NANOTECHOLOGIES IN NEW STRUCTURAL CONCRETES: PRACTICE AND OUTLOOK

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Abstract

The influence of nanomaterials and nanotechnologies in the construction segment is becoming more prominent. They have been shown to significantly enhance the performance of a variety of concretes and concrete composites. This will allow the concrete to remain the main structural material in the near future as well.

Keywords: Admixtures, Nanofibers, Nanoparticles, Nanotechnologies, Non-metal composite reinforcement, Photocatalysis, Performance

1 Introduction

The presence of nanomaterials and nanotechnologies in the construction segment is becoming more prominent. Today, on the total global market of nano-products, the construction industry "consumes" up to 3 % of volume and value terms of the total market of nanomaterials, and in some segments, such as nanocomposites, up to 11 % that leads with the "value added" in products, designs, buildings and structures to a possible sales volume of nanoproducts and nanoservice of approximately $ 95 to 100 billion (Gusev & al. 2013). By 2015, this market can grow to $ 400 billion. The list of basic research works in the field of construction nanomaterials and nanotechnologies performed in Russia and abroad is quite wide (Zhu, Bartos & Porro 2004).

Construction industry differs by its nature from other areas of human activity. Thus, construction is trying, more often than the others, to use the developments and inventions created in other areas of science and industry, rather than create them within branch. Historically, the construction has a very low level of investments in R & D (not more than 0.2 - 0.4 % of sales volume, with an average level of 3.5 - 4.5 % for the economy as a whole); that not only impedes the creation of new technical decisions, but also the adaptation of existing ones. And finally, a very high level of initial investments hinders the development of nanomaterials and nanotechnologies in construction, if we take into account that in this field mainly small and middle businesses are represented. For example, only 4 % of the construction market is "international", and the activity of its most members is very local.

All mentioned of the above determines the desire to shorten the innovation cycle and immediately to get a result: a new material, a new technology, a new decision related to the safety and environmental protection.

The detailed analysis and long-term forecast for the development of research and application of nanomaterials and nanotechnologies in construction shows that the cement and concrete cover over 40 % of the nanotechnology products in construction materials (market value is $ 5.6 billion) with a predicted annual growth more than 10 % in 2012…2015 (Falikman & Petushkov 2012).

2 Nanosized and Nanostructured Materials in Cement and Concrete

The concrete are composite materials, whose structure comprises hydrated cement phases with particle sizes of 1 to 100 nm, the cement grain, chemical admixtures and mineral additives, aggregates and fillers. The reduction of the size of the structural elements, and the formation of specific continuous filament structures formed as a result of three-dimensional contacts between nanoparticles of different phases, lead to a radical improvement in their performance characteristics.

Most of recent studies of the use of nanotechnology principles in concrete have been focused on the structuring of the cement materials and studying the mechanisms of their destruction.

The creep of the concrete is now associated with the reality of nanoscale globules C-S-H with changing of their packing characteristics: some of them are more "packless" and the others are more close-packed. The calcium hydrosilicate C-S-H (Fig. 1) is formed by "self-assembly" of globules of two structurally different but chemically identical phases, each of which has the maximum density of spherical packing: 64 % for the low-density gel (LDG), and 74 % for the high density gel (HDG) according to Jennings (2000). The third, a more close-packed phase C-S-H can be obtained by a careful and skilful control of production of concrete mix with nano- and microsilica, which fill the space between nanogranules C-S-H, usually being filled with water. This leads to an increased density of C-S-H-gel, which, in turn greatly restricts the migration of the globules C-S-H with time. Thus, considering the behavior of the cement stone with microsilica at the nanoscale, we can understand why the addition of microsilica reduces the creep of concrete that opens the way to get high-compacting materials with a slow creep. Using the nano-identification equipment, we can "feel out" and probe C-S-H-phase with the applied load and measure in minutes the creep characteristics, which are fully confirmed by long-term experiments on the macro level. The understanding of these mechanisms provides the opportunities of directed regulation of the structure of advanced cement composites and their properties.

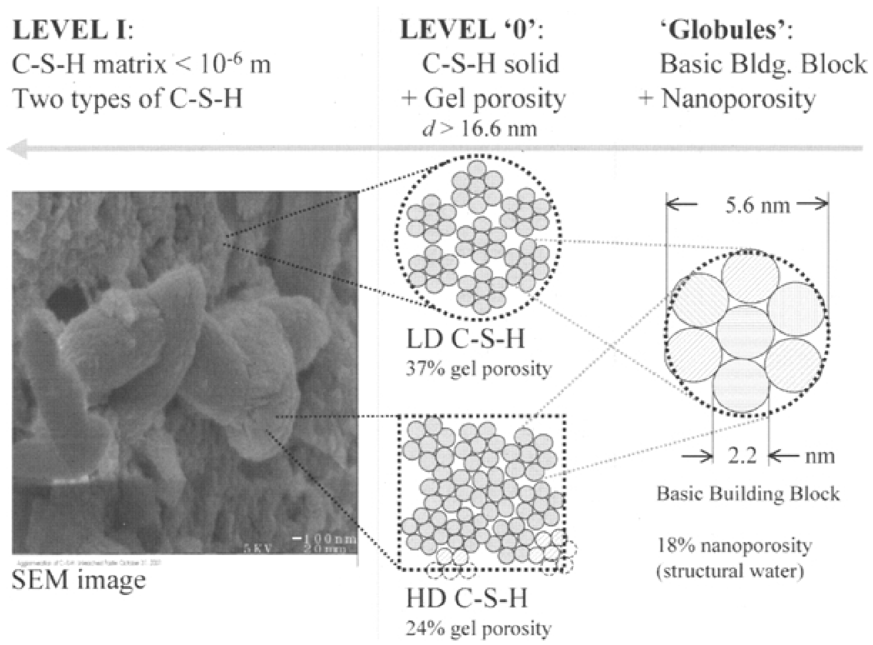

Fig. 1 The globular structure of calcium hydrosilicate (adapted from Jennings).

It is found that the inclusion of nanoscale particles (typically with the diameter of particle about 100 nm) in the concrete mixture has a significant influence on the concrete properties. Thus, the use of nanosilicates with a specific surface not less than 180 m^2/g (an order greater than the specific surface area of microsilica), and new polycarboxylates with special molecular structure, provides for the achievement of radically new structures and strength values of the cement stone, creating the preconditions for the further development of reactive powder composites with the compressive strength value about 800 MPa and the bending tensile strength value about 100 MPa.

When introducing nanoparticles SiO_2, the pozzolan activity of fly ash significantly increases, which leads to an increase in both early and grade concrete strength with a high content of fly ash. The introduction of nanosilica allows us to get self-leveling concrete mixes, to reduce bleeding and concrete segregation with very low impact on the workability. Currently a large range of additives based on nanosilicates are produced on an industrial scale for their use in SCC, in shotcrete, for concrete pouring into oil and gas wells, and for works on the seabed.

The use of concrete additive based on nanoparticles of calcium hydrosilicates, nanoparticles Fe_2O_3 and Al_2O_3, nanoscale spinel $MgAl_2O_3$, and nanoparticles of clays is widely known. As it have been shown in a number of works, they have a significant impact on the mechanical properties, the resistance to penetration of chlorides, reduce the permeability and shrinkage of concrete, and are also widely used in self-compacting concrete mixes (Falikman & Sobolev 2010).

The nanoparticles of calcium carbonate $CaCO_3$ look as a new type of concrete hardening accelerator. After 2 hours of hydration, we can observe around the nano-$CaCO_3$ a considerable increase in fibrous hydrosilicates C-S-H, which are the main product of the cement hydration. Using the nano-$CaCO_3$ as a hardening accelerator, we can compensate the delayed early hydration and ensure the development of the strength of the concrete containing large amounts of various mineral additives.

The nanoparticles of calcium hydrosilicates C-S-H, today produced by a number of companies and received through the preliminary hydration of silicates, perform the function of crystallization centers and contribute to a more rapid curing of cement systems. The use of such "nano-additives" ("seeds") allows reducing the time of thermal treatment of the precast concrete, reducing the energy intensity of production, and the influence on the environment.

The nanoparticles of clay, as it is shown in several studies, have the influence on the mechanical properties, the resistance to penetration of chlorides, reduce the permeability and concrete shrinkage, and are widely used in self-compacting concrete mixes as well. The chemical "graft" of polymers to blanched nanolayers of the clay with thickness about 1 nm with their full exfoliation provides "pillared clays" particles, which significantly improve properties of cement systems.

Thus, nano-modified montmorillonite reduces the permeability of the cement stone by about 50%. The maximum strength increase (almost 15 %) is achieved with the introduction of 0.6 % of the additive, although the maximum density is provided at the value of 0.4 %. Furthermore, nano-sized particles of clays act as a "seed" for the formation of C-S-H, and significantly improve the molding properties and the rheology of concrete mixes, especially for the self-compacting and high-stiff ones. Besides, the addition of small amounts of nanoclay (less than 0.5 % of the binder mass) considerably reduces the pressure on the formwork, what is often a problem when using a self-compacting concrete mixes.

It is necessary to mention so-called "nano-cements", which are prepared either in the process of "sol-gel" synthesis or by a superfine grinding of Portland cement components. Typically, these cements have the ultra-short terms of setting and a high early (at the age of 2 days) strength value, compared with ordinary Portland cement. The "nano-binders" produced by mechanical-and-chemical activation of cements, provide for the increase by more than 60 % of the concrete strength value.

To improve the properties of the final product, it is often sufficient to introduce a relatively small amount of "dopant" nanomaterials. Despite this, the commercial success of nanomaterials depends on the ability to produce them in large volumes and at reasonable prices comparable with the ultimate effectiveness of the nano-product. The technology of the production of nano-materials at an industrial scale is mainly associated with the use of plasma, chemical vapor deposition, electroplating, sol-gel synthesis, mechanical etching and the use of natural nano-systems.

An additional potential for the development of more durable structural materials with higher strength and stiffness is provided by carbon nanoparticles, nanotubes and nanofibers, which are produced now at an industrial scale by a lot of companies. In this way, however, at least two problems are kept: an increased tendency of carbon materials toward agglomeration, and, as a result, the difficulty of a uniform distribution of "nanofibers" in the composite, as well as insufficiently high bond between the cement matrix concrete and the nanotubes, which does not allow using wholly their high elasticity modulus (5 times higher than that of steel) and the strength (8 times higher than that of steel) with a very low density. A fundamentally new line of research in this area is "growing" of nanotubes directly from the gas phase on the particles of cement or microsilica.

When the nanotubes with a diameter value close to the thickness of the layers of C-S-H are introduced into the cement matrix, it results to a noticeable change in its properties, especially in the values of compressive and tensile strength, but this increase is not so significant, if we consider high cost of nanotubes. Much more important application is the reduction of cracking (Makar, Margeson & Luh 2005), especially in the surface layers of high performance cement composites (Photo 1) and in the strain hardening cement composites (SHCC) - "super- ductile concrete".

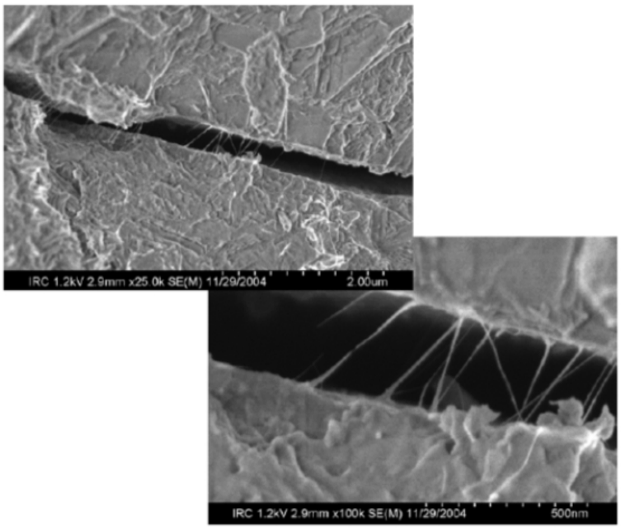

Photo 1 The cement matrix modified by carbon nanotubes (Makar, Margeson & Luh 2005).

The nanotubes are more and more used as the deformation sensors, especially in the bridges and road pavements. It is interesting that this has stimulated the research of cement composites reinforced by graphene as well.

Recently, in the production of new generation of concrete, high-effective polycarboxylate superplasticizers are used more often. These superplasticizers are intensively studied by many leading companies, a number of such admixtures are manufactured at an industrial scale. Polycarboxylate superplasticizers got the commercial name “hyperplasticizers”, because the real opportunities to reduce the water-cement ratio (up to 40 %) and to increase the concrete mix workability is considerably higher than that of traditional polymethylene naphthalene sulfonates (PNS) and polymethylene melamine sulfonates (PMS).

The basis of molecular design of high-effective water-soluble carbon-chain superplasticizers is a chemical modification of carboxylated polymers, which allows us to introduce into these macromolecules long side oligoalkilenoxidation chains through the formation of corresponding ether or amide groups. Numerous high-effective polycarboxylate superplasticizers are described. These carbon-chain polymers with the form of macromolecules known as “centipedes”, “comb” or “star-shaped” (Fig. 2) provide for practically unlimited possibilities to produce “tailor made concrete” by changing of the length of the main and side chains, the electrical charges, the density of side chains, and free functional groups (Falikman 2009). It is sufficient to say that on the basis of only three monomers we can “construct” more than a trillion of different macromolecules.

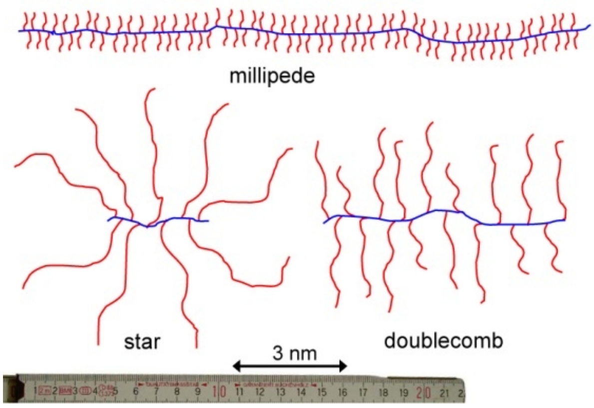

Fig. 2 Various shapes of the polycarboxylates molecules

The optimization of the chemical structure of polycarboxylates ethers through the use of nanotechnologies (nanoscale assembly of molecules of a given structure) significantly reduces their consumption in concrete, as well as allows minimizing their sensitivity to the chemical composition of the cement. For example, the increase of the water demand of the concrete mix is determined by electric charges and side chains; the concrete mix “shelf life” due to the polymers adsorption on the cement particles is determined by the functional monomers, and the development of early concrete strength is determined by the form (configuration) of the polymer molecule as a whole. The modern products usually contain several types of molecules, and often the action of each begins at a certain time.

In particular, these superplasticizers acquired a special role in the production of self-compacting (SCC) and self-leveling (SLC) concrete mixes, reactive powder concrete (RPC), which open new and very promising era of concrete technology development. Actually, only with the forthcoming of polycarboxylate superplasticizers the widespread production and use of these advanced concrete became real. New trends of research and modification of superplasticizers are associated with the attempts to control the rheology characteristics of SCC. So, in recent years the polyphosphonates are intensively developed, the application of which provides for the achievement of a higher yield with a lower plastic viscosity of the concrete mix (Bellotto & Zevnik 2013). Furthermore, to control the amount of the superplasticizer in concrete mix in time, the cross linked organic admixtures, whose structure is similar to the schistous layered hydroxides or to three-calcium aluminate hydrates and tetra-calcium alumoferrite hydrates is used as the basis. These studies open a new way for the nanocomposites synthesis using polymer particles and schistous materials; in such a manner it is possible to control the effect of admixtures on the hydration kinetics through programming the time of their selection from cross linked structures.

The active methods of influencing on shrinkage deformations of concrete are based on the use of a new generation of organic admixtures, so called “the organic shrinkage reducing admixtures” (OSRA), on the base of hydroxyl derivatives of ethoxylated or propoxylated aliphatic alcohols obtained under strictly controlled conditions, which ensures their constant chemical composition. The OSRA mode of action based on the variety of water bond forms in concrete and regulation of mass-transfer processes presents a much lesser hazard for the concrete structure than formation of calcium hydrosulfoaluminates typical for mineral expanding admixtures on the basis of sulfate and aluminate compounds. This favorably distinguishes the organic admixtures from traditional inorganic expanding additives. Autogenous shrinkage is regulated by superabsorbent polymers (Jensen 2008).

3 Environmental Effects of Nanomaterials Used in Concrete

The nanotechnologies play an important role in solving many problems associated with the environmental protection.

The experience of using titanium dioxide sensibilized through a nanotechnology is quite interesting (Falikman & Vainer 2009). As it is well known, the modified TiO_2, exposed to the ultraviolet light, acts as a photocatalyst, allocating atomic oxygen from ambient water vapor or oxygen. The amount of released active oxygen is enough for the oxidation and decomposition of organic pollutants, deodorizing of rooms, and destruction of bacteria.

Currently the nanoparticles of TiO_2 are widely used as additives in cement paints, special cements, mortars, concrete and asphalt road pavements, self-cleaning materials and structures, air-cleaning materials and structures, antibacterial materials and structures, plasters for external and internal works, etc.

Especially widespread is the use of such photosensitive catalysts in concrete self-cleaning surfaces due to open superhydrophilic properties which allows maintaining the aesthetic appearance of the structures unchanged for a long time.

The first application of photocatalytic cement materials with self-cleaning properties dates back to 1996, when Italcementi Group participated in the construction of Dives di Misericordia Cathedral in Rome (Photo 2). A complicated structure with three huge white sails was assembled from precast concrete. This project required the use of the concrete with unique properties, which besides high strength and durability had to maintain for a long time white color due to the self-cleaning properties of the surface.

Photo 2 Dives di Misericordia Cathedral in Rome (Photo: Dr. A. Skarendahl)

The photocatalytic cements have been used in other prestigious European architectural projects, primarily in France: Cité de la Musique in Chambery (2003), Hotel de Police in Bordeaux, as well as the construction of Saint John Court in Monte Carlo (Monaco), the schools in Mortara, Italy (1999), high-rise residential buildings in Ostende, Belgium. Moreover, the cement compositions of paints containing the photocatalysts have been developed, which are widely used in Italy in the process of construction of residential buildings.

The cement materials containing TiO_2, are interesting not only because of their self-cleaning properties. The studies show that these materials are good for the control over urban pollution. The photo catalytic system "TiO_2-cement" may destroy NO_x, SO_x, NH_3, CO, volatile organic hydrocarbons such as benzene and toluene, organic chlorides, aldehydes, and condensed aromatic compounds.

In Japan, Italy, France, Belgium and Nederland, the studies of concrete made with the use of nanocatalysts have been carried out. The Russian Engineering Academy implemented R & D supported by the Moscow Government, which resulted paints, plasters, and concretes for interior and exterior works based on the cement matrices modified by photo catalytic titanium dioxide. The experimental application will be done for the projects of residential and multifunctional buildings, as well as in the construction of special structures (tunnels, sewers), contributing to the improvement of the ecological situation and to the reduction of the content of harmful environment components, including the smoke and the gas-laden atmosphere.

Important changes have occurred in the development and application of a new generation of self-cleaning coatings for concrete. They are considered today in the general context of the struggle for a radical reduction of the cost and working time for the maintenance and repair works and the restoration of complex structures. Among the products, produced by a number of German and Spanish firms from the late of 1990s on the basis of nanotechnologies, the most important are the coatings for the full hydrophobization of the surfaces. They can be used to prevent the damage from graffiti, and to eliminate the potential sources of biological damage - mold, fungi, mosses and lichens.

The high-strength, high-resistant and shockproof coatings represent a special group; they are resistant to chemical actions and protect the reinforced concrete structures from corrosion. Almost all of them are the result of the "self-crosslinking" of properly selected components.

4 Reinforcement

The most significant example of a wide industrial application of nanotechnologies for reinforced concrete is the steel reinforcement with a modified nanostructure (Photo 3). It has a much longer service life in corrosive environment, which reduces the construction cost.

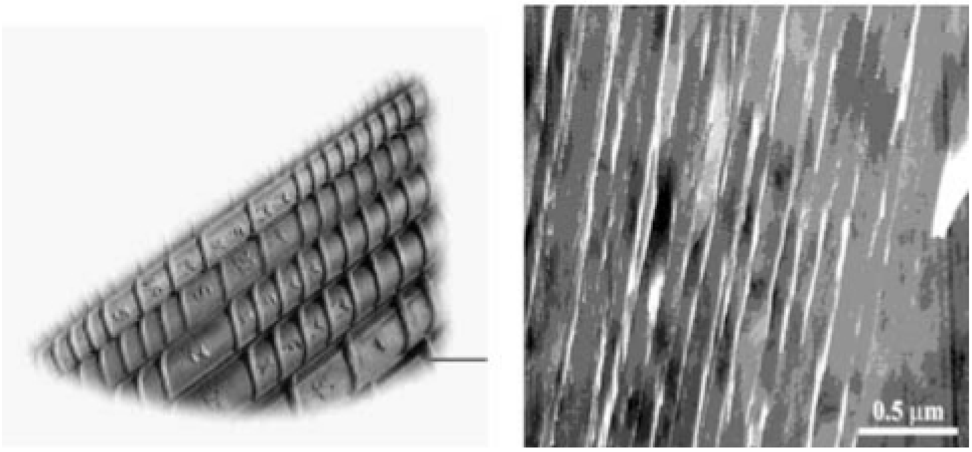

Photo 3 Nanolayer of austenite in a carbide-free "rail" of martensite, TEM, MMFX Steel Corp, USA

Another important and intensively developing line of research is the use of non-metal composite reinforcement, consisting mainly of longitudinal un-idirectional nanostructured fiber reinforced polymers, as well as the use of external reinforcement systems based on carbon fiber reinforced plastics. The nanomodification of binders allows creating the composites with fracture toughness by 5 to 10 times higher, and their thermal stability increases up to 180…340 °C. Much attention is paid to the parameters determining the workability of binders (lower viscosity of oligomer, acceleration of the curing process, the viability of large prepregs, etc.). The same principles may be applied to adhesion interaction of polymers with the surface of different fiber types, where the nanostructuring of the contact zone may play a decisive role in a significant improvement of structural and mechanical properties of composites.

5 What has tomorrow in store for us?

Thus, it is evident that nanotechnologies have already changed and will further change our views, expectations and opportunities in the field of control over the material world. Such changes will definitely have an impact on the construction and the building materials industry (Falikman & Sobolev 2010). The Portland cement is one of the most widely consumed materials; it has a huge, but at the same time, not completely explored, potential. A deeper understanding of the properties and the structure of cement materials at the nanoscale will certainly lead to the creation of a new generation of concrete with high strength and durability, with desired properties, resistant to stress, having a whole range of new features, such as electrical conductivity, ability to respond to the change of temperature, humidity and pressure. The development of materials with controlled deformation characteristics and low thermal expansion, the "smart" materials, such as sensors for monitoring stress, "bio-imitators" with unique properties is near at hand. These new concrete will be ecological, "friendly" to the environment, efficient (not expensive and energy-saving, i.e. demonstrating exactly the properties which will meet the needs of modern society. Mechanochemistry and nano-catalysis have to change the face of modern cement industry, which is responsible for about 5 % of global CO_2 emissions, or 2.1 billion tons of CO_2 yearly, reducing its impact on the environment by significant reduction of the temperature of clinker formation and perhaps even implementation of the "cold clinker burning" through "sol-gel" synthesis. Today the ways and mechanisms of "self-healing" of reinforced concrete structures are intensively studied. Adding of anaerobic alkaliphilic microorganisms (typical nanoobject) of a certain type to the mixing water allows reducing the permeability of cement-and-sand matrix due to the colmatage of pores by their metabolic products, primarily the calcite, and increasing its strength up to 25 % (Jonkers & Schlangen 2008). More and more the modified and activated geopolymers will be used (Davidovits 1991).

6 Conclusions

Recent progress in the field of nanotechnologies allows us to hope that in the coming decade, many problems, which may seem fantastic now, will be successfully solved.

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