Comparative analysis of strength characteristics of grouting mortars

Marina Panfilova¹, Nikolay Zubrev², Olga Novoselova¹ and Saniya Efremova³

¹ Moscow State University of Civil Engineering, Yaroslavskoe shosse, 26, Moscow, 129337, Russia
² Federal State Budget Educational Institution higher education "Russian University of Transport", Obraztsova, 9, Moscow, 127994, Russia
³ Penza State Technological University, PenzSTU, travel Baidukova , st. Gagarin, 1a/11, Penza, 44003, Russia

E-mail: 012340@mail.ru

Abstract. The practice of building in difficult geological and hydrogeological conditions found wide use grout mixes used to fill old mine workings or large underground cavities. However, the traditional oil well cementing cementing solutions causes a large flow rate of the solution in the absorbing horizons and its erosion under the influence of the tributaries of the water. A problem arises, which is associated with insufficient provision of guaranteed strength and durability fixed soil or structures, as well as in environmental and health safety used injectable compositions. A promising direction in the construction material science is the approach to the directed structure formation of composites that are initiated by the introduction of nanomodifiers, having ultra-small dimensions in super small quantities.

The aim of this work is to develop new cement compositions with improved processing characteristics, based on the comparison of the effect of additives aluminosilicate nanotubes (ANT) and boehmite on the structure formation of cement composites. The main components of the composite solution were: bentonite П2Т2А, ANT, bemit, cement and liquid glass.

Performed x-ray phase analysis of boehmite and ANT. Studied the structure formation of composite systems. It is established that the highest rate of structure formation is achieved at a concentration of boehmite 0.208% by weight of cement. Relative to the control sample, the rate of structure formation increases 1.3 times. With the introduction of additives ANT the greatest strength of the composite solutions was achieved with the introduction of 0.125% by weight of cement. It was found that cement compositions based on ANT after 28 days of storage the strength of the compositions is increased almost 2 times compared to the composite solution with additives boehmite. It is established that a promising direction for obtaining of composite systems is the modification due to the introduction of environmentally friendly aluminosilicate nanotubes based on natural mineral.

1. Introduction

In practice of building constructions in the composite geological and hydrogeological conditions broad application was found by the grouting mortars that are applied for the purpose of filling the aged excavations or large underground cavities arising because of filtration of underground water. At elimination of karst processes it is necessary to try to obtain the maximal simulated filling of
emptiness for the purpose of fixing the massif of the karstic rocks and the termination underground water's filtration. Filtration of underground waters can be achieved by squeezing of liquid silica glass, cement clay mud or bitumen into the cracks and emptiness as traditionally used mixes used for elimination of underground emptiness have slight durability. Therefore as grouting mortar use mixes with existence of the reinforcing element.

There are lot of different options of compoundings of grouting mortars that are presented in the works of Karimov, Ovchinnikov, Ryabokon, Frolov and others. However, particular mining-and-geological conditions, the purposes and methods of the carried-out injections demand further creation of options of grouting mortars. Especially it concerns the facilitated cements for cementation of wells in order to prevent the emergence of the significant forces of hydrodynamic pressure in underground waters leading to emergence of the karst phenomena [1].

Such a grouting mortars should have the under density and the corresponding modes of breakdown [2].

In the long term providing a structural complex with modern, competitive and innovative structural materials, considering up-to-date economic and ecological requirements, will be the primal problem of industry of structural materials according to "The forecast of long-term social and economic development of the Russian Federation until 2030 (developed by the Ministry of Economic Development of the Russian Federation)".

As such compositions grouting mortars with inclusion of nanotubes can be used (microscopic hollow tubes from several atomic layers of carbon polymers) [3-6].

2. Materials and methods
As is well-known, many perspective directions in construction connect with carbon nanotubes, but on an equal basis with CNTs they begin to use reinforcing nanoaluminosilicates - silica-alumina nanotubes (ANT). Such a material is received from natural mineral – the halloysite that consists of hydroaluminum silicate with the common formula $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4 \times n\text{H}_2\text{O}$, where $n = 0 - 2$. It is known that natural clay has multistratified structure, while halloysite represents the clay layers twirled in nanotubes on 95% [7].

Silica-alumina nanotubes represent a hollow tube with a caliber of 15 nanometers and external diameter about 50 nanometers. The wall twisted in a spiral consists of simple atomic layers of aluminosilicate and its thickness can be 20–30 layers. Besides, it is necessary to allocate especially that ANT relates to natural materials that are cheaper than CNTs but the biocompatibility of ANT is confirmed by numerous of experiments with alive simplest organisms.

Various chemical properties of ANT surfaces are explained by singular structure of aluminosilicates: nanoplates are twisted in such a way that on an internal surface of nanotubes there is an adamant attracting to itself negatively charged particles and on external – the silicon oxide having positive charge (Fig. 1).

![Figure 1. The structure of ANT](image-url)
Owing to existence of a cellular structure and high catalytic activity this material can be used as additives in composite (injection) solutions.

Except of silica-alumina tubes, recently it is used bemit as nanoadditives, which represents trimetric crystalline structure with the unit cells: \(a = 2.87\), \(b = 12.23\), \(c = 3.70\) Å (Fig. 2).

![Figure 2. The structure of bemit a - OH; b - hydrogen bridge](image)

In it ions of aluminum are surrounded with six ions of oxygen located on tops of the irregular octahedrons. The last are bound among themselves by edges except for one of axes where they connect in double layers to hydrogen bridges which form zigzag chains. On the one hand, the oxygen anion adjoining to cation of hydrogenium is bound to aluminum cation, and on the other hand, to three cations of hydrogenium. Thus the complete saturation of the valency of an ion \(\text{O}^2-\) is reached. The charge of anions of \(\text{O}^2-\) inside a double layer is also completely sated with the shares of valency of four \(\text{Al}^{3+}\) cations surrounding it. Thus, there are two types of ions of oxygen that corresponds to a formula \(\text{AlOOH}\) in the structure of bemit [8-14].

According to morfostructured classification of nanosystems, bemit is 3D-HKM – the nanocrystal modifier.

In this regard, the purpose of this work was development of new grouting compositions with the improved processing behavior with the given nanostructure. These studies were carried out on the basis of a comparison of the effect of additives of aluminosilicate nanotubes and boehmite (Table 1) on the structure formation of cement composites for 28 days.

| Principal specifications | Nanoadditives  | Bemit                  | ANT                  |
|-------------------------|----------------|------------------------|----------------------|
| 1 Outward               | Highly dispersive powder of white color | Hollow aluminosilicate tube |
| 2 The size in nanometers of crystal grains, | No more than 100 |                       |
The main components that were used when developing composite solutions: bentonite, M500 cement and liquid glass, as nanoadditives - ANT and bemit.

For improvement of grouting mortar's performance characteristics the bentonite of a brand P2T₂A is used as an additive [15].

On the basis of the roentgenogram of P2T₂A bentonite it is established that it consists of montmorillonite 75-80, quartz 15-17, kaolinite 1-2 and hydromica of muscovite type 1-2 (masses. %). Sodium fluid glass-silicate of sodium with a density of 1.46 g/cm³ and silica modul 2.7-3.4 also was used in work. Silicon dioxides 21-24; iron oxides and aluminas max. 0.25; calcium oxides max. 0.2; sulphuric anhydride max. 0.15; sodium oxides 7.9-8.8 are a part of a liquid silica glass, (masses. %) [16-18].

### 3. Results of the study

Composite systems were prepared in laboratory conditions. In the beginning the batter of ANT and the bemit (content of nanoadditives varied from 0 to 0.306% to the mass of cement) was carried out in reference mixers and bentonite and nanoadditives mixed up "dry". Then entered water for receiving 5% suspensions of bentonite. Cement, liquid glass and excipients were added into the prepared solution. Water and cement ratio 2:1. The exemplars had been prepared which were taken from forms in a day for determination of durability of grouting mortar. Before the test they were stored in the room with a temperature (20 ± 3)°C and the relative humidity (65 ± 10)%. Exemplars were taken from a form by a compression failure of cubes on a hydraulic press Controls 50-C0050/CAL50, defined compression strength in 1, 7, 14 and 28 days. Results of the pilot studies of influence of the bemit and ANT on durability of grouting mortar are given in Table 2.
Table 2. Strength of the composite solution with ANT and boehmite additives during storage

| №  | Nanodotubes | Nanoadditives, % to the mass of cement | Durability, $P$, MPa | The terms of concreting, days |
|----|-------------|--------------------------------------|---------------------|------------------------------|
|    |             |                                      |                     | 7                            |
| 1  | Control sample | 0.000                                     | 0.47                | 0.85                        |
| 2  | ANT         | 0.300                                    | 1.12                | 1.87                        |
| 3  |             | 0.150                                    | 1.65                | 2.23                        |
| 4  |             | 0.400                                    | 0.96                | 1.23                        |
| 5  |             | 0.450                                    | 0.95                | 1.37                        |
| 6  |             | 0.100                                    | 1.95                | 2.45                        |
| 7  |             | 0.125                                    | 2.15                | 2.67                        |
| 8  |             | 0.075                                    | 0.88                | 1.53                        |
| 9  | Bemit       | 0.600                                    | 1.13                | 1.46                        |
| 10 |             | 0.208                                    | 0.78                | 1.20                        |
| 11 |             | 0.133                                    | 0.75                | 1.15                        |
| 12 |             | 0.249                                    | 0.73                | 1.12                        |
| 13 |             | 0.100                                    | 0.70                | 1.10                        |
| 14 |             | 0.041                                    | 0.65                | 1.01                        |
| 15 |             | 0.306                                    | 0.60                | 0.99                        |
| 16 |             | 0.600                                    | 0.51                | 0.88                        |
| 17 |             | 0.700                                    | 0.43                | 0.77                        |
| 18 |             | 1.000                                    | 0.78                | 1.20                        |

From the analysis of tab. 2 it is established that strength indicators of composite solution increase because of structural change formed in a cement stone on a nanolevel. This is probably due to the introduction of nanoadditives, which gradually fill the voids between the grains of hydrating cement, acting as centers of crystallization, by colluding large pores. They form a more dense and homogeneous structure [19], leading to a more intensive growth of structure formation. On average, in the first 7 days the strength of the composite system is (in% of the final strength) with the introduction of ANT-78, after 14 days - 83; and for boehmite, respectively, 52 and 80 [20-23].

By results of a research (Table 2) the schedules of dependence of durability of composite solution on concentration of ANT (Fig. 3) and the bemit (Fig. 4) to the mass of cement were constructed and the schedule of dependence of durability of composite solutions on a shelf life are constructed at best values of concentration of ANT and the bemit to the mass of cement (Fig. 5).
Figure 3. Durability of Composite Solution from concentration of the bemit to the mass of cement, %

Figure 4. Durability of Composite Solution from concentration of ANT to the mass of cement, %

It is revealed that adding of ANT and the bemit in knitting with the corresponding concentration of 0.125% and 0.208% to the mass of cement cause essential increase in durability for the 28th days in comparison with a control specimen, (Fig. 3, Fig. 4).
From Fig. 5 it is visible that the largest durability of composite solution for the 28th days is reached by introduction of ANT with concentration of 0.125% to the mass of cement that more than by 2.5 times exceeds durability of a control specimen whereas for bemit - by 1.3 times, although the dynamics of the set of strength is almost the same. This effect is reached by thanks to interaction of ANT with brick minerals in a zone of particles' contact of these components. Moreover, ANT has the universal features, including a larger specific surface area in comparison with boehmite surface (Table 1), and also high porosity and tunable chemistry of a surface. At introduction of ANT there is a structuring a matrix of cement to formation of the dense faultless envelope on a surface of solid phases and as result - the improved coupling with the surface of filler. At the same time there is a self-tightening of cracks of a cement matrix due to inducing of the accelerated body height of new growths. At the same time framework cells are formed due to improvement of contact interaction of boundary layers, leading to modification of a cement matrix and emergence of space packing of a matrix, promoting increase in its strength properties.

4. Conclusions

1) It is established that at introduction of nanotubes there is an increase of durability of grouting compositions of rather control specimen
2) It has been shown experimentally that the optimal concentrations of additives (for cement mass,% for obtaining the maximum strength of the composite solution is - for ANT 0.125%, for boehmite – 0.208%.
3) It was found that the highest strength of the composite solution on day 28 is achieved when ANT is introduced at a concentration of 0.125% to the mass of cement, which is almost 2 times greater than the strength of the composite solution with boehmite additives.
4) It is defined that it is perhaps to influence targeted on processes of structurization of cement composites due to introduction of ecologically safe ANT on the basis of natural mineral and strengthening of power opportunities of each additive separately

The prospect of further development of the topic is research in the field of modification of slurry mortars with nano additives. One of the key problems of composite materials remains the study of the composition-structure-property relationship.
Acknowledgments
All tests were carried out using research equipment of The Head Regional Shared Research Facilities of the Moscow State University of Civil Engineering (RFMEFI59317X0006).

References
[1] Samsonenko N V The extending facilitated grouting cement: dis.... candidate of technical sciences: M., 2006. 157 p. (in Russia).
[2] Polyakov V N, Ishkayev R K, Lukmanov R R Technology of completion of oil and gas wells. Ufa: TAU, 1999. 408 p. (in Russia).
[3] Ponomarev A N Nanobeton-concepts and problems // Building materials. 2007. N 7. P. 2-4.(in Russia).
[4] Structural modification of neoplasms in a cement matrix by dispersions of carbon nanotubes and nanosilica / G I Yakovlev, I S Polyanskih, G N Pervushin et al. // Building materials. 2016. N 1/2. C. 16-20. (in Russia).
[5] Smilauer V, Hlavácek P, Padevet P Micromechanical analysis of cement paste with carbon nanotubes // Acta Polytechnica. 2012. V. 52. N 6. P. 22–28.
[6] Gesoglu M, Güneyisi E, Asaad D S Properties of low binder ultra-high performance cementitious composites: Comparison of nanosilica and microsilica // Construction and Building Materials. 2016. Vol. 102. N 1. P. 706–713.
[7] Halloysite Clay Nanotubes for Loading and Sustained Release of Functional Compounds / Y Lvov et al. // Adv. Mater. 2016. N 28. N 6. P. 1227–1250.
[8] Bukhalo A.B. Heat-insulating non-autoclaved aerated concrete with nanodisperse modifiers: Author's abstract. dis. ... cand. tech. sciences. Belgorod, 2010. 27 p. (in Russia).
[9] Chaly V P Hydroxides of metals. (Regularities of education, composition, structure and properties). Kiev: Naukova dumka, 1972. 160 p. (in Russia).
[10] Shelley D, Smale D, Tulloch A J Boehmite in syenite from NewZealand // Mineralogical Magazine . 1977. V. 41. P. 398–400.
[11] Nazarov V V, Pavlova-Verevkina O B Synthesis and the colloid chemical properties of hydrosols of the bemit // Colloid Journal.( Kolloidnyy zhurnal ). 1998. V. 60, No. 6. P. 797-807. (in Russia).
[12] Akselrod M S Optically stimulated luminescence of Al₂O₄ // Radiat. Meas. 1996. V. 29. P. 391–399.
[13] Sakka S Hand book of sol-gel science and technology processing characterization and applications. Boston: Kluwer academic publishers, 2005. 680 p.
[14] Jones R W Sol preparation of ceramic and glasses // Metal and Matireals. 1988. V. 4. N.12. P. 748-751.
[15] Panfilova M I, Zubrev N I, Fomina M V Foamed injection solutions in construction. Moscow: MGSU, 2015. 128 p. (in Russia).
[16] Brichka S Ya Natural aluminosilicate nanotubes: structure and properties / S Ya Brichka // Nanostructured Materials Science. 2009. N 2. P. 40-53. (in Russia).
[17] Radiographic analysis of galloidite nanotubes modified with cerium (IV) oxide [Text]: scientific publication / L Yu Kotel et al. // 2 All-Ukrainian Conference of Young Scientists "Modern Materials Science: Materials and Technologies". Kiev, 2011. P. 183. (in Russia).
[18] Burianov A F Effective gypsum materials and products using ultradisperse aluminosilicate additives and carbon nanomodifiers: the author's abstract. dis ... doc. those. sciences. Moscow, 2012. 38 p. (in Russia).
[19] Modification of cement concrete with complex additives based on polycarboxylate esters, carbon nanotubes and microsilica / E A Karpova, Mohamed Ali Elsaed, G Skripkjunas and others // Building materials. 2015. N 2. C. 40-48.
[20] Zhang X, Li Q, Holesinger T G Ultrastrong, stiff, and lightweight carbon-nanotube fibers // Advanced Materials (Stroitel'nuye materialy.) 2007. V. 19, N 23. P. 4198–4201. (in Russia).
[21] Strong luminescence of solubilized carbon nanotubes / J E Riggs, Z X Guo, D L Carroll et al. // Journal of American Chemical Society. 2000. V. 122. N 24. P. 5879–5880.

[22] Jong K D, Geus J W Carbon nanofibers: catalytic synthesis and applications // Catalysis Reviews: Science Engineering. 2000. V. 42. N 4. P. 481–510.

[23] Nanomodified cement-bentonite composites / M.I., Panfilova, N.I. Zubrev, D.A. Leonova et al. // XXI century: the results of the past and the problems of the present plus. (XXI vek: itogi proshlogo i problemy nastoyashchego plyus.) 2015. N 5 (27). P. 95-98. (in Russia).