as it moves away from the contact line. The study of the structure of contact zones of sulfur-containing binder stone with shredded mercerized reed on samples from binder dough with inclusion of shredded reed fiber showed that it has a dense and strong binder shell with a width of 35-60 microns.

So the microhardness of the contact layer of the sulfur-containing binder stone with shredded reed is equal to 1550 MPa, which is about 15% higher than the microhardness of the binder stone in the intergranular space. Due to the high porosity of the organic aggregate, the binder penetrates into the depth of the cellulose organic aggregate grain 105 - 135 microns. The porous shell of shredded cane due to the effect of self-vacuuming promotes the involvement of sulfur-containing binder inside the organic filler dough, which, interacting with the surface of the pore walls of the filler, activates them, while the sulfur-containing dough tightly adheres to the surface of cane particles. The contact zone between the sulfur-containing binder and the crushed reed is characterized by a dense structure, its width is 105-135 microns.

Microhardness and adhesion strength of organic aggregates in arbolite concretes are also determined by the nature of new formations arising in the contact zones as a result of physical and mechanical processes of interaction between the aggregate and components of sulfur-containing binder. Studies have shown that mercerized cane stalks have less effect on the setting time and strength gain of arbolite compared to untreated samples.

Apparently, water-soluble sugars, organic acids and mineral salts are leached from the cane stalks during such treatment. Therefore, in the process of making arbolite mercerization can replace the operation of preliminary soaking of cane in solutions of chemical additives. Determination of the compressive strength of sulfur-containing arbolites using rice husk, mercerized and unmercerized cane showed that intensive strength growth is observed in the first 14 days in all arbolites, further strength growth slows down (Fig.).

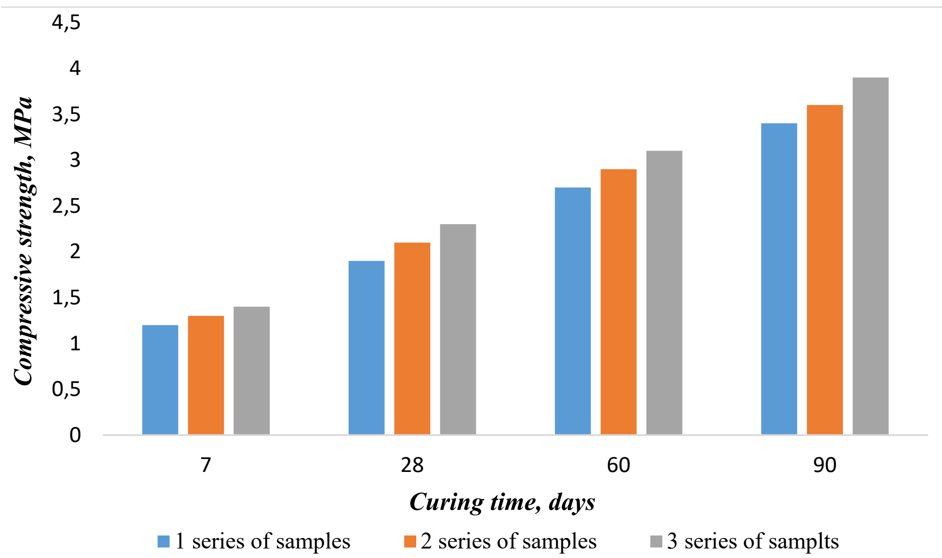

Figure 1. Compressive strength of sulphur-containing arbolite in depending on curing time and different organic aggregates:
1 - rice husk; 2 - untreated cane; 3 - mercerized cane

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The highest compressive strength after 28 days of curing is observed for samples based on mercerized cane stalks. Growth of strength of samples based on rice husk by 14 days is 2.1 MPa, on the basis of crushed cane stalks without treatment is 2.5 MPa and for samples based on mercerized cane stalks is 2.7 MPa. By 28 days, the strength growth of rice husk based samples is 3.0 MPa, based on crushed cane stalks without treatment is 3.5 MPa and for samples based on mercerized cane stalks is 4.0 MPa (Fig.). The results of the study, compositions and properties of the sulfur-containing arbolite are summarized in Table 5.

The obtained results confirm that mercerization of cellulose organic aggregates of sulfur-containing arbolites increases its adhesion ability.

Table 5. Compositions and properties of sulfur-containing arbolite based on mercerized reed stalks

Components of arbolite mixture	Units of measurement	Strength class arbolite	
		B 2,5	B 3,5
Cement	%	35	36
Mercerized cane stalks	%	20	21
Water per 1m^3 of mixture with dry organic aggregates	%	30	31
Industrial sulphur	%	3,2	3,6
Pyrite cinders	%	6,9	7,2
Mineralizers – calcium chloride; – barium chloride	%	 0,4 1,4	 0,5 1,6
Density	kg/m^3	550-590	590-650
Compressive strength	MPa	3,1	4,5
Water absorption	%	67	45
Frost resistance	cycle	50	75
Heat transfer coefficient	W/m*K	0,100	3,2

Findings/Discussion

The results of the study showed that mercerized cane stalks have less effect on the setting time and strength gain of arbolite compared to untreated samples. Apparently, water-soluble sugars, organic acids and mineral salts are leached from the cane stalks during such treatment. Therefore, in the process of arbolite production mercerization can replace the operation of preliminary soaking of cane in solutions of chemical additives. The increase in strength of sulfur-containing arbolite samples on mercerized cane can be explained by the fact that in addition to "tanning" of cane stalks there is also etching of its surface, nano-, micro- and macropores are formed in the material. Pores absorb sulfur from sulfur-containing compositions, which binds molecules on the surface of different phases during the subsequent hardening of the arbolite mixture.

The obtained results give grounds to assert that in the loaded state the mercerized organic aggregate has a high resistance to loads, hardens and can absorb even higher loads than in the unloaded state. Apparently, the formation of nano- and microstructure and strengthening of mercerized organic aggregate occurs due to the emergence of a kind of "tanning" effect in the fibers of reed stalk, similar to the effect of tanning leather and changes in the deformation modulus of the components of sulfur-containing arbolite under load. On the other hand, the reason for higher strength of sulfur-containing arbolite is the "colmatization" of nano- and micropores of mercerized cellulose with elementary sulfur from sulfur-containing composition of arbolite, which hardening causes an increase in the strength of the resulting product.

Conclusions

1. It was found that the highest index of efficiency coefficient equal to 1.02 and 1.01 have samples of sulfur-containing arbolite on the basis of shredded reed and cotton stalks.

2. study of the structure of contact zones of sulfur-containing binder with shredded mercerized cane on samples of binder dough with inclusion of shredded cane fiber showed that it has a dense and strong binder shell with a width of 35-60 microns.

3. The results confirm that mercerization of cellulosic organic aggregates of sulfur-containing arbolites increases its adhesion ability.

4. The obtained results of the study can be used for the manufacture of wall materials for low-rise construction.

The contribution of the authors

Isakulov B.R. – concept, methodology, resources, data collection, testing of experimental samples;

Tukashev J.B. – modeling, analysis;

Abdullaev H.T. – visualization, interpretation, writing;

Isakulov A.B. – editing.

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Күкіртті құрамалы арболиттің физикалық-механикалық және адгезиялық қасиеттеріне органикалық толтырғыштың әсерін зерттеу

Аңдатпа. Бұл зерттеудің негізгі проблемасы органикалық толықтырғыштардың кеуекті құрылымының цемент тасына және байланыс аймағының сипатына әсерін зерттеу болып табылады. Бұрыннан белгілі болғандай, кеуекті толықтырғыштар ылғалдың бір бөлігін цементті тастың іргелес қабаттарынан тартып алады және бұл құбылыс олардың тығыздалуына ықпал етеді. Өз кезегінде, күкіртті құрамалы тұтқыр байланыстырғыш заттың байланыс қасиеттері де өзгереді. Сондай-ақ, өндірісте күкірт және оның туындылары химиялық өңдеуге қосымша ретінде қолданылады. Күкірттің өзі күшті тотықсыздандырғыш екені белгілі, сондықтан күкіртті құрамалы арболиттердің органикалық толықтырғыштарының морфологиясы мен химиялық құрамына өз әсерін тигізуі мүмкін. Тиімділік коэффициентінің ең үлкен көрсеткіші 1,02 және 1,01-де ұсақталған қамыс пен мақта сабақтарына негізделген күкірт бар арболит үлгілері бар екені анықталды. Құрамында күкірт бар тұтқыр мен ұсақталған мерсерленген қамыстың түйісу аймақтарының құрылымын ұсақталған қамыс талшығының қосылуымен байланыстыратын қамыр үлгілерінде зерттеу оның ені 35-60 мкм тығыз және берік байланыстырушы қабығы бар екенін көрсетті. Нәтижелер целлюлоза-органикалық күкіртті арболиттердің мерсеризациясы олардың адгезия қабілетін арттыратынын растайды. Зерттеу нәтижелері аз қабатты құрылысқа арналған қабырға материалдарын өндіруде қолданылуы мүмкін.

Түйін сөздер: құрамында күкірт бар арболит, байланыс аймағы, тиімділік коэффициенті, күкірт, органикалық агрегаттың микроқаттылығы, мерсеризация, қысу беріктігі.

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Исследование влияния органического наполнителя на физико-механические и адгезионные свойства серосодержащего арболита

Аннотация. Основной проблемой данного исследования является изучение влияния пористой структуры органического заполнителя на цементный камень и на характер контактной зоны. Как известно, пористый заполнитель оттягивает часть влаги из прилегающих слоев цементного камня, что способствует их уплотнению. В свою очередь, контактные слои серосодержащего вяжущего также претерпевают изменения. Также в работе сера и ее производные используются в качестве добавки для химической обработки. Известно, что сера сама по себе является сильным восстановителем, поэтому она может влиять на морфологию и химический состав поверхности органического заполнителя серосодержащих арболитов. Установлено, что наибольший показатель коэффициента эффективности, равный 1,02 и 1,01, имеют образцы серосодержащего арболита на основе измельченного тростника и стеблей хлопчатника. Исследование структуры зон контакта серосодержащего вяжущего с измельченным мерсеризованным тростником на образцах из теста вяжущего с включением измельченного тростникового волокна показало, что оно имеет плотную и прочную связующую оболочку шириной 35-60 мкм. Полученные результаты подтверждают, что мерсеризация целлюлозно-органических агрегатов серосодержащих арболитов повышает их адгезионную способность. Полученные результаты исследования могут быть использованы при изготовлении стеновых материалов для малоэтажного строительства.

Ключевые слова: Серосодержащий арболит, зона контакта, коэффициент эффективности, сера, микротвердость органического заполнителя, мерсеризация, прочность на сжатие.

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