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HYDRAULIC ENGINEERING CONCRETE BASED ON A COMPOSITE BINDER USING DISPERSED PERLITE AND A COLLOIDAL ADDITIVE

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Abstract: Concreting of massive hydraulic structures is accompanied by the phenomenon of exothermic heating of structures caused by the process of cement hydration. Under natural conditions, the heat released in massive concrete is slowly removed from the structure. Often, a significant temperature difference occurs between the central part of the massif and its surface. If the critical value of the temperature difference is reached, temperature cracks occur, violating the monolithicity of the structures.

In order to solve the problem of crack formation, the article considers the possibility of obtaining hydraulic concrete using a composite binder based on finely dispersed aluminosilicate rocks - perlites, a colloidal additive in the form of silicic acid sol and a superplasticizer.

To obtain a composite binder, aluminosilicate materials - perlite rocks with different degrees of crystallinity were ground in a laboratory vibratory grinder to the required specific surface. To obtain a colloidal additive - silicic acid sol, the method of hydrolysis of soluble salts was used in the work, in particular sodium fluorosilicate Na_2SiF_6 without removing sodium cations Na^+. The crack resistance index of hydraulic concrete Ktr was determined indirectly by the ratio of the tensile strength of concrete under bending to the compressive strength - Rben/Rcom. The grade of concrete water resistance was assessed by an express method for determining the water resistance of concrete by its air permeability.

It has been established that the most rational compositions are composite binders containing 10-20% glassy perlite, with a specific surface area of 600 m^2/kg, a colloidal additive in the form of silicic acid sol in an amount of 0.4% of the cement weight and the Polyplast superplasticizer, which provides an increase in the compressive strength of hydrated stone after 28 days by 33% and an increase in bending strength by 40-45% compared to the control composition. At the same time, the crack resistance index of hydraulic concrete Ktr using finely dispersed perlite, silicic acid sol and the Polyplast polycarbide superplasticizer increases by 21% compared to the control concrete composition, the concrete grade for water resistance is W16, which is 60% higher than the water resistance grade of the control concrete composition.

Keywords: hydraulic concrete, plasticizing additive, silica sol, glassy perlite, crystallized perlite, degree of dispersion, specific surface, water resistance, crack resistance, compressive strength

ГИДРОТЕХНИЧЕСКИЙ БЕТОН НА ОСНОВЕ КОМПОЗИЦИОННОГО ВЯЖУЩЕГО С ПРИМЕНЕНИЕМ ДИСПЕРСНОГО ПЕРЛИТА И КОЛЛОИДНОЙ ДОБАВКИ

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Аннотация: Бетонирование массивных гидротехнических сооружений сопровождается явлением экзотермического разогрева конструкций, вызванного процессом гидратации цемента. В естественных условиях выделяемое в массивном бетоне тепло медленно отводится из конструкции. Часто между центральной частью массива и его поверхностью возникает значительный температурный перепад. В случае достижения критической величины температурного перепада возникают температурные трещины, нарушающие монолитность конструкций.

В статье для решения вопроса трещинообразования рассмотрена возможность получения гидротехнического бетона с использованием композиционного вяжущего на основе тонкодисперсных алюмосиликатных пород - перлитов, коллоидной добавки в виде золя кремниевой кислоты и суперпластификатора.

Для получения композиционного вяжущего алюмосиликатные материалы - перлитовые породы с разной степенью кристалличности измельчали в лабораторном виброистирателе до необходимой удельной поверхности. Для получения коллоидной добавки - золя кремниевой кислоты в работе применяли способ гидролиза растворимых солей, в частности кремнефтористого натрия Na_2SiF_6 без удаления катионов натрия Na^+. Показатель трещиностойкости гидротехнического бетона $K_{тр}$ определялся косвенно по отношению прочности бетона на растяжение при изгибе к прочности при сжатии - $R_{изг}/R_{сж}$. Марка по водонепроницаемости бетона оценивалась экспресс-методом определения водонепроницаемости бетона по его воздухопроницаемости.
Установлено, что наиболее рациональными являются составы композиционных вяжущих с содержанием 10-20% стекловидного перлита, с удельной поверхностью 600 м^2/кг, коллоидной добавки в виде золя кремниевой кислоты в количестве 0,4% от массы цемента и суперпластификатором Полипласт, обеспечивающим прирост прочности на сжатие гидратного камня через 28 суток на 33% и прирост прочности на изгиб - на 40-45% по сравнению с контрольным составом. При этом показатель трещиностойкости гидротехнического бетона $K_{тр}$ с использованием тонкодисперсного перлита, золя кремниевой кислоты и поликарбрксилатного суперпластификатора «Полипласт» увеличивается 21% по сравнению с контрольным составом бетона, марка бетона по водонепроницаемости составляет W16, что больше марки по водонепроницаемости контрольного состава бетона на 60%.

Ключевые слова: гидротехнический бетон, пластифицирующая добавка, золь кремниевой кислоты, стекловидный перлит, закристаллизованный перлит, степень дисперсности, удельная поверхность, водонепроницаемость, трещиностойкость, прочность при сжатии

INTRODUCTION

Currently, due to the development of hydraulic engineering construction in the Siberian and Far Eastern regions of Russia, there is a need for concrete for hydraulic engineering structures. According to GOST 26633-2015, it is recommended to use sulfate-resistant and pozzolanic cements as a binder for the production of hydraulic engineering concrete. However, the use of such cements leads to a significant increase in the cost of hydraulic engineering concrete, since these types of Portland cement are much more expensive than ordinary Portland cement and the production volume of such cements is limited [1].

Concretes for hydraulic engineering structures must meet increased durability requirements imposed on them under operating conditions at the boundary of air and water environments. Under such conditions, cracking in hydraulic engineering concrete is most dangerous. As a result of cement hydration, heat is released, which initially causes compressive stresses in hydraulic engineering structures. Then, as a result of a decrease in temperature, concrete shrinkage occurs and tensile stresses appear. At the moment when tensile stresses exceed the tensile strength of concrete, cracks are formed [2-4].

Improvement of the characteristics of hydraulic concrete can be achieved by introducing active mineral additives into Portland cement, which eliminate the negative impact of a high temperature gradient during cement hydration by modifying the structure of the cement stone, increasing water resistance, increasing corrosion resistance, reducing overall porosity, increasing the physical and mechanical and operational properties of hydraulic concrete [5-7]. In addition, the formation of the physical and mechanical characteristics of concrete is interconnected with the formation of new complex hydrate compounds with improved characteristics and a certain crystallization structure, which also affects the physical and mechanical properties of concrete. There are works on the use of microsilica in combination with surfactants, which, in accordance with their chemical nature, have a positive effect on improving the properties of artificial stone, but the effectiveness of their action as a result of limited reaction activity does not ensure the creation of concrete of a new level of properties [8].

In the presented work, perlite rocks subjected to mechanochemical activation in energy-intensive devices, an ultrafine silica additive and a superplasticizer based on polycarboxylate were used to obtain hydraulic concrete. An ultrafine silica additive in the form of a sol and an active mineral additive subjected to mechanical activation will contribute to improving the microstructure of cement stone due to water reduction of the cement system, the formation of a dense packing of particles of a dispersed composite binder and hydration interaction of Portland cement with silica-containing additives [9], improving the physical and mechanical properties of concrete with their use.

MATERIALS AND METHODS

To improve the properties and increase the crack resistance of hydraulic concrete based on finely dispersed, colloidal additives and surfactants, Portland cement CEM I 42.5 N GOST 31108-2020 OOO Timlyuycement was used as a binder. Finely ground glassy and crystallized perlite from the Mukhor-Talinskoye deposit (Republic of Buryatia) were used as active mineral additives depending on the composition. The chemical compositions of glassy and crystallized perlite are given in Table 1.

Table 1. Chemical composition of glassy and crystallized perlite, mass.%

Material	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	R_2O	p.p.p.
Perlite vitreous	68,40	13,75	0,50	0,06	0,50	0,30	0,15	0,10	3,91	3,37	-	5,97
Crystallized perlite	73,13	11,7	1,08	1,71	0,55	0,30	-	-	-	-	6,4	7,65

Perlites were pre-crushed in a laboratory vibratory grinder VI-4x350 to a specific surface of 550 - 600 m^2/kg. A superplasticizer based on modified polycarboxylates (OOO "Polyplast-Sibir") was used as a surfactant, introduced into the cement with mixing water in an amount of 0.2% of the cement weight. The basis of the superplasticizer "Polyplast" are polycarboxylate esters. To obtain a silicic acid sol - a colloidal additive, a method of hydrolysis of soluble salts was used in the work, in particular sodium fluorosilicate Na_2SiF_6 without removing sodium cations Na^+. The optimal concentration of the sol is 0.75%. Hydrolysis of sodium fluorosilicate occurs according to the following reaction:

$$Na_2SiF_6 + 4H_2O \rightarrow 2NaF + 4HF + H_4SiO_4, \quad (1)$$

The resulting silicic acid sol in the form of an aqueous solution has a density of 1.018 g/cm^3, the value of the hydrogen index pH = 4.5-4.8, was introduced into the composition of concrete with mixing water with an optimal concentration of 0.4% of the cement weight.

The superplasticizer "Polyplast PK type S" based on modified polycarboxylates (OOO "Polyplast-Sibir") was used as a surfactant, introduced into the composition of cement with mixing water. The basis of the superplasticizer "Polyplast" are polycarboxylate esters.

The binder was prepared by thoroughly mixing Portland cement and finely dispersed glassy and crystallized perlite, crushed to a specific surface of 550-600 m^2/kg.

Concrete mix using composite binder with workability grade P3 (cone slump 12 cm) was prepared by mixing in a laboratory concrete mixer for 1 min pre-dosed components - Portland cement, finely dispersed perlite, sand with fineness modulus Mkr. = 2.1, crushed stone of fraction 10-20 mm and water containing dosed silica-containing component - silicic acid sol and superplasticizer Polyplast. From concrete mix of equal mobility, cube samples measuring 100x100x100 mm were molded, which were tested according to standard methods. For each type of test, samples were made in accordance with the requirements of GOST 10181-2014 "Concrete mixes. Test methods", GOST 10180-2012 "Concretes. Methods for Determining Strength Using Control Samples", GOST 12730.5-2018 "Concrete. Methods for Determining Water Resistance", GOST 24452-2023 "Concrete. Methods for Determining Prism Strength, Elastic Modulus, and Poisson's Ratio". The crack resistance index of hydraulic concrete Ktr was determined indirectly by the ratio of concrete tensile strength under bending to compressive strength - Rben/Rcom.

RESULTS AND DISCUSSION

All the components under study in rational quantities provide improvement of physical and mechanical properties of hydraulic concrete (Table 2).

Table 2. *Effect of dispersed perlite, specific surface area of 600 m^2/kg and silica sol on physical and mechanical properties of hydraulic concrete*

Name	Compressive strength, in MPa, after hardening for			Bending strength, in MPa, after hardening for		Ktr (Rben /Rcom)
	3 days	7 days	28 days	7 days	28 days	
Control composition	24,6	34,8	38,7	4,1	7,1	0,18
PC+ 10% Vitreous perlite+ Polyplast	25,4	36,3	39,9	4,3	7,3	0,18
PC+ 20% Vitreous perlite+ Polyplast	25,6	37,4	40,7	4,5	6,9	0,17
PC+ Sol $_6$+ Polyplast	30,8	37,4	40,9	5,6	9,1	0,22
PC+ 10% Vitreous perlite+ + Sol + Polyplast	33,1	39,0	48,6	6,9	10,6	0,22
PC+ 20% Vitreous perlite + Sol + Polyplast	35,2	42,4	53,4	7,8	10,9	0,20
PC+ 10% Crystal-lized perlite + Sol + Polyplast	32,6	38,5	41,1	4,0	6,9	0,16
PC+ 20% Crystal-lized perlite + Sol + Polyplast	33,2	40,0	42,9	4,4	7,6	0,17

Introduction of finely ground perlite into the concrete composition leads to an increase in the water-binding ratio by 7-13%. The use of the polycarboxylate superplasticizer Polyplast in an optimal amount of 0.2% of the binder weight not only reduces water consumption by 9-16%, thereby compensating for the loss of strength of hydrated stone associated with a decrease in the amount of cement in the composition, but also changes the structure of hardened concrete.

Colloidal additive in combination with finely ground perlite and plasticizer has a positive effect on increasing the strength of concrete. The maximum values of compressive strength were shown by the compositions with the addition of vitreous perlite and silicic acid sol: PC + 20% vitreous perlite + sol in the amount of 0.4% of the cement mass + Polyplast - 53.4 MPa, which is 33% higher than the strength of the control composition, respectively.

The use of polycarboxylate polymer in combination with fine and ultrafine silica-containing additives, to the greatest extent, starting from an early age, increases the tensile strength of concrete in bending. The maximum values of concrete tensile strength in bending at the age of 28 days were shown by concrete compositions: PC + 10% vitreous perlite + sol in the amount of 0.4% of the cement mass - 10.6 MPa; PC + 20% vitreous perlite + sol in the amount of 0.4% of the cement mass – 10.9 MPa, which is on average 40-45% greater than the flexural strength of the control concrete composition.

The increase in strength is the result of the influence of perlite on the structure and chemical and mineralogical composition of hydraulic concrete on a composite binder. A significant role is played by the chemical factor of perlite action, which is expressed in a change in the balance between the hydrated phases in the composition of cement stone towards an increase in the volume of stronger and more stable low-base calcium hydrosilicates (CHS) with the formation of dense conglomerate structures [9, 10]. The amorphous phase of silica, contained in large volumes in vitreous perlite, leads to an increase in compressive strength due to the replacement of the mechanically weak phase of calcium hydroxide with a stronger hydrosilicate phase [11].

The presence of a glassy phase (60-80%) in the perlite composition causes an increase in the strength of composite cement compared to the use of crystallized perlite of equal chemical composition, which is associated with an increase in the content of the amorphous phase in aluminosilicate rocks, their further amorphization during fine grinding in energy-intensive grinders [12]. Amorphous silica in perlite binds free calcium hydroxide formed during cement hydration, with the formation of an additional amount of low-basic calcium hydrosilicates.

In addition, as studies have shown, the morphology of the particles of the original crushed materials of natural and artificial origin changes depending on the grinding method [13]. In an energy-intensive grinder, which includes a rod vibratory grinder, during the grinding of glassy perlite, more rounded grains of the material are formed with a small amount of roughness on the surface, as a result of which the particles fit more tightly to each other with an increase in the contact surface, which indicates the efficiency of grinding the raw material in the rod vibratory grinder. When grinding crystallized perlite, grains of a flat, elongated shape are formed with the formation of a less dense packing of mixtures using it.

A colloidal additive, represented by a silicic acid sol, turns into a gel, compacting the microstructure of the hardening system, and also enhances the hydration activity of silicate-containing minerals of Portland cement and interacts with hydrolytic lime, thereby ensuring the formation of tobermorite-like calcium hydrosilicates, which in turn reinforce the hardening system, providing increased bending strength [14].

The crack resistance index of hydraulic concrete Ktr, indirectly estimated by the ratio Rben/Rcom, using finely dispersed perlite and silica sol is 0.22, which exceeds the crack resistance index of concrete without additives by 21%.

The results of the physical and mechanical properties of concrete confirm the resistance of concrete based on a composite binder, with colloidal and plasticizing additives to crack formation. To increase the durability and crack resistance of hydraulic concrete, studies were carried out to determine the deformation properties of concrete (Table 3).

Table 3. Deformative properties of hydraulic concrete based on composite binder

Compound	Prism strength, MPa		Modulus of elasticity Eb, MPa × 10^3		Poisson's ratio	
	3 days	28 days	3 days	28 days	3 days	28 days
PC	19,8	34,6	22974	32362	0,18	0,216
PC + 20% vitreous perlite + Polyplast	23,4	40,2	24084	35680	0,18	0,202
PC + Sol + Polyplast	25,6	39,6	23742	34493	0,17	0,191
PC + 20% vitreous pearl + Sol + Polyplast	30,1	46,3	26247	37345	0,17	0,199

The prismatic strength of hydraulic concrete on the optimal compositions with the combined use of finely dispersed perlite, silica sol and superplasticizer Polyplast in relation to the compressive strength is 17%, while on the control samples this ratio is 9%, which confirms the increased resistance of concrete to cracking. The increase in the prismatic strength of hydraulic concrete is mainly due to the high cubic strength of the presented concrete compositions compared to the control sample.

The modulus of elasticity of the hydraulic concrete compositions using finely dispersed perlite + superplasticizer Polyplast and the composition of silica sol + superplasticizer Polyplast increased on average by 3-5% in 3 days and by 7-10% in 28 days compared to the control composition. The composition with the combined use of vitreous perlite, silica sol and the superplasticizer Polyplast increases the modulus of elasticity compared to the control composition at 3 days by 14%, at 28 days - by 15%, respectively. The increase in the modulus of elasticity of hydraulic concrete based on a composite binder occurs due to the compaction of the structure due to the interaction of perlite, sol and superplasticizer with cement hydration products and the formation of additional bonds in the form of calcium hydrosilicates. Also, the increase in the modulus of elasticity is associated with a lower water-cement ratio, at which porosity decreases, which causes an increase in the modulus of elasticity [15, 16].

The Poisson ratio at the age of 3 days for the composition with vitreous perlite remained unchanged compared to the control composition. The Poisson ratio for the compositions with silica sol + Polyplast and the composition with vitreous perlite + sol + Polyplast decreased by 5% compared to the control composition. At the age of 28 days, the Poisson's ratio for the compositions: vitreous perlite + Polyplast; sol + Polyplast; vitreous perlite + sol + Polyplast decreased by 6, 11 and 8%, respectively.

The decrease in the Poisson's ratio of modified concrete can be explained by the fact that when introducing a polycarboxylate superplasticizer and silicic acid sol, due to the modification of the concrete structure, a greater number of structural elements are formed in the hydrated shells of the grains, and, consequently, the sliding surface of the particles increases, which leads to a more intensive reduction in transverse deformations and a decrease in the Poisson's ratio [17, 18].

To ensure the durability of hydraulic concrete, it is important to ensure a high value of water resistance. The concrete grade by water resistance, estimated by the express method of determining the water resistance of concrete by its air permeability, for the compositions of hydraulic concrete using finely dispersed perlite + superplasticizer Polyplast and the composition of silica sol + superplasticizer Polyplast is W12 and W14, which exceeds the water resistance of concrete without additives by 20 and 40%, respectively (Table 4). The composition with the combined use of glassy perlite, silica sol and superplasticizer Polyplast increases the concrete grade by water resistance by 60% compared to the control composition - up to W16.

The increase in water resistance can be explained by the fact that during the polycondensation process, which takes place at all stages of the sol-gel process, microgel structures are formed containing molecules of different molecular weights (from monomer to polymers) [19-21]. Polycondensation in the volume of particles leads to their compaction. At the gelation stage, this reaction helps to strengthen the coagulation contacts between particles [22]. In turn, the gelation products fill the micropores of the concrete structure with sol particles and the products of its interaction, thereby creating a dense structure [23-25]. The introduction of perlite into the composition of concrete leads to the formation of low-basic calcium hydrosilicates, which in turn also increase water resistance.

Table 4. Concrete grade by water resistance

Compound	Time of pressure drop in the chamber of the VV-2 device, s	Concrete grade by water resistance
PC	186 сек.	W10
PC + 20% vitreous perlite + Polyplast	294 сек.	W12
PC + Sol + Polyplast	391 сек.	W14
PC + 20% vitreous perlite + Sol + Polyplast	573 сек.	W16

CONCLUSIONS

It is possible to obtain durable concrete for hydraulic structures with high initial strength, increased water resistance and crack resistance by using highly effective plasticizers, active mineral additives of natural origin, subjected to mechanical activation in order to obtain finely dispersed additives, and ultra-dispersed additives obtained using sol-gel technologies.

Thus, it can be concluded that the additive for hydraulic concrete using vitreous perlite, silicic acid sol and superplasticizer based on polycarboxylate polymers is effective, the use of which promotes the formation of low-basic calcium hydrosilicates, the formation of a denser microstructure of cement stone, while improving the strength properties of modified cement stone in concrete, which, in our opinion, can increase the thermal crack resistance of hydraulic concrete.

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