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Highly effective water-repellent concrete with improved physical and technical properties

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Abstract

The paper presents the research results of high performance modified concretes with complex hydrophobization modifiers and hydrophobic tragers. It is known that the concrete durability largely depends on its filtering characteristics, which can be lowered by adding hydrophobization additives to the concrete compositions, which, in turn, reduce the concrete strength and raise the concrete creep. The objective of the research was to develop a method of concrete hydrophobization without reducing its strength by applying hydrophobic water insoluble organic-and-mineral tragers. The paper provides the compositions of developed complex hydrophobization additives and water insoluble organic-and-mineral tragers. The influence of hydrophobization modifiers on the concrete workability has been studied as well. It was proved that complex hydrophobization modifiers allow producing high-mobility concrete mixtures and reducing their water separation value by 15...20% providing high preservation of concrete mixtures. The cube and prism strength values for concretes with modifiers are by 15...20% higher as compared to the concrete without additives. It was proved that the creep flow for all examined modified concrete samples was by 10...20% higher, and the concrete creep had damped characteristics. It was shown that the use of complex hydrophobization modifiers may reduce the water absorption as well as the capillary infiltration effect in concrete by 3...3.5 times. The concrete waterproofness is considerably improved as well; the waterproofness grade is almost 3 levels higher as compared to the concrete without additives.

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1. Introduction

The durability of concrete to a certain degree depends on the mass transfer processes of water or aqueous solutions of corrosive salts in its body. Hydrophobized concrete, being a more durable material, is produced by creating volume-hydrophobized cement stone structure by the use of known waterproofing additives such as GPD (direct emulsion of stillage residue of synthetic fatty acids in 50 % aqueous solution of sulfate-yeast mash), KOD-S (direct emulsion of soapstock in 30 % aqueous solution of sulfate-yeast mash), KOMD-S (KOD-S + sodium nitrite), OMD (GPD + nitrite-nitrate calcium chloride). The hydrophobic effect, as practical studies show, depends on the number of "phenocrysts" surface-active substance with the water-repellent action [1-4]. Formed in the cement stone meshwork (netlike structure) of hydrophobizator's "phenocrysts" does not preclude further cement hydration and improves the production of new fine-crystal dense formations, providing high durability of the material [5-9]. The increase of the hydrophobic effect, decreasing filtration characteristics of the concrete (water permeability, capillary suction, water absorption) and thus increasing its durability, can be achieved by increasing the content in its composition waterproofing additives, which at the same time leads to a considerable reduction in strength and the increase in the concrete creep [10-13].

2. Materials

The purpose of this research is to develop a method for increasing the concentration of the water-repellent in concrete composition to the level not less than 10 % (by the binder mass) without any strength reduction through the use of hydrophobic organic-and-mineral carriers as the granules of certain size distribution.

The use of hydrophobic carrier together with complex water-repellent modifiers allows us to manage the processes of water and mass transfer, to reduce a destructive effect of corrosion processes of the cement material and to improve the durability of concrete, reinforced concrete products and structures [14, 15].

The developed complex water-repellent additives and hydrophobic organic-and-mineral carriers, which allow purposefully controlling the properties of concrete mixtures and hardened concrete, include the following components:

- plasticizers - technical lignosulfonates, sour tarring, sodium salts of condensation products of naphthalene sulfonic acid and formaldehyde (superplasticizer C-3), sodium salts of aqueous product of condensation an sulfated aromatic hydrocarbon of catalytic cracking gas oil fractions and hydrolysis of oil and formaldehyde (with molecular mass of 6000 to 8000), sulfated melamine formaldehyde resins;
- water-repellent - soap stocks of vegetable oils, stillage residue of synthetic fatty acids (SRSFA), oil bitumen of low marks;
- regulating the kinetics of the curing (accelerators) - salts of inorganic acids, triethanolamine;
- dispersion fillers - wollastonite, fine rubber powder, fly ash.

Hydrophobization at the micro-level is achieved by using both known and new water-dilutable waterproofing additives, whose compositions are given in Table 1; at the macro-level by using of hydrophobic organic-mineral carriers.

Table 1. Compositions of hydrophobizing complex modifiers

Components	Content of component, mass %, in various modifiers		
	KMF	GKM-S	GKM-TR
Sour tarring	10.0-15.0	–	–
Sulfated melamine formaldehyde resins	–	10.0-30.0	10.0-30.0
Soapstocks of vegetable oils	10.0-30.0	5.0-15.0	5.0-15.0
Fly ash	28.0-52.0	–	20.0-25.0
Triethanolamine	–	0.30-0.50	0.30-0.50
Fine rubber powder	18.0-19.0	–	0.8-1.0
Water	The rest, to 100%		

3. Results and discussion

The influence of hydrophobizing modifiers on the concrete workability was studied. The results are shown in Figure 1.

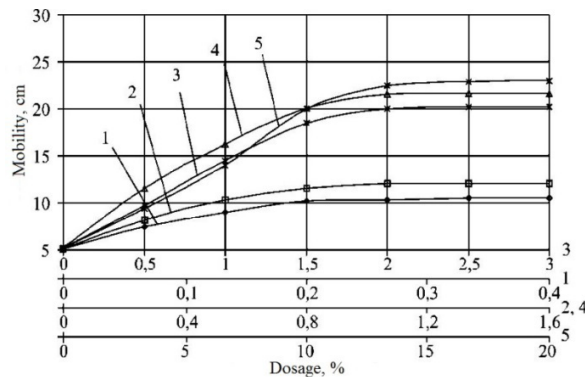


Fig. 1. The mobility of concrete mixture with various modifiers; 1 – modifier GPD; 2 – MGP-N; 3 – GKM-S; 4 – C-3; 5 – GKM-S + GC-M.

Figure 1 shows that the hydrophobizing complex modifiers allow us to get highly mobile concrete mixtures and they can compete with the superplasticizer with respect to the plasticizing effect. The highest concrete mobility value was observed in the area of optimal content the complex waterproofing additives GKM-S and hydrophobic carrier (1.5 % GKM-S + 10 % of GC-M). At the optimum content of the modifier GKM-S + GC-M, the concrete mobility increases significantly in comparison with the mobility of concrete mixtures with C-3 and GKM-S. This mobility increase is explained by the specific action of the hydrophobic carriers.

The superimposition of processes at different levels provides, as a consequence, the improvement of visco-plastic properties of cement materials, reducing the sliding friction between the components of the concrete mixture and increasing the water binding in the "semi-solid" aqueous shells, which, besides the lubricating action, give the stability to the concrete mixture [16, 17].

Plastification of the cement systems in the presence of complex hydrophobizing modifiers is caused by the following processes:

- formation of the meshwork films during the adsorption of hydrophilizing and hydrophobizing surface active substances (SAS) on the cement grains, providing the additional lubricating effect in cement systems;
- the influence of "semi-solid" aqueous shells, which also serve as lubricant solids cement systems;
- a decrease in the electrostatic adhesion forces resulting from the adsorption of SAS on the surface of the solid phases and creating the electric like charge, which also improves the visco-plastic properties of the concrete mixture [18].

The developed modifiers significantly reduce the water separation of concrete mixture by 15 to 20 %, ensuring high quality of contact between the layers of the concrete mixture during the concreting process, and thus the discontinuities of erected structures are excluded.

The peculiarity of concrete mixtures with GKM-S and GKM-S + GC-M is that with greater amounts of mixing water and the increase in fluidity of the concrete mixture, the uniformity of concrete mixture is preserved, i.e. the concrete mixture does not separate even at the flow rate of 220 liters per 1 m³ of concrete, while the concrete mixture without additives fully separates at the flow rate of 200 liters per 1 m³ of concrete.

The increased cohesion of concrete mixture with additives is explained through the slowing of diffusion processes. The complex hydrophobizing modifiers, providing dire concrete properties (workability, considerable reduction in exfoliation and water separation) allow us to create the optimal conditions of concreting at complex construction projects.

The study results showed that the developed complex hydrophobizing modifiers GKM-S and hydrophobic organic-and-mineral carriers GC-M allows us to change the concrete rheology in the right direction and thus allow to offer high quality concrete mixtures to the consumer in the accordance with the production requirements.

The influence of complex hydrophobizing modifiers on the deformability properties and on the strength of concrete was studied at the cement consumption $PC = 330 \text{ kg/m}^3$, the sand consumption $S = 625 \text{ kg/m}^3$ and the rubble consumption $R = 1270 \text{ kg/m}^3$. The analysis of the obtained results (Table 2) shows that the cube and the prism concrete strength with modifiers (consumptions 2 and 3) 15...20 % higher than the concrete strength without additives.

Table 2. Strength and deformation concrete properties

№	Composition, type and content of the modifier, % by cement mass	Strength, MPa			Elasticity module $E \cdot 10^3, \text{ MPa}$	Shrinkage, $\varepsilon_{sh} 10^{-5}$	Creep, $\varepsilon_{cr} 10^{-5}$
		Cube	Prism	Tensile strength in bending			
1	Without modifier (control sample)	32,5	27,6	3,7	34,4	41	29,2
2	With modifier 1.5 % GKM-S	41,4	33,1	5,6	35,1	37	33,7
3	With modifier 1.5% GKM-S + 10 % GC-M	40,5	32,4	5,2	34,7	36	34,5

The concrete with the complex water-repellent modifier 1.5 % GKM-S + 10 % GC-M have a tendency to ductile fracture. This phenomenon can be explained by the presence in the structure of the pore and capillaries walls the hydrophobizing phenocrysts and hydrophobic organic-and-mineral carriers, forming the contact water-repellent zone with the cement stone. These contact zones contribute to improving of the deformation properties of concrete. The destruction of concrete with these modifiers has the features of both the brittle destruction and the ductile one.

It was established that the creep deformation of all studied modified concrete samples increased by 10 to 20 %. The increased deformability of concrete with the studied modifiers can be explained by the fact that the micro particles of surface active substances are adsorbed on the surface of the growing crystals hydrosilicate, contributing to the formation of microcrystalline structure of the cement stone, which increased the creep of concrete.

The development of creep deformation of the concrete with the complex modifier GKM-S + GC-M (Table 2, composition 3) had its own features: the deformations developed immediately after the loading of the concrete, and then they slightly increased, i.e. the creep had a damped character. The time period of creep damping was reduced by 50 %.

For a better understanding of the developed modifier we performed X-ray analysis of the cement stone and carried out the studies of the material by X-ray small-angle scattering; the results of aforesaid studies are presented in Tables 4 and 5. The main products of cement hydration with water-repellent additives are:

- Hydrated gel phases with two reflections of X-ray scattering (max amorphous halo 7 and 14 Å) and a reflection of the X-ray scattering (max amorphous halo 9 Å) with two structural types of tobermorite-like hydrosilicates calcium. The amount of hydrate gel, which is characterized by the total intensity of these maxima, it ranges from 8 to 15 relative units;

- Crystalline hydrate phases: portlandite Ca(OH)_2 (4.39; 2.63; 1.92 Å) and low-alkali hydrous calcium SSN (1) (12.5; 3.04; 1.40 Å). Their quantity is estimated by total intensity of the main individual lines.

Table 3. Data of the X-ray phase analysis of a cement stone.

Additive	The intensity of X-ray scattering (relative units)				
	hydrate phase				clinker minerals $\sum J \text{ C}_2\text{S} + \text{C}_3\text{S}$
	amorphous		crystal		
	$\sum J 7 \text{ и } 14 \text{ \AA}$	$\sum J 9 \text{ \AA}$	$\sum J \text{ Ca(OH)}_2$	$\sum J \text{ CSH(1)}$	
Without additive	21,4	0,42	0,85	1,53	7,3
GKM-S	14,0	0,44	0,40	1,57	8,9
GKM-S + GC-M	13,8	0,42	0,39	1,57	8,8

The cement stone with water-repellent additives contains a certain amount of clinker minerals: tricalcium silicate (2.77; 2.59; 1.76 Å) and dicalcium silicate (2.81; 2.69; 1.58 Å).

The data in Table 3 show that the water-repellent additive promotes:

- increase in the amount of crystalline hydrate phase SCH(1), especially for the cement paste with additives GKM-S and GKM-S plus GC-M (ΣJ increases from 1.53 to 1.57 relative units);
- reduction of the number of gel-like hydrate amorphous components (ΣJ 7 and 14 Å is reduced from 21.4 to 14.0 relative units with additive GKM-S and up to 13.8 relative units with additive GKM-S plus GC-M);
- reduction in the amount of crystalline portlandite $\text{Ca}(\text{OH})_2$ (ΣJ is reduced from 0.85 to 0.4 relative units in GKM-S and to 0.39 relative units in GKM-S plus GC-M);
- reduction in the degree of hydration of clinker minerals ($\Sigma J \text{ C}_2\text{S} + \text{C}_3\text{S}$ increases from 7.3 to 8.9 relative units with the addition of GKM-S).

Research of microporous structure of a cement stone without additive or with water-repellent additives on the X-ray device KRM-1 (Table 4) shows that the cement stone without additive has the low-angle scattering which indicates the presence of non-uniform microstructure with an effective size of microheterogeneities $R_{\text{eff}} = 189 \text{ \AA}$ and a scatter size $\Delta R = 175 \text{ \AA}$. The nature of such scattering is probably due to micropores (density fluctuation $\Delta\rho < 1$) formed in the calcium hydrosilicates.

Table 4. Data of low-angle X-ray scattering of a cement stone.

Additive	Microstructure parameters		
	ΣJ_{SAXS} , relative units	R_{eff} , Å	ΔR , Å
Without additive	0,69	189	175
GKM-S	0,94	200	154
GKM-S + GC-M	1,01	219	160

Water-repellent additives lead to an increase in the intensity of small-angle scattering from the cement stone (from 0.69 to 1.01 relative units) which characterizes the increase in number of micropores in volume units.

Taking into account the long-term impact of water-repellent additives on the processes of modification of hydration products of clinker, which lead to the self-healing of structural defects of the cement stone, it can be concluded that the microstructure parameters are crucial in improving the frost- and corrosion resistance of cement materials. The positive impact of hydrophobic modifier on the parameters of a microporous structure is explained by favorable changes in the process of hardening the binder [19, 20]. There is a certain decrease in number of amorphous constituents of hydrated phases and portlandite $\text{Ca}(\text{OH})_2$, the ordering of the amorphous hydrated gel-like phase, the increase in number of CSH (1), the improvement of the microporous structure of hydrated tumors. Hydrophobic modifiers promote preservation of the stock of clinker minerals in a cement stone.

Next, we researched the degree of hydration of cement paste and microporosity. Crystalline and gel products, which are the result of interaction of cement with water, together with the non-hydrated cement stone granules are involved in the process of creation of 3D-framework.

In this regard, it is interesting to consider the effect of the degree of hydration of cement on microporous hardened cement paste with water-repellent additives. The data obtained from the diffraction patterns of the hydration degree as well as those of the microporosity of the cement stone without additives or with water-repellent complex modifiers are shown in Table 5.

Table 5. Cement hydration degree and microporosity of cement stone.

Additive	Hydration degree, %	Microporosity, relative units
Without additive	47	0,68
GKM-S	32	1,38
GKM-S + GC-M	33	1,40

The data in Table 5 show that the interaction of water with cement mineral phase forms hydrosilicate phases with the microporosity of 0.69 volume units, the amount of which is about 40% of the total mass of the cement paste. The hydration degree of the cement paste with water-repellent additives is reduced by 15...25%.

The presence of a water-repellent additive containing inorganic salts increases the hydration degree of cement

stone. Such a character of hydration can be explained by the change of the diffusion processes of the water mass transfer under the action of a hydrophobizing ingredient and a hydrophobic carrier. In turn, the mobility of the cement system with water-repellent additives is a source of increase (by 1.8 to 2.0 times) the microporosity due to the reduction in the number of larger pores, that is, the ordering of the system at the micro level takes place. It is known that such changes promote the increase in strength, water resistance, durability and improve other properties of cement materials.

The test results for water absorption, capillary suction and water resistance of modified concrete are shown in Figures 2, 3 and Table 6.

The analysis of the results shows that the complex water-repellent modifiers allow reducing water absorption and capillary leakage by 3 to 3.5 times. High resistance to the penetration of water apart through to the dense structure of concrete is provided at the micro level through the mesh "phenocrysts" of water-repellent additive in the volume of sub-microcrystals of cement stone and at the macro level through the hydrophobic field formed by the hydrophobic carriers in the volume of concrete.

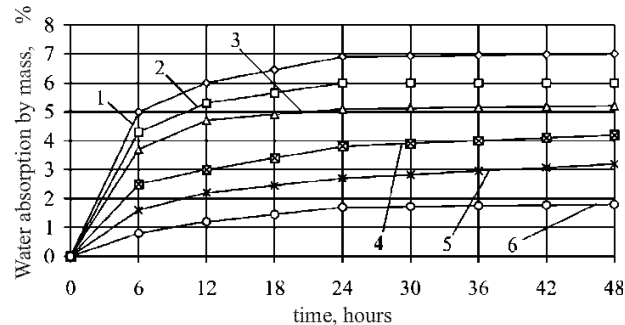


Figure 2. Kinetics of water absorption of concrete; 1 – without additive; 2 – 0.8 % C-3; 3 – 0.2% GPD; 4 – 1.5 % KMF-SA; 5 – 1.5 % GKM-S; 6 – 1.5 % GKM-S + 10 % GC-M.

Table 6. The influence of modifiers on the capillary suction of water in the concrete.

Additive	Capillary suction of water, mass. %, after time, hrs.						
	1	3	6	12	24	36	48
Without additive	1,65	2,86	3,37	4,2	4,8	5,2	6,2
0,8% C-3	1,20	2,15	2,95	3,72	4,13	4,74	5,30
0,2% GPD	0,82	1,83	2,31	3,00	3,62	4,15	4,60
1,5% KMF-SA	0,62	1,24	1,82	2,41	2,64	3,20	3,50
1,5% GKM-S	0,50	0,98	1,32	2,08	2,10	2,15	2,20
1,5% GKM-S + 10 % GC-M	0,25	0,75	0,96	1,20	1,43	1,68	1,95

Water resistance of concrete is also significantly improved by the application of water-repellent additives (Figure 3). A considerable resistance to the water penetration has the concrete laced with GKM-S plus GC-M: the water resistance is increased by nearly 3 steps compared to the concrete without a modifier.

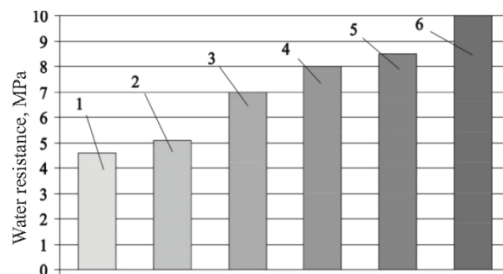


Figure 3. Water resistance of concrete.

4. Conclusion

Thus, the developed GKM type modifiers and waterproof organic-and-mineral carriers can be recommended for a wide use in the technology of hydro-engineering concrete and reinforced concrete products for special purposes (roads, foundations, drainage structures).

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