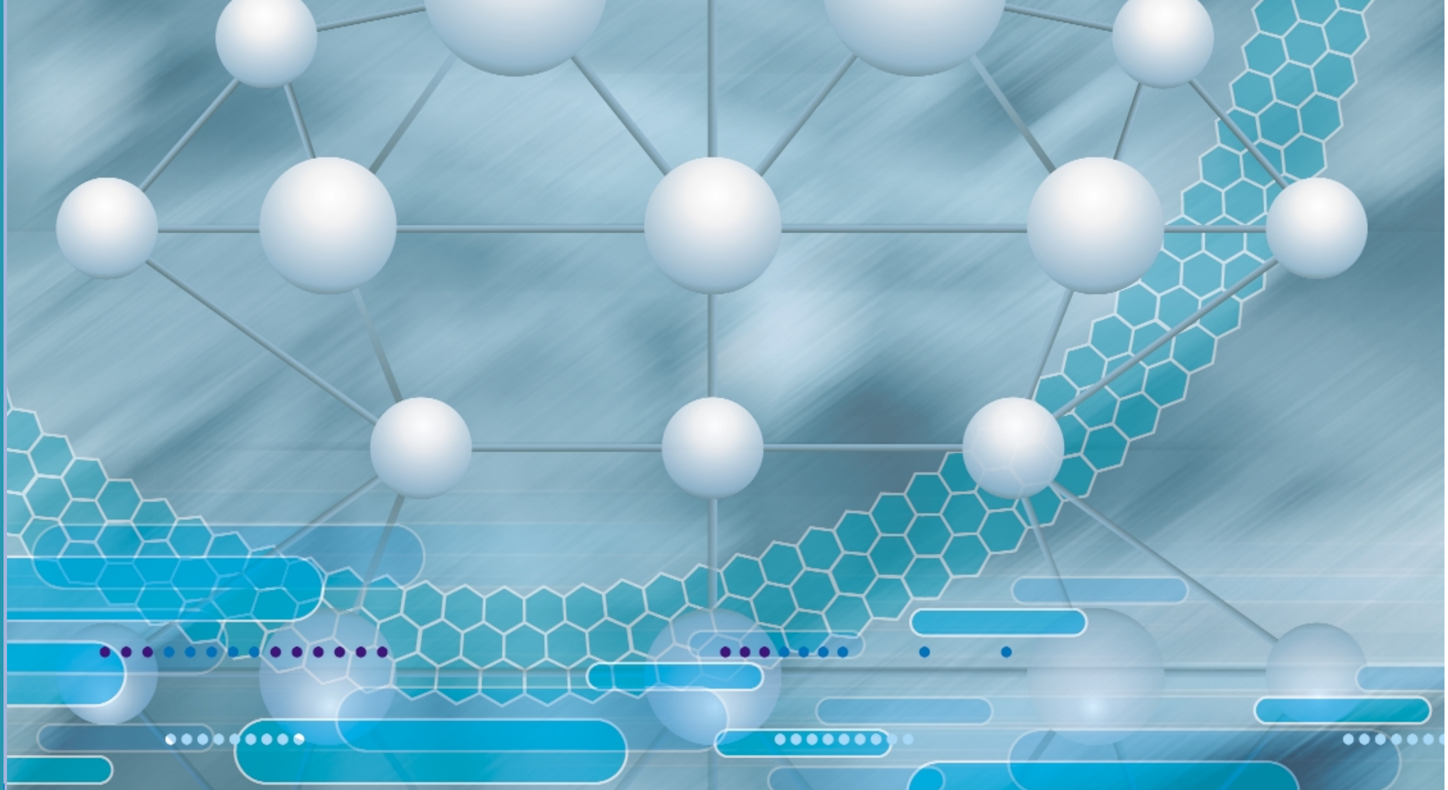

How Nanotechnology Can Change the Concrete World

Part Two of a Two-Part Series

Successfully mimicking nature's bottom-up construction processes is one of the most promising directions.

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A general overview of nanotechnology was presented in part one of this two-part series (see p14 in the October issue). In this part, potential applications of nanotechnology to concrete are presented.

How Nanotechnology Can Change Construction Materials

The majority of recent nanotechnology research in construction has focused on the structure of cement-based materials and their fracture mechanisms.[4,24,25,32] New advanced equipment makes it possible to observe a structure at its atomic level. Moreover, the strength, hardness and other basic properties of microscopic and nanoscopic phases of materials can be measured.[24]

Atomic force microscopy (AFM) has been applied to the investigation of the amorphous C-S-H gel structure. This has led to the discovery that this product has a highly ordered structure at the nanoscale (Fig. 6).[33]

Understanding of nanoscale structure helps to influence important processes related to production and use of construction materials, including strength development, fracture, corrosion and tailoring of desired properties. For instance, the development of paints and finishing materials that are self-cleaning, discoloration resistant, antigraffiti protected, high scratch resistant and wear resistant is extremely important for façade and interior applications. Self-cleaning Hydrotect tile, window glass, and water-based paint have been developed by TOTO based on photocatalyst technology.[16,17] The self-cleaning effect related to decomposition of organic pollutants and gases is achieved when titania

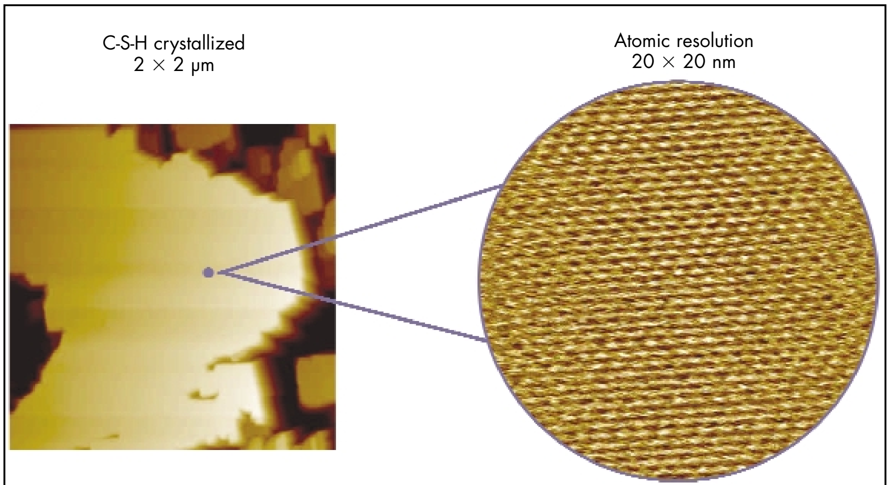

Figure 6 *Highly ordered structure of C-S-H gel (Ca/Si = 0.9) observed at a nanoscale.*[33] *Courtesy Eric Lesniewska, Nanosciences Group, Physics Lab, University of Bourgogne, France.*

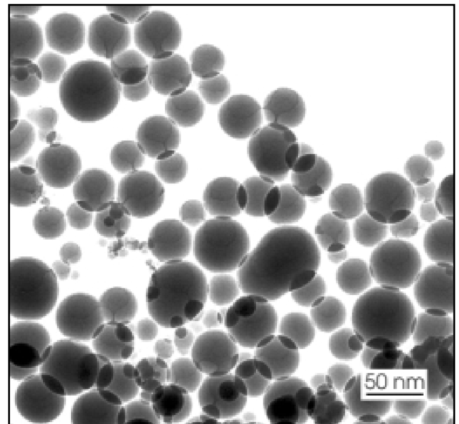

Figure 7 *Ultrafine fumed silica particles observed using TEM.*[37] *Courtesy Andri Vital, EMPA Mat'ls Testing & Research, Laboratory for High-Performance Ceramics, Duebendorf, Switzerland.*

photocatalyst thin film is set on a surface to emit active oxygen under ultraviolet light.

Another aspect of self-cleaning is provided by the hydrophilicity of the surface. This helps to rinse away dust and dirt. Other examples are related to nanometer-thin coatings of conducting polymers that protect carbon steel against corrosion[4,9,25] or window glass covered with an invisible silver nanolayer to enhance the thermal insulation of buildings.[4,9,25]

Nanochemistry with its bottom-up possibilities offers new products that can be effectively applied in concrete technology. One example is related to the development of new superplasticizers for concrete, such as polycarboxylic ether (PCE) polymer-based Sky. This product has been developed recently by Degussa. A nanodesign approach helped to realize the extended slump retention of concrete mixtures.[34]

It has been proposed that nanoparticles can be incorporated into conventional building materials. They then possess advanced or smart properties required for the construction of high-rise, long-span or intelligent civil and infrastructure systems.[4,24,25,35–39] For example, silica nanoparticles (nanosilica (Fig. 7)) can be used as an additive for high-performance and self-compacting concrete that has improved workability and strength.[35–37] Nanosilica has been proved to be an effective additive to polymers to improve strength, flexibility and durability.[39–41]

Kang et al.[39] investigated epoxy composites filled with functionalized nanosilica particles obtained using the sol–gel process. The synthesized uniform silica particles were either modified by substituting the surface silanol groups by epoxide ring, amine and isocyanate groups or by calcinating the nanosilica to remove surface silanol groups. It was found that modified particles could chemically bond to epoxy matrix, which resulted in a decrease in the coefficient of thermal expansion (CTE) of the composites. With increased nanosilica content, the composites exhibited an additional decrease in CTE, an increase in glass transition temperature and a decrease in damping.

The combination of carbon nanotubes and conventional polymer-based fibers and films is another challenge. For example, the incorporation of 10% SWNTs into the strongest artificial fiber, Zylon, results in a new material with 50% greater strength.[40] It is expected that better exfoliation (separation of the bundles to release the individual nanotubes) and improved dispersion and alignment of the individual nanotubes can increase the performance of composite fibers or decrease the volume of the nanotubes used.[40]

Based on research conducted at the University of Texas–Dallas, Dalton et al.[26,41] introduced a further breakthrough related to SWNT-reinforced fibers. The composite fiber comprising 60% of nanotubes and 40% of poly(vinyl alcohol) (PVA) produced by continuous spinning with a modified coagulation method achieved strengths of ≥1.8 GPa. These fibers matched the energy-absorbing capacity of spider silk up to the breaking point of silk at 30% (165 J/g) and continued to absorb energy until reaching a toughness of 570 J/g, as compared with 50 and 33 J/g for Spectra and Kevlar fibers, respectively.[26] Application of these new super fibers in composite materials is promising.

Concrete with Nanoparticles

Mechanical properties of cement mortars with nano-iron-oxide and nanosilica were studied by Li et al.[38] Experimental results demonstrated an increase in compressive and flexural strengths of mortars that contained nanoparticles. It was found that increased nanosilica content improved the strength of the mortars.

Table 1. Effect of Gaia on Performance of Concrete Mixtures†

Mixture parameters	Plain	With Gaia
Cement type (EN-197)	II/A-P 42.5R	II/A-P 42.5R
Cement content (kg/m^3)	460	460
Admixture dosage (%)		1.3
Air content (%)	2.7	1.1
Slump (mm)		
After 5 min	60	200
After 30 min	25	210
After 60 min	15	160
After 90 min		140
Ambient temperature (°C)	20	20
Compressive strength (MPa)		
At 1 d	22.7	68.2
At 7 d	32.7	77.3
At 28 d	45.2	91.7

†Reference 35.

Moreover, the strength of the cement mortars with nanoparticles was even higher than the strength of mortars with silica fume. SEM study proved that the nano-iron-oxide and nanosilica particles filled the pores and decreased the content of calcium hydroxide within the hydration products. These effects resulted in the improvement of the mechanical properties of the cement mortars with nanoparticles.

A laboratory study of high-volume fly-ash high-strength concrete that incorporated nanosilica was performed by Li.[42] Investigation of the hydration process confirmed that the pozzolanic activity of fly-ash can be significantly improved by the application of a nanosilica. It was concluded that the use of nanosilica led to increased early age and ultimate strength of high-volume fly-ash concrete. The developed concrete with nanosilica had a 3 d strength 81% higher compared with plain concrete. The 2-year strength of the developed concrete was 115.9 MPa (higher than the strength of reference portland cement concrete of ~103.7 MPa).

Collepardi et al.[36,37] investigated low-heat self-compacting concretes with mineral additives (ground limestone, fly-ash and ground fly-ash). Nanosilica (5–50 nm) at a dosage of 1–2% of cementitious materials was used as a viscosity-modifying agent. A constant water/cement ratio (*W/C*) of 0.58 was used for all mixtures, and a slump flow of 780–800 mm was maintained by adjusting the dosage of an acrylic-polymer-based superplasticizer. To maintain the specified slump flow, the superplasticizer dosage was increased by ~0.21% per each percent of nanosilica used. The addition of nanosilica made the concrete mixture more cohesive and reduced bleeding and segregation. At the same time, the nanosilica had little effect on the slump loss measured within the first 30 min.

Although the nanosilica did not affect the compressive strength of the concrete that contained various forms of fly-ash, the compressive strength of the concrete that contained ground limestone was slightly decreased. The best performance was demonstrated by concrete with ground fly-ash, 2% nanosilica and 1.5% superplasticizer. This concrete had the highest compressive strength of 55 MPa at an age of 28 d with the desired behavior in the fresh state, i.e., low bleeding, perfect cohesiveness, better slump flow and little slump loss. The investigation also showed that nanosilica did not affect concrete durability.[36,37]

One of the first commercial nanoadmixtures for concrete, Gaia, was developed by Ulmen S.A. and Cognoscible Technologies to substitute for silica fume at ready-mixed concrete facilities certified by ISO 14001, "Environmental Management Systems." This product is available in liquid form that facilitates the satisfactory distribution of nanosilica particles in concrete. Gaia combines the effects of water reduction and slump increase.[35] According to Ferrada et al.,[35] the concrete mixtures with Gaia exhibit perfect workability without segregation or bleeding. This makes the design of self-compacting concrete an extremely easy task. A slump loss of 30% in 1.5 h at an ambient temperature of 20°C has been reported for concrete mixtures that include Gaia (Table 1).

The application of Gaia at a dosage of 1.3% (by weight, as a dry content) provides almost a twofold increase in concrete compressive strength at ages of 7 and 28 d.[35] The early strength of the concrete with Gaia is 68.2 MPa, which is ~3 times higher than that of reference concrete (Table 1 and Fig. 8). The 28 d compressive strength of the concrete made with Gaia demonstrates a classical dependence on *W/C* **(Fig. 9)** and, based on the available test data, a single formula is proposed to predict the 28 d strength of the investigated concretes: $f_{28} = 208.38e^{-3.0881W/C}$ (at $R^2 = 97\%$).

Based on the available data, the positive action of the nanoparticles on the microstructure and properties of cement-based materials can be explained by the following factors:[35–38,44]

- Well-dispersed nanoparticles increase the viscosity of the liquid phase, which helps to suspend the cement grains and aggregates, which, in turn, improves the segregation resistance and workability of the system.
- Nanoparticles fill the voids between cement grains, which results in the immobilization of free water (filler effect).
- Well-dispersed nanoparticles act as centers of crystallization of cement hydrates, which accelerates the hydration.
- Nanoparticles favor the formation of small-sized crystals (such as calcium hydroxide and AF_m) and small-sized uniform clusters of C-S-H.
- Nanosilica participates in the pozzolanic reactions, which results in the consumption of calcium hydroxide and formation of an additional C-S-H.
- Nanoparticles improve the structure of the aggregate contact zone, which results in a better bond between aggregates and cement paste.
- Crack arrest and interlocking effects between the slip planes provided by nanoparticles improve the toughness, shear, tensile strength and flexural strength of cement-based materials.

Future Developments

Much progress in concrete science is to be expected in coming years by the adaptation of new knowledge generated by a quickly growing field of nanotechnology. The development of the following concrete-related nanoproducts can be anticipated:

- Catalysts for the low-temperature synthesis of clinker and accelerated hydration of conventional cements;
- Grinding aids for superfine grinding and mechanochemical activation of cements;
- Binders reinforced with nanoparticles, nanorods, nanotubes (including SWNTs), nanodampers, nanonets or nanosprings;
- Binders with enhanced/nanoengineered internal bond between the hydration products;
- Binders modified by nanosized polymer particles, their emulsions or polymeric nanofilms;
- Biomaterials (including those imitating the structure and behavior of mollusk shells);
- Cement-based composites reinforced with new fibers that contain nanotubes as well as with fibers covered by nanolayers (to enhance the bond and corrosion resistance or to introduce new properties, such as electrical conductivity);
- Next-generation superplasticizers for total workability control and supreme water reduction;
- Cement-based materials with supreme strength, ductility and toughness;
- Binders with controlled internal moisture supply to avoid/decrease microcracking;
- Cement-based materials with engineered nanostructures and microstructures that exhibit supreme durability;
- Ecobinders modified by nanoparticles and produced with substantially decreased volume of portland cement component (down to 10–15%) or binders based on the alternative systems (magnesia, phosphate, geopolymers and gypsum);
- Self-healing materials and repair technologies that use nanotubes and chemical admixtures;
- Materials with self-cleaning/air-purifying features based on photocatalyst technology;
- Materials with controlled electrical conductivity, deformative properties, nonshrinking and low thermal expansion; and
- Smart materials, such as temperature-, moisture- and stress-sensing or responding materials.

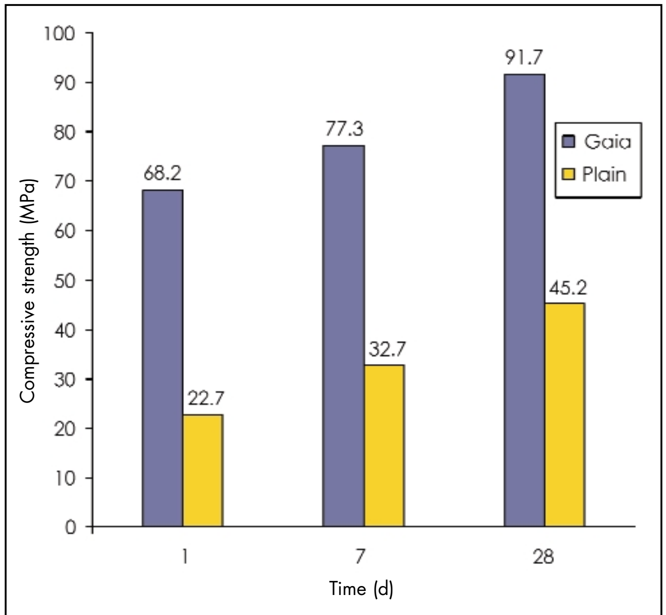

Figure 8 *Strength development of concrete with Gaia.*

Mechanochemistry and nanocatalysts could change the face of the modern cement industry by the great decrease of clinkering temperature and even realizing the possibility of cold sintering of clinker minerals in mechanochemical reactors. Nanobinder can be proposed as a logical extension of two concepts: densified system with ultrafine particles (DSP)[43] and modified multicomponent binder (MMCB)[44,45] down to the nanolevel **(Fig. 10)**.

In these systems, the densification of binder is achieved with the help of ultrafine particles: silica fume (SF) dispersed with superplasticizer (SP) in DSP and finely ground mineral additives (FGMA) and SF modified by SP in MMCB. These particles fill the gaps between cement grains. In these systems, portland cement component is used at its standard dispersion to provide the integrity of composition. In contrast to DSP and MMCB, the nanobinder can be designed with a nanodispersed cement component applied to fill the gaps between the particles of mineral additives (including FGMA).

In the nanobinder, the mineral additives (optionally, finely ground), which act as the main component, provide the structural stability of the system. The microsized or nanosized cementitious component (which also can contain the nanosized particles other than portland cement) acts as a glue to bind less-reactive particles of mineral additives together. Such nanosized cementitous component can be obtained by the colloidal milling of a conventional (or specially sintered/high C_2S) portland cement clinker (the top-down approach) or by self-assembly, which uses mechanochemically induced topochemical reactions (the bottom-up approach).

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