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USE OF OIL AND BITUMINOUS ROCKS AND WASTE FROM THEIR PROCESSING IN CREATION OF COMPOSITE SILICATE MATERIALS

Abstract. The article considers the issues of technology of silicate materials of dense and cellular structure with usage of oil bituminous rocks and waste from their processing, in particular: the optimization of the ratios of the raw components of a silicate materials mixture, the development of optimal technological parameters for the production of silicate materials, and the technological aspects of the production of the above materials.

The optimal compositions of binders with use of waste products from OBR are studied in this work as an activating component of lime or cement. The stability of the samples was studied in various media with a low and high content of basic calcium hydrosilicate. If they contain insoluble silicates and aluminosilicates containing silica, they are acid resistant. Alkali-resistant rocks containing oxides corresponding to strong bases are combined with oxides corresponding to weak acids, for example, calcium and magnesium carbonates.

As a result of the experimental work, technological processes for the manufacture of silicate materials (of dense and cellular structure) based on the OBR and waste from their processing are substantiated and developed. The paper reveals the chemical-mineralogical and the structural features of oil bituminous rocks and waste from their processing. The optimal ratio of the waste mixture of oil and bituminous rocks with lime and the technological parameters that ensure the grade of lime-sand binder from 400 to 500 are established. Silicate materials based on this mixture have high physical and mechanical properties and comply with the requirements of the ST standards of the Republic of Kazakhstan for silicate brick and GOST state standard for aerated concrete.

Thus, the compositions and conditions for the preparation of these binders with high resistance in large temperature, pressure and aggressive environments are proposed in this work.

Key words: oil bituminous rocks and waste from their processing, structure, mechanochemical activation, silicate materials, binder, cellular concrete, durability.

Introduction. One of the problems of the global scale of the twenty-first century is the human impact on the environment. In this regard, the utilization of oil bituminous rocks (hereinafter - OBR) and waste from their processing is given special attention [1].

The solution to the above problem is the creation and development of non-waste environmentally friendly and mobile technology in creating systems of silicate composite materials and technology for the synthesis of artificial stone, energy-saving and low-energy-consuming man-made products.

The presence of a large number of deposits of the OBR and bitumen-containing sands (hereinafter referred to as the Kir) in Kazakhstan, and as a result, replenishment of scarce oil products, determines the organization of the processing of the OBR with the receipt of 15-30% of bitumen and 70-85% of the mineral part of the sandy type feldspar-quartz, clay and carbonate composition. Currently, more than 50 deposits have been examined and developed only in the western regions of Kazakhstan and reserves of more than 20 million m3 have been determined [2].

The mineral part of the OBR under the microscope is represented by isometric grains of a darkish color, angular and low-rounded, 0.10-0.15 mm in size, which indicates fine grain size. The specified type of raw material contains up to 70% quartz, 24% feldspars, 3% calcite, single grains of sulfides, apatites, and barite. Voidness - 42%, average density - 1290 kg / m3. The chemical composition is presented in table 1.

Table 1 - chemical composition (%) of the mineral part of the OBR processing

Product name	SiO_2	Al_2O_3	Fe_2	Ca	M	K_2	Na	SO	C	П
Mineral part of the OBR processing	82,6	9,3	2,0	1,3	0,3	1,8	1,2	0,8	-	1,4

The OBR processing waste is a group of calcareous-siliceous materials that are dispersed systems of insoluble particulate matter of an amorphous or submicrocrystalline structure with a significant amount of free kinetic energy sufficient for the mutual attraction of the macroparticles with the formation of water-resistant structural bonds. This makes it possible to minimize fuel and energy processing costs, to carry out directional regulation of structure formation in materials hardening without heat treatment, thereby intensifying the technological process for the production of silicate materials and products based on them [3].

The physicochemical, mineralogical, and structural features of the OBR and mineral waste from their processing are represented by two main groups - siliceous materials containing more than 50% SiO_2 and limestone-siliceous materials containing 20-50% CaO and 20-50% SiO_2.

Materials and methods. In this work, we studied the optimal composition of binders using waste from the OBR processing as an activating component of lime or cement. To obtain comparative data, natural sand was used, the composition of which is identical to the waste of the OBR processing, i.e. quartz-feldspar mineralogical composition.

Mechanochemical activation was applied by co-grinding the components of the mixture [4]. Shredding of waste from the OBR processing occurs more quickly than its natural counterpart. This is facilitated by the presence of defects on the surface of the grains of the waste of the OBR processing; surface melting and deeper cracks along the cleavage of feldspar crystals and others in the process of heat treatment of the rock while removing bitumen.

Lime and sand binder. Obtained by co-grinding the waste from the processing of OBR with lime, to a specific surface of 300 m^2/kg. The optimal ratio of lime and waste from the OBR processing are in the range from 0.5:1 to 1:1, at which the activity of lime-sand binder has the highest rates, i.e. strength of 42-50 MPa.

The properties of samples of calcareous-sand binders, depending on the composition and conditions of hardening, vary significantly - samples subjected to autoclaving have a higher strength than samples steamed and hardening under ordinary conditions. It is possible to note the linear nature of the dependence of strength values in the direction of increase, with a corresponding increase in the content of lime in the composition of binders [5].

We studied the possibility of using OBR processing waste as an additive to cement. An evaluation criterion for mechanical activation was the heat of hydration of the activated mixture from the waste of the OBR and the strength of the composite materials based on it - binders with the addition of waste from the OBR are at the same level as with the addition of blast furnace clinker [6].

Results of research. Studies of the impact of additives from OBR processing waste showed that the compressive strength of samples depends on the hardening conditions - for samples with composition: 70% cement clinker and 30% of OBR processing waste hardening under ordinary conditions, compressive strength in 28 days is 46, 0 MPa. After autoclaving, the samples show composition: 50% cement clinker and 50% OBR processing waste, compressive strength is 50.0-53.8 MPa. This composition is optimal and the obtained results on compressive strength are objectively approximated with a normal density value of 27.3%, which is one of the smallest. Hence, it can be considered that the waste of the OBR processing is an active additive and increases the grade of cement.

Considering the fact that most of the known deposits of OBR are located near oil producing regions where cement with special properties (grouting) is used, the one in contact with various mineralized waters, accompanied by high temperature conditions and pressure, the possibility of OBR processing products as active additives to obtain special cements was reviewed.

Studies of the stability of binders in solutions of magnesium sulfate, sodium sulfate, magnesium chloride and sodium, in natural mineralized waters typical of Kazakhstan (sulfate-chloride and chloride-sulfate), resistance to atmospheric conditions and alternate freezing and thawing [7]. The mineralogical composition, structure and dispersion of the siliceous component have a great influence on the resistance of autoclaved materials to the aggressive action of sodium and magnesium sulfate solutions [8].

Lime-sand samples made from mineral wastes from OBR processing turned out to be more resistant than cement-sand samples made from traditional raw materials. But in sodium sulfate solutions, the above calcareous samples turned out to be less stable. Therefore, impurities of feldspar rocks in sands are not only acceptable, but also desirable, especially if the products are used under conditions of further exposure to magnesium-sulfate corrosion. The durability of lime-sand products can be increased by increasing the dosage of lime in lime-sand mixtures. The resistance of lime-sand products containing sodium salts can be increased by introducing a certain amount of ground sand [9]. The stability of the samples was studied in various media with a low and high content of basic calcium hydrosilicate. If they contain insoluble silicates and aluminosilicates containing silica, they are acid resistant. Alkali-resistant rocks containing oxides corresponding to strong bases are combined with oxides corresponding to weak acids, for example, calcium and magnesium carbonates.

We performed a series of experiments in which the test samples of cement containing up to 50% of the waste of the OBR processing were closed with a 5% solution of Na_2SO_4 in one case, and in the other with a 3% solution of $MgSO_4$. The experimental results are shown in table 2.

Table 2 - Influence of aggressive environments on the change in bending strength (MPa) of cements with the addition of OBR processing waste

Materials and conditions of preparation	Hardening conditions	Storage in 5% Na_2SO_4 for			Storage in 3% $MgSO_4$ for		
		1 day	6 day	12day	1 day	6 day	12day
cement with 50% of waste from OBR processing and sealed with water	under normal conditions	3,6	2,7	1,6	3,6	2,9	1,1
	steaming at 75^{0}C	4,4	4,1	3,3	4,4	4,0	3,0
	autoclaving at 175^{0}C	5,2	4,6	4,2	5,2	4,8	5,0
cement with 50% waste from the processing of OBR and sealed with 5% solution of Na2SO4	under normal conditions	4,0	3,6	3,8	4,6	4,4	4,4
	steaming at 75^{0}C	6,3	6,4	7,0	6,3	6,0	6,6
	autoclaving at 175^{0}C	7,4	7,6	7,8	7,4	7,6	7,8
cement with 50% waste from OBR processing and cured with 2% MgSO4 solution	under normal conditions	4,2	4,8	4,4	4,2	4,9	4,6
	steaming at 75^{0}C	5,8	5,5	5,8	5,8	5,9	6,0
	autoclaving at 175^{0}C	6,2	6,4	6,6	6,2	6,5	6,8

After molding, part of the samples hardened under ordinary conditions, the other was steamed at 75 ^{0}C, and the third part was autoclaved at 175 ^{0}C. Hardened samples were placed in solutions of sodium sulfate and magnesium. After the expiration of the storage period, they were subjected to a strength test.

Mixing with sulfate solutions, increasing the temperature of the hardening conditions, storage in aggressive solutions - all these improves the strength of the samples. In particular, samples made from a mixture inoculated with a 5% sodium sulfate solution and hardened under conditions of steaming at 75 °C, after 12 months of storage in solutions of 5% Na2SO4, and 3% MgSO4, reduced the strength by 5% (table 3.2.1) and the samples made from the mixture, sealed with a 3% MgSO4 solution and solidified under the same conditions, after storage in a 5% sodium sulfate solution and after the same test periods, not only did not reduce the strength, but, on the contrary, increased it by 5%, and when stored in 3% MgSO4, these same samples reduced strength by 4% [10] .

It should be noted that samples hardened in hydrothermal conditions at 175 °C have absolute resistance, which not only does not decrease, but, on the contrary, increases in aggressive sulfate solutions.

From this it follows that when using cements with the addition of waste products of the OBR processing used for laying boreholes, sulfate resistance can be improved by introducing sulfate salts into their composition. This mechanism of action, conventionally called the “affinity” of the composition of cement with the test medium, can be common for other types of binders and aggressive environments [11].

Silicate materials with a cellular structure. We studied silicate materials of a cellular structure based on OBR and waste from their processing. The ratio of cement to lime was established on experimental basis: the ratio of the waste of the processing of OBR and binder (50% lime and 50% cement) is accepted - 1.5: 5 and 1.75: 1 and they correspond to a water-hard ratio - 0.45 and 0.44. Under these conditions, the compressive strength of the samples is 5.1 and 5.2 MPa, with a density of 730-742 kg/m3. When the ratio of the waste of processing OBR and binder (60% lime and 40% cement) is 1.5: 1 and 1.75: 1, the density of the samples is 738-742 kg / m3, and the compressive strength is 5.2 and 5, 1 MPa. Data strength characteristics of these compositions are presented in table 3.

Table 3 - The effect of the ratio of the mixture components
on the density and strength of samples with a cellular structure

The ratio (products of processing OBR: astringent)	The composition of the binder (50% lime and 50% cement)			The composition of the binder (60% lime and 40% cement)		
	W/H	Density, kg/m^3	Compressive strength, MPa	W/H	Density, kg/m^3	Compressive strength, MPa
1:1	0,48	720	4,01	0,46	730	3,8
1,25:1	0,47	723	4,6	0,47	733	4,3
1,5:1	0,45	730	5,1	0,45	738	5,2
1,75:1	0,44	736	5,2	0,44	742	5,1
2:1	0,43	740	3,38	0,44	750	3,6

The structural properties of cellular concrete indicators and a number of its properties are influenced by the amount of blowing agent [13]. The compressive strength of the samples increases with the consumption of aluminum powder of 0.058 by weight of the dry components for the mixture, where the ratio of the components of the waste of the processing of OBR and binder is 1.5: 1, and with a ratio of 1.75: 1, the optimal consumption of aluminum powder is 0.060%.

Thus, the waste of OBR processing both in milled and not in milled form is suitable as a siliceous component for the production of silicate materials with a cellular structure that meet the requirements of the standards with respect to its properties [14].

In order to reduce water absorption and increase the hydrophobic properties of cellular concrete, natural OBR is introduced into the mixture in an optimal dosage of 10%. Natural OBR contained in the mixture up to 10% ensures the hydrophobicity of products: reduces water absorption by 25%, vapor permeability by 45%, shrinkage by 20%, adsorption moisture by 2.2 times. In addition, it contributes to the modification of the capillary-porous structure in the intergranular space of the material and the creation of fine crystallinity and fine porosity, which leads to a decrease in deformation stresses by 4.3 times compared to materials without additives. Samples made from a mixture with the addition of 10% OBR are more frost-resistant than those without the additive — they withstood up to 100 cycles without destruction [15].

Silicate materials of dense structure. Dense silicate materials based on OBR and their waste were studied. To increase the activity of the interaction of the components, the raw material was partially milled (to activate it) and introduced into the mixture from 10 to 20%. A positive effect of the addition of the ground part of the OBR processing waste on the strength of pressed silicate samples was observed. Combined grinding of waste products from OBR and lime significantly contributes to an increase in the strength of the samples - up to 30 MPa, with a binder content of 22-25%.

With a constant ratio of binder and waste processing OBR, equal to 1: 3, with an increase in press pressure increases the density of the samples and at the same time decreases water absorption [16].

With a constant composition of a mixture of a binder -25% and non-ground product of processing OBR - 75% and a pressure of 20.0 MPa, with increasing humidity of the mixture, the density of the samples increases, and the compressive strength increases to a certain value of the moisture of the mixture - 7-9%, in which the density and strength are respectively 1810 and 1826 kg / m; 24.84 and 25.1 MPa. With increasing temperature of the processed medium, the strength of the samples increases. Strength and density indicators of the tested samples are shown in table 4.

Table 4 - the Effect of hardening conditions on the properties of silicate material based on waste processing OBR

Mixture composition, %		Hardening conditions	Density, kg/m^3	Compressive strength, MPa
Binding	OBR processing waste			
25	75	steaming at 80^{0}C	1830	10,8
25	75	steaming at 120^{0}C	1840	16,4
25	75	autoclaving 175^{0}C	1858	25,0

Frost resistance of pressed samples after 25 cycles of alternate freezing and thawing, in general, meets the requirements of GOST 379-2015 [17] on silicate stones and bricks: compressive strength - 29.7 MPa; density - 1870 kg / m; water absorption - 9.2%; frost resistance - 25 cycles; brand - 250.

Thus, as a result of the tests we were able to establish the technological aspects of obtaining silicate materials based on OBR and waste from their processing.

The quality of silicate products is closely related to the composition and structure of the neoplasms represented by CSH (1) and tobermorite, the structure of which varies from gel to fine crystalline.

The parameters of the microporous structure of phase-forming calcium hydrosilicates vary from the hardening conditions and determine the operational properties of the material. The less porous and more homogeneous structure that takes place during hardening of samples under wet conditions or by steaming corresponds to the highest strength and frost resistance of materials [18].

The strength of the samples both after molding and after hardening increases with increasing pressure. The strength of samples after molding intensively increases by more than three times with an increase in pressing pressure from 5.0 to 20.0 MPa, then with a further increase in pressure from 30.0 to 40.0 MPa, the strength of samples after molding increases by 19%.

The increase in the strength of the samples with increasing pressure is due to the fact that during compaction by pressing, “constrained” conditions are created under which the interacting particles are significantly closer to each other, the solvated solid phase is densely packed, and the polarization interactions of the particles of the components are greatly enhanced. With less pressure, the distance between the particles is greater meaning that the concentration of the solid phase decreases and the solvated particles of the components are disconnected, and the water contained between them has thick interlayers, which leads to a weakening of the polarization interaction and reduces the rate of formation of cement substances [19].

On the basis of non-ground waste from the processing of OBR, it is possible to manufacture cellular concrete products with a density of 700-728 kg / m3 and compressive strength of 5.4 - 5.9 MPa. In the manufacture of cellular concrete with the addition of 10% natural OBR, the hydrophobicity of products is achieved up to 85%.

According to their physical and mechanical properties, pressed silicate materials and products meet the requirements of standards: stamp 75 to 250, density 1810-1920 kg / m, water absorption 7-10%, frost resistance 15-50 cycles. Silicate brick based on the non-ground product of processing OBR and lime-sand binder during autoclaving has the brand name “200”, and with the addition of an additional 5% cement, the autoclave treatment can be replaced by steaming.

Conclusion. Based on the results of the work, technological processes for the manufacture of silicate materials (dense and cellular structure) based on OBR and the waste from their processing are substantiated and developed. The chemical-mineralogical and structural OBR and waste from their processing have been identified [20], namely:

− OBR of semi-dark color contains up to 15% of the organic part and up to 85% of the mineral part, including 70% of quartz and 30% feldspar minerals. The structure of grains along cracks, cleavages and surface grooves is saturated by the organic components (bitumen);

- waste from OBR processing consists of a fine-grained sandy substance of feldspar-quartz composition.

The surface of the grains of quartz and feldspar is darkly colored, slightly melted, has numerous defects and cracks along the cleavages. In terms of chemical composition, in addition to silicon dioxide, aluminum oxides and alkali metals are present [21].

It was determined that the optimal ratio of the mixture of waste from OBR processing with lime and the technological parameters ensure that the lime-sand binder is 400 to 500 grit. Silicate materials based on it have high physical and mechanical properties and meet the requirements of ST for silicate brick and GOST for cellular concrete.

In addition, the presence in OBR system of up to 15% bitumen does not significantly affect the phase composition of hydrated components having less crystallinity, a more gel-like structure; promotes the formation of a thin film on the surface of the interacting particles, reducing the speed of their interaction. Hydrated neoplasms in the studied materials have a microporous structure. These factors have a positive effect on the strength characteristics of the material.

Silicate materials of a cellular structure made on the basis of OBR in an amount of 10% in a mixture of waste from OBR, lime or cement achieve significant hydrophobicity, which positively affects the reduction of water absorption by 25%, sorption moisture by 2.2 times, shrinkage by 20%, vapor permeability up to 2 times, which significantly improves the performance of products.

Cementing materials based on wastes from processing of OBR in a mixture with lime or cement, have low heat and in heat-moisture conditions they intensively gain the required grade, have high sulfate resistance, in conditions of elevated temperature and hostile environment, which simulates working conditions when drilling boreholes. The compositions and conditions for the preparation of these binders, which are highly resistant under conditions of high temperature, pressure and aggressive environment, are proposed.

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МҰНАЙ БИТУМИНОЗДЫ ЖЫНЫСТАР МЕН ОЛАРДЫ ӨҢДЕУДІҢ ҚАЛДЫҚТАРЫПАЙДАЛАНЫП ЖӘНЕ ӨҢДЕП СИЛИКАТТЫ МАТЕРИАЛДАРДЫН ЖАСАУ

Аннотация. Мақалада мұнай битуминозды жыныстарды және оларды қайта өңдеу қалдықтарын қолдана отырып, тығыз және ұяшықты құрылымдағы силикатты материалдар технологиясы, атап айтқанда: силикатты материалдар қоспасының шикізат құрамдастарының арақатынасын оңтайландыру, силикатты материалдарды дайындаудың оңтайлы технологиялық параметрлерін әзірлеу, жоғарыда аталған материалдар өндірісінің технологиялық аспектілері мәселелері қарастырылған.

Мұнай битуминозды жыныстар мен оларды қайта өңдеу қалдықтарының химиялық-минералогиялық және құрылымдық ерекшеліктері анықталды. Шикізаттың химиялық-минералогиялық құрамын, оның контактілі-конденсациялық қасиеттерін назарга ала отырып, жұмыста әктің немесе цементтің активтендіруші компоненті ретінде МБЖ қайта өңдеу қалдықтарын пайдалана отырып тұтқыр заттардың оңтайлы құрамы зерттелді. Тұтқыр қасиеттерді айқындау және күшейту үшін қоспа компоненттерін бірге ұсақтау жолымен механикалық-химиялық активациялау қолданылды. Дисперсиялықтың жоғарылауы және сонымен бірге шикізаттың белсенділігі көп дәрежеде жоғары қаттылықпен сипатталатын материалдарды бірге ұнтақтау кезінде байқалады.

Мұнайбитуминозды жыныстар минералдарының жоғары ерігіштігі олардың әкпен өзара әрекеттесуін белсендіреді. Әктасты-құмды тұтқыр материалдар үлгілерінің қасиеттері, құрамы мен қатаю жағдайларына байланысты айтарлықтай өзгереді - автоклавты өңдеуден өткен үлгілер буландырылған және әдеттегі жағдайларда қататын үлгілерге қараганда беріктігі жоғары болады. Байланыстыргыш құрамындағы әктас мөлшерінің тиісті ұлгаюымен беріктілік мәндерінің ұлғаю жағына тәуелділігінің сызықтық сипаты белгіленеді. Мұнай битуминозды жыныстарды қайта өңдеу қалдықтар қоспасының әктаспен оңтайлы арақатынасы және технологиялық параметрлер анықталды, олар әктас-құмды тұтқыргыштың маркасын 400-ден 500-ге дейін қамтамасыз етуге мүмкіндік береді.

МБЖ қайта өңдеу қалдықтарын цементке қоспа ретінде пайдалану мүмкіндігі зерттелді. Механикалық активтендірудің бағалау критерийі МБЖ қайта өңдеу қалдықтарынан белсендірілген қоспаныың гидратациялау жылылығы және оның негізіндегі композициялық материалдардың беріктігі болып табылады - МБЖ қайта өңдеу қалдықтары қосылған байланыстыргыш домна қожын қосқандағыдай деңгейде болады.

Сығылуға беріктігі бойынша алынған нәтижелер ең аздарының бірі болып табылатын қалыпты қоюлықтың мәнімен объективті түрде апроксимацияланады. Меншікті беті аз мұнай битуминозды жыныстарды қайта өңдеудің құмды өнімдерін қосқан кезде цемент үлгілерінің жұқа ұсақтауға қарағанда беріктігі жоғары болуы тиіс. Мұнай битуминозды жыныстардың қайта өңделген меншікті беті аз құмды өнімдерін қосқан кезде цемент үлгілері ұсақ майдалангандарға қарағанда беріктігі жоғары болды. Мұны суспензиядағы материалдың ірі фракциялары pH-ортаның мәнін төмендететіні түсіндіреді, бұл цемент сияқты сілтілі реакциясы бар аралас байланыстырғыштың гидратациясы мен гидролизін жеделдетуге ықпал етеді. Мұндай механизм цементтің мұнайбитуминозды жыныстарды қайта өңдеудің құмды өнімдерімен қышқылдық-негіздігімен өзара әрекеттесуіне негізделген. МБЖ қайта өңдеу қалдықтары белсенді қоспа болып табылады және цементтің маркалығын арттырады, сондай-ақ жылу өңделген алюминосиликат құрамы сазы, күл-шығару, шлактар және басқа да техногендік заттар түріндегі пирогенді өнімдермен салыстырылатын белсенді қоспа болып табылады, бұл олардан мұнай өнімдерін алу процесіндегі термиялық әсермен түсіндіріледі. Мұнайбитуминозды жыныстардың белгілі кен орындарының басым бөлігі арнайы қасиеттері бар (ауырлатылған, тұзға төзімді, ыстық пен тұзға төзімді, тампонаждық) цементтер көп мөлшерде тұтынылатын мұнай өндіруші аудандарға жақын орналасқанын ескере отырып, мұнайбитуминозды жыныстарды қайта өңдеу өнімдерін арнайы цементтер алу үшін белсенді қоспалар ретінде пайдалану мүмкіндігі қарастырылды. Кальцийдің төмен және жоғары негіздегі гидросиликаттарының үлгілері түрлі орталарда төзімділігі зерттелді.

Атап айтқанда, құрамында мұнай битуминозды жыныстарды қайта өңдеудің құмды қалдықтары бар сыналатын цементтер магний мен натрийдің сульфатты ерітінділеріне салынып, автоклав жағдайында қатайтылғаннан кейін сульфатты ерітінділерде сақталды. Жасалған үлгілер осы агрессивті ерітінділерде абсолютті төзімділікті көрсетті. Бұл әрекет механизмі цемент құрамының пайдалану ортасымен "туыстық" деп шартты түрде атадық. Көрсетілген қағида тұтқыр материалдар мен агрессивті орталардың басқа түрлеріне қолданылуы мүмкін. Құрамында кремнезем бар ерімейтін силикаттар мен алюмосиликаттар болған жағдайда олар қышқылға төзімді болып табылады. Жүргізілген эксперименталдық жұмыстар нәтижесінде МБЖ және оларды қайта өңдеу қалдықтары негізінде силикатты материалдарды (тығыз және ұяшықты құрылымды) дайындаудың технологиялық процестері негізделді және әзірленді. Мұнай битуминозды жыныстардың қайта өңделген техногенді минералдық өнімдері ұнтақталған, сондай-ақ ұнтақталмаған түрінде қасиеттері бойынша стандарт талаптарына сай ұяшықты құрылымдағы силикатты материалдарды өндіру үшін кремнеземдік компонент ретінде жарамды болып табылады. Силикатты қоспаға табиғи мұнай битуминозды жыныстың 5% - ға дейінгі қоспасы бұйымдардың гидрофобиялығын қамтамасыз етеді: су сіңірілуін 25% - ға, бу өткізгіштігін 45% - ға, адсорбциялық ылғалдылықты 2,2 есе, капиллярлы сору 7 есе, аязға төзімділікті 100 циклге дейін азайтады. Силикат қоспасына мұнайбитуминозды жынысты қосу капиллярлы-кеуекті құрылымды модификациялауға және ұсақ кристалдылықты және ұсақ кеуекті құруға ықпал етеді.

Әк бар мұнай битуминозды жыныстарды қайта өңдеу қалдықтарынан алынған әк-құмды байланыстырғыш негізіндегі силикатты материалдардың жоғары физикалық-механикалық және пайдалану қасиеттері бар және олар силикатты кірпіш пен ұяшықты бетонға қойылатын нормативтік талаптарға сәйкес келеді.

Түйін сөздер: мұнай битуминозды жыныстар мен оларды өңдеудің қалдықтары, құрылым. механохимиялық активтендіру, силикатты материалдар, тұтқыр, ұялы бетон, беріктік.

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ИСПОЛЬЗОВАНИЕ НЕФТЕБИТУМИНОЗНЫХ ПОРОД И ОТХОДОВ ИХ ПЕРЕРАБОТКИ В СОЗДАНИИ КОМПОЗИЦИОННЫХ СИЛИКАТНЫХ МАТЕРИАЛОВ

Аннотация. В статье рассмотрены вопросы технологии силикатных материалов плотной и ячеистой структуры с применением нефтебитуминозных пород и отходов их переработки, в частности: оптимизация соотношений сырьевых составляющих смеси силикатных материалов, разработка оптимальных технологических параметров изготовления силикатных материалов, технологические аспекты производства вышеуказанных материалов.

Выявлены химико-минералогические и структурные особенности нефтебитуминозных пород и отходов их переработки. Принимая во внимание химико-минералогический состав сырья, его контактно-конденсационные свойства, в работе исследовались оптимальные составы вяжущих веществ с использованием отходов переработки НБП, как активизирующего компонента извести или цемента. Для проявления и усиления вяжущих свойств была применена механохимическая активация путем совместного

измельчения компонентов смеси. Повышение дисперсности и вместе с тем активности сырья в большей степени отмечается при совместном помоле материалов, характеризующихся повышенной твердостью.

Повышенная растворимость минералов нефтебитуминозных пород активизирует их взаимодействие с известью. Свойства образцов известково-песчаных вяжущих материалов, в зависимости от состава и условий твердения, изменяются в значительных пределах - образцы, прошедшие автоклавную обработку, имеют более высокую прочность, чем образцы, пропаренные и твердеющие в обычных условиях. Отмечается линейный характер зависимости значений прочности в сторону увеличения, с соответствующим увеличением содержания извести в составе вяжущих. Установлено оптимальное соотношение смеси отходов переработки нефтебитуминозных пород с известью и технологические параметры, которые позволяют обеспечить марочность известково-песчанного вяжущего от 400 до 500.

Изучалась возможность использования отходов переработки НБП как добавки к цементу. Оценочным критерием механической активации явилась теплота гидратации активизированной смеси из отходов переработки НБП и прочность композиционных материалов на ее основе - вяжущие с добавкой отходов переработки НБП, находятся на том же уровне, что и при добавке доменного шлака. Полученные результаты по прочности на сжатие, объективно апроксимируются со значением нормальной густоты, являющийся одной из наименьших. При добавке песчаных продуктов переработки нефтебитуминозных пород с меньшей удельной поверхностью цементные образцы имели более высокую прочность, чем при более тонком измельчении. Это объясняется тем, что более крупные фракции материала в суспензии снижают значение pH среды, что способствует ускорению гидратации и гидролиза смешанного вяжущего, имеющего щелочную реакцию, как и цемент. Такой механизм основан на кислотно-основном взаимодействии цемента с песчаными продуктами переработки нефтебитуминозных пород. Отсюда можно считать, что отходы переработки НБП являются активной добавкой и повышают марочность цемента, а также являются активной добавкой, сравнимой с пирогенными продуктами типа термообработанных глин алюмосиликатного состава, золы-уноса, шлаков и других техногенных веществ, что объясняется результатом термического воздействия в процессе извлечения из них нефтепродуктов.

Учитывая то, что большинство известных месторождений нефтебитуминозных пород находятся вблизи нефтедобывающих районов, где потребляются в больших количествах цементы со специальными свойствами (утяжеленные, солестойкие, термосолестойкие, тампонажные), рассматривалась возможность использования продуктов переработки нефтебитуминозных пород в качестве активных добавок для получения специальных цементов. Изучалась стойкость образцов в различных средах низко-и высокоосновных гидросиликатов кальция. В частности, испытываемые цементы, содержащие песчаные отходы переработки нефтебитуминозных пород, затворяли сульфатными растворами магния и натрия, с последующим твердением в автоклавных условиях и последующим хранением в сульфатных растворах. Полученные образцы имели абсолютную стойкость в этих агрессивных растворах. Этот механизм действия нами назван условно «родственностью» состава цемента с средой эксплуатации. Указанный принцип может быть распространен на другие виды вяжущих материалов и агрессивных сред. При наличии в них нерастворимых силикатов и алюмосиликатов, содержащих кремнезем, они являются кислотостойкими.

В результате проведенных экспериментальных работ обоснованы и разработаны технологические процессы изготовления силикатных материалов (плотной и ячеистой структуры) на основе НБП и отходов их переработки. Техногенные минеральные продукты переработки нефтебитуминозных пород как в молотом, так и в немолотом виде являются пригодными в качестве кремнеземистого компонента для производства силикатных материалов ячеистой структуры, по свойствам отвечающим требованиям стандарта. Добавка в силикатную смесь до 5 % природной нефтебитуминозной породы обеспечивает гидрофобность изделий: уменьшает водопоглощение на 25 %, паропроницаемость на 45 %, адсорбционную влажность в 2,2 раза, капиллярный подсос в 7 раз, морозостойкость до 100 циклов. Добавка нефтебитуминозной породы в силикатную смесь способствует модифицированию капиллярно-пористой структуры и созданию мелкокристалличности и мелкопористости.

Силикатные материалы на основе известково-песчаного вяжущего, полученного из отходов переработки нефтебитуминозных пород с известью, имеют высокие физико-механические и эксплуатационные свойства и соответствуют нормативным требованиям к силикатному кирпичу и ячеистому бетону.

Ключевые слова: нефтебитуминозные пород и отходы их переработки, структура, механохимическая активация, силикатные материалы, вяжущее, ячеистый бетон, долговечность.

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