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Modifying the Structures of Composite Grouts with Aluminosilicate Nanotubes

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Abstract

When building a subway, composite grouts are used more often due to their ability to strengthen cement grouts.Attempts are being made to add carbon nanostructures into cement compositions, with a view to improving the physical and mechanical properties of the cement grout and concrete based thereon. Various studies have considered improving the strength and cold resistance of composite grouts by modifying cement stone with aluminosilicate nanotubes.The studies found that the addition of aluminosilicate nanotubes in an amount of 0.125% of cement mass produces a composite material with increased strength. Thus, the analysis of studies shows that the addition of small concentrations of nanotubes changes the kinetics of structure formation and facilitate an increase in strength and density of the composite grout, which allows using it in more difficult operating conditions of transport constructions.

Keywords: Composite material; Aluminosilicate nanotubes;Bentonite; Liquid glass;Cement stone modification

INTRODUCTION

When building a subway, composite grouts are injected to protect it from subsidence under buildings that are located near the lines and consolidate the ground during tunneling.

Compounds that are added in such a way increase the strength of the soil and reduce its compressibility, water permeability, and high humidity sensitivity (1-3).

The disadvantages of this technique include the insufficient strength of consolidated soil masses and the environmental friendliness of the compositions of the injected compounds.

A promising approach in construction material studies is the controlled structure formation of composites, which is initiated by adding very low amounts of ultra-small carbon nano-modifiers(4-6). Attempts are being made to add carbon nanostructures into cement compositions, with a view to improving the physical and mechanical properties of the cement grout and concrete based thereon (7, 8).

The vast potential of nanotubes used in cement-based materials has been shown by various researchers, who found that nanotubes increase the strength of the cement matrix. At that, carbon nanotubes work as a “nano-reinforcement” due to their high tension strength (9).

Some studies investigated nano-modification and its effect on the physical and chemical properties of mixing water, the structure formation during the hydration of cement stone compounds, and the development of the final strength of composite systems (10, 11).

For instance, adding 0.08% of multilayer carbon nanotubes to the cement grout increases its bending strength and reduces porosity, while simultaneously homogenizing the distribution and size of pores. The microstructure of modified samples shows that multilayer carbon nanotubes ensured an even distribution of the load in case the composite had cracks and cavities (12).

The possibility of using 20-100 nm fulleroid materials as modifiers was presented in study (13).

The modification of the structure of new-generation construction composites with nano-elements increases the volume of pores with a minimum radius (14).

For instance, the addition of 0.0005-0.001% of the carbon material taunite (fullerene-like tubulate bonds and beams of carbon nanostructured material) into a concrete mixture forms, by regulating crystallization processes, a three-dimensional network that covers the entire volume of the cement stone (15, 16).

The production of high-strength fine-grain concrete based on cementing materials with low water demand uses fine powders of silicon dioxide Taroxyl-05 and Taroxyl-20, the average particle size of which is 2053 nm, while the specific surface is 50.6-139 m^2/g, which increases strength by 30-45% and 50-60%, respectively (17).

In order to modify foam concrete, it is possible to use nanotubes based on $Al(OH)_3$, AlOOH and Al_2O_3, which are pure nanocrystal aluminum oxides and hydroxides with a well-developed surface structure (boehmite and corundum). Such form concrete has a stable porous structure and increased mechanical strength.

Boehmite hydrosols were used as an additive when preparing non-autoclaved aerated foam concrete during construction(18, 19). Obtained results showed a 20-25% gain in strength when boehmite was added to the grout (20-22).

The analysis of literature showed that nano-additives were capable of compensating, to a considerable extent, for the flaws in cement composites, which confirms the need to develop technologies of modified composite grouts capable of forming cement stone with perfect technological properties and improved operating properties.

In recent years, aluminosilicate tubes manufactured by Nanotechnologies and Innovations JSC have come into use. These tubes are based on aluminum and silicon.

Based on the analysis of information found in literary sources regarding the modification of cement systems, the purpose of this study was set as follows – to improve the strength and cold resistance of the composite grout (or cement slurry) by modifying the cement stone with nano-additives.

The objectives of the study were as follows: to rationalize the possibility of increasing the cold resistance of the composite grout via modification of the cement stone with nano-additives; to determine the dependency between the strength properties of the composite grout and the concentration of modifying additives.

This study used high-performance catalytic aluminosilicate nanotubes with a general formula $Al_2[Si_2O_5](OH)_4 \times nH_2O$, where n=0÷2 (Figure 1, Table 1), P2T2A bentonite containing, in wt%, 75-80 montmorillonite, 15-17 quartz, 1-2 kaolinite, and 1-2 hydrous muscovite mica.

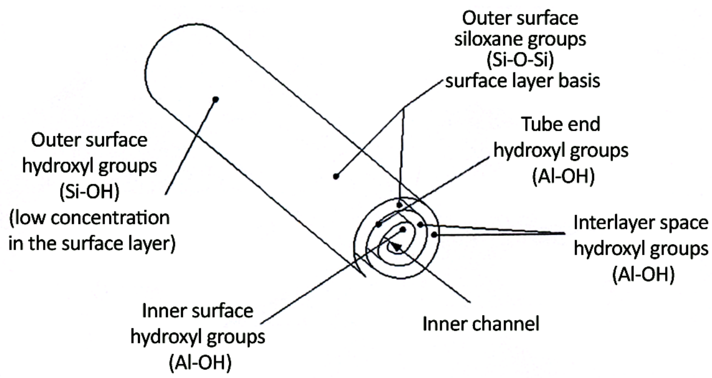

Figure 1. Aluminosilicate nanotube structure

Table 1: Tube specifications

Characteristic	Parameters
Bulk density	0.624 g/cm^3 – 624 kg/m^3
Specific weight	2.55
Specific surface area	20 m^2/g
Nanotube size	
- outside diameter	50-120 nm
- length	0.5 – 2.0 µm
X-ray phase analysis	
Halloysite at least	77%
Quartz and	less than 13.4 %
Cristobalite less than 25%	less than 25 %
Unidentified impurities (other) less than	2%
aqueous suspension pH	3.5 - 4.5
Moisture content less than	4 %

Since the composition of aluminosilicate nanotubes is mostly aluminum and silicon, which are also found in cement and bentonite, one can assume that they are capable of modifying the strength of composite grouts significantly.

MATERIALS AND METHODS

The study used M500 Portland cement, P2T2A bentonite, and TEKS universal liquid glass (GOST 13078-81).

The effect of the addition of aluminosilicate nanotubes on the changes in the structure formation of composite grouts during storage was studied at aluminosilicate nanotube concentrations in cement mass ranging from 0.000% (sample zero) to 1%.

The effect of aluminosilicate nanotubes on changes in the strength characteristics of composite grouts during storage was studied at a 2:1 water to cement ratio.

In order to produce the composite grout, we prepared a 5% bentonite suspension with added aluminosilicate nanotubes, added water, and stirred at 600 rpm for 15 minutes. Cement and liquid glass in an amount of 5% of the mixture weight was added.

The strength of modified composite grouts was measured using a Controls 50-C0050/CAL50 hydraulic press after 7, 14, and 28 days of cementing (%)(Table 2).

Table 2: Structure formation of a composite grout based on P2T2A bentonite with added aluminosilicate nanotubes (ANT) during storage

No.	ANT, % of cement mass	Density, P, MPa			
		Hardening time, days			
		7	14	21	28
1	0.000	0.92	1.23	1.27	1.38
2	0.300	1.12	1.87	2.29	2.55
3	0.150	1.65	2.23	2.45	2.63
4	0.080	0.84	1.35	1.55	1.91
5	0.400	0.96	1.23	1.45	1.61
6	0.250	0.98	1.54	1.67	1.78
7	0.450	0.95	1.37	1.7	1.97
8	0.100	1.95	2.45	2.75	2.95
9	0.125	2.15	2.67	2.95	3.2
10	0.075	0.88	1.53	1.86	2.21
11	0.006	1.13	1.46	1.61	1.7

The data presented in Table 2 were used to draw a diagram of changes in the strength of composite grouts depending on the hardening time (Figure 2).

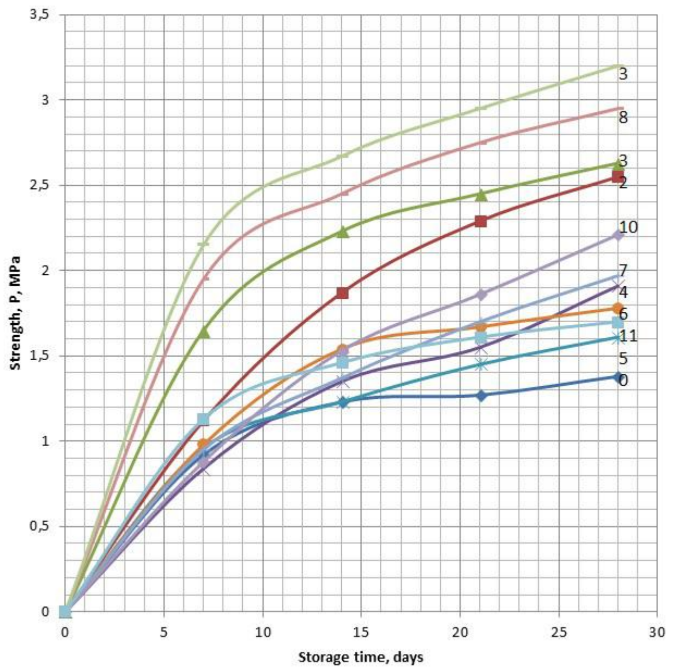

Figure 2: Composite grout strength, depending on storage time with different concentrations of ANT in the cement mass, %

1-0.000; 2 – 0.300; 3 – 0.150; 4 – 0.080; 5 – 0.400; 6 – 0.250; 7 – 0.450; 8 – 0.100; 9 – 0.125; 10 – 0.075;11 – 0.006.

RESULTS AND DISCUSSION

The analysis of Table 2 and Figure 2 shows that the addition of aluminosilicate nanotubes increases the strength and changes the nature of structure formation. It was discovered that adding aluminosilicate nanotubes in an amount of 0.125% of the cement mass significantly increased strength versus the control sample, while also intensifying structure formation. For instance, the strength reached 70% of its final level after the first seven days and 90% after 14 days.

An important stage in the creation of the final strength of a composite grout is the formation of the structure of the modified system during the initial stage of setting, since the crystallization compound of cement stone forms out of the coagulation structure during this period.

The rate of structure formation of the composite grout during the initial stage was measured based on the slope ratio (130). This was followed by the drawing of a diagram of changes in the rate of structure formation depending on the concentration of aluminosilicate nanotubes in the cement mass (Figure 3).

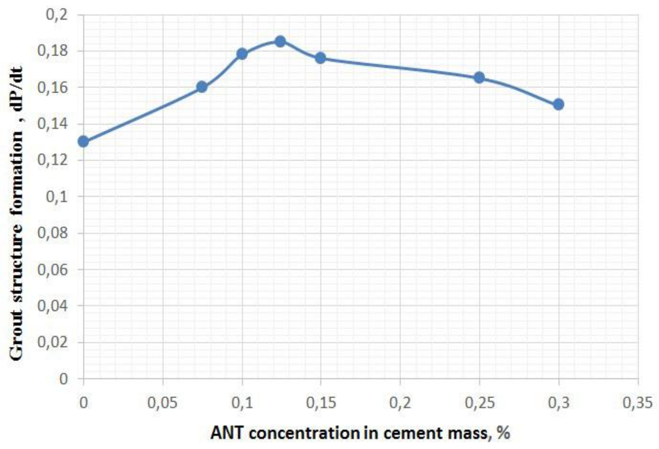

Figure 3: Structure formation kinetics, depending on nanotube concentration

Figure 3 shows that with the increase in aluminosilicate nanotube concentration in the composite grout, the structure formation rate increased at first and then, when the concentration of aluminosilicate nanotubes reached 0.125% of the cement mass, it started to drop gradually. The rate of structure formation at 0.125% aluminosilicate nanotube concentration increased by almost 1.5 times versus the control sample. This effect may be caused by the interaction between nanotubes and clinker minerals in the area where these components come into contact. The optimal concentration of nanotubes obviously ensures a dense packing of the cement stone, which increases the strength of the composite system.

Nowadays, new achievements in the technologies of composite materials require manufacturers to learn to immaculately design composites with preset properties, including cold resistance.

The durability and cold resistance of cement composites largely depends on the porous structure of the cement stone, which drops with the cement hydration temperature. In sub-zero temperatures, water that enters the pores of the material freezes and generates tension stress in the structure of the material due to volume gain.

Compounds with identical fluidity were produced to test the cement composites for cold resistance. Six samples were made: 70x70 mm cubes made out of a composite compound that contained aluminosilicate nanotubes. The samples were stored for 28 days in a moisture chamber. Tests were conducted with multiple freezing and thawing (a total of 20 cycles) using the accelerated method in a 5% NaCl solution at a temperature of -25±5°C. Strength was measured using an IP-1A-1000 press. It was found that the cement composites had 1% strength loss, which corresponded to the F100 cold resistance class.

The presence of aluminosilicate nanotubes in the composite grout intensified the hydration of cement and formed a stronger and denser structure, which provided for increased indices of grade strength and cold resistance, thus increasing the life of the composite grout and the durability of constructions.

The processes of structure formation of the composite grout were studied using the ultrasound method. In building, it is necessary to check the quality of constructions, since the solid mass may still contain air bubbles, a low-quality grout may have been used or the structure may change during operation due to freezing. Even with high-quality preparation of the grout on the surface, the construction may hide flaws that can cause the entire structure to collapse. Therefore, special techniques are used to monitor its structure and composition.

The most practical ones are nondestructive methods that yield maximum information. The most effective one of them is the ultrasound method, which is based on the measurement of ultrasound wave velocity when they pass through the composite grout and its subsequent comparison to the control sample.

An important feature of this method is the sensitivity of the ultrasound vibration velocity in the material during all stages of its hardening and with various contacts, both coagulation and crystallization.

The ultrasound vibration velocity depending on the concentration of aluminosilicate nanotube concentration was measured using a PULSAR 1.1 ultrasound concrete strength-measuring device.

Table 3. Ultrasound vibration velocity depending on ANT concentration

Concentration of ANT in the cement mass, %	0.000	0.100	0.125	0.150	0.300	0.400	0.450	0.600
Ultrasound vibration velocity, V, m/s	1379	1597	1680	1659	1387	1295	1265	1207

The data presented in Table 3 were used to draw a diagram of dependency of ultrasound vibration velocity on aluminosilicate nanotube concentration (percentage) in the cement mass (Figure 4).

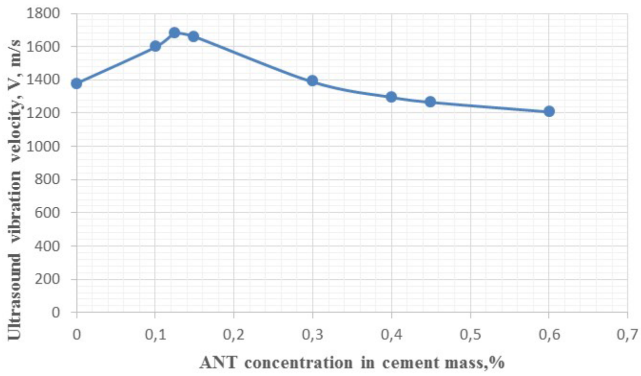

Figure 4. Dependency of ultrasound vibration velocity on ANT concentration in the cement mass, %

It was found that the increase in the aluminosilicate nanotube concentration increased strength at first and then decreased it. The strength of the system increased with the addition of aluminosilicate nanotubes in an amount of 0.125% of the cement mass and the ultrasound vibration velocity increased by 1.22 times versus the control sample, which was indicative of the consolidation of the material structure and the creation of additional contacts between particles, which meant that cavities were being filled. Obtained results are in line with the data on the measurement of the composite grout strength.

We have found that the addition of ANT to the stone-sand-cement mixtures makes it possible to regulate their physical mechanical properties by changing the percentage of the additive. This feature makes it possible to set the required quality of strength.

CONCLUSIONS

The analysis of studies shows that the addition of small concentrations of nanotubes changes the kinetics of structure formation and increases the strength of the composite grout due to nanoparticles entering small pores of the cement stone. Such material is quite dense. This affects its longevity. Its density has been checked by ultrasonic methods that has showed a high result.

This grout will help to improve the reliability of structures and significantly reduce the risk of destruction in building subways.

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