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HIGH–REACTIVE POWDER CONCRETE ON THE BASIS OF ORGANIC NANOMODIFIKATOROV

A significant range of organic and mineral binders produced by the industry allows for a wide variety of combinations, providing a variety of resulting compositions. This, in turn, makes it necessary to establish general regularities in the formation of their properties. An attempt is made in this article. The results of studies of the properties of concrete, which are a composition of Portland cement, fine aggregate and mineral–organic complex, intended for the creation of special structures. It is shown that the use of the organic component of the mineral–organic complex of micelle–forming surfactants or polyalcohols leads to the sealing of the inner surfaces of the pores that are formed in concrete, which leads to an increase in the strength of concrete. It has been proven that the most effective use of the mineral is as a mineral component of complex organic compounds containing so–called d–elements, such as iron. The currently widely used mineral–organic compositions of the first type are, as a rule, "mineral binder – organic polymer" or "mineral binder – bitumen (tar)" systems. These types of mineral–organic compositions have undergone quite serious tests and have been tested in operation and have not sufficiently confirmed their effectiveness. But, as you know, these types of organic materials have the disadvantage of aging, which is accompanied by depolymerization (polymer) or a change in structure (asphalts, tars). Therefore, the durability of this type of resistance is limited by the organic component of the mineral–organic composition. It is known that the adsorption properties of derivatives of higher fatty acids depends on the length of the hydrocarbon radical. This is due to the strength of attachment of derivatives of higher fatty acid to the mineral surface. This largely depends on the solubility of the compositions are formed. The solubility of these compounds is, in turn, is determined by the order of solubility of the corresponding salts higher fatty acids. The solubility of these compounds, in turn, determined by the solubility of the respective salts of fatty acids. The authors obtained a mineral–organic material which is a system of "mineral binder based on calcium – fatty acid – a substance containing iron". Mechanism of structure obtained mineral–organic material explained as follows. As is well known, are unsaturated higher fatty acids with two or more double bonds with oxygen independently oxidized.

Keywords: concrete, cement, construction, mineral–organic complexes, surfactants.

Materials for repair of building structures, in particular, concrete should have a number of special properties that define the possibility and scope of their application. Thus, these materials should have: the required compressive strength; necessary deformable under load; minimum own deformations (shrinkage and swelling); high adhesion to concrete structures repaired; Non–corrosive to concrete structures repaired; resistance to external influences; durability.

Currently widely developed complex binders, which include both mineral and organic components. This type of binding materials have properties that distinguish them from the "traditional" mineral binders.

A considerable range of organic matter and mineral binders, which produces industry, allows combinations vary widely, providing diversity derived compositions. This, in turn, makes it necessary to establish the general laws governing the formation of their properties. Attempt it and done in this paper.

Analysis of the known mineral–organic compositions allows, in general, be divided into three types:

1. The mineral–organic compositions, the formation of the structure and, as a consequence, the physical and mechanical properties of which there is no interaction between their mineral and organic components.

2. Of the mineral–organic compositions, the formation of the structure and, as a consequence, the physical and mechanical properties which is due to the interaction between their mineral and organic components.

3. Mineral–organic compositions structure formation and, as a consequence, the physical and mechanical properties which is due to the interaction between their mineral and organic components, as well as products of their interaction.

The basis of the Structure of the mineral–organic compositions of the first kind, which got at the moment, the most widely used is the so–called "rule of domination," suggested Professor Sivertsev G.N. This rule is the basis of the formation of the properties of such complex binding as slag cement, gypsum cement and other binders. According to this rule, the basis of the properties of the compositions of this type creates their most active component.

Mineral–organic compositions of the species, have specific characteristics:

- One component of the mineral–organic compositions or the products of its structure formation does not need to be aggressive to another component of the mineral–organic compositions or the products of its structuring;
- The most active component of the mineral–organic compositions or its products of structure should not affect the structure formation of the less active component;
- Product structure formation less than the volume of the active component mineral–organic compositions must not exceed the pore volume formed during the structuring over the active ingredient. Otherwise, in the rock formed during the structuring of the most active component of the mineral–organic compositions, there will be internal stresses and, as a consequence of heterogeneity, which will contribute to the deterioration of its properties;

Should provide a high adhesion between the products of structure of all components of the mineral– organic compositions.

Widely used at present mineral–organic compositions first type generally are systems "mineral binder – organic polymer" or "mineral binder – bitumen (tar)." These types of mineral–organic compositions were quite serious trials and tested in operation and underconfirmed their effectiveness. However, as is known, these types of organic materials have the drawback of aging, which is accompanied by depolymerization (polymer) or a change in structure (asphalts, tars). Therefore, the durability of this type of resistance is limited by the mineral–organic compositions organic component.

Thus, the known complex binders which include the mineral–organic compositions of the first kind, have a fairly serious constraints in their production technology. This reduces the amount mineral–organic compositions first type, which can be obtained on the basis of their.

In the mineral–organic compounds of the second variety also has its own characteristics. The main feature – is the strength and stability of the products of the interaction of components of these compositions, as well as the possibility of forming products of their interaction, which weaken the structure.

Mineral and organic compounds of the second type – silicon–organic Compound obtained first. They have a lot of properties that can be used for the repair of reinforced concrete structures. From this point of view a sufficient interest is the question of obtaining mineral–organic compositions second type based on organic materials, polymerized under certain conditions (in particular, polyhydric alcohols). Since it is known that the replacement of unsaturated alcohols, such as vinyl, active hydroxyl hydrogen or an alkyl radical acid residue formed ethers or esters – quite stable compounds. They are easily polymerized to form polymers (e.g. polyvinyl converted into polyvinyl alcohol – resistant polymer product).

It is known that polyhydric alcohols readily react not only with the alkali metals, but also with hydroxides of heavy metals. Moreover, the elimination of water from alcohols such results, depending on reaction conditions to form a polymer:

$$nHOCH_2\text{-}CH_2OH \rightarrow [\text{-}CH_2\text{-}CH_2\text{-}O\text{-}]_n + n\,H_2O.$$

The most prominent representative of the composition of the second type has a cement–based trivalent alcohol – glycerine and lead oxide. This cement within a few hours of hardening has a compressive strength of up to 40.0 MPa and adhesion to steel up to 3.5 MPa, due to the formation of glycerate lead – PbC_3H60_3 by the reaction:

$$PbO + C_3H_8O_3 \rightarrow PbC_3H_6O_3 + H_2O.$$

This – early strength cement, substantially dimensionally stable cover which can be used for various soedineniyat materials used at elevated temperatures (250°C), by the action of water, hydrochloric acid at any concentration and dilute sulfuric acid.

However, it should be noted that in the process of forming the structure of this mineral and organic compounds released water species that is the source of structural defects in the composite material, and as a consequence limits the potentially achievable strength. This same drawback also have mineral–organic compounds which are soluble in water.

This inconvenience, obviously, can be eliminated by introducing in the mineral–organic compounds of the second "water absorbent". These are substances that bind water liberated in the course of the main reactions. Absorbent water should generate little or insoluble substances containing a significant amount of chemically bound water. Thus, a study conducted by the author, it was found that the use of mineral–organic compounds, which is a system of "polyol – multivalent metal oxide," the place of PbO or PbO together with gypsum or Portland cement improves the strength of the resulting composite material 1.5 ... 2.0 times for securing released water. This is the third type of mineral and organic compounds compositions.

It is known that the adsorption properties of derivatives of higher fatty acids (HFA) depends on the length of the hydrocarbon radical. This is due to the strength of attachment of derivatives of higher fatty acid to the mineral surface. This largely depends on the solubility of the compositions are formed. The solubility of these compounds is, in turn, is determined by the order of solubility of the corresponding salts higher fatty acids. The solubility of these compounds, in turn, determined by the solubility of the respective salts of fatty acids. For example, the ability to dissolve oleates can be positioned in a certain sequence, ascending ability to dissolve: $Fe^{3+} < Pb^{2+} < Mn^{2+} < Mg^{2+} < Al^{3+} < Ca^{2+}$. From this it follows that the higher the salt of d–elements of fatty acids (e.g., iron salts or manganese salts) have very low solubility. Ions – d–element (such as iron) are stronger polymerizer fatty acids, for example, by reacting:

$$3\cdot[CH(CH_2)_7COOH{=}CH(CH_2)_7COONa] + Fe(OH)_3 =$$
$$Fe[CH(CH_2)_7COOH{=}CH(CH_2)_7COO]_3 + 3\cdot NaOH.$$

On the surface of minerals containing iron, creates a solid molecular layer of iron salts of higher fatty acids.

The presence of iron broken double bonds in the unsaturated fatty acid radical and the degree of polymerization. This, as is known, leads to an increase in strength and length of the polymer. Thus, upon reaction d–elements (e.g., iron) salts of fatty acids and polymerization occurs under normal conditions of organic compounds, which enables to form a polymer having a branched structure.

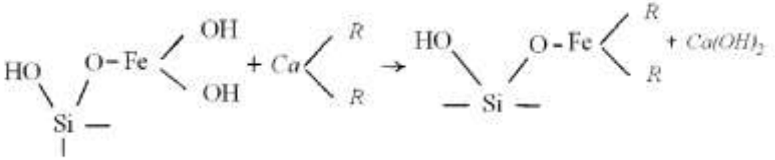
The resulting reaction product of the organic component and d–member new item (e.g., sodium hydroxide) is reacted with a mineral component (gypsum or Portland cement) and allows to increase the strength of the resulting composite material.

Thus, the effect of the polymerization revealed the presence of fatty acid salts using a d–element ions (e.g., iron).

Based on this effect, the authors obtained a mineral–organic material which is a system of "mineral binder based on calcium – fatty acid – a substance containing iron". Mechanism of structure obtained mineral–organic material explained as follows. As is well known, are unsaturated higher fatty acids with two or more double bonds with oxygen independently oxidized. In the first step of the hydroperoxide groups formed by oxidation type

$$-CH{=}CH-CH_2-CH{=}CH- \xrightarrow{O_2} -CH{=}CH-\overset{\overset{O-O-H}{|}}{CH}-CH{=}CH-$$

Then, using piroksidnyh bridges (—O—O—), individual radicals higher fatty acids are interconnected to form the spatial structure of the polymer. At the same time part of the molecules of higher fatty acids with a greater or lesser rate of splitting water – to hydrolysis, which is amplified by the hydroxyl ions.



In the presence of alkali (carrier which, in this case, is a mineral binder based on calcium derivatives higher fatty acids cleaved with formation of a polyhydric alcohol and a calcium salt higher fatty acids – Ca–

Liberate calcium hydroxide is reacted with a polyol, thereby forming its calcium derived, for example,

$$Ca(OH)_2 + C_3H_8O_3 \rightarrow CaC_3H_6O_3 + 2 \cdot H_2O.$$

Providing that in water, according to, is chemically bonded to the mineral binder based on calcium, resulting in dehydration of the remaining alcohol. This in turn allows, as stated above, its polymerization and, consequently, to increase the strength of the resulting composite material.

This type of mineral–organic material can be used for the repair and strengthening of structures, including those operating in conditions hostile environment.

The adhesion of concrete on the basis of this type of mineral–organic material 50 ... 70% higher than that of concrete without additives. Consequently, these concretes can be used effectively in the repair of reinforced concrete structures, including the exposed to high temperatures.

The research lead to the following conclusions: theoretically justified and experimentally confirm the role of substances containing d–elements (iron, manganese, etc.). Fatty acids, polyalcohols and their derivatives, which are polymerized d–elements allow to obtain a new type of mineral and organic materials effective for repair of building structures having high physical and mechanical properties, in particular compressive strength and adhesion to concrete existing building structure.

Applied conditions determined way to obtain concrete, which exhibit high strength.

Concrete, intended for the production of special construction must have certain properties. Chief among these is the high strength and high strain. Improved deformation for a particular construction enable the emergence of vibrations muffle, e.g., seismic effects, which together with the increased strength will improve the reliability of buildings.

High–strength concretes appeared in foreign practice in the early 60–ies of the last century. Especially promising are obtained at the end of the 80s of the twentieth century in France, the so–called reactive powder concrete – Reactive powder concretes (RPC). This new generation of concrete with a compressive strength of 200 to 800 MPa and a tensile strength of 25 to 150 MPa. Components of the concrete are Portland cement, fine ground quartz, fine sand, steel and microfiber super– plasticizer at water–solid ratio in the range 0.12–0.15. Concrete called "reactionary powder" due to the high dispersion of the components and the increased number of hydraulically active materials. The concept of RPC is to provide mothers with a minimum of structural defects – of microcracks and pores. Optimizing the particle size distribution of concrete components it provides a very high density. In this regard, the use of high– strength concrete provides fine ground fillers.

So ground limestone in the concrete composition is widely used in France and Germany [3]. Significantly higher sealing effect in the structure of concrete is achieved using of ultrafine silica fume [1]. Using fly ash reduces the water consumption while maintaining the mobility of the concrete mix, modifying the composition of cement hydration products [5]. Acceleration of hydration and increase in strength provided by the use of said concrete in their composition nano dispersed substances, in particular, silica and other serpentine minerals [2, 4, 8, 9].

For adjustment of the properties and obtain highly ductile concrete mixtures with low water–cement ratio, with high cohesion and resistance to stratification used superplasticizers – organic polyelectrolytes, whose main function is to disperse the chemical environment in heterogeneous systems [7].

Analysis of the results of scientific research in the field of surface–active substances (SAS) showed that almost all modern plasticizers used in concrete technology, refer to molecular. At the same time, in terms of physical and chemical mechanics, the most rational use of colloidal or semi–colloidal (according to the classification of Academician PA Rehbinder) surfactants. These types of surfactants which form micelles. At a certain concentration, the molecules of these substances are combined into micelles, whose properties differ from the properties of the molecules. In the first place, the micelles have the size and shape corresponding to the shape and size of nanoparticles that can be attributed to their nanoparticles. These nanoparticles – micelles, to a much lesser extent in comparison with molecular surfactant shield the cement particles, which reduces their impact on the timing of setting and hardening of concrete. Besides micelles S–surface–active substances practically not lead to a hydrophobic surface of cement particles, while absorbing hydrophobic particles which might fall into the concrete mix or specially introduced into it.

Virtually all types of RPC, which are at present, the broader scientific development, based on Portland cement, the activity of which is limited, and, apparently, to date, been exhausted. At the same time, has long been known as a kind of binders slag–alkaline knitting [6], the activity of which, even without the use of special techniques, which are used to improve the strength Portland cement concrete reaches 80 MPa. The disadvantage slag–alkaline concrete considered their increased deformability, but modern types of high– strength concrete (eg, Reactive powder concretes – RPC) based on Portland cement also have increased de– formability comparable with deformable slag–alkaline concrete. Development of these types of concrete is obtained RPC [8,9], modified polyols. At the same time demonstrated [10] that in the technology of porous concrete effectively use polyols instead of alkali salts of organic acids that are micelle–forming surfactants.

The aim of this study is to determine the effect of the strength of the micelle–forming surfactant RPC.

Experiments were conducted in accordance with standard techniques. Checking the stability of the samples was performed on a universal machine UMM–100. The date of manufacture of Portland cement concrete used M400 as fine aggregate – iron ore tailings. As a micelle–forming surfactants (SSAS) – sodium oleate.

Studies have revealed that S–surface–active substances micelles during the setting and hardening of cement are adsorbed at the interface "hydration products of cement – water" or "grain cement, which has not hardened – water", they formed on the inner surface of pores and cracks, keeping this surface by chemisorp– tion.

The experimental results showed that the introduction of the Reactive powder concretes (RPC) S–surface– active substances which are chemically adsorbed on the surface of the pores and cracks in the body of cement paste, leads to consolidate their inner surface, which entails an increase in strength of cement, and as a consequence, concrete in compression.

Thus, it was found that an increase in S–surface– active substances to a predetermined concentration (micelle concentration) leads to dramatic decrease in interfacial tension in the system. A further increase in the content of S–surface–active substances does not change the surface tension.

It should be noted that increasing the concentration S–surface–active substances to a concentration corresponding to micelle formation is accompanied not only by reducing the surface tension but also increase the strength of concrete. Contents corresponding S–

surface–active substances their critical micelle concentration, the system has the lowest surface tension and maximum strength, which in this case is 120 to 250% of the strength of concrete without additives depending on its composition.

A further increase in the content of S–surface–active substances over their critical micelle concentration does not change the surface tension, and is accompanied by a decrease in the strength of concrete. This is due to the fact that excessive molecule S–surface–active substances shield binder particles, reducing the degree of hydration.

Conclusion.

Studies and analysis of their results suggest the following conclusions:

1. Established that introduction of reactive powder concretes – Reactive powder concretes (RPC) micelle– forming surfactants which have dimensions and properties of the nanoparticles leads to an increase in the strength of concrete.

This process occurs by reducing the surface tension of molecules S–surface–active substances and chemisorption of these molecules at the inner surface of the pores and cracks in the concrete, which in turn provides a strengthening of the wall.

2. It is proved that there is content in the S–surface– active substances RPC, which ensures the formation of the great strength of concrete.

3. It has been shown that the optimal content S– surface–active substances in RPC meets their critical micelle concentration. At the moment, the original system (concrete) has the lowest surface tension and resulting in the process of hardening concrete – maximum strength.

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Високореактивний порошковий бетон на основі органічних наномодифікаторів

Значний асортимент органічних і мінеральних в'яжучих, що випускаються промисловістю, дозволяє здійснювати найрізноманітніші комбінації, забезпечуючи різноманітність одержуваних композицій. Це, у свою чергу, зумовлює необхідність встановлення загальних закономірностей у формуванні їх властивостей. Наведено результати досліджень властивостей бетонів, що представляють собою композицію портландцементу, дрібного заповнювача та мінерально-органічного комплексу, призначеного для створення спеціальних конструкцій. Показано, що використання в якості органічної складової мінерально-органічного комплексу міцелоутворюючих ПАР або поліспиртів призводить до ущільнення внутрішніх поверхонь пір, які утворюються в бетоні, що призводить до підвищення міцності бетону. Доведено, що найбільш ефективне використання в якості мінерального компонента складних сполук, що містять так звані d-елементи, наприклад залізо. Широко використовувані в даний час мінерально-органічні композиції першого типу - це, як правило, системи «мінеральне в'яжуче - органічний полімер» або «мінеральне в'яжуче - бітум (дьоготь)». Дані види мінерально-органічних композицій пройшли досить серйозні випробування і випробувані в роботі і недостатньо підтвердили свою ефективність. Але, як відомо, ці види органічних матеріалів мають такий недолік як старіння, яке супроводжується деполімеризацією (полімери) або зміною структури (асфальти, гудрони). Тому довговічність даного типу матеріалу обмежена органічною складовою мінерально-органічного складу. Відомо, що адсорбційні властивості похідних вищих жирних кислот залежать від довжини вуглеводневого радикала. Розчинність цих сполук, у свою чергу, визначається розчинністю відповідних солей жирних кислот. Автори отримали мінерально-органічний матеріал, який являє собою систему «мінеральний композит на основі кальцію - жирної кислоти - речовини, що містять залізо».

Ключові слова: бетон, цемент, будівництво, мінерально-органічні комплекси, поверхнево-активні речовини

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