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Structure Formation and Properties of Concrete Based on Organic Hydraulic Binders

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Abstract. The article addresses the issues of structure formation of road composite materials containing hydraulic (portland cement) and organic (bitumen) binders. It has been determined that organic and hydraulic binders, being thermodynamically incompatible, are capable of interaction and complement each other. Structure formation processes are associated with inter-phase transition layers interaction mechanism and the direct formation of phase contacts with cement crystallohydrates. The interphase boundary is diffuse and is established through interphase transition layers. The emergence of interfacial layers is thermodynamically advantageous, since it contributes to a decrease in Gibbs free energy and does not contradict modern concepts of solid state physics. It was established that with cement content of about 30 % of complex bitumen-cement binder volume, there will appear (nucleate) phase contacts that will prevail in the binder structure when the cement content is more than 60 %. In the case phase contacts prevail, concrete will demonstrate significant strength at high temperatures, but low temperature and fatigue crack resistance, which will lead to their durability loss. The cement content of 30–40 % of the total complex binder can be considered optimal.

Keywords: concrete based on organic-hydraulic binder, structure, bitumen, cement, interphase layer, phase contact, filler

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Процессы структурообразования и свойства бетонов на органогидравлических вяжущих

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Реферат. Рассмотрены вопросы структурообразования дорожных композитных материалов, содержащих в своем составе гидравлические (портландцемент) и органические (битум) вяжущие. Установлено, что, являясь термодинамически несовместимыми, органические и гидравлические вяжущие способны к взаимодействию и дополняют друг друга. Процессы структурообразования связаны с механизмом взаимодействия межфазных переходных слоев и непосредственного образования фазовых контактов кристаллогидратами цемента. Исследования процессов срастания кристаллогидратов цемента через органические пленки, микроскопический и рентгеноструктурный анализ подтвердили данные результаты. Граница раздела фаз является размытой и осуществляется через межфазные переходные слои. Процесс появления межфазных слоев выгоден с термодинамической точки зрения, поскольку способствует уменьшению свободной энергии Гиббса и не противоречит современным представлениям физики твердого тела. При содержании цемента около 30 % от объема комплексного битумно-цементного вяжущего начнут появляться (зарождаться) фазовые контакты, которые будут преобладать в структуре вяжущего при содержании цемента более 60 % по объему. В случае преобладания фазовых контактов бетоны будут обладать значительной прочностью при высоких температурах, но низкой температурной и усталостной трещиностойкостью, что приведет к потере их долговечности. Оптимальным можно считать содержание цемента в количестве 30–40 % от общего объема комплексного вяжущего.

Ключевые слова: бетон на органогидравлическом вяжущем, структура, битум, цемент, межфазный слой, фазовый контакт, наполнитель

Introduction

Recently, new materials, including composites, have been used in road construction. Composites refer to materials consisting of two or more dissimilar materials and having properties that the original materials do not have. Road composites is a narrower class of composites. Their main difference is the use of two or more thermodynamically incompatible binders, which form bonds of different nature, strength and deformability in the structure of the material. Such binder compositions include, for instance, cement-asphalt, sulfur asphalt, asphalt with fatty acids, polymer modified asphalt, etc.

In road building practice, cement-asphalt compounds of various composition designs and technological processes for their preparation are widely used. In the future, we will call them concretes based on organic hydraulic binders (hereinafter referred to as OHB concretes).

OHB concrete is manufactured construction material that combines the properties of thermodynamically incompatible organic (bitumen, tar) and hydraulic (cement, gypsum, ash, etc.) binders in its structure. The invention of OHB concrete in road construction was associated with a number of reasons:

1) the lack of reliability and durability of conventional asphalt concrete in response to present-day traffic loads;

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2) the introduction of new energy and resource-saving technologies that require the presence of water in the structure of the material (emulsions, foamed bitumen, wet organic-mineral mixtures, etc.);

3) the emergence of new technologies for repair and reconstruction of road surfaces (e. g. cold recycling).

New materials require the study of the peculiarities of their performance in a temperature-time field in order to develop objective technical requirements for their physical and mechanical properties, which ensure the required strength and reliability values. In addition to the authors, the issues of obtaining and optimizing the composition and structure of OHB concrete are dealt with by experts in most countries of the world [1–6]. The main technological parameters for concrete production have been established, studies of composition effect on strength have been carried out, and in-use life has been examined [7–11]. A significant role of cement in the processes of structure formation is recorded. In particular, it has been found that at low cement content, or its absence, the durability of the material in road surfaces is very low [12]. All this requires a more detailed analysis of the processes of OHB concrete structure formation.

The structure of OHB concrete includes two thermodynamically incompatible binders (cement and bitumen) and water. This provides the grounds for creating a complex structure, which cannot be attributed to crystallization (cement concrete), or coagulation (asphalt concrete). A fundamental issue is the purpose and effective use of cement in the process of OHB concrete structure formation. In some cases, its content is limited and considered a filler that absorbs excess water, in others it is an independent binder that increases the strength of the composite, especially at high operating temperatures. It is known that bitumen and cement are antagonists. Oil fractions of bitumen harm the structure formation of cement; water and hydration products interfere with the formation of bitumen bonds. This prevents a clear understanding of the processes of structure formation. The question of determining technical requirements to similar materials, designing road structure, and evaluating their reliability and durability is also unclear. To solve these problems, it is necessary to under-stand the processes of structure formation of OHB concretes and obtain theoretically and experimentally proved models of their behavior in temperature-time fields under loads. New materials warrant further study of the peculiarities of their behavior in a temperature-time field in order to develop objective technical requirements, which can provide the required values of strength and reliability. At the first stage, studies were performed aimed at investigating the processes of structure formation and the structural peculiarities of complex binders, that have a significant effect on the properties of OHB concrete.

Body

During the preparation of concrete based on organohydraulic binders, aggregates of cement grains of various nature and structure are formed. Regardless of the preparation technology, there are conditions for water to penetrate into these aggregates and hydrate them. The possibility of hydration of the mineral binder makes it relevant to study the formation of direct crystallization (phase) contacts of cement aggregates of the optimal (effective) volume, including the case organic binder films are present in between, which is an important task for optimizing the properties of OHB concrete at the design stage of the composition to achieve maximum parameters of their operational reliability under the influence of weather and climate factors and traffic.

When studying the structure of OHB concretes, the question of the possibility of forming phase contacts between particles of hydrated cement in the presence of aqueous dispersions of bitumen or bitumen films is of paramount importance.

According to these ideas, during the hardening of binders, crystallization structures appear in the system. The basis of their development is the bridging of particles (crystalline or amorphous) of hydrated neoplasms in the process of separation of a new phase from supersaturated solutions. It is the bridging of particles – the formation of strong contact bridges between them – that is the main condition for the transformation of a dispersed system into an artificial stone exhibiting mechanical strength. Depending on the nature of particles interaction, it is advisable to distinguish between two main types of contact between particles (respectively, two types of dispersed structures),

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which are commonly referred to as coagulation and phase. In coagulation contacts (or structures), the cohesion of the particles of the dispersed phase is limited by their simple "contact", either directly or through the residual layer of the dispersion medium, mainly due to molecular (van der Waals) forces. Such contacts are of low strength (10^{-9}–10^{-7} N) and mechanically reversible, which determines the viscoplastic and thixotropic properties of coagulation structures.

Unlike cements and concrete, the dispersed medium of cement-bitumen systems is not the aqueous phase, but the aqueous emulsion of bitumen, which contains, in addition to purely oil phase, many different active centers and surface-active substances (hereinafter referred to as surfactants). Therefore, the formation of strong structures in such systems, of course, will differ in certain properties. However, general fundamental laws apply in this case as well.

Let us consider several possible situations of contacting cement particles and its hydrates in water-bitumen emulsion and evaluate the possibility of bridging.

If the cement particles are in contact in one phase, the hydration process will be accompanied by the growth of hydrated neoplasms and the formation of strong phase contacts between them. The bridging can be slowed down due to the adsorption of surfactants, due to a decrease in the probability of bridging, but not suspended, as evidenced by experiments on the bridging of modified surfactants of gypsum crystals [13]. The possibility of bridging of particles in the presence of an oil phase is not excluded.

In bitumen emulsions and dispersions, the growth of crystals in the presence of films between them (and the creation of the crystallization pressure necessary for breaking through the films) can be carried out both by diffusion of ions over the surface of growing crystals (surface diffusion) and by diffusion through the volume of oil phase, followed by release in areas not occupied by surfactant molecules. The formation of phase contact between individual aggregates of hydrated cement can also occur as a result of rupture of bitumen films during compaction, as well as cement contraction during hydration. Contractional deformations of various cement constituents are in the range of 3–10 % [14], which in some cases exceeds the ultimate deformation of bitumen film, especially of a reduced thickness, which makes 1–10 % [15].

In general, the probability of a crystal bridging in the presence of bitumen phase will be determined, first of all, by the size of the crystals formed and the thickness of the bitumen film. The larger the crystals and the thinner the bitumen film is, the higher the probability of crystal bridging is. The sizes of crystals of hydrosilicates (alite, tobermorite) are 0.25–0.50 microns, lime – 1–2 microns, ettringite – 16–20 microns [16]. If the thickness of the bitumen film scales to the double size of the crystals, then they can bridge.

It was decided to carry out experimental confirmation of the possibility of establishing phase contacts between hydrated cement aggregates when the dispersion medium is a bitumen emulsion or an aqueous dispersion of bitumen, by analyzing the direct processes of intergrowth of individual crystals in dispersion medium. This study is important, as it will allow us to focus on the effective concentration of a hydraulic binder in the design process of OHB concrete compositions which ensures the formation of a structure of complex binders with the required strength and deformation qualities. These effective concentrations, along with the peculiarities of the interaction of a complex binder and aggregates (granules from milling of road asphalt concrete pavements (hereinafter referred to as asphalt granules) or stone particles) will determine the reliability and durability of the composite.

First experimental studies of individual intergrowth contacts, which allowed to identify the patterns and mechanism of the formation of phase (crystallization) contacts between binder hydrate particles, was conducted under the supervision of Academician E. D. Schukin at the Department of Colloid Chemistry of Moscow State University and at the Laboratory of Physical and Chemical Mechanics of the Institute of Physical Chemistry Russian Academy of Sciences [13].

These studies were based on the measurements of adhesion forces between individual particles under conditions that actually occur during mineral binders hardening. They made it possible to establish the dependence of bridging process on such hardening factors as the metastability of the initial medium (supersaturation), the residence time of

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particles in the coagulation contact, the presence of impurities in the medium – various ions, surfactants, etc. As a result, the role of mechanical efforts was established – the compression of particles to each other. Such compression can be provided both by applying external stresses, and due to the development of internal stresses in the forming hardening structure, as a result of crystallization pressure. In addition, in systems with two-phase dispersion medium (for example, bitumen emulsions), the compression of particles can be the result of capillary pulling forces of the menisci, which are formed in the contact between the particles due to selective wetting. Capillary forces contribute to the fixation of particles in a coagulation contact and considerably determine the behavior of the system at the initial stage of its formation.

In connection with the above, the precision technique developed at the Department of Colloid Chemistry of Moscow State University was used to measure adhesion forces in the contacts between individual particles [13]. It is based on the use of a galvanometer sensitive magnetoelectric system as a power meter. This technique allows you to adjust the force during the compression of particles and directly measure the adhesion forces in the contacts between them in a wide range of values: from very small components of $\sim 1 \sim 10^{-8}$ N to relatively large – $\sim 10^{-3}$ N.

Gypsum was taken as the object of research, as it resembles the materials under consideration in its behavior the most, and at the same time, it is a fairly uniform and stable material. Calcium sulfate dihydrate crystals ($5 \times 5 \times 0.5$ mm in size) were used. The dispersed medium was a supersaturated solution of calcium sulfate obtained by dissolving semi-aqueous gypsum in water (three times more soluble than calcium sulfate dihydrate), followed by filtering the solution and diluting it to the

desired concentration C was obtained. This allowed to vary the degree of solution supersaturation $\alpha = C/C_0$ (C_0 – the solubility of calcium sulfate dihydrate) from 1 to 3. To model bitumen dispersions and emulsions, surfactants were used that did not lead to a significant change in the optical properties of the medium (octadecylamine, gelatin, dimethyldichlorosilane). A direct analogue of emulsions based on octane (oil phase) and cetylpyridinium bromide (emulsifier) was also used.

The idea of the experiments was as follows. Two particles placed in a supersaturated solution were brought into contact with a predetermined force *f*, kept in such fixed position for a certain period of time *t*, and then parted. The force needed to detach the particles was measured, which was identified with the strength of the individual contact p_1.

Since crystal bridging is a probability process, the results were subjected to static analysis and the bridging probability was estimated:

$$W_{cp} = \frac{W_t}{W_0}, \qquad (1)$$

where W_t – number of "strong" contacts; W_0 – total number of contacts registered.

"Strong" (phase) contacts are contacts with a force of more than 10^{-6} N. Weak (coagulation) contacts are those with a limiting separation force of less than 10^{-7} N.

Studies of the bridging of individual particles, the surface of which was modified by a surfactant, showed (Tab. 1) that in all cases a decrease in the bridging probability is observed. In this case, the reduction bridging effect W_b depends on the symbols of the approaching faces, which is associated with their different adsorption capacity and their growth rate.

Table 1

The effect of surface modification of crystals on the probability of their bridging W_b in supersaturated calcium sulfate solutions

Crystal in contact	Surface modifier	W_b, %	α	*t*, s
Gypsum-gypsum	ODA	36 (67)	1.8	1000
Gypsum-quartz	ODA	27 (68)	1.8	1000
Gypsum-quartz	DMS (quartz)	32 (69)	1.8	3000
Gypsum-gypsum	Gelatin	42 (49)	1.8	100
Gypsum-quartz	Gelatin	38 (68)	1.8	1000

Note. The values specified in parentheses are for unmodified crystals. ODA – octadecylamine; DMS – dimethyldichlorosilane, was used for preliminary hydrophobization of quartz surface.

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With rapid crystallization (and rapid growth of faces), molecules or ions of a crystallizing substance will interfere with the adsorption of surfactants and may displace part of them from the surface. At the same time, the difficulty of bridging of neoplasm particles at the initial stage of hardening will favorably affect the strength of the finally formed structure, since it inhibits the formation of a primary rigid frame capable of accumulating elastic stresses. Internal stresses developing during the formation of the structure can lead to its irreversible destruction, especially in the late stages of hardening (when new contacts scarcely occur), and to a decrease in the final strength. Therefore, this behavior of surfactants at their optimal proportioning provides the conditions for creating a stronger final structure with fewer residual internal stresses.

Thus, the presence of a surfactant in dispersion medium does not prevent the appearance of phase contacts, but the probability of such contacts is reduced by two or more times. Therefore, when using bitumen emulsions, the bridging of crystals through emulsion dispersion medium will occur and a crystallized framework of reduced strength will be created.

To directly confirm the bridging of crystals in direct emulsions, an attempt was made to measure the adhesion forces of gypsum crystals in emulsions containing 50 % (by volume) of oily dispersed phase (octane) in supersaturated solution of calcium sulfate. Cetylpyridinium bromide was used as an emulsifier. However, experiments with such emulsions are difficult due to their large turbidity, which does not allow to register the moment of particles joining and the moment of contact rupture. In addition, the appearance of sufficiently large adhesion forces between gypsum crystals ($>10^{-7}$ N) in emulsions cannot be considered as direct evidence of their bridging, since such adhesion forces can also be associated with the manifestation of capillary forces due to the appearance of a meniscus in the contact zone. To give a clear answer, it is necessary to separate the contribution of capillary forces p' and the contribution of cohesion forces p'' at bridging in the total contact strength p_1 establishing between gypsum crystals with the presence and isolation of a new phase in the contact zone.

This can be done by simulating various situations that may occur when particles are in contact in emulsions. It is such model experiments that will ascertain the fact of particle bridging in two-phase liquid medium more objectively.

For this purpose, contact strength was measured for the contact between gypsum crystals placed in octane medium when a drop of calcium sulfate solution – saturated and supersaturated towards gypsum crystals – was introduced into the contact zone.

Preliminary experiments were conducted to select the optimal volume of droplets introduced into the contact zone, which was necessary to obtain reproducible results. The optimal volume proved to be 0.5–0.6 mm^3.

The crystals brought together were compressed with force f, kept in this state for a predetermined amount of time t (100 or 1000 s). Then a negative force was applied to them (tensile force f_p). The f_p value at which the crystals detach from each other, i. e., the individual contact strength p_1 was measured. Each measurement was reproduced at least 30–50 times (depending on the distribution of values p_1) in order to ensure sufficient results for an objective analysis of statistics.

Studies have shown that at low force f, time t and low supersaturation, the contact forces do not exceed 10^{-4} N, i. e., the contact strength resulting from the action of menisci. Crystal bridging occurs in this case as well though, but the strength due to cohesion forces p'' shows at or below the strength associated with the manifestation of capillary forces, i. e. $p_1'' < p_1'$. The fact of bridging is evidenced by the nature of the separation of particles from each other, observed visually (by a microscope).

In the absence of bridging, the supply of tensile force f_p (separating the particles) from the very beginning leads to the emergence of a gap between the particles and the gradual "stretching" of the meniscus, which increases as the force builds up. Separation of particles occurs at the time of rupture of the meniscus column under the action of critical force f_{p_c}. This force determines the contact strength due to the action of capillary forces p'.

The occurrence of bridging contacts manifests itself in the fact that, when applying tensile

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force f_p, the gap between the crystals appears only when a certain critical force is achieved, corresponding to the contact strength due to cohesion forces $f_{p_c} = p''$. When this force is exceeded $(f_{p_c} > p'')$, the gap increases and the meniscus stretches, rupturing upon reaching $f_{p_c} > p'$. In this case, the strength of the contacts due to bridging p'' is lower than the meniscus rupture force p'.

It is possible to observe the occurrence of bridging contacts with strength exceeding the meniscus rupture force. A bar graph in Fig. 1 presents the strength of the contacts arising between gypsum crystals located in the octane medium in the presence of a drop of a calcium sulfate supersaturated solution in the contact zone ($\alpha \cong 3$). The contact time was 100 and 1000 s, the compressive force was 10^{-6} and 10^{-5} N. The figure shows that most of the bridging contacts have the strength p'' of the same order as the strength due to the capillary forces of the meniscus p'. At the same time, these contacts are of fundamentally different nature: their occurrence is the result of crystal bridging in the process of separation of a new phase from a supersaturated solution in the contact gap. Therefore, unlike contacts due to the action of menisci, they are destroyed irreversibly. After damaging such contacts (when moving the particles apart) to restore them, it is not enough to bring the crystals into contact again. In this case, only the meniscus is restored in the contact zone, and the bridging forces and the nature of subsequent separation of the particles corresponds to the action of only capillary forces. To restore the bridging contact, it is necessary to provide supersaturation

in the contact meniscus and sufficient time of crystals being in contact in order for the contact nucleus to appear and grow. Only after this the nature of the separation of the crystals becomes different. If, under these conditions, the growth process has managed to cover a sufficiently large part of the contact gap, then the measurements reveal contacts with higher strength associated with the binding action of the meniscus.

Thus, the appearance and development of phase (crystallization) bonds in the structure of OHB concrete is possible and likely. This should lead to an increase in strength at high temperatures and a decrease in the temperature-time sensitivity. However, this probability will be manifested at appropriate concentrations of cement in the total volume of binder, also depending on the properties and quality of the aggregate.

The appearance of phase contacts in the structure of the material will lead to a number of peculiarities in the behavior of the material, its properties and reliability in road structure. The result of phase contacts will be the strength increase, especially at high temperatures, as well as stiffness (elastic modulus). However, there will be a downward trend in temperature crack resistance and fatigue life. In this case, it is important to find the optimal amount of these contacts that do not reduce the level of reliability in general.

At the same time, and at lower cement concentrations, various physical and chemical processes are possible at the interface between organic and hydraulic binders, due to adsorption-solvation phenomena and the interaction of active groups of organic binder with hydration products.
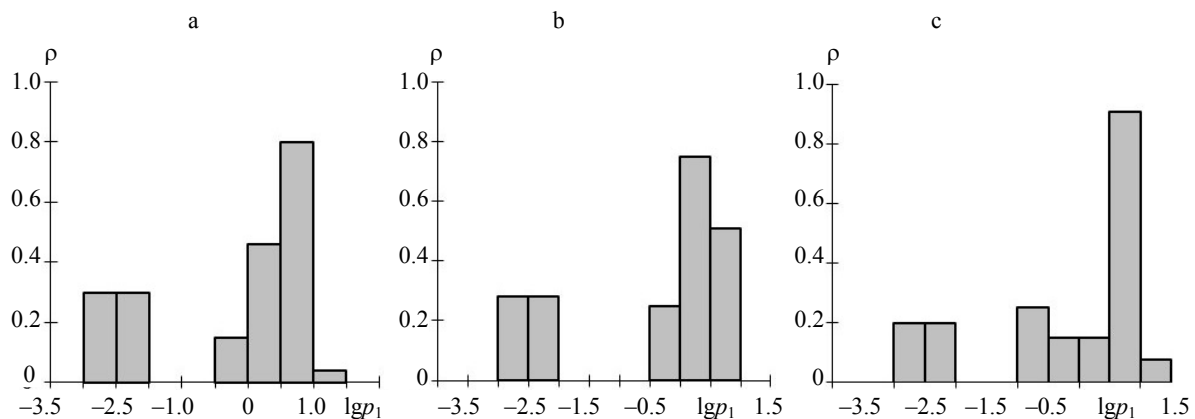

Fig. 1. Histograms showing contact strength in calcium sulfate dihydrate crystals in the presence of meniscus in supersaturated aqueous solution in the contact zone: a $-f = 10^{-6}$ N, $t = 100$ s; b $- 10^{-6}$ N, 1000 s; c $-f = 10^{-5}$ N, $t = 100$ s

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In our opinion, the process of structure formation of OHB concretes can be mainly caused by the appearance of interfacial layers of various lengths [17, 18]. For OHB concretes these layers can be formed by molecular and intermolecular clusters of various sizes and structures.

The length of the interfacial layer is different and depends on the properties of the substrate and the type of adsorbent [17, 18]. With regard to polymers, this layer can reach 50–60 μm [19], for bitumen 0.8 μm [20]. This difference is related to the structure of polymer molecules and their ability to conformation. When cement hydration products are used as a substrate, the thickness of the oriented polymer layer increases by an average of 1.5–1.9 times [21].

Therefore, the transition layer of bitumen during cement hydration can reach 1.2–1.5 microns.

The formation of interfacial layers will be affected by both physical (adsorption, crystal intergrowth and destruction of bitumen associates, ion transfer, etc.) and chemical (formation of Me + _OOCR bonds, hydrogen bonds–H–O, etc.) processes. The bonds of Me + _OOCR type will be formed by metal ions, their oxides and hydroxides that occur during hydration of the mineral binder, due to interaction with oxygen, hydroxyl and carboxyl groups of the organic binder. Hydroxyl groups of hydration products and, accordingly, hydroxyl, nitrogenous and sulfur compounds of bitumen (tar) will participate in the formation of hydrogen bonds. The volume of these compounds can be very small and cannot be detected by existing methods of analysis, however, their role as interfacial layers can be very significant.

The presence of a transition layer in OHB concretes allows us to prove that despite the absence of chemical interaction between hydration products and the organic binder or the formation of a crystallization bond through organic films, the "organic – mineral binder" system is not a physical mixture of two substances.

To study the conditions for the appearance of interphase layers and their structure, it is necessary to develop special theoretical and experimental approaches based on modern ideas about the structure of solids at the level of valence bands, in particular, involving the theory of atomic and configuration models of solids [22].

Theoretically, the structure of any of the compositions of the "cement–bitumen–water" system can be represented as a set of the following elements: cement, bitumen, water, cement–bitumen interface, bitumen–water interface, cement–water interface, cement–bitumen–water interface. The quantitative ratio between bitumen–water interface, cement–water interface, cement–bitumen interface, and cement–bitumen–water interface is determined by the ratios X/Y, Y/Z, X/Z in the system $X_{cement} + Y_{bitumen} + Z_{water}$. The interface can be quite large, depending on the affinity of the composition to the solubility limit of the system. With this representation of the "cement–bitumen–water" system, the question of the physical model of the system's interface remains the most important. The physical model of the boundary can be represented on the basis of the electronic model [23], which was developed in the study of various materials characterized by the eutectic type of reaction [24].

Specifying the above mentioned with respect to the "cement–bitumen–water" system, it can be said that nanoareas are areas formed due to charge transfers of SiO_2–Fe_2O_3–Al_2O_3–CaO–$CnHm$–H_2O complexes. In other words, these are nanoscale areas arising at SiO_2–H_2O, SiO_2–$CnHm$, CaO–H_2O, CaO–$CnHm$ interfaces, etc. Thus, based on modern concepts of interfaces in mechanical mixtures, it is possible to substantiate the formation of cluster areas with an electronic structure different from the components that make up the system.

Since hydraulic and organic binders are thermodynamically incompatible and cannot form a stable single-phase system, the phase boundary is blurred and contacts are made through interfacial transition layers. The formation of interfacial layers is influenced by both physical (crystal intergrowth, adsorption, destruction of bitumen associates, ion transfer, formation of double electron layers) and chemical (formation of Me + OOCR, hydrogen–H–O bonds, etc.) processes.

Let us formulate the thermodynamic approach to the conditions for the formation of interfacial transition layers.

Interfacial Gibbs energy, for example, "hydrated cement–bitumen" (F_{HC-B}), taking into account the formation of transition layers of a cluster type at the interface, can be determined from the following condition:

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$$F_{HC-B} = (1 - x_1 - a_1 x_1)F_C +$$
$$+ (x_1 - b_1 x_1)F_B + (a_1 x_1 - b_1 x_1)F_{C-BI} +$$
$$+ 2RT[a_1 x_1 \ln(a_1 x_1) + b_1 x_1 \ln(b_1 x_1)], \quad (2)$$

where F_C, F_B – Gibbs energy of hydrated cement and bitumen respectively; x_1 – bitumen mole fraction in relation to cement; a_1, b_1 – ratios of cement and bitumen characterizing the proportion of molecules in the transition layer, the values of which are less than one; F_{C-BI} – Gibbs energy of the transition layer interface molecules of cement-bitumen particles; T – temperature; R – absolute gas constant.

Since Gibbs energy is always negative, then F_{C-BI} is less than zero and, therefore, the more $a_1 x_1 + b_1 x_1$ is, the lower Gibbs energy of the whole F_{HC-B} system is.

The contribution of $a_1 x_1 \ln(a_1 x_1) + b_1 x_1 \ln(b_1 x_1)$ to model (2) allows one to take into account the molecules mixing entropy in the transition layer of cement–bitumen particles and characterizes the number of "permutations" formed by unlike particles of transition layers of cement and bitumen, since $a_1 x_1 < 1$ and $b_1 x_1 < 1$, the contribution of these layers in model (2) gives a negative value (the logarithm of the number is less than one), which also leads to a decrease in Gibbs energy in "cement–bitumen–water" system. Thus, the appearance of transition layers reduces total Gibbs energy and, therefore, is a thermodynamically favorable process.

The experimental evidence of the presence of cluster type transition layers was carried out by photoelectron spectroscopy methods that prove to be most effective in the studies of materials chemical bonding. Using the photoelectron spectra of various "cement–bitumen–water" systems, the nature of bonds at the level of valence bands was determined with subsequent mathematical processing and analysis.

As a result of comparing the experimental data and the spectra obtained by computer simulation methods (Fig. 2), it was found that the introduction of water into the cement–bitumen system leads to the formation of transition areas with a certain chemical bond energy. The presence of such a bond indicates a considerably strong and stable structure of complex binders of OHB concrete to both mechanical loads as well as weather and climate factors.
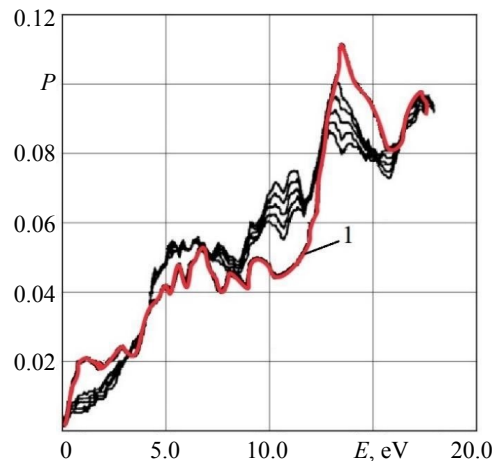

Fig. 2. Standardized valence bands x (cement) + y (bitumen) ($0.5 < x < 0.9$; $0.1 < y < 0.5$) and cement + bitumen + water (experiment) (curve 1)

On the basis of theoretical and experimental studies, a structural model of OHB concrete complex binder has been developed, which is represented by cement aggregates that have been hydrated to varying degrees and a number of interfacial transition layers (Fig. 3).
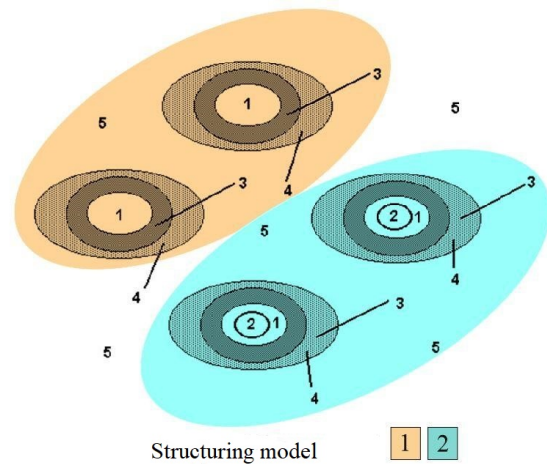

Fig. 3. Structural model of OHB concrete complex binder: 1 – area of hydrated cement, for which the interaction energy of cement and bitumen particles is zero; 2 – non-hydrated cement area; 3 – interfacial transition layer on the cement side; 4 – interfacial transition layer on the bitumen side; 5 – area of bitumen, for which the interaction energy of cement and bitumen particles is zero (unstructured bitumen)

The appearance of interfacial layers will also contribute to an increase in the strength of the composite prepared on a complex bitumen-cement binder, but at the same time, its temperature crack resistance will be maintained with an increase in fatigue life.

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Depending on cement phase volume fraction, cement structural aggregates can interact with each other through layers of bitumen, transition layers, or directly with each other, forming phase contacts.

In accordance with the proposed structure formation scheme, the effect of a hydraulic binder on the structure and properties of concrete will be manifested by the filler mechanism.

At the same time, it is a special filler. First of all, it is a reinforcing filler forming secondary structures in a bitumen matrix. The secondary structures of the mineral binder can interact with each other through phase contact, or transition layers with higher strength than the bitumen matrix. As a result, a spatial reinforcing mesh is formed with a "hinged" connection at nodes of various degrees of mobility. A mineral binder will also have a bridging effect, since mineral binder aggregates, in contrast to inert fillers, will become a fairly monolithic system after hydration.

Hydraulic binder is a more active filler in terms of physical and chemical interaction with organic binders, compared, for example, with mineral dolomite powders. This is due to the appearance of more extended interfacial cluster type layers associated with the interaction of hydrated neoplasms and an organic binder. This is due to the higher activating effect of cement in comparison with lime and other inactive binders.

Thus, the mineral binder in the structure of OHB concrete is manifested by the mechanism of the active, bridging and reinforcing filler, which determines the interaction of the complex bitumen-cement binder with the macrostructure and mesostructure of the composites, composed of stone aggregate, or granular asphalt. Therefore, the effect of introducing a mineral binder will depend primarily on its volume concentration in the complex binder and its threshold concentrations can be determined using percolation theory [25].

In percolation theory, two main tasks are distinguished: the bonding problem and the node problem. The issue of the formation of percolation "bridges" in secondary structure aggregates of composite binders is a typical task of nodes. The solution to this problem for two environments is known. According to [25], the formation of a percolation framework occurs when the volume content of clusters is more than 0.17. However, percolation bonds at this content are still rare and

the hardening of the structure is insignificant. Noticeable effect of clusters occurs when their volume content reaches 0.33 [26]. Consequently, the effect of the secondary structure on the properties of concrete will manifest itself with a volumetric content of at least 0.33 of the main binder. Further increase in the content of the secondary structure leads to more frequent contacts of clusters; with a volume content of about 0.67 [26], a continuous lattice of the secondary structure is formed. The material acquires basic properties of a secondary binder and a further increase in its volumetric content is not significant. However, the percolation theory makes it possible to establish only boundary concentrations without constructing a complete curve illustrating the dependence of the number of contacts between particles on their volume. Given the presence of a number of transition layers (Fig. 3), it is advisable to use mathematical modeling methods to construct a visual model of structure formation [27]. To simulate the process of structure formation, a special program has been developed.

The program is based on the solution of the problem of maximum filling a square of side A with circles of radius R. The following conditions have been accepted. Let A be a fixed number, let X, Y and R be independent random variables, where X and Y are evenly distributed on intervals $[0; A]$, and R has a normal distribution with parameters $R_0 > 0$ (mathematical expectation) and $\sigma > 0$ (standard deviation; if $\sigma = 0$, then the random variable $R = R_0$ is a constant).

It is required by mathematical modeling method to determine the maximum fillability of the square of side A with disjoint circles of radius R with centers at points with coordinates $(X; X)$. Fillability stands for the ratio of the total area of circles to the square area. Fillability is considered to be maximum if, as a result of N-fold (N – set value) modeling, it is not possible to place a circle in a square so that it does not intersect with the circles already placed and the borders of the square. Each circle of radius R is covered with a film (transition zone) $d = y(R)$ thick, where $y(R)$ is a function depending on R by one of the mathematical functions (hyperbole, exponent, etc.), that is, the sizes of the transition zones are also defined according to random distribution.

Two design patterns similar to the proposed model of a binder composite material (Fig. 3) have

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been considered. The first pattern involves changing the size of the transition layer by increasing the external dimensions of the structural aggregate while maintaining the size of the hydrated core (Fig. 3, model 1). The second pattern keeps the external diameter constant, developing a transition layer inwards the aggregate (Fig. 3, model 2). In this case, the contacts of the balls through the inner circles (dry contact) were not allowed. In accordance with this pattern, the higher the degree of hydration is, the larger the size of the transition layer is.

As a result of the calculations, the dependencies of the number of contacts (interactions) of structural complexes on the volume content of the mineral binder and the size of the transition layers have been obtained. One of these dependencies is shown in Fig. 4.
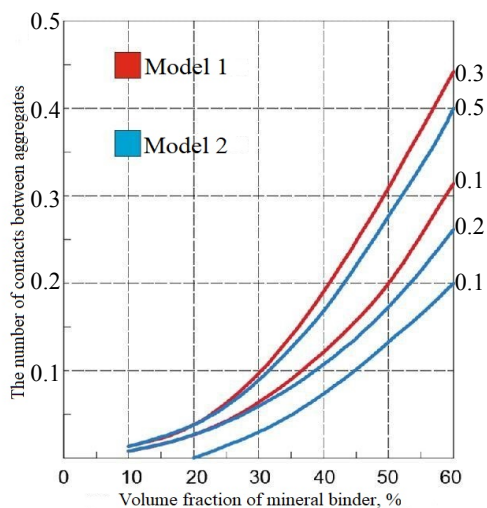

Fig. 4. Dependence of the number of contacts between structural aggregates of OHB concrete binder: the values on the curves denote the specific length of the transition layer (of the aggregate size)

As a result of data analysis, Fig. 4, the following conclusions can be made:

1) the number of percolation contacts increases in power-law dependence with an increase in the cement phase volumetric content;

2) due to the presence of transition layers, the percolation thresholds of structure formation are shifted downward. This reduction can reach 50 %;

3) with an increase in the hydration of unreacted grains, the number of contacts and the strength of the system increase. Other things being equal, preliminary hydration of cement allows to increase

the number of structural aggregates by 1.3–1.5 times.

In general, the volumetric content of mineral binder necessary for the formation of percolation transitions depends on the structure formation model and the specific length of the transition layers (Tab. 2).

Table 2

Volume fractions of mineral binder necessary for the formation of percolation transitions

Volume fraction of percolation transitions, %	Average specific length of a transition layer		
	0.1	0.3	0.5
17	0.15 0.07	0.14 0.15	0.12 0.13
34	0.26 0.31	0.20 0.27	0.16 0.22
67	0.30 0.44	0.20 0.37	0.09 0.21

Note. The numerator shows the data for structure formation model 1, the denominator – model 2 (Fig. 3).

Analysis of bitumen-cement system structure was performed using an electronic scanning microscope. The surface of the samples examined had been prior subjected to shearing and grinding.

The presence of transition zones between organic and mineral binders has been established. The photographs clearly show aggregates and clusters of hydrated particles, "connecting" larger hydrated neoplasms through bitumen films. The structure of the transitional layer itself is granular with a gradual size reduction (Fig. 5). The extent of the zone can be quite large and able to connect aggregates separated by an organic binder film. Large intergrown crystals and clusters of smaller neoplasms are clearly visible, gradually turning into molecular regions (Fig. 5a). At the presence of cement phase, there appear phase contacts (Fig. 5b).

Thus, direct experiments have shown the possibility of phase coalescence of particles and the formation of a crystallization bond in the presence of a two-phase (for example, emulsion) medium. At the same time, the bridging probability and the strength of the contacts are significantly reduced.

Calculations show that the appearance of phase contact is real at bitumen film thickness of less than 1–2 microns.
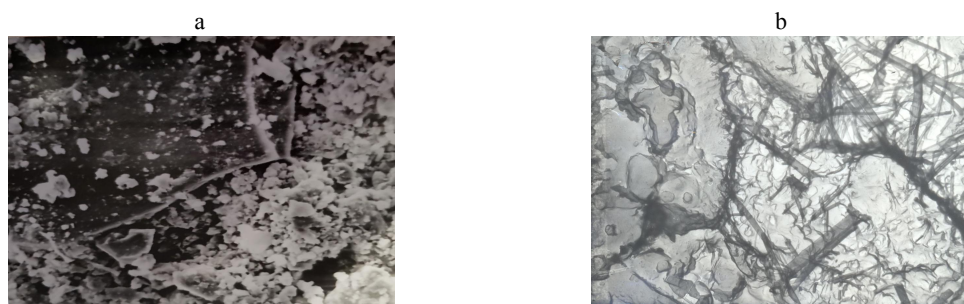
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a   b

Fig. 5. Image of OHB concrete microstructure: a – granular structure; b – cement phase

The presence of transitional interfacial layers and phase contacts in the structure of OHB concrete is confirmed by a number of experimental studies. Experimentally, this is confirmed, for example, by the decrease in the strength of OHB concrete obtained by mixing mineral material, bitumen emulsion and cement, while destroying the original samples and their recycling. In the presence of phase contacts and transition zones, the strength of the recycled samples decreases, since these contacts are destroyed irreversibly. With this in mind, it is possible to identify onset zones of cement influence on the structure of concrete (8–10 %) and the zones of the appearance of a continuous network of phase contacts (50–60 %), which fully confirms the above provisions. The optimum cement content, taking into account the probabilistic nature of this value, can be considered 30–40 %, which will largely allow both strength and deformability of the composites.

At the same time, the study was aimed at studying the processes of structure formation in a complex bitumen-cement binder, the main results of which can be extended to the properties of OHB concretes when sealable stone aggregates act as a filler. The situation is a little different when granular asphalt is used as a filler, where the main part of the surface of the polygranular particles are covered with old bitumen. For such composites, a more detailed study of the processes of bitumen involvement in deformation process is needed, when most solid phase contacts develop through aggregate particles not coated with bitumen with the formation of a continuous condensation-crystallization structure. In this case, whiskers partially penetrate into bitumen films and during the interaction of hydration products with bitumen active components on the surface of granular asphalt particles, and the spatial condensation-

crystallization structure formed this way, determines the elastic properties of the composite. All this considerably determines the properties of cold regenerated mixtures based on asphalt granules, up to 100 % of their content.

Based on the complexity of the processes that occur during the formation of the structure of composites based on asphalt granules and organic-hydraulic binders, an important question arises of providing and predicting their physical and mechanical properties, which should be solved at mixture composition design stage depending on the quality of the original components. The questions are being resolved by our research team at the moment.

CONCLUSIONS

1. Regardless of the method of water supply and the technology of OHB concrete preparation, aggregates and cement floccules are formed in the binder structure, surrounded by direct and reverse emulsion (dispersion) of the organic binder. This creates the condition for the interaction of cement with water and its hydration. Due to partial mutual solubility of the components, the accumulation and retention of water at the active centers of the organic binder, diffusion, rupture of bitumen films due to intracrystalline pressure, conditions arise for the bridging of individual aggregates by a chemical bond. However, the strength of this bond is significantly lower than the strength of cement.

2. The effect of cement injection cannot be explained only by the surface interaction of active groups with hydration products. The OHB concrete structure formation process is caused by a complex of physical (intracrystallization pressure, crystal intergrowth into bitumen films, their rupture, etc.), physical and chemical (destruction of bitumen associates and chemisorption interaction of bitu-

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men components and hydration products) and chemical (interaction of organic binder active groups with active groups, oxides and hydroxides of hydration products) processes. Taken together this all leads to the appearance of cluster type interfacial transition layers, which play the main role in structure formation of OHB concrete.

3. Despite the fact that organic and hydraulic binders are thermodynamically incompatible products and cannot form a stable single-phase system, the phase boundary is blurred and shows as interfacial transition layers. These layers have a certain chemical bond energy, the value of which will determine the strength and stability of the final structure. The emergence of interfacial layers is thermodynamically advantageous, since it contributes to a decrease in Gibbs free energy and does not contradict modern concepts of solid state physics. It is the effect of the appearance of such layers that can explain the higher "activating" ability of cement in mixtures on cationic emulsions and neutral bitumen.

4. Using the obtained model ideas about the number of contacts of structure-forming complexes with different transition layer thicknesses, one can imagine the influence of the structure and properties of individual complexes on the properties of the system as a whole at the phenomenological level. As a result of theoretical and experimental studies, the following practical conclusions can be drawn:

• the effect of cement on the properties of a complex bitumen-cement binder and concrete prepared on its basis will manifest itself at the content of about 8–10 % of the total volume of the binder;

• when cement content is about 30 %, phase contacts will appear, which will prevail when the cement content is more than 60 % of the total binder. If such contacts prevail, concrete will demonstrate high strength at high temperatures, but low temperature and fatigue crack resistance, which will lead to a significant reduction in the durability. The optimum cement content, taking into account the probabilistic nature of this value, can be considered 30–40 %, which will largely allow both strength and deformability of the composites;

• for concrete obtained by mixing granular asphalt, bitumen emulsion and cement, the optimum cement content at the design stage should be estab-

lished not only based on the structural formation of a complex bitumen-cement binder, but also taking into account the involvement of old bitumen covering the particles of this polygranular aggregate in the deformation process.

5. It is necessary to develop a methodology for selecting OHB concrete composition based on the optimization of their elastic and viscous properties, taking into account the properties of granular asphalt and the amount of cement, which will effectively control the durability and reliability of such composites.

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