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## Improving durability of cement composite materials

Sofia F. Korenkova<sup>a</sup>, Yulia V. Sidorenko<sup>a\*</sup>

<sup>a</sup> Samara State University of Architecture and Civil Engineering, 194 Molodogvardeyskaya st., Samara, 443001, Russia

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### Abstract

One of the problems of modern construction material science is to provide durable composite materials based on affordable and low-cost local raw materials (natural resources, industrial wastes, etc.). The application of two-component nano- and microdispersed fillers is approved which were actively involved in structure formation of hardened cement paste, adhesive strength, as well as a closed system of microvoids. Their polyfunctional effect on structure properties of cellular and heavy concrete, mortars, etc. was identified. Reorganization of the pore space by introducing two-component fillers leads not only to the strength increase, water and cold resistance, but to the durability of cement composite materials.

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### 1. Introduction

The analysis of Russian and foreign scientific papers on the impact of fine-dispersed mineral components, industrial waste of sludge on structure and properties of cement-containing and also silicate, composite and other kinds of materials shows that implementation of active mineral fillers as an independent component is one of the essential provisions of structure optimization, improvement of construction and technological properties and durability as a whole [1-11].

However, despite the rather large amount of data in this field, there is no consensus on how high dispersion mineral fillers effect on durability, structure and properties of cement or lime-silica stone. At present plasticizing,

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\* Corresponding author. Tel.: +7-846-242-37-02 .  
E-mail address: [sm-samgasa@mail.ru](mailto:sm-samgasa@mail.ru)

stabilizing and structuring modifiers, hardening regulators, additives that add special properties to concrete and mortar, as well as complex polyfunctional modifiers are widely used.

In this paper, we consider the issues of improving durability of materials made with chemically active fillers – sludge waste and two-component (binary) components

## 2. Methods

### 2.1. Sludge wastes

A group of inorganic fillers, used to control the sorption process in water binding mixtures, are industrial sludge wastes formed by the type of sol-gel technology, particularly sediments after water-purification, water treatment processes and water softening [2, 5, 8, 10-18]. The superatomic sludge structure research shows that particle sizes are at the average from 40 to 80 nm; specific features of sludge formation (in the form of wastewater sludge) can be attributed to nano-technogenic raw material [2, 5, 10-15].

The main ingredients allow us to classify sludges into mineral and organomineral. Depending on the scope of an industrial enterprise and sludge formation, there are carbonate, calcium aluminum, aluminum alkaline and polymineral sediments [2, 5]. The feature of sludges is a high degree of self-organization determined by uniformity coefficient, that is, the quality of solid particles packaging in the filled systems at the stage of materials structure formation. It is known that self-organization processes are related to the motion of particles and dependent on their diameter, density, ability to encounter and interact with other particles. Movable and nanoparticles of sludges transfer to a stable state by a non-equilibrium, which determines a high degree of randomness and the ability to self-organization. This fact determines their final high degree of uniformity. Such fillers are distinguished by excess energy, chemical interaction and the contact zone formation between binder (cement, lime, etc.) and filler with good adhesive strength. In particular, carbonate sludge is one of the most efficient nanoscale fillers for cement- containing materials, and it is actively involved in shaping the structure and properties of the contact zone in the manufacture of various types of concrete, dry mixtures, solutions, etc. [2, 5, 12].

### 2.2. Binary fillers

Estimating the effect of fine (nano- and micro-sized) particles on the structure and properties of cement paste, we note that they are additional crystallization centers, also, they increase the surface energy, which in turn favorably affects the strength characteristics as well as water and frost resistance of cement stone [13, 19, 20].

The two-component (binary) fillers combining tougher particles with soft ones, more active with less active (represented by  $\text{CaCO}_3$  and  $\text{MgCO}_3$  compounds as nanosized particles, and micro-sized particles of sand), and they differ in surface energy and damping properties; dust of building enterprises can be classified among such fillers [21-24]. Nanoparticles allow the filler to actively participate in physical and chemical processes, as they differ in fractal dimension and high degree of self-organization. This process is one of the key to obtain a stable structure, and the desired properties of the filled materials. The purpose of quartz is to change pores (of capillary porosity) dimensions and form finely porous stone structure, thereby providing the increased cold and water resistance.

The second component ( $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ) is less durable and more reactive, it is involved in the physical and chemical processes of interaction in coarse cements, which are characterized by high pore volume, including open and interconnected.

Carbonate incorporations are damping components and additional crystallization centers. Moreover, they participate in the formation of new crystalline compounds (in particular, calcium hydrocarboaluminates), which together with previous measures favorably affects the strength characteristics, water and frost resistance of cement stone.

Another important factor is an early strength increase (7-10 days) when implementing the two-component nanosized filler. In conjunction with the porous structure reorganization of the macropore volume at an early age, there is a reduction of pore sizes in 3.6-4.5 times. Thus, the reorganization of the pore space by implementing the two-component filler causes not only the increase in strength, but also the durability of cement compositions.

### 3. Results

In accordance with the Polystructural Theory of Composite Construction Materials by prof. V.I. Solomatov), the composites structure may be regarded as an interrelated whole – from the atomic-ion level to coarse macroscale objects [25]. The composite materials properties at the level of microstructure are determined by the degree of filling, dispersiveness of fillers, active interaction between binders and fillers and other factors. For instance, binary fillers create not only the content of binders, but also improve the possibility of chemical interactions between the hydrolysis and hydration, thereby laying the foundation for higher durability of the material under operating conditions. However, in our opinion, the preparation and application of fillers different in composition, properties, dispersiveness require new methods of research raw mixtures and finished products. Technological modes for the filled cement-containing materials preparation have to provide heterogeneity of the system, that is, to create conditions for cluster formation of dispersed particles. The role of cluster formation is not sufficiently appreciated that substantially reduces the significance of the fillers role in a complex filled system [25].

Thus composite is a system with several structural levels arranged across the interface into a single unit on the basis of structural organization [25-28]. Cluster structures are particles aggregates that are combined by binders and connected with surface forces. The interaction between the filler and the binder in the process of technological conversions produces a synergistic effect (material is of new quality) [25-28]. In the compositions undergoing mixing step, sealing, heat treatment, etc., there are self-organization processes of structure typical for the cluster system caused by free surface energy excess of the dispersed particles. A cluster is a spontaneously occurring collection of many particles connected with interaction forces, preserving their individuality in the microstructure [25]. The cluster can be regarded as a kinetic element of the structure, as it arises and is formed in the material formation processes (nucleation, phase transitions, phase separation, and others).

### 4. Discussion

Thus a positive role in enhancing the durability of cement-containing building materials perform nanoparticulate fillers, that under pressing conditions form a monolithic material structure. It is desirable that nanofillers have chemical activity, and among other recommendations we mention the following [1-5, 24-28]:

It is preferable to use multicomponent compositions, components must be partially in unstable active form, and the part – in the form of crystalline compounds. Unstable components containing  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and basic oxides, which with alkaline form the tumors group of different activities are the basis of hardening;

- Complex binders' activity is largely determined by surface activity, so it is preferable to use fillers in nano- and microdispersed state;
- Products preparation on the basis of such compounds and compositions is desirable to carry out by the method of pressing or hyperpressing (contact-condensation hardening) to provide contact between the particles under the water shortage conditions (including free water) in the system;
- Hardening conditions also play an important role, and it is preferable if the process is carried out at low temperature exposure ( $\sim 80 \dots 1050^\circ\text{C}$ ).

In general, the processes of cluster formation, reorganization of cement-containing, silicate pore space systems by nanofillers implementation allow eventually obtain materials with improved operating characteristics that determine their durability.

### 5. Conclusion

At present there is an increase in creating progressive, environmentally safe mineral binders and composite building materials based on them that are distinguished by low power consumption, low cost of the production establishment that allow to obtain the construction products with high functional properties and durability. In this regard, during the construction of the region housing there is a need for intensive use of local raw material resources; strive to increase the diversity of output products, including small-pieces and small-format products and materials as well as implementation of low power technology [29-30]. Theoretical studies development should serve as an impetus for the local manufacture of efficient binders and materials. A variety of industrial and household

waste, which can be used as additives, fillers, including nano-technogenic raw material, under the terms of its formation, aggregation state, activity, chemical and mineralogical and phase composition allow not only to expand the resource base of these materials, but also to greatly improve their properties due to the formation of self-organization structure processes at all technological stages.

## References

- [1] V.S. Ramachandran, R.F. Feldman, M. Kolleparadi, Additives for Concrete: Reference Book; Ed. V.S. Ramachandran, (Russ. eds. T.I. Rosenberg, S.A. Boldyrev), M., Stroyizdat, 1988, p. 575.
- [2] A.A. Novopashin, T.B. Arbuzova, Ways of Using Alumina-Containing Sludges in the Production of Building Materials, Environmental Technology. Recycling of industrial wastes into building materials: Proceedings of Ural Polytechnic Institute, Sverdlovsk, 1984, pp.19-25 (in Russian).
- [3] A.A. Portik, A.V. Savinyh, Foamed Concrete, SPB, Nauka, 2004, p.270 (in Russian).
- [4] A.P. Proshin, V.A. Beregovoy, A.A. Krasnoshekov, A.M. Beregovoy, Foamed Concrete: Composition, Properties, Usage, Penza, PGUAS, 2003, p.161 (in Russian).
- [5] H. Schmidt, Inorganic-Organic Composites by Sol-Gel Techniques. Journal of Sol-Gel Science and Technology, 1, 217–231, 1994, DOI:10.1007/BF00486165
- [6] M.I. Balzannikov, N.V. Ahrameeva, Ecological Problems of Manufacturing Building Products, Environmental and hydraulic structures: Problems of construction, operation, environment and training: proceedings of the International Scientific and Technical Conference, Samara, Samara State University of Architecture and Civil Engineering, 2014, pp. 46-51 (in Russian).
- [7] I.V. Nedoseko, V.V. Babkov, S.S. Yunusova, A.R. Gaitova, I.I. Ahmadulina, Gypsum and Gypsum Slag Compositions Based on Natural Raw Materials and Industrial Wastes, Building Materials, 2012, no. 8, pp. 66-68 (in Russian).
- [8] S.F. Korenkova, N.G. Chumachenko, Y.V. Sidorenko, A.I. Hlystov, Perspectives of Application Nano-technogenic Sludge Waste in the Production of Modern Building Materials, Proceedings of the IV International Kazan Innovation Nanotechnological Forum (NANOTECH'2012), Kazan, GUP RT "Tatarstansky TsNTI", 2012, pp. 412-414 (in Russian).
- [9] B.V. Gusev, S.Y. Yin, T.V. Kuznetsova, Cement and Concrete – Development Trends, ed. B.V. Guseva, M., Nauchnyi mir, 2012, p. 136 (in Russian).
- [10] S.F. Korenkova, Y.V. Sidorenko, A.M. Guryanov, The three-dimensional technogenic origin nano-structures, European Journal Of Natural History, 2012, № 2, pp. 34-36.
- [11] A. Guryanov, S. Korenkova, V. Lebedev, V. Lebedev, Y. Sidorenko, Investigation of Cement Structure Formation by Small-Angle Neutron Scattering Experiments, The II International Conference "Modern problems in the physics of surfaces and nanostructures (ICMPSN2012)": Book of abstracts, May 23-25, 2012, Yaroslavl Branch of the Institute of Physics and Technology of Russian Academy of Sciences, Yaroslavl, Russia, 2012, pp. 131. av. at: [http://www.yf-ftian.ru/icmpsn/abstract/book\\_of\\_abstracts.pdf](http://www.yf-ftian.ru/icmpsn/abstract/book_of_abstracts.pdf)
- [12] S.F. Korenkova, A.M. Guryanov, Y.V. Sidorenko, Nanodispersed Technogenic Raw Materials for Multicomponent Mixtures of Raw Materials, Construction dry mixtures, 2012, no. 3, pp. 17-19 (in Russian).
- [13] S.F. Korenkova, A.M. Guryanov, Y.V. Sidorenko, The Quality Control Concept of Building Materials Using Nano-Technogenic Raw Materials, Scientific Review, 2014, No. 6, pp.61-63 (in Russian).
- [14] S.F. Korenkova, Y.V. Sidorenko, K. Voprosu, On the Question of the Fractal Dimension of Nano-Technogenic Raw Materials, Nanotechnologies in construction: a scientific online magazine, 2010, Vol.2, No. 3, pp. 26-32 (in Russian).
- [15] A.M. Guryanov, Particles Formation during Hydration of Cement according to the Small-Angle Neutron Scattering, Proceedings of the 70-th Russian scientific conference on the results of research in 2012 "Tradition and innovation in construction and architecture", Samara, Samara State University of Architecture and Civil Engineering, 2013, pp. 107-108 (in Russian).
- [16] M.V. Nazarov, Water and Sewage Purification by Electrochemical Filtration, Vestnik of SSUACE. Town Planning and Architecture, 2013, Vol.1, pp. 51-60 (in Russian), doi:10.17673/Vestnik.2013.01.9
- [17] A.A. Sizov, N.S. Serpokrylov, Y.U. Kamenev, Selection Methods of Purification Technologies of Periodic Wastewater Discharges, Vestnik of SSUACE. Town Planning and Architecture, 2012, Vol. 4, pp. 71-74 (in Russian), doi:10.17673/Vestnik.2012.04.13
- [18] I.V. Nedoseko, M.V. Okolzina, Treatment Facilities Reconstruction of the "Krasnousolskiy" Resort Using Multilayered Polycarbonate, Vestnik of SSUACE. Town Planning and Architecture, 2013, Vol. 3, pp. 51-54 (in Russian), doi:10.17673/Vestnik.2013.03.10
- [19] D.V. Popov, Operational Acoustic Control Method of Concrete Permeability of Hydraulic Structures, Vestnik of SSUACE. Town Planning and Architecture, 2012, Vol. 3, pp. 66-67 (in Russian), doi:10.17673/Vestnik.2012.03.14
- [20] D.V. Popov, Operational Method for Determining the Permeability of Hydraulic Concrete on the Basis of Fracture Mechanics, Vestnik of SSUACE. Town Planning and Architecture, 2012, Vol. 4, pp. 76-77 (in Russian), doi:10.17673/Vestnik.2012.04.14
- [21] N.E. Pospelova, E.H. Timirbulatova, Some Features of the Technological Processes and the Level of Air Pollution Caused by Emission Sources of Construction Enterprises, Vestnik of SSUACE. Town Planning and Architecture, 2014, Vol. 3, pp. 84-88 (in Russian), doi:10.17673/Vestnik.2014.03.15
- [22] N.E. Pospelova, E.H. Timirbulatova, Study of Atmospheric Pollution by Emission Sources of OAO "Tyazhmash" in Syzran, Vestnik of SSUACE. Town Planning and Architecture, 2013, Vol. 3, pp. 103-107 (in Russian), doi:10.17673/Vestnik.2013.03.20
- [23] P.A. Sidiyakin, N.A. Marinin, S.V. Shulga, K.O. Chichirov, Road Construction Works as Source of Dust Air Pollution, Vestnik of SSUACE. Town Planning and Architecture, 2014, Vol. 2, pp. 72-76 (in Russian), doi:10.17673/Vestnik.2014.02.12

- [24] S.F. Korenkova, Y.V. Sidorenko, Binary Fillers for Building Materials, *International Journal of Applied and Basic Research*, 2014, no. 6, pp. 39-40 (in Russian).
- [25] V.I. Solomatov, *Polystructural Theory Development of Composite Building Materials*, The success of modern materials science: proceedings of the Anniversary Conference, RAASN, MGUPS, Moscow, 2001, pp. 56-66 (in Russian).
- [26] Y.V. Sidorenko, S.F. Korenkova, *The Multilevel Synergetic Approach to the Hardening Mechanism Formation of Contact- Condensation Systems of Silicate Type: Monograph*, Samara, SGASU, 2005, p. 112 (in Russian).
- [27] V.I. Solomatov, S.F. Korenkova, Y.V. Sidorenko, *Thermodynamic Aspects of Contact Condensation of Unstable Silicate Systems*, Proceedings of Higher Educational Establishment. Construction, 2001, no. 2-3, pp. 38-44 (in Russian).
- [28] V.I. Solomatov, S.F. Korenkova, S.A. Piyavsky, Y.V. Sidorenko, *Numerical Simulation of Unstable Silicate Binders in the Isothermal Reactor Crystallizer*, Proceedings of Higher Educational Establishment. Construction, 2001, No. 12, pp. 22-24 (in Russian).
- [29] T.E. Gordeeva, *Replanning Features of an Apartment in a Large-Panel House*, *Vestnik of SSUACE. Town Planning and Architecture*, 2013, Vol. 3, pp. 55-59 (in Russian), doi:10.17673/Vestnik.2013.03.11
- [30] Y.S. Vytchikov, I.G. Belyakov, *Mathematical Modeling of Heat-Shielding Characteristics of Masonry Blocks from Claydite*, *Vestnik of SSUACE. Town Planning and Architecture*, 2013, Vol. 4, pp. 82-86 (in Russian), doi:10.17673/Vestnik.2013.04.14

Mechanical Properties and Durability of CNT Cement Composites. by MarÃa Del Carmen Camacho, Oscar Galao , Francisco Javier Baeza, Emilio Zornoza and Pedro GarcÃas \*. Civil Engineering Department, Universidad de Alicante, Ctra San Vicente s/n, San Vicente del Raspeig 03690, Spain.Â Multifunctional cementâ€matrix composites are useful as structural materials that provide functional properties, which allow applications such as electrical grounding, electrical contacts for cathodic protection, deicing, electromagnetic interference (EMI) shielding, antistatic flooring and strain sensing.Â In any case, structural characteristics should be maintained or improved [5,12,13]. Carbon nanotubes (CNT) are one of the additions that can be used to create multifunctional materials.