Composite grouting mortar based on 3D-NKM - nanocrystalline inoculant

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Abstract. For the waterproofing of tunnels and the uniform distribution of space between the lining of tunnels and rock, composite injection solutions are used. To improve the physical and mechanical properties of cement composites, the nanoconstruction effect is used, which is possible when using nanoparticles with extended geometry. Nano-additives and nanomodifiers consisting of nanoparticles, both natural and artificial and technogenic, can be used for the production of cement-containing solutions and concretes. For example, under certain conditions nanocrystalline powder of oxides and hydroxides of aluminum to nanotechnogenic raw materials can be referred to wastes of technogenic origin. The paper investigated the effect of nano-additives-boehmite, which is a waste of production, to increase the strength and frost resistance of plugging materials made on the basis of cement when administered. It is established that the use of boehmite as an additive in cements leads to an increase in the strength properties of concrete and increase its frost resistance, which is a prerequisite for long-term and reliable operation of the composite solution. Thus, the composite solution modified by boehmite is the basis for the creation of plugging solutions

1 Introduction

Concrete is the most popular building material of the 21st century. Environmental protection and modern environmental requirements require the development of new types of concrete with a given set of properties. In the Strategy of Innovative Development of the Russian Federation, nanotechnologies and composite materials are considered as the main directions.

For the waterproofing of tunnels and the uniform distribution of space between the lining of tunnels and rock, composite injection solutions are used. Due to the growth of scope of grouting work in the northern regions, specific problems related to the strengthening of soils in permafrost have become urgent. Conventional injection solutions

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are of little use, since in permafrost they do not adhere well and have a reduced rate of hydration, even with the introduction of accelerating agents such as calcium chloride.

In order to full realization the potential of cement, traditionally to control the formation of the structure and properties of cement stone, nanoadditives are used, which use by-products of industry, which is economically justified and contributes to the improvement of the ecological situation. At the same time, the performance characteristics of the resulting materials are improved, such as the strength, crack resistance and durability, meaning the maintenance of the required performance properties during the normalized service life, under the influence of the environment.

Since the mechanical strength of injected grouting mortars can change under conditions of temperature change during freezing, in conditions of permafrost it is necessary to control the change in strength properties of composite solutions from porosity, pore type and frost resistance, which is a characteristic of the durability of the material. The structure of porous space of cement stone, determining its frost resistance, depends on the water-cement ratio, the degree of hydration of cement, the conditions of hardening and the fineness of cement grinding.

Of great importance is the protection of building materials and structures from destruction, which ensures the extension of their service life. It is known that the introduction of nanotubes into mortars provides high strength, watertightness, crack resistance and durability of the construction. To improve the physical and mechanical properties of cement composites, the nanoconstruction effect is used, which is possible with the use of nanoparticles with elongated geometry [1-4].

The increase in frost resistance and strength characteristics of cement concretes and solutions modified by carbon nanoparticles is caused by the compaction of their structure, which is noted in the works of domestic and foreign scientists A.N. Ponomareva, V.R. Falikman, V.A. Perfilova, T.A. Nizina, G.I. Yakovleva, I.A. Pudova, A.F. Khuzina, A.V. Yeletsky, M.S. Dresselhaus, T. Kazuyoshi, M.F. Yu, G.Y. Li, De Ibarra, X.J. Xiang, J.M. Makar et al. [5-9]. It is the formation of a larger number of crystalline hydrate neoplasms of increased density and strength and causes a densification of the structure of the cement stone[10-11].

2 Methods

Fullerenes, astralenes and carbon nanotubes are most often used as carbon nanoparticles for modifying cement matrices [12].

The polyhedral structure of astralene particles consists of 20-50 flat graphene sheets of average size ~ 15 nm, connected by edge defect areas, predominantly of a pentagonal structure. Around astralenes there is a starlike "growth" of the cement stone, with further penetration into the thickness of the fillers by an additional nano-polar bond.

Carbon nanotubes (CNTs) - graphene planes folded into tubes [13,14], can be single-layer (with diameter $d = 1-1.5$ nm) or multilayered, with a separation between layers of 3.4 nm. The introduction of CNTs makes it possible to increase the strength of the cement composite, to reduce the formation of cracks in the early periods of hardening, to improve the quality of the interface between the phases of the matrix filler [1, 15].

The limited introduction of carbon nanoparticles is connected to their propensity for agglomeration and uneven distribution of the volume of the composite cement mixture [16-18]. This requires the use of special technologies.

For the production of cement-containing solutions and concretes, nanoadditives and nanomodifiers consisting of nanoparticles, both natural and artificial and technogenic, can be used. Some kinds of industrial waste can be referred to nanotechnogenic raw materials under certain conditions [19], for example, a nanocrystalline powder of aluminum oxides

and hydroxides. Such a waste is formed with the technology of hydrogen production by burning aluminum and is pure nanocrystalline oxides and aluminum hydroxides, with developed surface structure, and obtaining particles up to ten microns in size.

The aim of the work was to study the increase in strength and frost resistance of grouting mortars made on the basis of cement with the introduction of additive - boehmite, which is a waste of production. During the experiment, M500 cement, modified with bentonite of grade P2T2A, nanocrystalline powder - boehmite, and liquid glass of the brand "TEX" (GOST 13078-81), with water-cement ratio in the composite system of 2:1.

Bemit-orthorhombic crystal structure with elementary cells: $a = 2.87$, $b = 12.23$, $c = 3.70 \text{ \AA}$ (Figure 1).

Fig. 1. The structure of boehmite a-OH; b-hydrogen bond.

In it, aluminum ions are surrounded by six oxygen ions, located at the vertices of irregular octahedra. Oxygen ions are bound by the ribs, located at the vertices of irregular octahedra. Oxygen ions are bound by the ribs, with the exception of one of the axes, where they join into double layers with hydrogen bonds, which form zigzag chains. On the one hand, the oxygen anion adjacent to the hydrogen cation is linked to the aluminum cation. On the other hand, the bond is carried out with three hydrogen cations, which leads to a saturation of the valence of the O^{2-} ion, which is also fully saturated in the double layer by the valence of the four Al^{3+} cations surrounding it. Therefore, the boehmite structure corresponds to the formula $AlOOH$. The particle size distribution is shown in Figure 2.

Fig. 2. Distribution of boehmite particles by size.

3 Results

X-ray method revealed the size of crystals: 30-60 nm, with the primary aggregate size of primary particles - 1-3 μm, which gives nanosized particles. Therefore, when boehmite is added to the composite system, a dense packing of the cement stone takes place due to the filling of voids. Based on the morphostructural features of the structure of nanoscale particles, boehmite refers to the 3D nanocrystalline type of substances (3D-NCM - nanocrystalline modifier). Based on the x-ray phase analysis (BPA) of boehmite, it was suggested that this modifier has a developed phase interface, and therefore introducing it into the binder will have a significant effect on hydration (Table 1).

Table 1. Physico-chemical indicators of boehmite.

№ п/п	Description	Value
1	2	3
1	Appearance	Fine powder of white color
2	Structure of the crystal	Bemit
3	The size of the crystallites, nm, (FullProf) Particle size, nm, (FEC)	10 140
4	Mass fraction of impurities (in terms of on calcined substance),%, not more than: silicon dioxide (SiO ₂), iron oxide (Fe ₂ O ₃), sodium oxide (Na ₂ O)	0,05 0,05 0,05
5	Mass fraction of water,%, not more than	1,5
6	Specific true density, g / cm ³ , not more than	3,06
7	Bulk density, kg / m ³ , not more than	600
8	Porosity (BET method) - no more than,%	30
9	Loss of mass upon calcination (at temperatures up to 1100 ° C),% no more	17
10	Active specific surface area (BET method), m ² / g	55,9
11	Disperse composition by fractions,%: 1 ÷ 5 μm 5 ÷ 10 μm 10 ÷ 20 μm > 20 μm	55 35 10 0

The main component of the injection solution is cement. The integral and differential particle size distribution and the granulometric composition of M500 cement are presented in Table 2 and in Figure 3.

Table 2. Granulometric composition of cement.

Sample	Maximum particle size d95, μm	Average particle size d50, μm	Particle less than 2 μm,% by mass
Cement M 500	56,828	15,061	12,95

Interpolation Values... C:\Program Files\q22 32\ritsch\HMMNT 1.FPS											
0.000-	0.500μm=	0.00%	0.500-	0.500μm=	2.41%	0.500-	1.000μm=	3.62%			
1.000-	2.000μm=	7.02%	2.000-	3.000μm=	5.54%	3.000-	4.000μm=	4.57%			
4.000-	5.000μm=	3.87%	5.000-	10.000μm=	13.77%	10.000-	20.000μm=	19.22%			
20.000-	30.000μm=	15.41%	30.000-	40.000μm=	10.93%	40.000-	50.000μm=	6.79%			
50.000-	60.000μm=	3.89%	60.000-	70.000μm=	2.21%	70.000-	80.000μm=	1.20%			
80.000-	90.000μm=	0.58%	90.000-	100.000μm=	0.08%	100.000-	120.000μm=	0.00%			
120.000-	150.000μm=	0.00%	150.000-	200.000μm=	0.00%						

Interpolation Values... C:\Program Files\q22 32\ritsch\10_90.FPV											
5.0 % <=	1.010 μm	10.0 % <=	1.899 μm	15.0 % <=	2.522 μm						
20.0 % <=	3.528 μm	25.0 % <=	4.752 μm	30.0 % <=	6.234 μm						
35.0 % <=	8.036 μm	40.0 % <=	10.140 μm	45.0 % <=	12.504 μm						
50.0 % <=	15.061 μm	55.0 % <=	17.781 μm	60.0 % <=	20.630 μm						
65.0 % <=	23.841 μm	70.0 % <=	26.909 μm	75.0 % <=	30.529 μm						
80.0 % <=	34.694 μm	85.0 % <=	39.728 μm	90.0 % <=	46.348 μm						
95.0 % <=	56.828 μm	99.0 % <=	76.813 μm	100.0 % <=	99.534 μm

Fig. 3. Integral and differential particle size distribution in a sample of M500 cement.

According to the results obtained, the recycled cement M500 with a specific surface area of 450 cm²/g has a predominant particle size of 1 to 90 μm. About 88% of the particles have a size of less than 57 μm, and the rest - less than 2 μm. Bentonite P₂T2A contains montmorillonite - 75-80%, quartz - 15-17%, kaolinite - 1-2%, and mica-muscovite-type hydromica - 1-2%. The integral and differential particle size distribution and granulometric composition of bentonite are presented in Table 3 and in Figure 4. The granulometric composition of bentonites is presented in Table 3.

Table 3. Granulometric composition of bentonite.

Sample	Maximum particle size d 95, μm	Average particle size d 50, μm	Particle less than 2 μm,% by mass
Bentonite P ₂ T2A	12,270	2,969	34,23

Interpolation Values... C:\Program Files\22 32\ritsch\HMNT 1.FPS											
0.000-	0.300µm=	0.00%	0.300-	0.500µm=	2.86%	0.500-	1.000µm=	9.00%			
1.000-	2.000µm=	22.38%	2.000-	3.000µm=	17.21%	3.000-	4.000µm=	12.30%			
4.000-	5.000µm=	8.81%	5.000-	10.000µm=	20.00%	10.000-	20.000µm=	7.73%			
20.000-	30.000µm=	0.72%	30.000-	40.000µm=	0.00%	40.000-	50.000µm=	0.00%			
50.000-	60.000µm=	0.00%	60.000-	70.000µm=	0.00%	70.000-	80.000µm=	0.00%			
80.000-	90.000µm=	0.00%	90.000-	100.000µm=	0.00%	100.000-	120.000µm=	0.00%			
120.000-	150.000µm=	0.00%	150.000-	200.000µm=	0.00%						

Interpolation Values... C:\Program Files\22 32\ritsch\W0_90.FPV											
5.0 %	<=	0.713 µm	10.0 %	<=	0.962 µm	15.0 %	<=	1.181 µm			
20.0 %	<=	1.396 µm	25.0 %	<=	1.614 µm	30.0 %	<=	1.843 µm			
35.0 %	<=	2.088 µm	40.0 %	<=	2.354 µm	45.0 %	<=	2.645 µm			
50.0 %	<=	2.969 µm	55.0 %	<=	3.334 µm	60.0 %	<=	3.751 µm			
65.0 %	<=	4.236 µm	70.0 %	<=	4.808 µm	75.0 %	<=	5.500 µm			
80.0 %	<=	6.383 µm	85.0 %	<=	7.558 µm	90.0 %	<=	9.278 µm			
95.0 %	<=	12.270 µm	99.0 %	<=	18.789 µm	100.0 %	<=	26.312 µm

Fig. 4. Integral and differential particle size distribution in bentonite.

It has been found that bentonite has a specific surface area of 290 cm²/g and a predominant particle size in the range of 1 to 10 µm. Moreover, 66% of the powder particles have a particle size of less than 12 µm, and only 34% of the particles are less than 2 µm. To reduce the time of setting, liquid glass (GOST13078-81) - universal, brand TEX - was introduced. In the composite system the water-cement ratio was 2:1. To prepare the composite solution, the mixture was first made by dry mixing of cement, bentonite with boehmite additives, then water was added and, mixing at 600 rpm, and 5% water glass to the weight of the mixture.

In previous studies it was established that after 28 days of storage the maximum rate of the process of structure formation is achieved when the optimal concentration of boehmite is 0.208% to the mass of cement (Figure 5). Compared to the control sample, the rate of structure formation increases almost 1.2 times.

Fig. 5. Structurization of a composite solution with an optimal adding of boehmite.

4 Discussion

For the frost resistance test, samples were prepared: cubes 70x70 mm, made from a composite composition containing boehmite (W6 on the composition selection chart), and stored for up to 28 days in a normal hardening chamber (6 samples). The frost resistance of the samples was determined by repeated freezing and thawing (in accordance with GOST 10060-2012 and GOST 5802-86), accelerated by the method of 5% NaCl solution at minus temperature ($25 \pm 50^{\circ}\text{C}$). Tests of strength samples were carried out in accordance with GOST 10180-2012 on the press IP-1A-1000 (certificate of verification No.AA 2217924 until 09.07.2016). A sample saturated with NaCl solution was placed in a dilatometer and held for 30 minutes, then placed in a freezer and frozen at a temperature drop of minus ($25 \pm 5^{\circ}\text{C}$) at a rate of $0.3^{\circ}\text{C}/\text{min}$. Frost resistance of the brand of the mixture was determined by (in accordance with GOST 10060.3-95). On the basis of the graph of the dependence of the maximum relative difference between the volume deformations of the cured composite solution and the standard sample on the freezing temperature, (Table 4).

Table 4. Effect of boehmite additive in the composite mixture on frost resistance.

Characteristics of the sample	Freezing, cycles	Compressive strength, MPa		Loss of strength,%	Mass loss,%	Frost resistance, F
		experience	control			
Bemit (0.208% of cement mass)	20	3,17	3,20	1,0	0,4	100
Without additives	20	1,35	1,38	1,0	0,5	50

To determine frost resistance, the method of alternating freezing and thawing of samples is applied. The criterion for frost resistance of cement stone is the number of cycles when the loss of mass of the sample is less than 5%, and the reduction in strength should not be more than 25% of the original value.

The loss of strength of the composite solution with the addition of boehmite does not exceed 1%, and the mass loss through 100 cycles of freezing and thawing is 0.4. Frost resistance of the modified composite solution corresponds to the brand F100. This proves that the addition of nanoadditives to cement leads to more intensive hydration of cement, increasing the density of cement stone [20-21].

5 Conclusion

1. Experimental studies have established that the use of boehmite as an additive in cements leads to an increase in the strength properties of concrete.
2. As a result of the experiments carried out, it was noted that the frost resistance of concrete based on the proposed composite portland cement with the addition of boehmite is higher than for the control composition, which is a prerequisite for a long and reliable operation of the composite solution
3. Frost resistance of concrete is enhanced by modifying the cement stone with a new boehmite additive. This allows you to influence the formation of the structure and phase composition of the cement stone. Thus, the composite solution modified by boehmite is the basis for the creation of oil wells.

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