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Review

Nanotechnology in concrete – A review

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ABSTRACT

This paper reviews the state of the field of nanotechnology in concrete. Definitions of nanotechnology, including nanoscience and nano-engineering in concrete, are provided. The impact of recent advances in instrumentation and computational materials science and their use in concrete research is discussed. Recent progress in nano-engineering and nanomodification of cement-based materials is presented.

Contents

1. Introduction

Since nanotechnology was introduced by Nobel laureate Richard P. Feynman during his now famous 1959 lecture "*There's Plenty of Room at the Bottom*," [1] there have been many revolutionary developments in physics, chemistry, and biology that have demonstrated Feynman's ideas of manipulating matter at an extremely small scale, the level of molecules and atoms, i.e., the nanoscale.

While the meaning of "nanotechnology" varies from field to field and country to country and is widely used as a "catch all" description for anything very small, nanotechnology is commonly

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defined as the understanding, control, and restructuring of matter on the order of nanometers (i.e., less than 100 nm) to create materials with fundamentally new properties and functions [2]. Nanotechnology encompasses two main approaches: (i) the "top-down" approach, in which larger structures are reduced in size to the nanoscale while maintaining their original properties without atomic-level control (e.g., miniaturization in the domain of electronics) or deconstructed from larger structures into their smaller, composite parts and (ii) the "bottom-up" approach, also called "molecular nanotechnology" or "molecular manufacturing," introduced by Drexler et al. [3], in which materials are engineered from atoms or molecular components through a process of assembly or self-assembly (Fig. 1). While most contemporary technologies rely on the "top-down" approach, molecular nanotechnology holds great promise for breakthroughs in materials and manufacturing, electronics, medicine and healthcare, energy, biotechnology, information technology, and national security.

To date, nanotechnology applications and advances in the construction and building materials fields have been uneven [4]. Exploitation of nanotechnology in concrete on a commercial scale remains limited with few results successfully converted into marketable products. The main advances have been in the nanoscience of cementitious materials [5,6] with an increase in the knowledge and understanding of basic phenomena in cement at the nanoscale (e.g., structure and mechanical properties of the main hydrate phases, origins of cement cohesion, cement hydration, interfaces in concrete, and mechanisms of degradation). Recent strides in instrumentation for observation and measurement at the nanoscale are providing a wealth of new and unprecedented information about concrete, some of which is confounding previous conventional thinking. Important earlier summaries and compilations of nanotechnology in construction can be found in [5,7–11]. This paper reviews the main developments in the field of nanotechnology and nanoscience research in concrete, along with their implications and key findings. The paper is divided into three main sections: (i) definitions of nanotechnology in concrete, (ii) advances in instrumentation and computational materials science, and (iii) nano-engineering of cement-based materials.

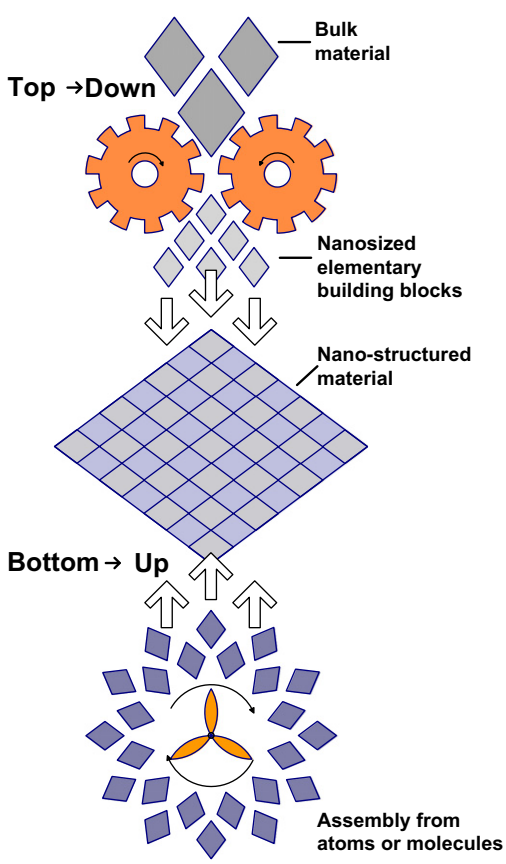

Fig. 1. Illustration of the "top-down" and "bottom-up" approaches in nanotechnology. Adapted from [108].

2. Nanotechnology and concrete: definitions

2.1. Concrete: a complex, nano-structured material

Concrete, the most ubiquitous material in the world, is a nano-structured, multi-phase, composite material that ages over time. It is composed of an amorphous phase, nanometer to micrometer size crystals, and bound water. The properties of concrete exist in, and the degradation mechanisms occur across, multiple length scales (nano to micro to macro) where the properties of each scale derive from those of the next smaller scale [12–14]. The amorphous phase, calcium–silicate–hydrate (C–S–H) is the "glue" that holds concrete together [15] and is itself a nanomaterial (Fig. 2).

Viewed from the bottom-up, concrete at the nanoscale is a composite of molecular assemblages, surfaces (aggregates, fibers), and chemical bonds that interact through local chemical reactions, intermolecular forces, and intraphase diffusion. Properties characterizing this scale are molecular structure; surface functional groups; and bond length, strength (energy), and density. The structure of the amorphous and crystalline phases and of the interphase boundaries originates from this scale. The properties and processes at the nanoscale define the interactions that occur between particles and phases at the microscale and the effects of working loads and the surrounding environment at the macroscale. Processes occurring at the nanoscale ultimately affect the engineering properties and performance of the bulk material [5,12,13,16–18].

2.2. Definition of nanotechnology in concrete

The nanoscience and nano-engineering, sometimes called nanomodification, of concrete are terms that have come into common usage and describe two main avenues of application of nanotechnology in concrete research [5,6,19,20]. *Nanoscience* deals with the measurement and characterization of the nano and microscale structure of cement-based materials to better understand how this structure affects macroscale properties and performance through the use of advanced characterization techniques and atomistic or molecular level modeling. *Nano-engineering* encompasses the techniques of manipulation of the structure at the nanometer scale to develop a new generation of tailored, multifunctional, cementitious composites with superior mechanical performance and durability potentially having a range of novel properties such as: low electrical resistivity, self-sensing capabilities, self-cleaning, self-healing, high ductility, and self-control of cracks. Concrete can be nano-engineered by the incorporation of nanosized building blocks or objects (e.g., nanoparticles and nanotubes) to control material behavior and add novel properties, or by the grafting of molecules onto cement particles, cement phases, aggregates, and additives (including nanosized additives) to provide surface functionality, which can be adjusted to promote specific interfacial interactions.

3. Advances in instrumentation and computational materials science

Advances in the characterization of the nanoscale structure of cement-based materials and in computational materials science have provided scientists and engineers with promising new tools

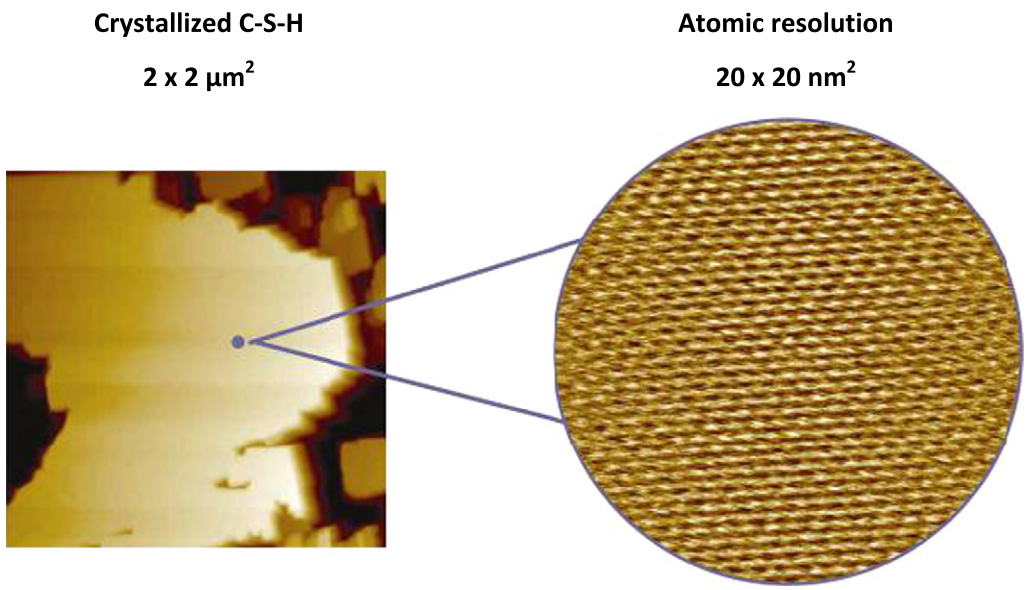

Fig. 2. Nanoscale structure of C–S–H crystallized on calcite substrate and revealed by AFM (Ca/Si = 0.9). Reprinted with permission from the American Ceramic Society Bulletin, 2005, Vol. 84, N 11 [7].

to better understand and engineer the structure of concrete and to improve concrete performance and durability. It is now clear that the important features of the structure of C–S–H and other cement phases exist on the nanometer scale and that a fundamental understanding of the nanoscale and microscale physical and chemical processes is necessary to predict and control the material properties and performance through to the macroscale. This understanding is essential to transition from traditional empirically driven approaches that are inherently limited in their range of applicability to more rigorous design methods. An important challenge in this endeavor is building the bridge between the nano and macroscopic length and time scales. The ongoing advances in material characterization techniques and computational materials science are providing the capabilities to make this possible.

3.1. Advances in instrumentation

The development of instrumentation with high spatial resolution has made it possible to observe the structure of concrete at the nanoscale and to measure the physical, chemical, and mechanical properties of its microscopic and nanoscopic phases. Pioneering applications of nanotechnology in materials science and engineering have been in the characterization of material mechanical properties by nanoindentation. Atomic force microscopy (AFM) was one of the enabling techniques that gave rise to the nanotechnology revolution and has been key to many of the advances in molecular nanotechnology. Other modern characterization tools include small-angle neutron scattering (SANS), ultrasmall-angle X-ray scattering (SAXS), quasi-elastic neutron scattering (QENS), nuclear magnetic resonance (NMR) spectroscopy, and nuclear resonance reaction analysis (NRRA). The following highlights several key findings in the nanoscience of concrete as a result of the application of these tools.

3.1.1. Atomic force microscopy

AFM has proved to be a powerful tool for investigating the surface structure of hydrating cements, the changes in cement paste surface morphology in response to exposure to relative humidity, the carbonation process of cement phases, and the forces acting at the origin of cement cohesion [21,22]. AFM imaging has revealed that, while generally thought of as an amorphous phase, C–S–H is in fact a well-ordered structure composed of nanoparticles, and direct observations of C–S–H growth by AFM during the hydration of tricalcium silicate grains indicated that the formation of C–S–H occurred as an agglomeration of identical elementary clusters with sizes on the order of $60 \times 30 \times 5$ nm^3 [23,24]. Furthermore, AFM measurements of the forces acting between C–S–H surfaces or between cement grains have shown to be electrostatic in nature and thus not representable by the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory as previously supposed [22,25]. AFM investigations of the surface of cement paste in a humid air environment revealed a change in the surface structure of the paste from coarse to fine grains for relative humidities between 3% and 30% [21]. Understanding the role of condensation damage as a function of relative humidity is important to the design of durable structures.

3.1.2. Nanoindentation techniques

Nanoindentation rendered possible the measurement of local mechanical properties of cement-based materials at the nanoscale [26], and the recent use of a "Triboindenter" and AFM in contact mode enabled researchers to attribute the local nanomechanical properties to individual phases due to the instruments' in situ imaging capability [24,27]. Notably, work by Ulm and coworkers [26,28–30] revealed that C–S–H exists in at least three structurally different forms – low density, high density, and ultra-high density – that have different mean stiffness and hardness values and different volume fractions. The mean stiffness and hardness values were found to be intrinsic properties of the C–S–H and to not change from one cement-based material to another. It was also found that the high density C–S–H degrades much less during calcium leaching (decalcification) than the low density C–S–H. These results indicate that the ratio of low to high density C–S–H in the final product may have important implications for cement mix design and optimization. Imaging techniques combined with nanoindentation additionally have proved useful in determining local mechanical properties and is providing new insight into resolving the question of the existence of the interfacial transition zone (ITZ) around aggregates. Using nanoindentation with in situ scanning probe microscopy imaging, Mondal et al. [31,32] found that, contrary to conventional thought, the elastic modulus of the ITZ does not increase with distance from the interface, thus questioning

the existence of the ITZ and implying that interface failure is most likely governed by the extreme heterogeneity of the interface and poor bonding between the paste and the aggregates.

3.1.3. Nuclear techniques

Solid-state NMR spectroscopy, including ^{27}Al, ^{1}H, ^{17}O, ^{29}Si, and ^{33}S NMR, has proven useful over the past two decades for providing quantitative and structural information on the anhydrous and hydrated phases of Portland cement and details about the pore structure (i.e., porosity, pore size distributions, and interconnectivity) of cement-based materials (a few examples are [33–45]). NMR allows for the quantification of Si and Al substituted tetrahedral chain lengths and structural positioning and the identification of nearest and next-nearest neighboring elements. The technique has contributed greatly to the ongoing debate concerning the appropriate model for the structure of C–S–H [38,43,44,46,47]. This includes discussions on the relative importance of tobermorite and jennite and the levels of disorder and of substitution of portions of the structure by hydroxide, calcium hydroxide, and "impurity" elements such as Al. In combination with XRD spectra, it has clearly confirmed that the structure of the (aluminum) silicon dimers and higher order polymerized chains and the associated calcium layers are highly dependent on the Ca/Si ratio, the production method used (hydration of oxides versus precipitation from aqueous solution), and the presence of chemical and mineral admixtures [43]. Recently, NMR was used on C–S–H-based nanohybrids to reveal details about the structural position of organic-based grafts into defect locations on the silicate structure. It was determined that the effectiveness of the grafting process is dependent on the Ca/Si ratio [19,39,40,48]. ^{1}H NMR has been applied to the investigation of the hydration kinetics of cement. It was used to determine the relative percentages of free water, C–S–H interlayer (physically bound) water, and C–S–H gel (chemically bound) water [49–51] and has been lately proposed [52] to be utilized for the study of changes in early-age hydration due to internal curing. ^{1}H NMR has also provided information on the gel and capillary pores in white cement paste where the pore size distribution was found to be clustered in multiple, discrete ranges between 0.9 and 600 nm [45,53,54].

NRRA has provided new insights into the mechanisms that control the setting and curing of concrete and the effect of temperature, retarders, accelerators, and superplasticizers on the mechanisms and kinetics of cement hydration [55–58]. This method, which gives in situ measurements of hydrogen concentration as a function of depth at a resolution of a few nanometers, provided a strong indication that the hydration rate of calcium silicate during the induction period is controlled by the development of a semi-permeable surface layer and that of tricalcium aluminate by the formation of a crystalline layer. There has been some controversy over the mechanisms of the induction period in the early stages of hydration, and several competing physico-chemical models have been proposed [47,59]. Results from NRRA analysis may provide the information necessary to help resolve this question.

3.1.4. Neutron and X-ray scattering techniques

SANS and SAXS experiments have permitted researchers to shed new light on the evolution of the microstructure in cement systems during hydration at the nanometer scale as well as on the composition, solid density, and dimensions of nanoscale C–S–H [60–62]. These techniques provide direct data on particle morphology, surface area, and pore size distribution and have been applied to better understand creep, shrinkage, and the effects of aging. Based on the results from SANS and SAXS observations, Jennings [63–66] constructed a model of the structure of C–S–H at the nanoscale as an aggregation of brick shaped, nanometer sized particles. This colloidal–granular approach describes the C–S–H as particles that agglomerate over time, increasing the average degree of polymerization of the silicate chains and the C–S–H stiffness, strength, and density. In this approach, the pore structure consists of the void spaces between granules and depends on the packing arrangement that fills the space at a specific packing density. This is different from the view of C–S–H as a continuum permeated by a pore structure. In this colloidal–granular approach, the aging of cement paste due to external influences can be related to changes in the orientation and (re)packing of the nanosized C–S–H particles [62,65].

An important and strongly debated issue concerning C–S–H structure is the function and state of water at the nanoscale. QENS is a useful technique for studying the dynamic processes of confined or near surface water. It provides information about the state of water, allowing for differentiation between chemically bound water, physically bound water that interacts with the surface of gel pores, and unbound water confined within capillary pores of cement paste [67]. In studies of hydrating and hardened cement pastes, QENS helped determine the rate of conversion of free water to bound water and has shown that a greater degree of hydration is achieved at lower initial curing temperatures [67–74]. Information from QENS analysis has been utilized in the development of a mathematical model of the hydration reaction kinetics [73,75]. Improved knowledge of the interaction of cement phases and water is critical to the understanding of many properties of cement, including mechanical and transport properties, creep, and shrinkage.

3.2. Advances in computational materials science

Continually increasing computing power has allowed computational materials science to predict the microstructure and properties of concrete by integrating physics and chemistry [76]. Atomic scale modeling by ab initio, molecular dynamics (MD), and energy minimization techniques has offered new potentials in cement science and is shedding light onto the processes occurring at the nanoscale that are of importance for understanding material properties at the macro-level and for developing strategies to improve concrete performance. Recent years have seen an increased interest in the use of atomic scale modeling in cement science for the study of the structure of C–S–H [77–81], the interaction of water and solutes with various cement phases [82], the origin of the cohesion of cement pastes [83,84], and, more recently, for studying the tuning of the mechanical performance of cement systems by engineering the bonding scheme in C–S–H [85] and the molecular interaction with graphitic structure reinforcements [86,87]. While atomic scale modeling provides an unprecedented ability to manipulate, through simulation, individual atoms and molecules, one needs to ensure that the improvements achieved at the nano-level can be translated into beneficial material properties at the macro-level. There is a significant research need in the development of relations bridging the nano/micro and the macroscale.

While observations by NMR, AFM, and SANS have been used to characterize the structure of C–S–H, ab initio and MD simulations are probing its internal behavior and providing details of the structure that cannot be obtained through experimental techniques. Using structural prototypes such as tobermorite and jennite, insights into C–S–H structural parameters, hydrogen bond connectivity, and the positioning of water molecules and their dynamics in the interlayer have been obtained [77–80,88]. MD simulations by Dolado et al. [89] on the polymerization of silicic acids in the presence of calcium ions showed that increasing the calcium content (in effect the Ca/Si ratio) slows down the polymerization of the cementitious silicate chains and prevents them from forming rings and three-dimensional structures [89]. This structural information is important to developing a fuller understanding of the mechanical and chemical behavior of concrete and the mechanisms by

which it degrades. The ability to directly manipulate through simulation the structure and composition of C–S–H and interlayer species and then estimate their properties is an important, complementary tool to the experimental techniques previously described.

MD simulations have been applied to the interaction of liquid phases and cement phase surfaces. As has been generally found for water molecules near surfaces, the liquid phase of various water–hydroxide phase (portlandite, brucite, gibbsite, tobermorite, and jennite) interfaces was found to be highly structured and a function of the liquid phase composition, the solid phase surface charge, and the surface's ability to facilitate formation of hydrogen bond networks [90,91]. The simulations showed that the ordering of water at interfaces modifies a range of surface behavior such as diffusivity and hydration energies. Knowledge of the nanoscale interactions between species dissolved in the aqueous phase with cement phases is central to understanding the long-term durability of concrete. The sorption of chloride ions and associated cations onto the surface of calcium hydroxide, hydrated calcium aluminate phases, and calcium silicate phases (tobermorite) has been simulated by MD [92]. These studies of the adsorption of solutes from liquid phases showed that the chloride binding capacity decreases in the sequence calcium hydroxide, ettringite, and tobermorite (in agreement with ^{35}Cl NMR studies), which indicates a low sorption capacity for C–S–H and that chloride binding on C–S–H may be due to sorption on surface sites similar to those of calcium hydroxide [92]. These results provide insight and understanding of the molecular scale behavior of water and solutes in cement that can be used to devise interface and pore surface modification strategies that can positively impact the properties of cement-based materials.

Molecular simulations studies also have strongly indicated that the cohesion of C–S–H is mainly due to short- and medium-range attractive electrostatic forces and that van der Waals attractions only marginally contribute to cement paste cohesion [83,84]. These findings open the door for developing ways to control the overall cohesion and ultimately the mechanical performance of cement-based materials. Pellenq et al. [85] proposed two strategies for tuning molecular level interactions: (i) by altering the bonding scheme of cohesion of C–S–H or (ii) by covalent hybridization of the hydrates with small organic moieties or polymeric chains.

MD modeling has also been used for characterizing local molecular structure and bonding behavior at reinforcing structure–cement phase interfaces [86,87], both of which are important to the load-transfer capacity of the interface and, in turn, the macroscopic constitutive behavior of the composite material. Simulations performed on the interaction of surface functionalized graphitic structures and a tobermorite prototype (Fig. 3) have demonstrated the dominant role of electrostatic forces in the interfacial interactions and indicated that the polarity of the functional group can be used as an indicator of affinity the surface has to C–S–H [86]. The MD simulations further revealed that an optimal number of polar oxygen containing groups may exist for efficient graphitic structure–cement phase interaction and emphasized the mediating role of Ca^{2+} counter-ions. These results provide insight into ways of improving the bonding between graphitic structures and cement phases through appropriate surface treatment.

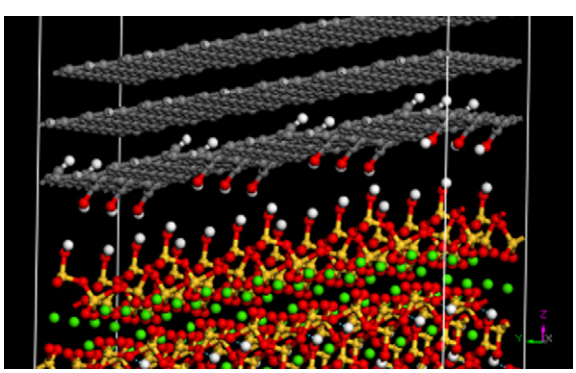

Fig. 3. Snapshot of the interaction of a surface functionalized graphitic structure and a tobermorite prototype.

The information obtained from simulation and computational modeling leads to better designs; reduces cost by explaining, suggesting or replacing experiments; and provides new opportunities for the exploration of novel materials [76]. Continued validation and correlation with experimentally determined material properties is critical to improving the accuracy of molecular scale models.

4. Nano-engineering of cement-based materials

Nano-engineering, or nanomodification, of cement is a quickly emerging field. Synthesis and assembly of materials in the nanometer scale range offer the possibility for the development of new cement additives such as novel superplasticizers, nanoparticles, or nanoreinforcements. Methodologies for hybridization and grafting of molecules allow for the direct manipulation of the fundamental structure of cement phases. These techniques can be used effectively in a bottom-up approach to control concrete properties, performance, and degradation processes for a superior concrete and to provide the material with new functions and smart properties not currently available. Engineering concrete at the nanoscale can take place in one or more of three locations [20]: in the solid phases, in the liquid phase, and at interfaces, including liquid–solid and solid–solid interfaces. While nano-engineering of cement-based materials is seen as having tremendous potential, nonetheless, several challenges will need to be solved to realize its full potential, including the proper dispersion of the nanoscale additives, scale-up of laboratory results and implementation on larger scale, and a lowering of the cost benefit ratio.

The following summarizes the effects of the addition of nanoparticles and nanoreinforcements to cement and the recent developments in hybridization of hydrated cement phases. Superplasticizers and chemical admixtures, which have been widely used in high performance and self-compacting concrete for many years, are not part of the scope of this paper and are not discussed in the following. Recent innovations on their use can be found in [5].

4.1. Addition of nanosized and nano-structured materials

For millennia, nanoparticles have been added to the production of ceramics; however, it is their conscious, scientific utilization that constitutes nanotechnology. Nanosized particles have a high surface area to volume ratio (Fig. 4), providing the potential for tremendous chemical reactivity. Much of the work to date with nanoparticles has been with nano-silica (nano-SiO_2) [93–102] and nano-titanium oxide (nano-TiO_2) [97,103]. There are a few studies on incorporating nano-iron (nano-Fe_2O_3) [96], nano-alumina (nano-Al_2O_3) [104], and nanoclay particles [105,106]. Additionally, a limited number of investigations are dealing with the manufacture of nanosized cement particles and the development of nanobinders [7,107]. Nanoparticles can act as nuclei for cement phases, further promoting cement hydration due to their high reactivity, as nanoreinforcement, and as filler, densifying the microstructure and the ITZ, thereby, leading to a reduced porosity. The most significant issue for all nanoparticles is that of effective dispersion. Though it is particularly significant at high loadings, even low loadings experience problems with self-aggregation, which reduces the benefits of their small size and creates unreacted pockets leading to a potential for concentration of stresses in the material.

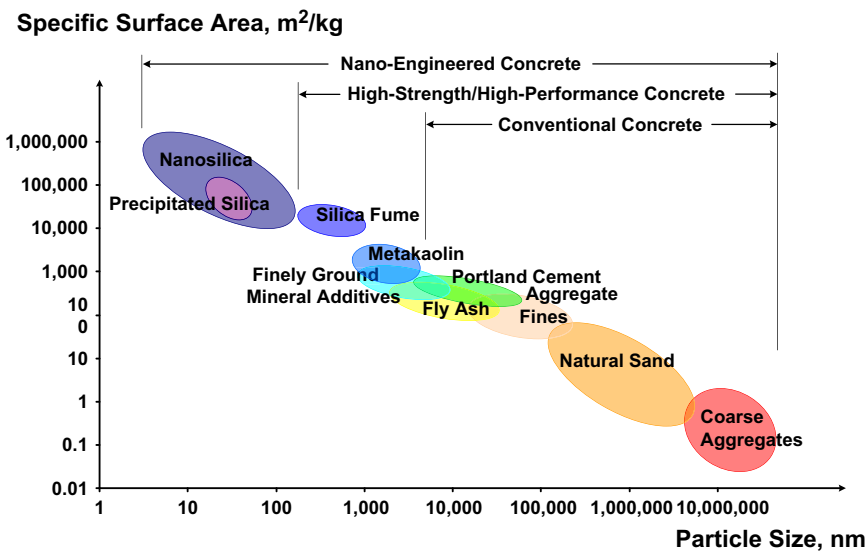

Fig. 4. Particle size and specific surface area related to concrete materials. Adapted from [108].

Nano-SiO_2 (Fig. 5) has been found to improve concrete workability and strength [101,108,109], to increase resistance to water penetration [94], and to help control the leaching of calcium [110], which is closely associated with various types of concrete degradation. Nano-SiO_2, additionally, was shown to accelerate the hydration reactions of both C_3S and an ash–cement mortar as a result of the large and highly reactive surface of the nanoparticles [93,99]. Nano-SiO_2 was found to be more efficient in enhancing strength than silica fume [95,98]. Addition of 10% nano-SiO_2 with dispersing agents was observed to increase the compressive strength of cement mortars at 28 days by as much as 26%, compared to only a 10% increase with the addition of 15% silica fume [109] (Fig. 6). Even the addition of small amounts (0.25%) of nano-SiO_2 was observed to increase the strength, improving the 28 day compressive strength by 10% and flexural strength by 25% [101]. It was noted that the results obtained depended on the production route and conditions of synthesis of the nano-SiO_2 (e.g., molar ratios of the reagents, type of reaction media, and duration of the reaction for the sol–gel method) and that dispersion of the nano-SiO_2 in the paste plays an important role. Nano-SiO_2 not only behaved as a filler to improve the microstructure but also as an activator to promote pozzolanic reactions [95].

Nano-TiO_2 has proven very effective for the self-cleaning of concrete and provides the additional benefit of helping to clean the environment (Fig. 7). Nano-TiO_2 containing concrete acts by triggering a photocatalytic degradation of pollutants, such as NOx, carbon monoxide, VOCs, chlorophenols, and aldehydes from vehicle and industrial emissions [111,112]. A detailed discussion of the mechanisms of TiO_2-based photocatalysis can be found in [113]. "Self-cleaning" and "de-polluting" concrete products are already being produced by several companies for use in the facades of buildings and in paving materials for roads and have been used in Europe and Japan (e.g., the Jubilee Church in Rome, Italy; a 230-m long stretch of road surfaces outside of Milan, Italy). In addition to imparting self-cleaning properties, a few studies have shown that nano-TiO_2 can accelerate the early-age hydration of Portland cement [114], improve compressive and flexural strengths, and enhance the abrasion resistance of concrete [97,103]. However, it was also found that aging due to carbonation may result in loss in catalytic efficiency [115].

Nano-Fe_2O_3 has been found to provide concrete with self-sensing capabilities as well as to improve its compressive (Fig. 6) and flexural strengths [96,109]. The volume electric resistance of cement mortar with nano-Fe_2O_3 was found to change with the

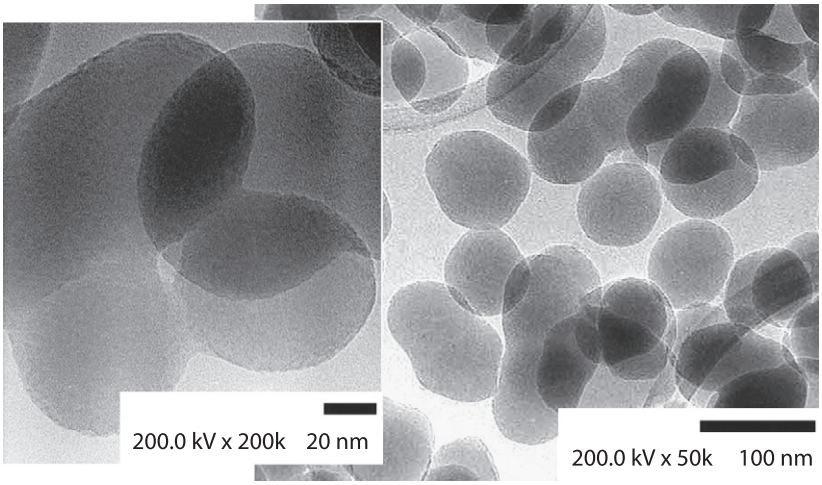

Fig. 5. Spherical nano-SiO_2 particles of uniform distribution observed using TEM. Courtesy of I. Flores and E.L. Cuellar (Universidad Autonoma de Nuevo Leon, Mexico).

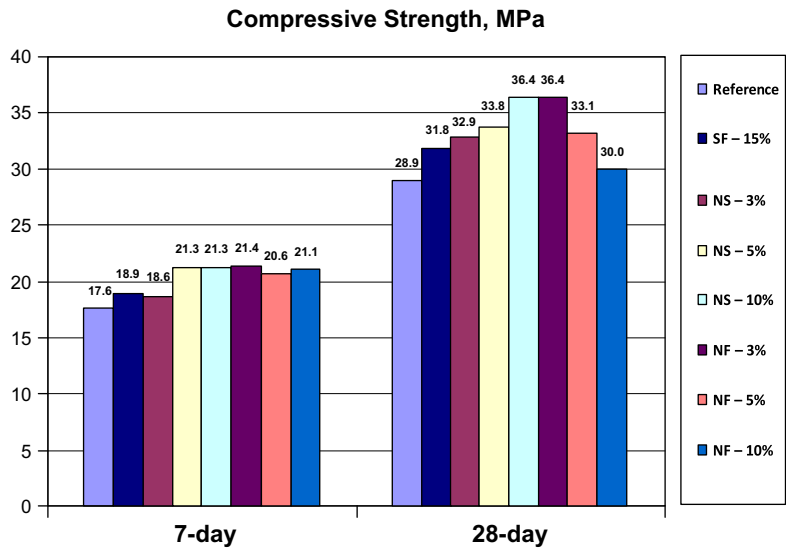

Fig. 6. Compressive strengths of cement mortars with different dosage of nano-SiO_2 (NS) and nano-Fe_2O_3 (NF) vs. reference portland cement and silica fume (SF) mortars. Adapted from [109].

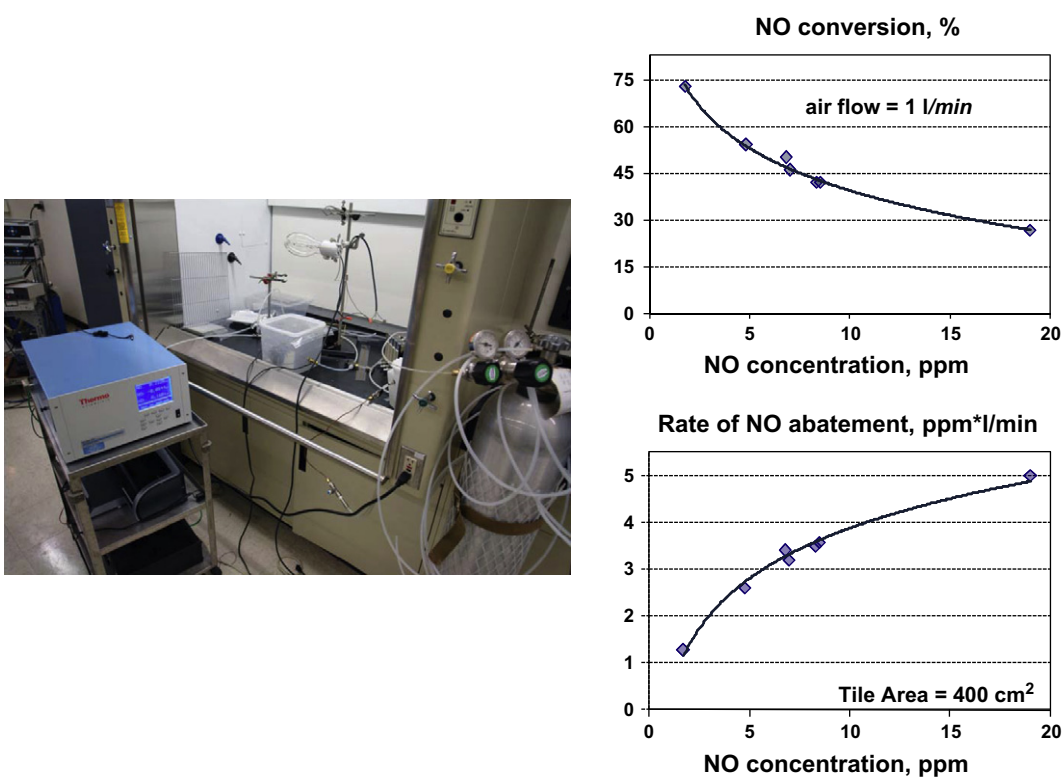

Fig. 7. Experimental setup for investigation of NO depollution effect (left) and performance of architectural concrete with nano-TiO_2 (right). Courtesy of A. Skliarov (University of Wisconsin-Milwaukee, USA).

applied load, demonstrating that mortar with nano-Fe_2O_3 could sense its own compressive stress. Such sensing capabilities are invaluable for real-time, structural health monitoring and for the construction of smart structures as they do not involve the use of embedded or attached sensors.

Nano-Al_2O_3 has been shown to significantly increase the modulus of elasticity (up to 143% at a dosage of 5%) but to have a limited effect on the compressive strength [104], and no novel properties have been reported.

Nanosized cement particles and nanobinders have been proposed as a way to improve cement performance while reducing carbon emissions [7]. Two avenues have been reported for creating nanosized cement particles: (i) high energy milling of conventional Portland cement clinker (top-down approach) [7] and (ii) chemical synthesis (bottom-up approach) [107]. Cement pastes made with nanosized cement particles have shown faster setting times and an increase in early compressive strength compared to pastes prepared with common, commercially available cement [107].

Recently, the concept of a nanobinder has been proposed [7]. This concept involves mechano-chemical activation that is obtained by inter-grinding cement with dry mineral additives in a ball mill [7,101,116]. Mechano-chemical modification of cement with high volumes of blast furnace slag has been shown to increase the compressive strength by up to 62% [116].

Nanoclay particles have shown promise in enhancing the mechanical performance, the resistance to chloride penetration, and the self-compacting properties of concrete and in reducing permeability and shrinkage [105,106,117,118]. Clay and the properties of clay that are important as admixtures to cement exist on the nanoscale. Individual, natural clay particles are micron and sub-micron in size, and the base structure of clay is composed of crystalline layers of aluminum phyllosilicates with thicknesses on the order of *ca*. 1 nm. Exfoliated layers are true nanoparticles. The effect of clay in cement is not a new subject and most applications utilize calcined clay (metakaolin, e.g., [119]). There has been a recent resurgence, however, focused on the possibilities of the nanoengineering of clays. Much of this work is looking at natural (non-calcined) clays. Because clay particles are typically highly hydrophilic, the control of water requirements in clay–cement composites is important. A reduction in the amount of water needed can be achieved by organic cation exchange modification, where organic cations replace sodium or calcium in the interlayer, reducing the hydrophilicity [106]. Chemical binding of PVA (polyvinyl alcohol) to exfoliated clay particles recently has been proposed to create linked clay particle chains that, when incorporated in cement, were shown to improve the post-failure properties of the material [120]. Additionally, non-modified, nanosized smectite clays were observed to act as nucleation agents for C–S–H and to modify the structure of C–S–H [121,122].

4.2. Hydrate hybridization

Modification of the structure of C–S–H at the nanoscale to create hybrid, organic, cementitious nanocomposites lately has received attention due to the interest in more sustainable concrete structures [19,39,40,48,123,124]. The layered structure and the propensity to have structural defects in the silicate chains (missing bridging tetrahedra) of C–S–H [35,125] offer the potential for creative manipulation by the insertion of a variety of organic molecules into the basic C–S–H structure. Three schemes for hybridizing, or incorporating "guest molecules" into, C–S–H have been proposed. The first scheme intercalates organic molecules into the C–S–H layer [126]. In the second, the "guest molecules" are covalently bound to the silicate structure [124]. The third scheme involves grafting the "guest molecules" at the defect sites of the silicate chain [39,40,48]. These schemes are already a source of debate, though relatively few publications are available in the literature. Work by Minet et al. [123] demonstrated that small sized organic groups directly linked to the silicate chains can be accommodated in the interlayer space of C–S–H. Phase separation was observed for larger sized or highly hydrophobic organic groups. Covalently bonded polymer–C–S–H hybrids, also, have been successfully prepared by Franceschini et al. [124] using organic chains containing T-silane groups that link to the silicate C–S–H chains with no modification of the internal structure of the C–S–H lamellas. Beaudoin et al. [39,40,48] reported the adsorption, or grafting, of HTDMA (hexadecyltrimethylammonium), PEG (polyethylene glycol), and methylene blue dye at sites of missing silica tetrahedra in C–S–H. However, partial intercalation into the interlamella space of the C–S–H could not be ruled out. Temperature and drying conditions were found to affect the process, and the effectiveness of the grafting was dependent on the Ca/Si ratio of the C–S–H [19]. To date, the focus has been on the synthesis of hybrid, organic C–S–H. Much research remains to be done to evaluate the mechanisms of hydration, mechanical performance, and long-term durability of these novel hybrids.

4.3. Nanoreinforcements: nanotubes/nanofibers

Carbon nanotubes/nanofibers (CNTs/CNFs) are potential candidates for use as nanoreinforcements in cement-based materials. CNTs/CNFs exhibit extraordinary strength with moduli of elasticity on the order of TPa and tensile strength in the range of GPa, and they have unique electronic and chemical properties [127–129]. CNTs/CNFs, thus, appear to be among the most promising nanomaterials for enhancing the mechanical properties of cement-based materials and their resistance to crack propagation while providing such novel properties as electromagnetic field shielding and self-sensing [130,131]. Single-wall CNTs (SWCNTs), multi-wall CNTs (MWCNTs), and CNFs are highly structured graphene ring-based materials with very large aspect ratios (of 1000 or more) [132] and very high surface areas. SWCNTs are single graphene cylinders and MWCNTs are multiple, concentric graphene cylinders coaxially arranged around a hollow core. Unlike CNTs, CNFs present numerous exposed edge planes along the surface that constitute potential sites for advantageous chemical or physical interaction. Compared to CNTs, vapor grown CNFs have a lower production cost (about 100 times lower than SWCNTs [133]) and are suitable for mass production. While CNTs/CNFs have been extensively studied in polymeric composites [134–136], their use in cement has, to date, remained limited. Most research efforts have focused on CNTs compared to CNFs and have been performed on cement pastes [130,137–141]. Only few investigations [131,142] have dealt with incorporation of CNTs into mortar. One of the main challenges is the proper dispersion of CNTs/CNFs into cement paste, partly due to their high hydrophobicity and partly due to their strong self-attraction. Incorporating the unique mechanical properties of CNTs/CNFs in cement composites has proven to be rather complex and to date mixed results have been obtained. Nonetheless, good interaction between CNTs/CNFs and cement phases has been demonstrated (Fig. 8), indicating the potential for crack bridging and enhanced stress transfer. A number of methods have been investigated to improve dispersion and to activate the graphite surface in order to enhance the interfacial interaction through surface functionalization and coating, optimal physical blending, and/or the use of surfactant and other admixtures.

Makar et al. [130] were among the first to indicate, using hardness measurements, that CNTs can affect early-age hydration and that a strong bond is possible between the cement paste and the CNTs. Their dispersion process consisted of sonication in isopropanol followed by cement addition, evaporation, and grinding, which produced cement particles coated with CNTs. Both MWCNTs and SWCNTs, when added to cement paste as a pre-mix with gum Arabic (a water-soluble gum used as a dispersing agent), were shown to increase the Young's modulus and hardness as determined by nanoindentation measurements but to worsen the mechanical properties when no dispersing agent was used [140]. A study by Cwirzen et al. [139] indicated that MWCNTs (0.006–0.042 wt.% loadings) introduced as a water suspension with added surfactant admixtures did not increase the compressive and bending strengths, though good dispersion was obtained. They also found the bonding between the MWCNTs and the cement matrix to be very weak, where, under tension, the MWCNTS were easily pulled off the matrix. Further work utilizing functionalization combined with "decoration" of MWCNTs with polyacrylic acid polymers [138] found improved dispersion, good workability, and increased compressive strength (nearly 50%) for loadings between 0.045 and 0.15 wt.%. In contrast, a study of the effect of CNT surface structure [143] comparing pristine MWCNTs, annealed MWCNTs, and carboxyl group functionalized MWCNTs found that flexural and

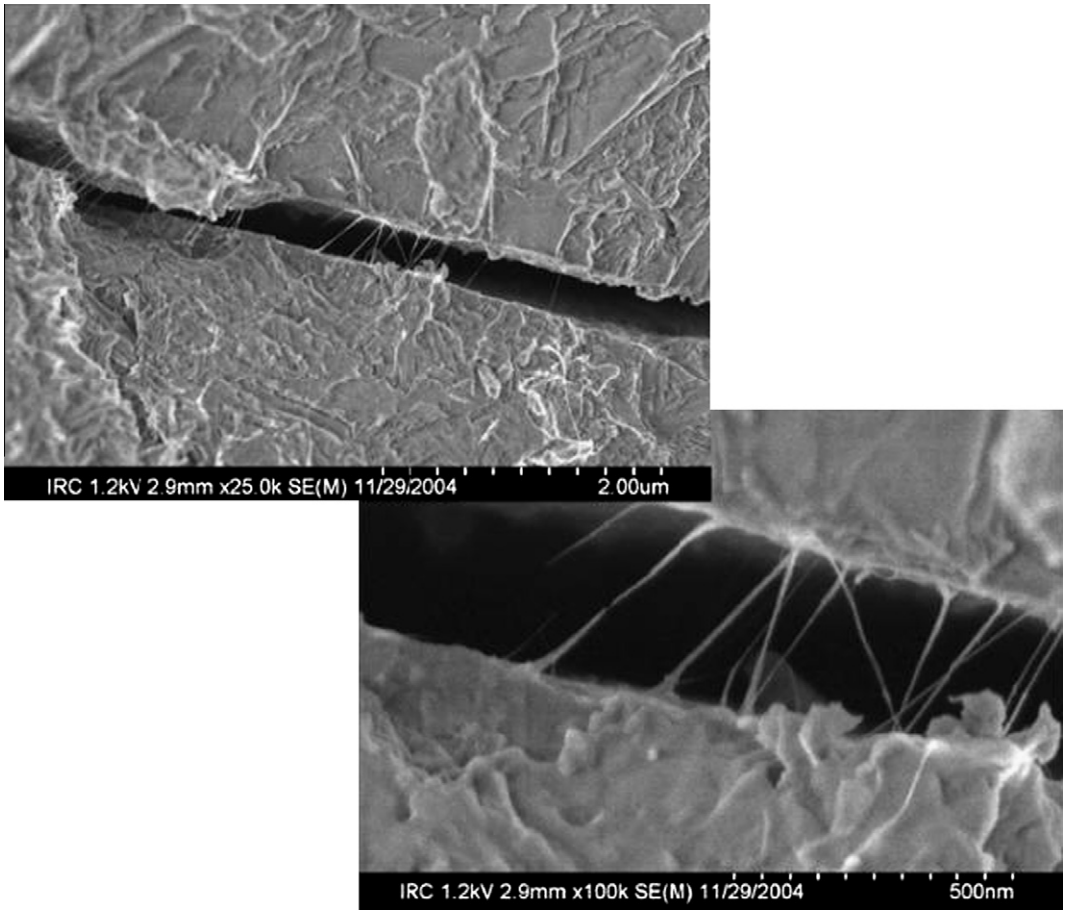

Fig. 8. Crack bridging observed in cement-CNT composites. Reprinted with permission from the proceedings of "The 3rd International Conference on Construction Materials: Performance, Innovations and Structural Implications" (Eds: N. Banthia, T. Uomoto, A. Bentur and S.P. Shah) [130].

compressive strengths were significantly reduced for functionalized MWCNTs while they were increased by 10–20% for the pristine and annealed MWCTs. The study used 0.5 wt.% MWCNTs that were first dispersed using acetone and ultrasonic vibration and a superplasticizer and a viscosity modifying agent that were added during the mixing stage. Lately, Shah et al. [137] found that, after dispersion in water using surfactant and ultrasonic energy, small amounts of CNTs (0.048 wt.% and 0.08 wt.%) produced a significant (50%) increase in the Young's modulus of cement pastes. Further investigation using nanoindentation found that the CNTs modified the C–S–H, increasing the quantity of high stiffness C–S–H, reinforcing the cement paste matrix at the nanoscale, and decreasing the porosity [141].

Investigations utilizing CNFs indicated that addition of silica fume (for 0.002–2 wt.% CNFs) [144], surface treatment of CNFs with nitric acid (for 0.5 wt.% CNFs) [12], and pre-dispersion in acetone (for 0.5 wt.% CNFs) [145] facilitated the dispersion of individual CNFs in Portland cement pastes, though pockets of agglomerated CNFs remained, and improved the interfacial interaction between the CNFs and the cement phases. While no change in compressive or splitting tensile strengths was observed, the presence of CNFs provided the composite with residual load-bearing capacity.

In mortar, a study using untreated CNTs and CNTs pre-treated with sulfuric and nitric acid found an increase in compressive strength up to 19% and in flexural strength up to 25% and that CNTs can decrease the electrical resistivity and improve the pressure-sensitive properties of mortars [142].

An alternative approach was recently developed by Cwirzen et al. [146] for a hybridized Portland cement that incorporated CNTs and CNFs grown in situ on the cement particles using a modified chemical vapor deposition method. The resulting hybrid cement, called Carbon Hedge Hog (CHH), allows for a composite containing up to 20% CNTs/CNFs. No significant change in the flexural strength was found; however, the electrical conductivity was increased by one order of magnitude.

These studies on CNTs/CNFs emphasize that resolving the issues related to dispersion and understanding the complexity of the fundamental mechanisms within the paste and the interactions at interfaces are key to optimizing the benefits of CNTs/CNFs addition to concrete.

5. Conclusions

The present paper reviews the current state of the field of nanotechnology in concrete and recent key advances. The potential of nanotechnology to improve the performance of concrete and to lead to the development of novel, sustainable, advanced cement-based composites with unique mechanical, thermal, and electrical properties is promising and many new opportunities are expected to arise in the coming years. The advances in instrumentation and computational science are enabling scientists and engineers to obtain unprecedented information about concrete, from the atomic through the continuum scale, and the role of nanoscale structures on performance and durability. This information is crucial for predicting the service life of concrete and for providing new insights on how it can be improved. New developments have taken place in the nano-engineering and nanomodification of concrete;

however, current challenges need to be solved before the full potential of nanotechnology can be realized in concrete applications, including proper dispersion; compatibility of the nanomaterials in cement; processing, manufacturing, safety, and handling issues; scale-up; and cost. Additionally, introduction of these novel materials into the public sphere through civil infrastructure will necessitate an evaluation and understanding of the impact they may have on the environment and human health. What is clear, however, is that, now, 50 years after Feynman's famous treatise, nanotechnology is changing the way scientists and engineers look at one of the world's oldest man-made materials, concrete.

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