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Composite binders for concretes with improved shock resistance

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Abstract. The qualitative and quantitative composition and properties of the initial materials, composite binders and concrete samples were studied. Optimal compositions of concrete for protective structures that provide the maximum static and dynamic strength characteristics are selected. In this case, the effect of increasing the shock endurance increases to 6 times. It has been found that concretes with a small number of defects, high packing density and uniformity, good adhesion between the aggregate and cement stone, an increased ratio of static tensile strength to static compressive strength R_{tens} / R_{compr} and ductility have the best resistance to dynamic impact. It is proved that this ratio can be increased, in the case of the use of dispersed reinforcement of concrete (so-called fibrous concrete). In experimental studies on penetration of both unreinforced and fiber-reinforced concrete slabs, it was noted that samples of unreinforced concrete were completely destroyed in large and small pieces, while samples of fiber-reinforced concrete were not completely destroyed, and only through penetration at the impact site was observed; that is, fibrous concrete has the best impact resistance. These results can be applied to the design of various special structures, such as protective structures of civil defense and emergency situations, concrete structures of nuclear power plants, etc.

1. Introduction

In the modern world, which saturated with natural and man-made hazards, the protection of human life must be ensured by the optimization of the "man-material-habitat" system through the continuous improvement of structural materials for protective structures. In view of the fact that the large-tonnage production of cement also significantly worsens the ecological habitat of humans, its use should be minimized. Thus, the increase in the efficiency of concrete must be achieved through the use of a composite binder (CB).

There are several technological ways to solve the problem of increasing the shock endurance of concrete. One of them is an increase in the static strength of concrete, and this way is practiced in a number of foreign countries. It is based on the use of high-quality cements, fractionated aggregates, superplasticizers. Another direction is the technology of modifying the structure of concrete by introducing into the concrete mixture the porous dispersed components (damping additives). This method of increasing the shock endurance of concretes was researched by R. Oyguc [1], M. Kristoffersen [2], A. Maazoun [3], Z.I. Syed [4], K. Makita [5], etc. However, these concretes provide a relatively moderate increase in shock endurance – up to 2–4 times, which is not sufficient for protective structures in conditions of the action of the means of destruction, which create high dynamic loads on the enclosing structures.

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The use of fiber-reinforced concrete for the production of enclosing structures of protective structures is promising (the studies of V.S. Lesovik [6–7], R.S. Fediuk [8–9], A. Abrishambaf [10], D.-Y. Yoo [11–13], N. Ranjbar [14–15]), because it has high impact resistance. Dispersed reinforcement allows to substantially increase the whole set of mechanical characteristics of concrete, such as static strength, crack toughness, impact resistance [5].

However, the application of new types of nanodispersed mineral additives, as well as the principles of their compatibility to ensure the required performance characteristics of CBs, have not been studied sufficiently. In particular, the study of shock endurance of composites of various compositions has not been practically investigated.

To expand the use of composite binders in construction, it is necessary to study the compositions of Portland cement and multicomponent finely dispersed mineral and organic additives to obtain the required properties of binders and composites based on them for protective structures.

Thus, the goal of the paper is the development of composite binder for concrete enhanced impact resistance.

To achieve the paper goal, composite binders were prepared, obtained by joint grinding of the following components: 52–59 % of Portland cement, 30–32 % of rice husk ash (RHA), 5–7 % of quartz sand, 6–8 % of limestone crushing waste, 2–4 % hyperplasticizer (HP). Water was added in the amount necessary to ensure the same mobility, but from the calculation of the water-binding ratio not higher than 0.25. Cement stones were studied at the age of 1, 3, 7, 28 days.

2. Methods

The study of qualitative and quantitative compositions and properties of raw materials, composite binders and concrete samples was carried out using standard methods. The study of the morphological features of the microstructure was carried out using the Carl Zeiss CrossBeam 1540XB scanning electron microscope. The study of the mineral composition and structure was carried out using X-ray diffraction analysis by the D8 Advance powder diffractometer (Bruker AXS). Derivatograms of the samples were obtained by the Shimadzu DTG-60H thermogravimetric analyzer.

Specific surface of binders as well as mineral additives was measured by the device PSH-11, which operates on the principle of air permeability through a layer of pre-compacted material.

The compressive strength at the static load action (cubic strength), prismatic strength and modulus of elasticity were determined on the cubes with an edge of 150 mm and prisms with a base of 100×100 mm and a height of 400 mm.

The modulus of elasticity was calculated for each sample at a loading level of 30 % of the destructive one, according to formula

$$E_{\sigma} = \frac{\sigma_1}{\varepsilon_{1y}},$$

here σ_1 is the increment of the voltage from the conditional zero to the level of the external load equal to 30 % of the destructive one;

ε_1 is the increment of the elastic relative longitudinal deformation of the sample, corresponding to the load level $P_1 = 0.3P_d$ and measured at the beginning of each stage of its application;

P_d is the destructing load measured on the scale of the press (machine).

To study the shock endurance, two series of tests were carried out: on panels and on cylinders.

Panels measuring 600×600×50 mm were removed from the mold 24 hours after casting and left in the laboratory until the testing age. The impact capacity of the panels was tested on day 28.

The shock endurance test was carried out with the aid of a falling hammer based on the international regulatory document ACI Committee 544, in which the impact-resistant specimen was subjected to repeated shocks at the same location. In this test, a hammer weighing 10 kg falls from a height of 600 mm on the panel. The number of impacts that caused the first visible crack and destruction was observed and used to calculate the first crack and the impact energy for destruction of concrete, respectively. The impact energy is given in the following equation:

$$E_{sh} = m \cdot g \cdot h \cdot N,$$

here E_{sh} is the shock energy,

J ; m – mass of the hammer = 10 kg;

$$g = 9.81 \text{ m/s}^2;$$

N is the number of impacts.

The ratio of the number of shocks causing the failure, N_f to the number of shocks causing the first crack, N_c is defined as the impact coefficient $\mu_i = N_f/N_c$. The width of the crack of the entire fiber-reinforced concrete panel was measured using the Dino-Lite AM3713TB microscope immediately after the appearance of the first crack, and the crack growth was studied.

3. Results and Discussions

At the first stage, an almost linear dependence of the required time of grinding of the CB was revealed to achieve a different specific surface in the range from 280 to 900 m²/kg (Figure 1, a, b). Obviously, with these data, the required grinding time can be predicted to reach a certain specific surface area. After grinding the CB components and measuring the surface area, water was added and the compressive strength was measured after 28 days. The results are shown in Figure 1, a. It can be seen that the maximum compressive strength was obtained at a surface area of 550 to 600 m²/kg. The increase in the surface area does not lead to a further increase in strength, and even to a decrease. This is due to the excess of fine particles, because the superplasticizer limit was reached, which we investigated earlier [16]. This behavior was also observed in the change in the viscosity of the mixture when the surface area of the particles was above 600 m²/kg. It is expected that an increase in the amount of superplasticizer will lead to the creation of concrete with an even greater compressive strength.

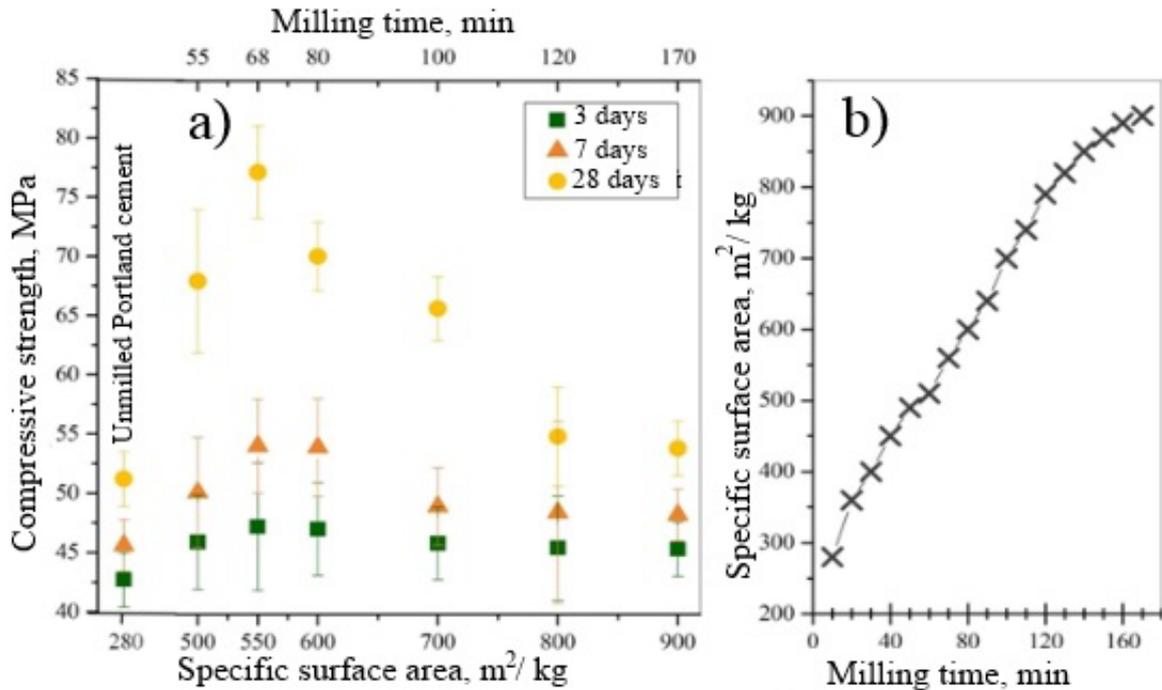


Figure 1. Microphotographs of cement stone without additives (a) and cement stone with replacing 25 % of cement by rice husk ash (b).

The microstructural analysis showed that cement matrix from a no-additive cement is characterized by a matrix with a large number of voids and microcracks, the overwhelming majority of which is represented by poorly crystallized and amorphous neoplasms, against which hexagonal plates of portlandite are visible (Figure 2, a, c).

The use of the developed composite binder allows to compact the microstructure, to obtain clearly distinguishable systems of needle and lamellar neoplasms filling anisometric and isometric voids (Figure 2, b, d). This leads to the formation of a rigid matrix with reduced porosity, which, in turn, leads to hardening of the cement stone [17–19].

Based on the results of XRD for the diffractogram of cement stone of the developed CB (Figure 3), the intensity of the peaks corresponding to clinker minerals is characteristic: an alite with $d/n = 3.04; 2.97; 2.78; 2.74; 2.75; 2.61; 2.18; 1.77 \text{ \AA}$ and belite with $d/n = 2.89; 2.67; 2.72; 2.76; 2.75; 2.78; 1.77 \text{ \AA}$, which indicates the acceleration of hydration processes when using the CB. In addition, the CB contributes to a decrease in the intensity of the portlandite peaks with $d/n = 4.93; 2.63; 1.93 \text{ \AA}$.

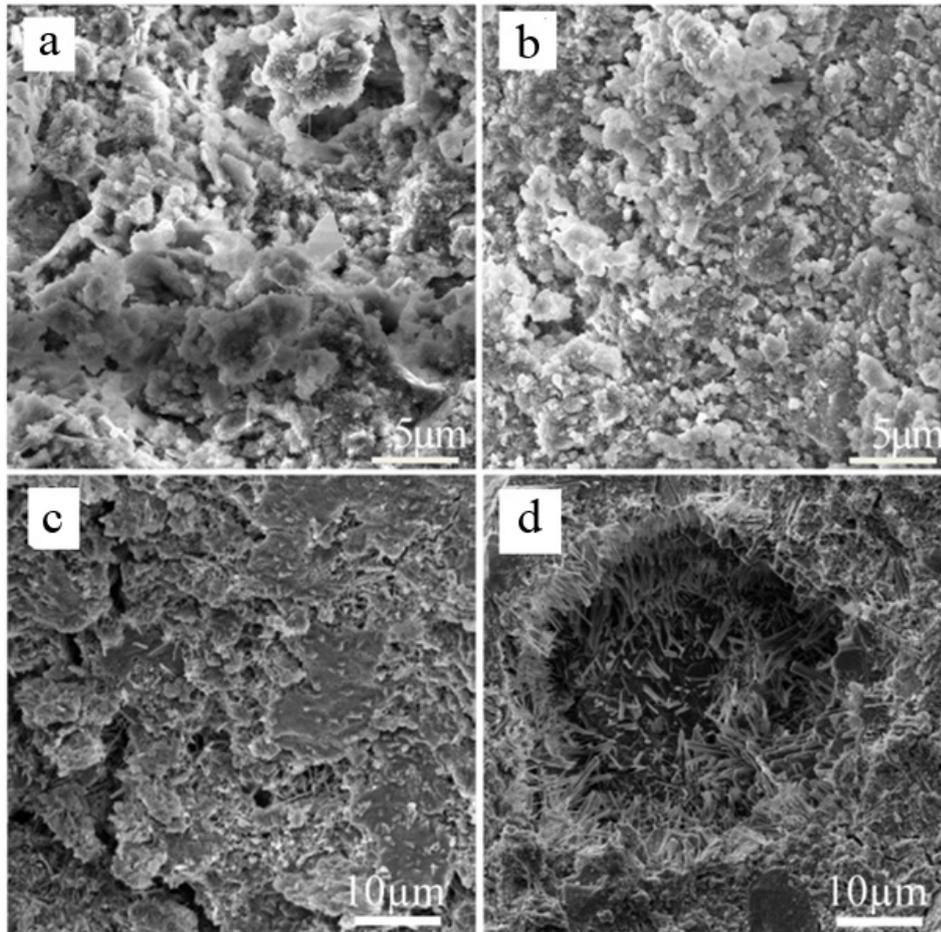


Figure 2. Microstructure of neoplasms (age 28 days): pure cement stone (a, c) and cement stone of the developed CB (b, d).

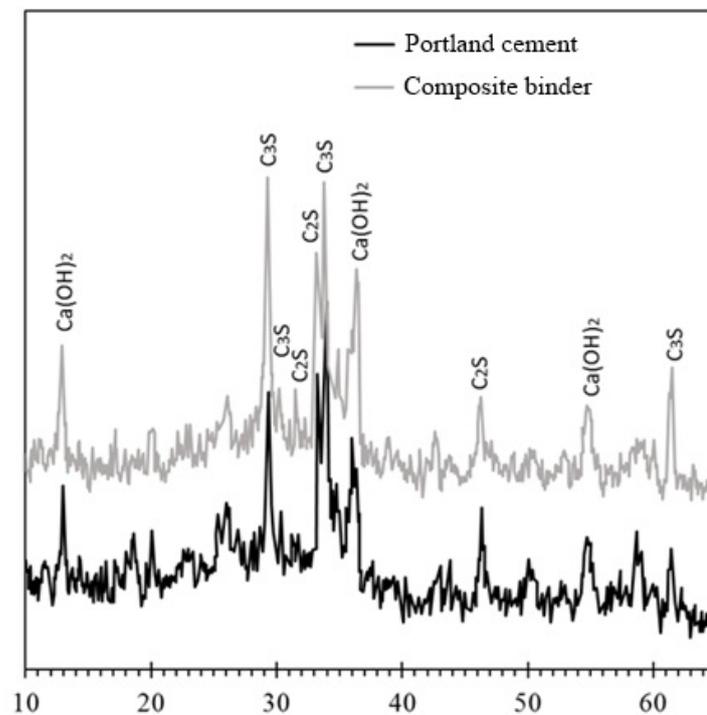


Figure 3. XRD of neoplasms.

Differential-thermal analysis (DTA) of the Portland cement stone and cement stone of the CB showed the presence of three main endothermic effects (Figure 4). The first (at a temperature of about 160 °C) is caused by the loss of adsorption water from the gel-like hydration products. Reduction of the area of this effect on the results of DTA cement stone of the CB, shows a decrease in the content of gel-like neoplasms as a result of their transition to a crystalline state.

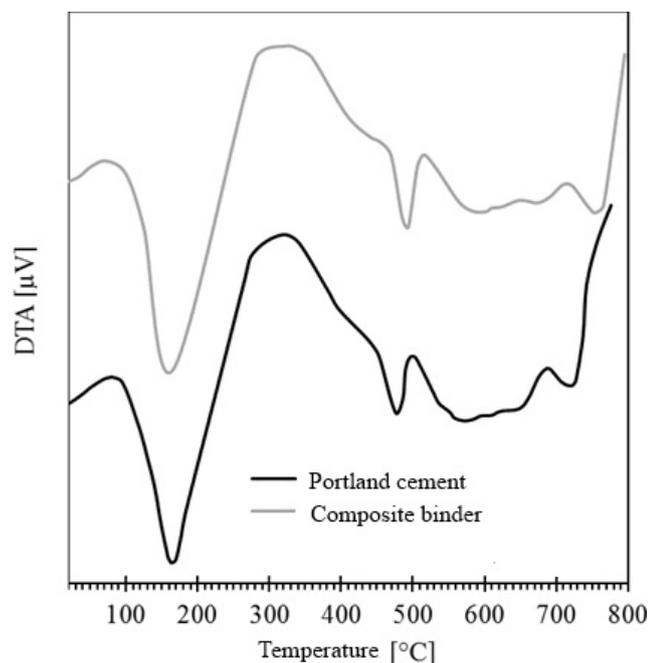


Figure 4. DTA results for pure cement stone and cement stone of the CB.

The next endothermic effect (at a temperature about 475 °C) corresponds to the dehydration of calcium hydroxide. The increase in the area of this peak on the thermogram of the no-additive cement stone shows a greater content of portlandite in its composition.

The last endothermic effect (at a temperature of 525–650 °C) can be associated with the decomposition of calcium carbonate.

In the initial period of curing, due to the fact that the crystal hydrates occupy an insignificant volume, the chemical and mineralogical characteristics of the additives and their pozzolanic activity practically do not affect the basic properties of the binder system.

In the second stage of hydration of the composite binder, the role of chemical processes that contribute to a significant modification of the phase composition of the system increases: the balance shifts from primary crystalline hydrates (calcium hydroxide and highly basic calcium hydrosilicates) toward more stable secondary fine crystalline hydrates represented by low-basic CSH. Mainly, the balance shift depends on the chemical composition and activity of the fine-milled additives. An obligatory condition of compaction, and, accordingly, hardening of cement stone is the shift of balance towards increasing the amount of low-basic calcium hydrosilicates CSH (I). Obviously, this condition will be sufficient until an excessive amount of filler will not envelop the surface of new phases, thereby preventing the formation of contacts and the fusion of crystalline hydrates. Proceeding from this, we conclude that in the mixed system is the optimum volume concentration of the ultradispersed additive taking into account its pozzolanic activity. When an inert filler is used, its optimum dosage will be determined by the amount of capillary pores necessary to seal the structure of the material.

Thus, it is possible to single out a number of positive factors leading to optimization of the physical and mechanical properties of cement stones as a result of the use of the developed CB:

- the speed of strength growth of the composite is increased in the early period as a result of the fact that the silica-containing components play the role of nucleation centers of neoplasms;
- Increasing the fineness of the particles and the concentration of the filler in the volume leads to a decrease in the total porosity of the composite;
- hydrosilicates of the second generation appear as a result of the reaction of amorphized RHA with portlandite;
- due to the large surface energy of the particles of the binder, clusters “binder – filler” are formed.

Investigation of the mechanical properties of fine-grained concrete (Table 1) showed that the use of composite binder allows to increase the technical characteristics of concrete, in comparison with similar compositions made with the use of traditional binder materials. This fact is explained by the denser structure of the cement stone of the developed composite binder, with a lower porosity, due to less water in the concrete. The best mechanical characteristics showed composition 2-2. It should be noted that with an increase in the amount of ash and a decrease in the amount of cement to ensure the uniformity of the formulations, it is necessary to increase the amount of water introduced into the concrete mix.

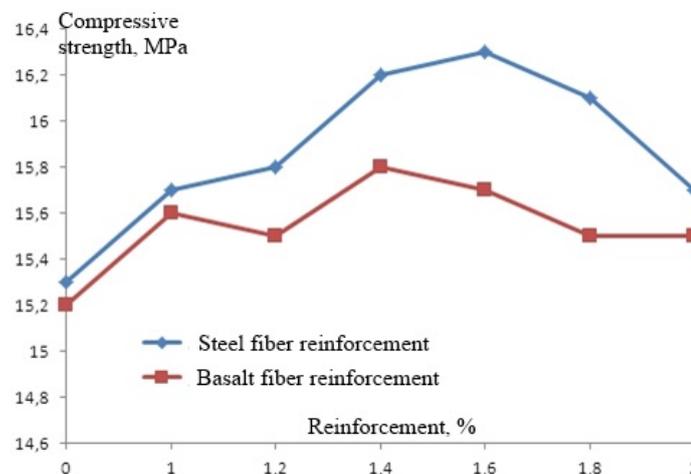
Table 1. Mechanical characteristics of fine-grained concrete depending on the composition of the binder.

Composition	Consumption of materials per 1 m ³				Cubic strength, MPa	Prism strength, MPa	Elastic modulus, GPa
	Cement, kg	Fillers of CB, kg	Aggregates, kg	Water, l			
1-2	646	508	1020	223	73.6	54.0	41.0
2-2	606	548	1020	231	82.6	65.2	55.3
3-2	565	589	1020	236	75.3	50.3	41.3
CEM I 42.5 N	545	-	1634	218	62.9	41.8	35.2
CEM I 42.5 N +31% RHA*	376	169	1634	241	71.2	52.3	44.0
CEM I 42.5 N +3% HP	512	33	1634	182	65.3	49.2	41.2

* – rice husk ash was crushed to 550 m² / kg

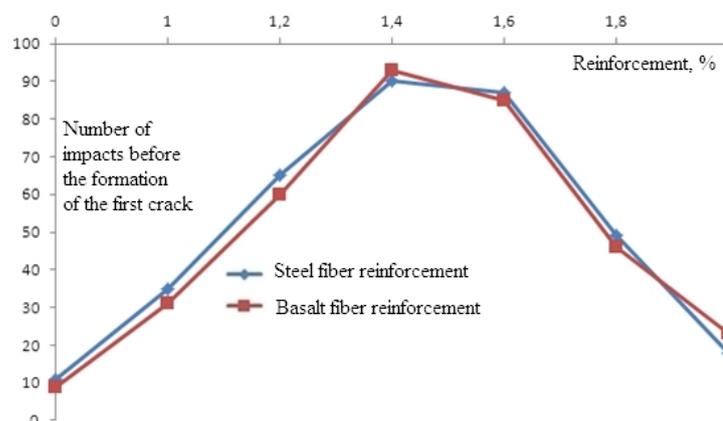
In order to obtain high density fibrous concrete, the effect of introducing reinforcing fibers into the concrete matrix was studied. As a basis for the concrete matrix was adopted the composition of 2-2 according to Table. 1.

To determine the optimal percentage of reinforcement of fine-grained fibrous concrete, samples of concrete of the same composition (2-2) with different contents of steel- and basalt fiber were molded. The results of the study of the dependence of the strength properties on the percentage of reinforcement by different types of disperse reinforcement are shown in Figure 5.

**Figure 5. Dependence of tensile strength of fiber-reinforced concrete on the percentage of reinforcement by different types of fiber.**

In the study of shock endurance of fiber-reinforced concrete with different types of fiber, the following results were obtained (Figure 6, 7).

Figure 6, 7 present that after the addition of steel or basalt fiber, the concrete strength (before the formation of the first crack) is increased to 9 times in comparison with the corresponding mixtures without fiber. Both steel and basalt fibers were effective in preventing the growth of microcracks and reducing the spread of these cracks before the cracks were combined with the formation of macrocracks.

**Figure 6. Dependence of the number of strokes before the formation of the first crack on the volume concentration of fiber.**

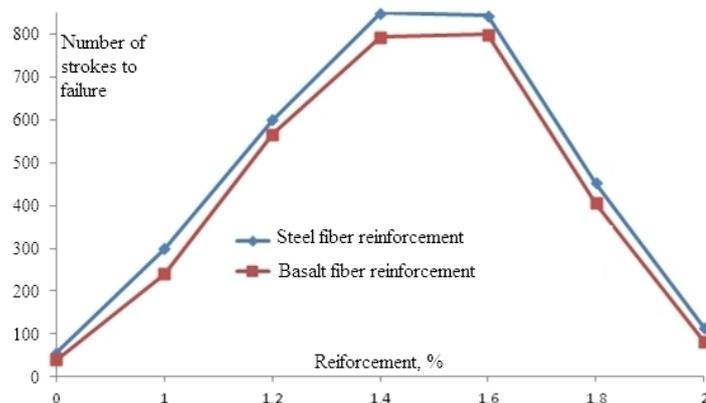


Figure 7. Dependence of the number of impacts to the destruction of fiber-reinforced concrete on the volume concentration of fiber.

The destruction scheme in samples with fibers and without is shown in Figure 8. The unreinforced concrete panel was broken into four parts after the destruction (Figure 8, a). The sample lost its structural integrity and geometry, reaching the energy capacity of the impact. The destruction of the fiber-reinforced concrete slab (Figure 8, b) was due to the perforation of the panels by the falling hammer, and the sample was not broken up into pieces, unlike simple concrete panels. This behavior showed that the fiber-reinforced concrete panels remained structurally integral, as well as viscous. Figure 8, b shows a significant number of secondary cracks.

Dynamic impacts are characterized by a continuous change in parameters, high intensity and short duration. Shock-, or dynamic strength, to a greater extent than static, depends on the initial defects in the structure of the concrete due to the reduction in the possibilities of redistribution of stresses due to the delay in the development of microplastic deformations. Fibers, influencing the processes of structure formation, help to reduce internal stresses and reduce the number of foci of occurrence of internal defects of concrete and their dimensions, thus preventing their further development.

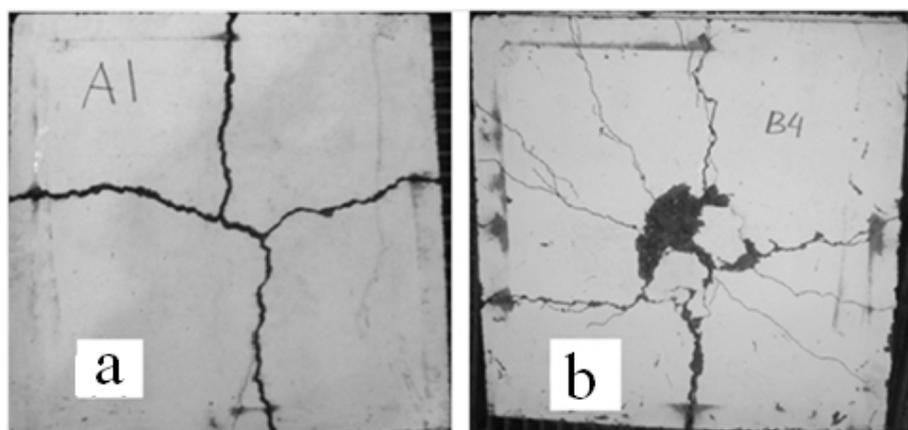


Figure 8. Destruction of samples without fiber and with fiber.

Further, studies were carried out of various compositions of fiber-reinforced concrete for impact endurance. It was revealed that the maximum number of blows withstands composition 2-2. Despite the fact that the largest coefficient of impact strength showed sample 1-2, this parameter can not be decisive in the design of protective structures, and its number of strokes to the first crack and the number of strokes before the destruction of the sample showed low results (Table 2).

Table 2. Shock resistance of fiber-reinforced concrete depending on the composition of the binder (1.4 % steel fiber reinforcement).

Composition (labeling according to Table 1)	Number of strokes for the first crack	Shock energy (first crack), J	The number of shocks for destruction the sample	Shock energy (destruction of the sample), J	Coefficient of impact strength, μ
1-2	6	354	198	11682	33
2-2	9	531	242	14278	27
3-2	8	472	191	11269	24
CEM I 42.5 N	1	59	6	354	5
CEM I 42.5 N +31% RHA	1	59	15	885	15
CEM I 42.5 N +3% HP	3	177	51	3009	17

Table 3 shows the width of the crack and the number of secondary cracks before the panel is destroyed. The initial width of the crack was used as a comparative study to determine the efficiency of steel fiber in bridged microcracks in fiber-reinforced concrete.

Table 3. Investigation of crack formation during fracture of samples.

Composition (labeling according to Table 1)	Opening of the first crack, mm	Crack opening before sample breaking, mm	Number of secondary cracks
1-2	0.132	1.789	13
2-2	0.095	1.876	18
3-2	0.187	1.843	14
CEM I 42.5 N	0.234	1.112	7
CEM I 42.5 N +31% RHA	0.187	1.160	10
CEM I 42.5 N +3% HP	0.197	1.324	12

The fiber bridge determines the absorption of the impact energy after the beginning of the cracking and, consequently, the shock plasticity of the concrete. The coefficient of impact strength μ_i , expressed as the ratio between the final and initial impact energies and shown in Table. 2, is a good indicator of the plasticity of concrete subjected to shock loading. Obviously, the final shock energy (before destruction) is much higher than the energy expended for the appearance of the first crack. Even after the formation of the first cracks, the sample was able to withstand a large amount of shock load before it destructed. The ultimate shock energy (before destruction) exceeded the published results for high-strength concrete [20–24]. This means that the developed fiber-reinforced concrete has a high impact strength and an excellent potential for use as a structural material for protective structures.

4. Conclusion

1. Principles of increasing the efficiency of fiber-reinforced concrete are proposed, which consist in the complex influence of the composite binder on the processes of structure formation of cement stone. In this case, the effect of increasing strength in static compression of fiber-reinforced concrete increases by 31%, and shock endurance – up to 6 times.

2. The best resistance to dynamic impact is possessed by concretes with a small number of defects, high density and uniformity, good adhesion between the aggregate and cement stone, an increased ratio of static tensile strength to static compressive strength R_{flex}/R_{compr} and ductility. This ratio can be increased if dispersed reinforcement of concrete is used.

3. The complex analysis of the system "composition (raw materials) – structure (raw materials, material) – properties (material)" is the methodological basis of the scientific research carried out. The results of the work were obtained using modern scientific methods of research, using standardized methods for determining the composition and properties of raw materials, binder and concrete using certified and certified equipment of the Far Eastern Federal University, as well as the Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences.

4. It has been established that the use of CB consisting of 55.5 % cement, 31 % RHA, 10.5 % inert filler complex and 3 % hyperplasticizer, which is comminuted to a specific surface area of 550 m²/kg, helps optimize the structure of the cement stone and increase its limit compressive strength of more than 60 %.

5. Compositions were designed on the basis of certain natural technogenic resources of the Primorye Territory, which have high adhesion to the cement matrix and close coefficients of deformation characteristics.

6. Comparison of the results of the tests carried out on fiber-reinforced concrete showed that with an increase in the deformation rate, an increase in strength was observed both during compression and in tension. In addition, a careful analysis of the experimental data has proved the fulfillment of the main provisions of the methods used, and the obtained dependences of the dynamic hardening coefficient on the strain rate qualitatively and quantitatively agree well with the results of domestic and foreign studies of various concretes.

7. In the penetration experiments it was noted that samples of unreinforced concrete were completely destroyed in large and small pieces, while the samples of fibrous concrete were not completely destroyed, and only through penetration at the impact site was observed; that is, fiber-reinforced concrete has better impact resistance.

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Композиционные вяжущие для бетонов повышенной ударной стойкости

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Ключевые слова: самоуплотняющийся бетон, зола рисовой шелухи, пуццолановые материалы, ударная выносливость, свойства бетонной смеси, механические свойства.

Аннотация. Исследованы и предложены химико-технологические принципы оптимизации физико-механических свойств и эксплуатационных характеристик дисперсно-армированных композиционных материалов, заключающиеся в комплексном влиянии композиционного вяжущего на процессы структурообразования цементного камня. Изучен качественный и количественный состав и свойства исходных материалов, композиционного вяжущего и бетонных образцов. Подобраны оптимальные составы бетонов для защитных сооружений, обеспечивающих максимальные статические и динамические прочностные характеристики. При этом эффект увеличения ударной выносливости возрастает до 6 раз. Выявлено, что наилучшим сопротивлением динамическому воздействию обладают бетоны с небольшим количеством дефектов, высокой плотностью упаковки и однородностью, хорошим сцеплением между заполнителем и цементным камнем, повышенным отношением статической прочности на растяжение к статической прочности на сжатие $R_p/R_{сж}$ и пластичностью. Доказано, что это отношение можно повысить, в случае применения дисперсного армирования бетонов (так называемые, фибробетоны). В экспериментальных исследованиях по пробитию, как неармированных, так и фибробетонных плит отмечено, что образцы неармированного бетона полностью разрушались на крупные и мелкие куски, в то время как образцы фибробетона разрушались не полностью, а наблюдалось только сквозное их пробитие в месте воздействия ударника; то есть фибробетон обладает лучшей ударной стойкостью. Данные результаты могут быть применимы при проектировании различных специальных сооружений, таких как защитные сооружения гражданской обороны, бетонные конструкции атомных электростанций и т.д.

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