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ДОБАВКИ ДЛЯ ТЯЖЕЛОГО БЕТОНА НА ОСНОВЕ ТЕХНОГЕННЫХ ОТХОДОВ ХИМИЧЕСКИХ ПРОИЗВОДСТВ

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Исследовано влияние комплексной добавки, содержащей суперпластификатор С-3, на свойства тяжелого бетона. Выявлена эффективность пластифицирующего действия указанной добавки на стадии приготовления бетонной смеси и последующем формовании бетонных изделий. Доказано, что на стадии твердения бетона исследуемая добавка способствует формированию более однородной коллоидно-кристаллической структуры и образованию плотных кристаллогидратных комплексов цементного камня к моменту завершения твердения бетона. Объектами исследования выбраны образцы бетона марки В22,5 без добавок; содержащие монодобавку - суперпластификатор С-3; содержащие комплексную добавку. При проектировании состава добавок для тяжелого бетона исходили из фундаментальных положений строительной науки, что комплексность действия добавок заключается в оптимальном сочетании двух основных противоположных по действию процессов, протекающих во времени и объеме бетонной матрицы. Применение синтезированного в ходе данного исследования олигомера капролактама позволяет решить проблему вовлечения в производственный оборот концентрированных отходов производства капролактама. Полученные олигомеры капролактама могут использоваться в строительстве в качестве пластификаторов бетонных смесей, как ингибиторов коррозии стальной арматуры при производстве железобетонных изделий. Были синтезированы водорастворимые олигомеры капролактама, которые сокращают время растворения суперпластификатора С-3 и диспергирования низкотемпературного катализатора в объеме затворяемой бетонной смеси. Было установлено, что в присутствии олигомера капролактама в количестве от 10 до 20% масс. скорость растворения суперпластификатора С-3 в воде при температуре 20-21 °С увеличивается в 2,0-2,2 раза. Это способствует более качественному перемешиванию компонентов бетонной смеси, прежде всего улучшению диспергирования комплексной добавки в объеме бетонной смеси. Используемый в настоящей работе олигомер капролактама является эффективным водорастворимым смачивателем поверхности частиц цемента, песка и щебня, что весьма важно для активизации гидрационных и сорбционных процессов при затворении бетонной смеси. Повышенные смачивающие свойства олигомера капролактама характеризуются углом смачивания, величина которого составляет 19,6°.

Ключевые слова: бетон, капролактам, техногенные отходы, низкотемпературный катализатор, ускоряющее-пластифицирующая добавка, водопоглощение

ADDITIVES FOR HEAVY CONCRETE BASED ON INDUSTRIAL WASTE FROM CHEMICAL INDUSTRIES

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The effect of a complex additive containing superplasticizer C-3 on the properties of heavy concrete has been investigated. The efficiency of the plasticizing action of the specified additive at the stage of preparation of the concrete mixture and subsequent molding of concrete products has been revealed. It is proved that at the stage of concrete hardening, the investigated additive promotes to the formation of a more homogeneous colloidal-crystalline structure and the formation of dense crystalline hydrate complexes of cement stone by the time of completion of concrete hardening. The objects of investigation were samples of grade B22.5 concrete without additives; containing a monoadditive - superplasticizer S-3; containing the complex additive. When designing the composition of additives for heavy concrete, we proceeded from the fundamental provisions of construction science that the complexity of the action of additives lies in the optimal combination of two main opposite processes in time and volume of the concrete matrix. The use of the caprolactam oligomer synthesized in the course of this investigation makes it possible to solve the problem of involving concentrated wastes of caprolactam production in the production turnover. The obtained caprolactam oligomers can be used in construction as plasticizers of concrete mixtures, as inhibitors of corrosion of steel reinforcement in the production of reinforced concrete products. Water-soluble oligomers of caprolactam, which reduce the time of dissolution of the superplasticizer C-3 and the dispersion of low-temperature catalyst in the volume of the concrete mixture being mixed, were synthesized. It was found that in the presence of the oligomer caprolactam in an amount of 10 to 20% of the mass. the dissolution rate of S-3 superplasticizer in water at a temperature of 20-21 °C increases by 2.0-2.2 times. This contributes to a better mixing of the components of the concrete mixture, primarily to improve the dispersion of the complex additive in the volume of the concrete mixture. The caprolactam oligomer used in this research work is an effective water-soluble wetting agent for the surface of particles of cement, sand, and crushed stone, which is very important for activating hydration and sorption processes during mixing of a concrete mixture. The increased wetting properties of the caprolactam oligomer are characterized by a wetting angle of 19.6 °.

Key words: concrete, caprolactam, technogenic waste, low temperature catalyst, accelerating-plasticizing additive, water absorption

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One of the main conditions for high quality of industrial and civil construction is a reduction in the period of concrete strength gain and an increase in the pot life of concrete mixtures, which is important when transporting concrete to objects remote from reinforced concrete production facilities.

Considerable attention is paid to this problem in concrete science [1-6]. Nevertheless, in the presence of many ways to achieve the tempering strength of concrete and reinforced concrete products in the early stages, this problem is not completely solved at this time [7-8].

This work shows the results of investigations on the study of the effect of complex additives containing industrial waste production of caprolactam, the well-known superplasticizer S-3 and synthesized plasticizer of concrete mixtures based on the oligomerization of caprolactam in a mixture of polyhydric alcohol and amino alcohol. For research work, a grade B 22.5 concrete mixture with the indicated plasticizing additives was prepared.

When designing the composition of additives for heavy concrete, we proceeded from the fundamental provisions of construction science that the complexity of the action of additives lies in the optimal combination of two main opposite processes in time and volume of the concrete matrix [9-14]. At the first stage of the process, when a dry concrete mixture is mixed with water, an important factor is the time of hydration of the cement grains, which correlates with the rate of wetting of their surface and the capillary penetration of water molecules into the lower layers of the grains. It should be noted that this effect is enhanced by the use of plasticizers, super- and hyperplasticizers, or by an increase in the water-cement (W/C) ratio. The second method is rarely used, since it reduces the strength characteristics of concrete. The description of the second method of additives preparation and the establishment of its ineffectiveness are presented in the articles [15-17].

At the second stage of the formation of the structure of the concrete matrix, the main conditions are those when the colloidal structures of the cement paste pass through the colloidal crystallization into the hard crystallization phase. This process is intensified by the action of hardening accelerators of inorganic and organic nature and consists in increasing the degree of saturation of the system with calcium oxide hydrate (CH) and the subsequent active formation of crystals of calcium hydrosilicate (CHS) [18-20]. In this case, a certain number of particles of hardening accelerators simultaneously form hydrate complexes with water molecules and thereby reduce the W / C ratio, which also contributes to accelerating the rate of concrete hardening [21].

In the experimental part, an additive was prepared based on the superplasticizer C-3 and a water-soluble caprolactam oligomer (I-60P) at a ratio of 0.5 : 1.0 (additive No. 3). Another additive was prepared on the basis of a mixture of C-3 superplasticizer, deactivated LTC and water-soluble caprolactam oligomer (I-60P) in a component ratio of 0.2 : 0.5 : 0.8 (additive No. 4).

The components were preliminarily subjected to joint grinding in a laboratory vibrating mill to the degree of dispersion of solid particles of the LTC to 20-30 μm.

The concrete mixture of grade B22.5 was prepared in accordance with [22]. For the manufacture of sample cubes, we used cement grade CEM I 42.5 N GOST 31108-2003, quartz sand with a size modulus of 2.0-2.5 in accordance with GOST 8736-85, crushed stone of granite fraction 5.0-20.0 mm in accordance with GOST 10268-80, tap technical water in accordance with GOST 10268-80 GOST 2874-82. The mixing of the concrete mixture was carried out at a water-cement ratio (W/C) of 0.4. Additives were added with mixing water at a concentration of 0.35% (wt.) of the cement weight.

The results of testing samples are cubes of concrete B22.5 with a size of 100×100×100 mm are shown in the Table. To calculate the compressive strength of concrete and water absorption, six sample cubes were tested.

The average values of each indicator were determined. Strength tests were carried out in accordance with GOST 1080-90 on a P-125 hydraulic press with a scale of 62.5 tf. When calculating the strength of concrete, a table was used to recalculate the compressive load taking into account the correction factor K = 0.95, taking into account the size of the face of the cube of the test sample (100 mm), since cubes with a face size of 150 mm are standard according to GOST 10180-90, GOST 18105-86.

After placing concrete in molds and vibrating on a laboratory vibrating table the samples were placed in a chamber for heat and moisture treatment (HMT) according to the following mode:

- temperature rise from +20 °C to +80 °C within 3 h;
- exposure at 80 °C within 8 h;
- cooling from +80 °C to + 20 °C within 4 h;
- exposure at +20 °C within 9 h.

Further, the samples were removed from the molds, examined in order to identify external defects of the cubes, then tests for strength and water absorption were carried out (Table).

As a comparison of the effect of additives on the properties of concrete, samples of concrete without additives (1) and with the addition of C-3 superplasticizer (2) were investigated.

Table

Physical and mechanical characteristics of B22.5 grade concrete
***Таблица.* Физико-механические характеристики бетона марки B22,5**

№	Grade B22.5 concrete samples	Additive amount, %	Setting time, min, GOST 310.3		Compressive strength, MPa, GOST 10180		Water absorption, % GOST 12730.0
			Beginning	End	1 day	28 days	
1	Without additives		175	252	19.6	29.8	1.88
2	With the S-3 addition	0.35	198	288	20.8	35.6	1.26
3	With S-3 additive and caprolactam oligomer I-60P	0.35	186	208	23.2	37.4	0.88
4	With S-3 additive and caprolactam oligomer I-60P and LTC	0.35	207	302	24.9	42.6	0.65

Investigation have shown a positive effect of additives on the properties of B22.5 grade concrete. The data in the Table indicate that the maximum effect of increasing concrete strength and reducing water absorption is achieved by using a complex additive (4) based on the composition of superplasticizer C-3, caprolactam oligomer I-60P, deactivated LTC, which is a technological waste of caprolactam production [23-24]. This is due to the fact that the caprolactam oligomer I-60P is an effective wetting agent and emulsifier dispersed systems of the "water-oil" type. In its presence, the amount of C-3 superplasticizer required for mixing the concrete mixture at 20 °C dissolves in water in 48 s, while without I-60P in 57 s. The adsorption properties of the caprolactam oligomer I-60P are characterized by the wetting angle of the glass plate surface, the value of which is 19.2 °. Consequently, due to this factor, the rate and specific area of wetting of the surface of cement particles, as well as of the low-temperature NTK catalyst, increases. The carbonates, calcium and zinc oxides included in its composition intensify crystallization processes, the rate of which increases in proportion to the decrease in time in the concentration of plasticizing additives in the concrete matrix – superplasticizer C-3, caprolactam oligomer I-60P. It should be assumed that the end time of the plasticizing effect of the additives coincides with the beginning of active concrete hardening.

The investigation have established the effectiveness of the action of additives No. 3,4, which exhibit a plasticizing effect at the stage of preparation of the concrete mixture and the formation of a coagulation structure, and at the subsequent stage as accelerators of hardening, increasing the strength of concrete under compression.

It can also be concluded that the combination of superplasticizer C-3 and caprolactam oligomer I-60P increases the degree of hydration not only cement grains, but also accelerates the reaction of mixing water with calcium oxide contained in the catalyst for cyclohexanol dehydrogenation [25]. The resulting calcium hydroxide and then calcium hydrosilicate accelerate the main processes of cement hydration. The results of the additive action of C-3 superplasticizer, caprolactam oligomer I-60P, cyclohexanol dehydrogenation catalyst (LTC) are: 1) an increase in the degree of cement hydration due to the synergy of the wetting properties of C-3 superplasticizer together with I-60P oligomer; 2) an increase in the period of the beginning and end of the setting of the concrete mixture contributes to the formation of a denser crystallization structure; 3) the oxides, hydroxides, calcium and zinc carbonates contained in the LTC are additional crystallization centers that additionally contribute to the formation of a denser concrete structure. For this reason, the indicators for the strength and water absorption of concrete are significantly improved, which is typical for additives No. 3.4 (Table).

Thus, additives No. 3, 4, according to their functional properties, can be attributed to the group of accelerating-plasticizing, which have prospects for use in construction production. An important advantage of using the additives is a stable domestic raw material base, manufacturability of preparation, competitive price and high quality.

It should be noted that in the preparation of the additives, the superplasticizer C-3 and the deactivated LTC are used without preliminary preparation. Caprolactam oligomer of I-60P was obtained by the method of low-temperature synthesis from concentrated wastes of caprolactam (CWC) in a mixture of glycerin and amino alcohols.

Practical application of the investigated additives 3 and 4 simultaneously solves the problem of complex use of secondary wastes of chemical production, which are concentrated wastes of caprolactam and deactivated LTC.

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