

ACI 241R-17

Report on Application of Nanotechnology and Nanomaterials in Concrete

Reported by ACI Committees 236 and 241



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Report on Application of Nanotechnology and Nanomaterials in Concrete

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Report on Application of Nanotechnology and Nanomaterials in Concrete

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Members of Committees 236 and 241 thank J. Beaudoin, M. Rahman, J. Kim, L. Brown, C. Gay, and T. Sato for their contributions to this report.

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ACI 241R-17 was adopted and published January 2017.

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This report presents information on nanotechnology of concrete, including recent developments related to investigation of nanostructure and nanodesign of cement-based materials, the effects of nanoparticles, field applications, and health and environmental safety concerns related to the use of nanomaterials.

Keywords: biomimicry; carbon nanofibers; carbon nanotubes; nanobinder; nanoclay; nanoindentation; nanoparticles; nanosilica; nanotechnology; nanotitanium dioxide; superhydrophobic concrete.

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CHAPTER 1—INTRODUCTION AND SCOPE

1.1—Introduction

Nanotechnology is a multidisciplinary field of science and engineering focused on understanding and controlling matter at dimensions between 1 and 100 nanometers, where unique phenomena enable novel applications.

Nanotechnology was first introduced by Feynman (1960) and is rapidly becoming an interdisciplinary field; many developments have emerged in physics, chemistry, biology, and engineering in the study of various materials or substances at the nanoscale.

There are two main approaches in nanotechnology: 1) the top-down approach, in which larger structures are reduced in size to the nanoscale while maintaining their original properties without atomic-level control (for example, miniaturization in the domain of electronics), or deconstructed from larger structures into smaller, composite parts (top part of Fig. 1.1a); and 2) the bottom-up approach, also called molecular nanotechnology or molecular manufacturing, introduced by Drexler et al. (1991), in which materials are engineered from atoms, or molecular components, through a process of assembly or self-assembly (bottom part of Fig. 1.1a). While most contemporary technologies, including concrete, rely on the top-down approach, molecular nanotechnology holds great promise for advancement in materials and manufacturing, electronics, medicine and healthcare, energy, biotechnology, information technology, and national security.

Nanoscience and nanoengineering are commonly-used terms that describe nanotechnology applications in concrete (Sobolev and Ferrada-Gutiérrez 2005a; Scrivener and Kirkpatrick 2008; Scrivener 2009; Raki et al. 2009; Garboczi 2009). To date, nanotechnology applications and advances in the fields of construction and building materials have been inconsistent (Bartos 2009; Sanchez and Sobolev 2010; Sobolev and Sanchez 2012). Implementing nanotechnology into concrete on a commercial scale remains limited. Some research developments, however, have been successfully converted into marketable products. The main advances have been in nanoscience of cementitious and pozzolanic materials, providing an increase in the knowledge and understanding of basic phenomena in cement at the nanoscale (Scrivener and Kirkpatrick 2008; Scrivener 2009). Examples include structure and mechanical properties of the main hydrate phases, origins of cement cohesion, cement hydration, interfaces in concrete, and mechanisms of degradation. Recent innovations in instrumentation for observing and measuring at the nanoscale are providing a wealth of new and unprecedented information about concrete. This information is crucial for a better understanding of mechanisms and factors influencing performance requirements, as well as predicting the service life of concrete and providing new insights for improvement. Important summaries and compilations of nanotechnology in construction can be found in Sobolev and Ferrada-Gutiérrez (2005a), Bartos et al. (2006), de Miguel et al. (2006), Scrivener and Kirkpatrick (2008), Sobolev and Shah (2008), Sobolev et al. (2008), and Shah (2008).

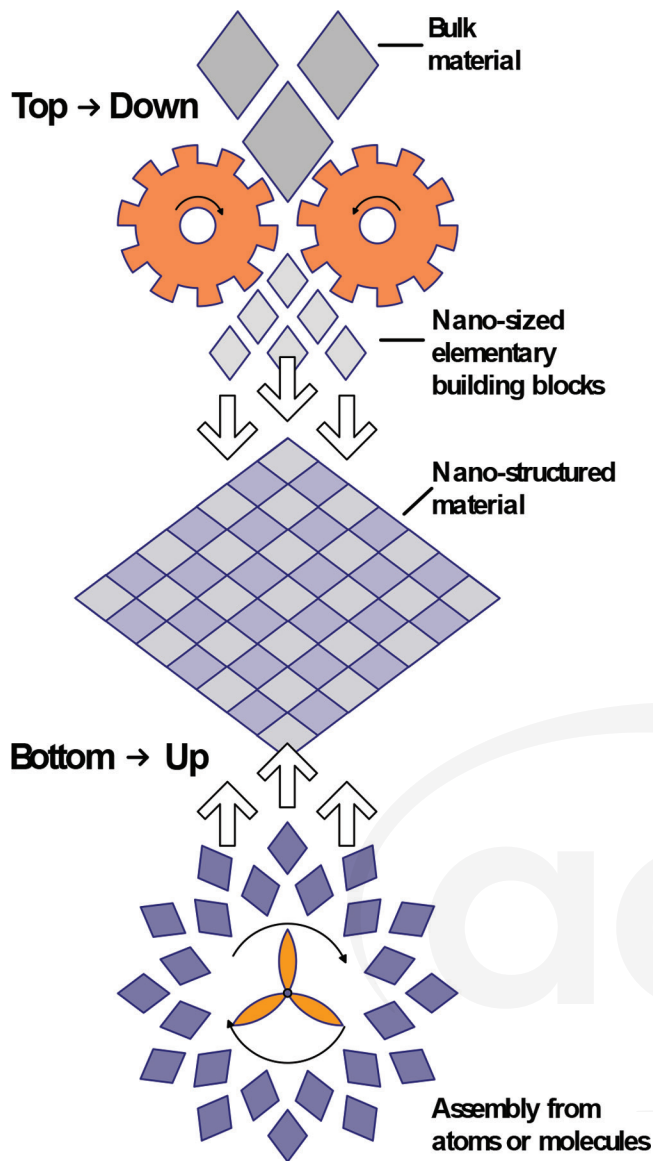


Fig. 1.1a—Illustration of the top-down and bottom-up approaches in nanotechnology (Sobolev and Ferrada-Gutiérrez 2005a).

and Sobolev (2010), Sobolev and Sanchez (2012), and Birgisson et al. (2012).

Concrete, the most ubiquitous construction material, is a “nanostructured, multiphase, porous composite material, composed of amorphous phases, nanometer- to micrometer-size crystals, and bound and free water” (Sanchez and Sobolev 2010). The properties of concrete exist at multiple length scales, nano to micro to macro (Fig. 1.1b). The properties of each scale derive from those of the next-smaller scale (Jennings et al. 2008; Sanchez et al. 2009). The amorphous phase, calcium-silicate-hydrate (C-S-H), is the phase that holds concrete together (Chong and Garboczi 2002), and is itself a nanostructured material (Fig. 1.1c).

Viewed from the bottom-up, concrete at the nanoscale is a composite of molecular assemblages, surfaces such as aggregates and fibers, and chemical bonds that interact through local chemical reactions, intermolecular forces,

and intra-phase diffusion. Properties characterizing this scale include surface properties and chemical bond properties such as type, length, strength/energy, and density. Structures of the amorphous and crystalline phases and the interphase boundaries originate from this scale. Properties and processes at the nanoscale define interactions that occur between particles and phases at the microscale, 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 (Garboczi and Bentz 1996, 1998; Xi et al. 2000; Jennings et al. 2008; Scrivener and Kirkpatrick 2008; Sanchez et al. 2009).

1.2—Scope

This report provides information for those involved in concrete design and construction so they are familiar with the factors involved in the effective use of nanomaterials and nanotechnology. This document is not intended as a primary reference source for researchers. Rather, it is aimed at engineers and architects who wish to gain further understanding of the effects of nanomaterials and nanoadditives being used or proposed for application in concrete.

Application of available technology is demonstrated for a range of nanoconcrete structures to show that technological risks are at a known and acceptable level and high industry standards maintained. An overview reports on the main developments in the fields of nanotechnology and nanoscience that are related to concrete, along with their implications and key findings. Factors affecting performance of fresh and hardened concrete are discussed to enable those involved in the evaluation and formulation of concrete mixtures to determine the effects of these factors.

The potential of nanotechnology to improve concrete performance can lead to the development of novel, sustainable, advanced cement-based composites with unique mechanical, thermal, and electrical properties. New developments have already taken place in nanoengineering and nanomodification of concrete. Current challenges, including proper dispersion, compatibility of the nanomaterials in cement, processing, manufacturing, safety, handling issues, and cost all need to be solved before the complete potential of nanotechnology can be realized in concrete applications. Additionally, introduction of these novel materials into the construction practice requires an evaluation and understanding of their potential impact on the environment and human health.

CHAPTER 2—NOTATION AND DEFINITIONS

2.1—Notation

A	= aluminum oxide (Al_2O_3)
A_i	= area of indentation impression, μm^2
C	= calcium oxide (CaO)
CaCO_3	= calcium carbonate
CH	= calcium hydroxide
C/S	= the molar or mass ratio of calcium oxide (CaO) to silicon dioxide (SiO_2)
C-S-H	= amorphous calcium silicate hydrate phase

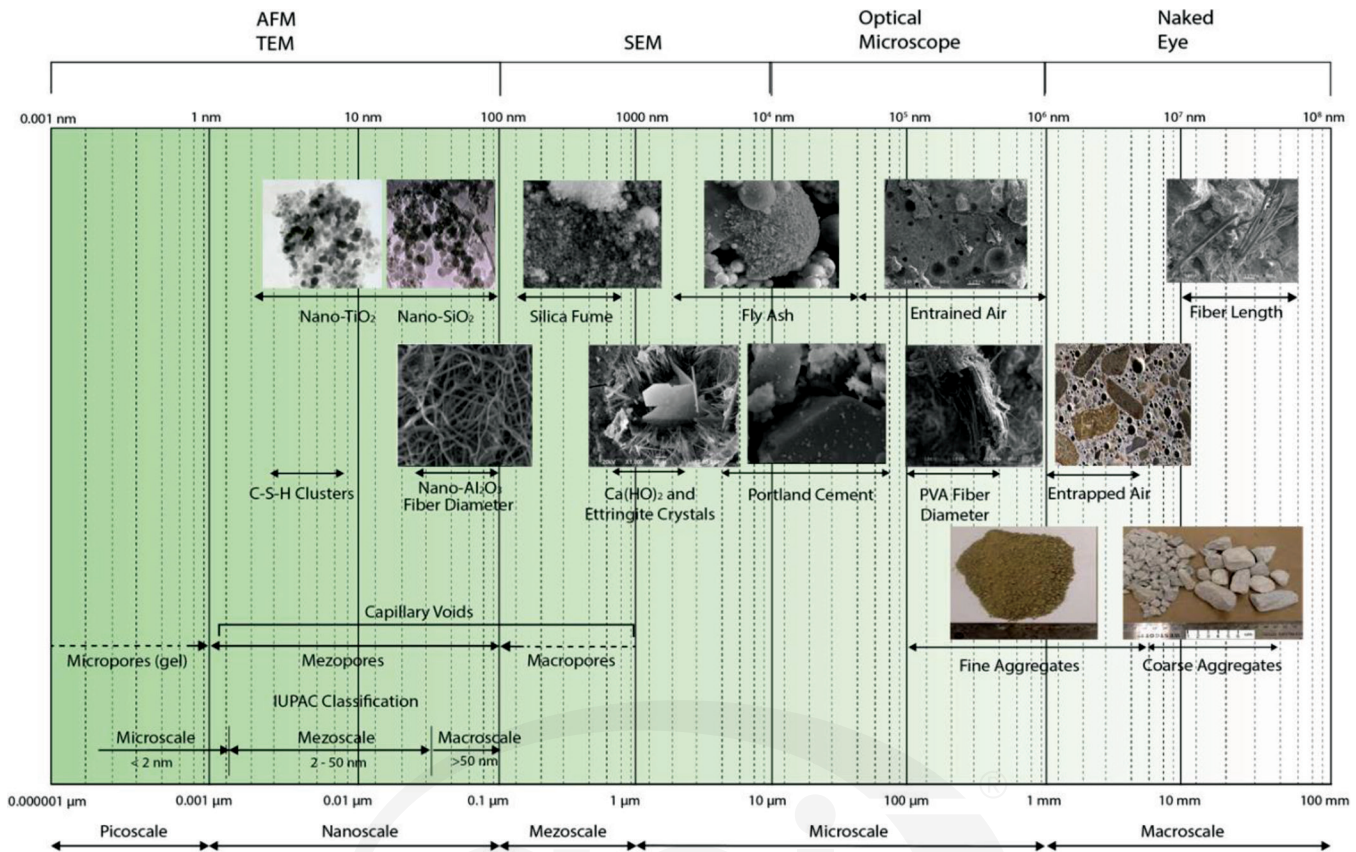
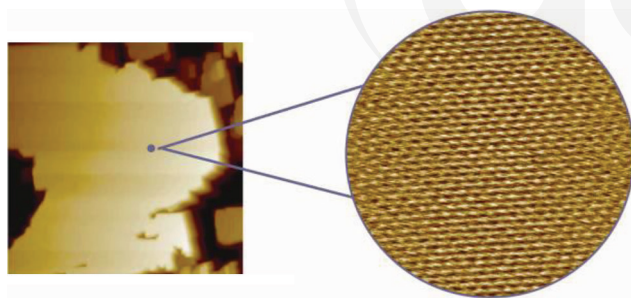


Fig. 1.1b—The multiple length scales related to concrete technology (Sobolev 2016).



Crystallized C-S-H
2 x 2 μm²

Atomic resolution
20 x 20 nm²

Fig. 1.1c—Nanoscale structure of C-S-H crystallized on calcite substrate as revealed by atomic force microscope (AFM) (Sobolev and Ferrada-Gutiérrez 2005a).

- C_3A = tricalcium aluminate
 C_3S = tricalcium silicate, alite
 E = Young's modulus, GPa
 E' = storage modulus, GPa
 E_i = Young's elastic modulus of the indenter, GPa (for diamond, $E_i = 1141$ GPa)
 E_r = reduced modulus of concrete, GPa
 F = iron oxide or ferric oxide (Fe_2O_3)
 H = concrete hardness, Pa
 h_a = displacement of surface at perimeter, nm
 h_e = elastic impression depth, nm
 h_p = contact indentation depth, nm

- h_r = residual impression depth, nm
 h_t = total impression depth, nm
 k = stiffness of probe cantilever ($k = 3EI/L^3$), N/m
 k^* = contact stiffness, N/m
 $MgAl_2O_4$ = magnesium aluminum oxide
 $m\%$ = percent by mass
 NO_x = nitrogen oxide
 P = load, N
 P_t = maximum indentation load, mN
 S = silica dioxide (SiO_2)
 S_c = contact stiffness or compliance
 $\tan\delta$ = internal friction
 TiO_2 = titanium dioxide
 $vol\%$ = percent by volume
 $ZnFe_2O_4$ = zinc iron oxide
 β = coefficient for Berkovich indenter (= 1.034)
 $\beta-C_2S$ = β -dicalcium silicate, belite
 λ^* = eigenvalue
 Θ = contact angle, degrees
 ν_c = Poisson's ratio of concrete
 ν_I = Poisson's ratio of indenter

2.2—Definitions

ACI provides a comprehensive list of definitions through an online resource, "ACI Concrete Terminology" (https://www.concrete.org/portals/0/files/pdf/ACI_Concrete_Terminology.pdf). Definitions provided herein complement that resource.

biomimetic (bionics)—approach that applies biological methods and systems found in nature to the study and design of engineering systems and modern technology.

bottom-up—approach that seeks to arrange smaller components into more complex assemblies (for example, classical chemical synthesis).

compliance—ability of an object to yield elastically when a force is applied, defined by the ratio of strain over stress.

contact angle (thermodynamic)—angle that a liquid makes with a solid in a given vapor environment and the interior angle is defined by the tangent planes of: 1) liquid-solid contact area; and 2) liquid-vapor surface, both planes being erected at the three-phase junction between vapor, liquid, and the solid.

engineered nanoparticles—nanoparticles manufactured to have specific properties or a specific composition.

functionalization—approach that develops components of a desired functionality (the particular set of properties for which material is designed) without regard as to how they might be assembled.

loss modulus—describes the energy dissipated as heat, the viscous response or the time-dependent part of the material response in viscoelastic materials.

nanocement—portland cement or binder material with particles less than 100 nanometers in size.

nanoeengineering—the techniques of manipulating a structure at the nanoscale to develop a new generation of tailored, multifunctional, cementitious composites and nanocement with superior performance and durability; also called **nanomodification**.

nanoinindentation—test method to determine near-surface mechanical properties of a material, which involves indenting the specimen with a diamond tip to a specific load in the range of nano-to milli-Newton and unloading the specimen, leaving an indentation impression with nanometer depth resolution.

nanomaterial-modified cementitious composites—materials that result from either the incorporation of nano-sized materials, including nanoparticles and nanoobjects (for example, nanotubes) into concrete or by grafting of molecules onto cement particles, cement phases, aggregates, and additives to promote specific interfacial interactions and provide surface functionality.

nanomaterials—materials having unique properties arising from their nanoscale dimensions.

nanoparticles—particles with three dimensions at the nanoscale.

nanoscale—matter having one or more dimensions less than 100 nanometers (Fig. 1.1b).

nanotechnology—science related to understanding and control of matter at the nanoscale, where unique phenomena enable novel applications.

overhydrophobic—property of water-repellent surfaces with a water contact angle between 120 and 150 degrees.

reduced modulus—the elastic modulus measured from indentation experiments as it represents a combined elastic modulus of the indented material and the elastic modulus of the indenter tip; as indenter tips (typically diamond) have

relatively high elastic modulus, the measured value is very close to the elastic modulus of the indented material.

storage modulus—describes the stored energy, the elastic response or the time-independent part of the material response in viscoelastic materials.

superhydrophobic—property of water-repellent surfaces with a water contact angle above 150 degrees.

top-down—approach that seeks to create smaller devices by using larger ones to direct their assembly.

CHAPTER 3—INVESTIGATION AND MODELING OF NANOSTRUCTURE AND HYDRATION MECHANISMS

3.1—Investigation of nanostructure

3.1.1 Calcium silicate hydrate (C-S-H)—The hydration of portland cement results in the formation of various products ranging from a few nanometers to several micrometers in size. The nature of these products may vary with time at different stages of hydration. Calcium silicate hydrate (C-S-H) is the dominant phase among the hydration products that is produced during the reaction between the calcium silicate phases and water, and forms up to 60 volume percent of the hydrated cement paste (Mehta and Monteiro 2006). C-S-H primarily contributes to properties of the hardened concrete such as strength and volume stability. The nanostructure of this hydrated phase has not been fully resolved, and the debate over its structural properties continues. Resolving the structure of this material at the nanoscale is an essential part of understanding and predicting its behavior, as is its importance in the context of modification and development of novel C-S-H systems. This section will address some of the significant aspects of the nature of C-S-H.

3.1.1.1 Formation of C-S-H—C-S-H is produced along with the calcium hydroxide in the chemical reaction of the calcium silicate phases with water. This type of C-S-H is generally referred to as the C-S-H gel. Although extensively studied, the hydration of portland cement has many ambiguous features. There are several theories to describe the hydration mechanism of calcium silicate compounds in portland cement (Odler 1998; Garraut and Nonat 2001; Gartner et al. 2002; Bullard et al. 2011). Makar and Chan (2008) suggest that a hydrated calcium silicate phase formed primarily during the preinduction period has low lime content and different anion structure compared to a more stable C-S-H existing at later times.

C-S-H can also be prepared synthetically during the reaction between lime and silica in excess water or by hydrothermal co-precipitation in the presence of calcium salts (for example, calcium nitrate) with sodium silicate. The composition of the C-S-H can be more readily controlled in these methods. Several types of C-S-Hs can be formed through synthetic methods (depending on the C/S ratio, pH, and reaction temperature) such as 1.4 nm tobermorite, jennite, C-S-H(I), and C-S-H(II). These materials are more ordered than the cement-derived C-S-H gel. They have relative crystalline structure and have been extensively studied.

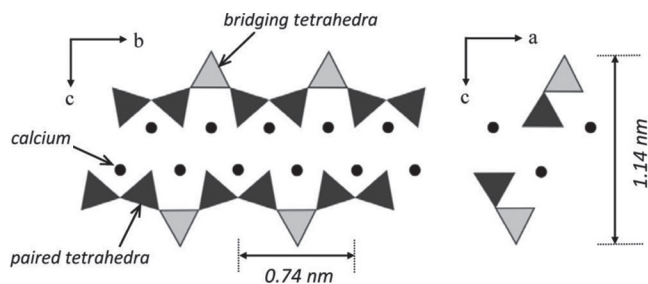


Fig. 3.1.1.2—Simplified molecular structure of a single sheet of the tobermorite-like material (after Taylor [1997] and Raki et al. [2010]).

analogs of the C-S-H gels (Taylor 1997; Tennis and Jennings 2000; Jennings 2000; Foley et al. 2012).

3.1.1.2 Characteristics of C-S-H—The C-S-H gel is a nearly amorphous material that does not have an ordered structure at length scales greater than 100 nm (Fig. 1.1c). The C-S-H gel is structurally related to the more-ordered synthetic materials such as tobermorite and jennite. In these systems, layers of CaO are flanked on both sides by chains of silicate tetrahedra. A stacking of these sheets with water molecules, hydroxyl groups, and calcium ions in between forms C-S-H. Figure 3.1.1.2 shows a schematic of the tobermorite-like layer. The broad range of stoichiometries in C-S-H can be obtained by omission of the bridging tetrahedra, by further defects in the silicate structure, and by the inclusion of more calcium ions in the interlayer region (Cong and Kirkpatrick 1996; Chen et al. 2004; Nonat 2004; Richardson 2004).

The C/S ratio in C-S-H is one of the main parameters that defines and controls the properties of a C-S-H system. This value varies from 1.2 to 2.1 in hydrated silicate phases of portland cement and has an average of approximately 1.75 (Richardson 1999). The C/S ratio can be decreased through decalcification of C-S-H gel in distilled water or ammonium nitrate solution (Alizadeh 2007). Synthetic C-S-H systems cover a wider range of C/S ratios. The C-S-H systems may be divided into low and high lime content categories partitioned by the C/S ratio of approximately 1.1, where chemical and physical properties change noticeably (Nonat 2004; Alizadeh et al. 2007; Kim et al. 2013). The main feature in C-S-H that is related to its C/S ratio is the mean length of silicate tetrahedra chains, which is a measure of polymerization extent. Longer silicate chains exist in low-C/S ratio C-S-H materials. The abundance of Si-OH and Ca-OH links also depends on this parameter. Experimental investigations by Alizadeh (2007) and Begaye et al. (2013) demonstrated that lowering the C/S ratio results in increasing stiffness and reducing creep of synthetic C-S-H of similar porosity levels. This was attributed to the increased level of silicate polymerization (for example, producing longer silicate chains) that tends to stiffen C-S-H. Note that C-S-H produced in hydration of portland cement is similar to high C/S ratio ≈ 1.5 to 1.8 (Foley et al. 2012).

The state of water in a C-S-H system is also vaguely defined. Water can be present within the interlayer structure of C-S-H, either in the form of H_2O or OH^- . Water

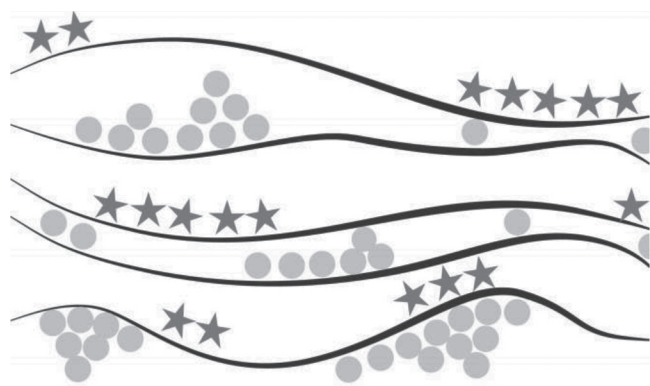


Fig. 3.1.1.3—Schematic physical model proposed by Feldman and Sereda (1968) for C-S-H in the hydrated portland cement. Dark lines are tobermorite-like sheets, circles are physically adsorbed water, and crosses are interlayer water.

molecules can also be physically adsorbed on the surface of solid particles. Finally, the capillary pores between C-S-H clusters can contain free water. Distinction of water states is not simple, as the energy by which the water molecules are held in C-S-H varies over a wide range and may overlap for different locations (Ramachandran et al. 1981).

3.1.1.3 Nanostructure of C-S-H—Early investigations on the hydrated cement products were conducted using mainly surface area and density measurements, and weight and length change isotherms to characterize this material (Taylor 1997; Ramachandran et al. 1981). In the last few decades, many new aspects of the C-S-H have been revealed with the advancements in the analytical techniques and application of new methods, such as nuclear magnetic resonance (NMR) spectroscopy (Nonat 2004). A clearer image of the C-S-H at the nanolevel has now emerged.

The nanostructure of C-S-H is not fully resolved, although it has been the subject of much research. Several models have been suggested, ranging from gel-like to layer-like to describe the physical properties of C-S-H. One of the first physical models was proposed by Powers and Brownyard (1946-1947), in which C-S-H was depicted as a gel-like material. In this model, the gel particles are held together mainly by Van der Waals forces, and the space between them is called gel porosity, which is accessible by water or other small molecules. A more comprehensive model was developed later by Feldman and Sereda (1968) based on extensive experimental studies of hydrated cement systems (Feldman and Sereda 1968; Jennings 2008). The role of water in this model is explained in more detail. The main feature of their model (Fig. 3.1.1.3) is concerned with the layered nature of the C-S-H. Structural roles assigned to the interlayer water explain irreversible behavior during the adsorption and desorption processes. Changes in the mechanical properties of C-S-H related to water content can be easily described using this model.

Jennings' colloid model features globules of approximately 5 nm in diameter for C-S-H and proposes the existence of intra-globular pores (IGP) and small gel pores

(Jennings 2008). The viability of using a layered model for the C-S-H in cement paste was more plausibly investigated using a helium inflow technique as a nanostructural probe along with the X-ray diffraction (XRD) method (Alizadeh et al. 2007). Changes at the nanolevel in the properties of C-S-H(I), a layered semi-crystalline material, were followed after the removal of adsorbed and interlayer water. The helium inflow results are analogous to those for C-S-H in hydrated portland cement. They are best explained by a layered model for C-S-H in cement paste.

3.1.2 Other cementitious nanostructures—There are limited reports on nanocharacteristics of other cementitious nanostructures. Recent efforts on nanocharacteristics of calcium hydroxide (CH) phase have been reported. Work by Beaudoin (2000) on microcharacterization of CH provides key information about CH crystals.

3.2—Nanocharacterization

3.2.1 Nanoindentation—Nanoindentation can be used to test microhardness (or microstrength). The test can also provide well-defined mechanical parameters such as Young's elastic modulus of the interfacial zone and C-S-H that can be used for modeling the composites. Studies using depth-sensing microindentation have been reported by Zhu et al. (2004), Nemecek et al. (2006), Sonebi (2008), Mondal et al. (2008), and Foley et al. (2012). The depth-sensing microindentation and nanoindentation method was first successfully used for microstrength testing and fiber push-in testing to assess interfacial and bond properties in glass fiber-reinforced cementitious composites (Zhu and Bartos 1997). Since then, significant advances have been made in improving the micro/nanoindentation test methods and in theoretical analysis of the test data (Oliver and Pharr 1992; Trtik and Bartos 1999). The depth-sensing microindentation and nanoindentation methods now offer great advantages over the conventional Vickers microhardness testing.

One challenge in identifying the nanoscale characteristics of materials is the preparation of a specimen that can be tested to identify the material properties at this length scale. There is an obvious difficulty in creating a nanoscale specimen that can be tested under tensile or compressive stresses. However, surface probing using depth-sensing indentation (hardness) tests were used as a nondestructive test for metals for the last 100 years (Mehta and Monteiro 2006). Indentation depends on pushing a hard indenter, typically diamond-based, into the surface of the material and recording the load and indentation depth. Quantitative analysis of the material response during unloading in indentation can reveal almost all the elastic mechanical and fracture characteristics of the material, including its hardness, stiffness, and toughness. By considering material response with time, other characteristics such as creep compliance and fatigue resistance can also be identified (Fischer-Cripps 2004). The loading and unloading process and the parameters used in nanoindentation analysis are schematically shown in Fig. 3.2.1a. (Oliver and Pharr 1992). Recent advances in hardware control and load and displacement measurements at the nanoscale made

nanoindentation a technology that is both robust and reliable for material mechanical characterization.

Nanoscale investigations of cement have enabled better understanding of the physical properties of cementitious materials. Moreover, it has been demonstrated that nanoscale elastic moduli and hardness values are consistent with values obtained at the microscale (Velez et al. 2001), confirming the possible correlation across scales. Nanoindentation of cementitious materials, especially of the C-S-H phase, was reported by several researchers (Acker 2001; Constantinides and Ulm 2004; Mondal et al. 2007; Qiao et al. 2006; Sorelli et al. 2008) and was strongly correlated to micromechanical properties and microstructure of concrete (Zhu et al. 2004, 2007; Sonebi 2008; Reinhardt et al. 2009). Although the nanoindentation technique provides knowledge at the nanoscale in indenting depth, nanoscale investigation in spatial resolution is sometimes required. Considering the residual mark of nanoindentation larger than 1 by 1 μm , the result is affected by the pore phase as well as solid hydrates because the capillary pores are distributed within the range of 10 nm to 10 μm . The mechanical properties of pure hydrates, such as C-S-H, cannot be measured accurately by nanoindentation; however, inverse analysis, or grid indentation with the aid of statistical analysis, can be used to provide a good estimate of those properties (Constantinides and Ulm 2004). This report uses the term “measuring” in the following paragraphs to indicate providing accurate estimates using a large number of nanoindentations.

For example, using depth-sensing microindentation, Sonebi (2008) studied the micromechanical properties such as Young's elastic modulus and microhardness of the interfacial transition zone (ITZ) around the aggregate-matrix interface for underwater concrete (UWC) and around steel reinforcement for self-consolidating concrete (SCC). Scanning electron micrograph of nanoindentation of cement paste and the micromechanical properties, represented by Young's modulus ITZ at top and bottom of steel bar in concrete, are shown in Fig. 3.2.1b and 3.2.1c. Another method, an atomic force microscope (AFM), was effectively used because of its accurate positioning capabilities (S  ez de Ibarra et al. 2006). Mondal et al. (2008), who studied techniques to image the nanostructure of hardened cement paste using an AFM and nanoindentation to determine Young's modulus of cement paste (Fig. 3.2.1d), reported that AFM is a promising technique to image and characterize cement paste microstructures and nanostructures. Mondal et al. (2008) reported that Young's modulus of C-S-H varied widely from 10 to 35 GPa and for residual cement particles ranged from 100 to 130 GPa.

Although there is extensive investigation of hydrated cement paste using nanoindentation (Constantinides and Ulm 2004; Mondal et al. 2007), the nanoindentation of pure C-S-H phase is rarely studied (Alizadeh 2007; Foley et al. 2012). The relation between the chemical composition of the C-S-H and its mechanical response was recently examined (Kim et al. 2013; Begaye et al. 2013). The intrinsic modulus of elasticity of C-S-H appears to be independent of its stoichiometric ratio and degree of polymerization (Beaudoin and Feldman

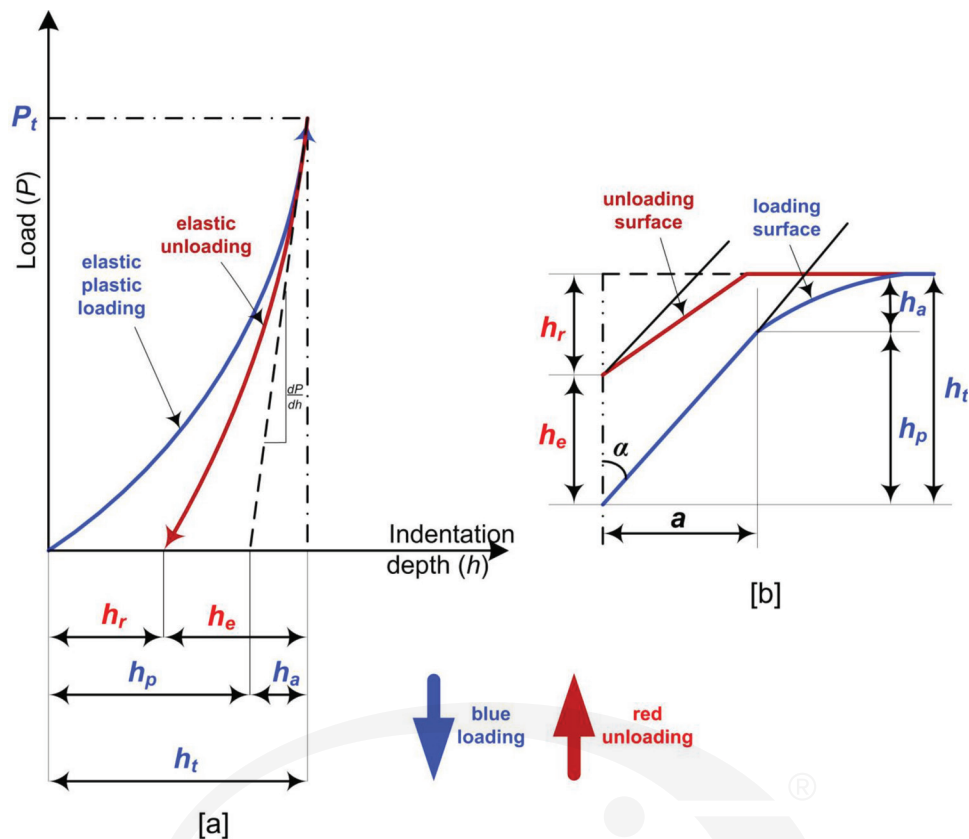


Fig. 3.2.1a—Schematics of loading and unloading in nanoindentation: (a) loading and unloading curves; and (b) loading and unloading of nanoindentation surfaces (Begaye et al. 2013). Indentation depths: h_t is total depth at load P_t ; h_e is elastic depth rebound at unloading; h_r is residual impression depth after unloading; h_a is the displacement of the surface at the perimeter; and h_p is the contact indentation depth.

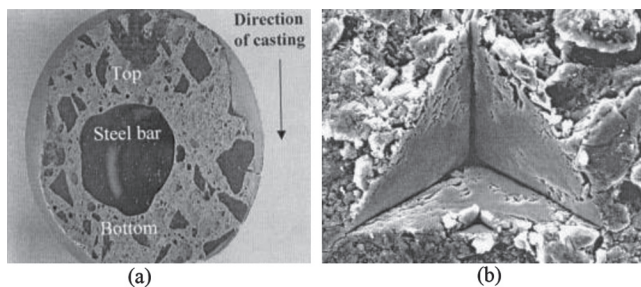


Fig. 3.2.1b—(a) Specimens for studying the ITZ (Zhu et al. 2004); and (b) scanning electron microscope (SEM) image of a typical indent (Sonebi 2008).

1986). Two types of C-S-H, both low and high density, are suggested (Constantinides and Ulm 2004; Mondal et al. 2007). The low and high density C-S-H phases, with a volume fraction (of total C-S-H) of 30 and 70 percent in hydrated portland cement, have a mean stiffness of approximately 21.7 and 29.4 GPa, respectively. AFM nanoindentation was used to measure the Young's elastic modulus of C-S-H prepared on the surface of a calcite crystal in sodium silicate solution (Plassard et al. 2004).

3.2.2 Nano compliance measurement—Two approaches were suggested for measuring compliance of the different cement phases (C-S-H and CH) at the nanoscale. These

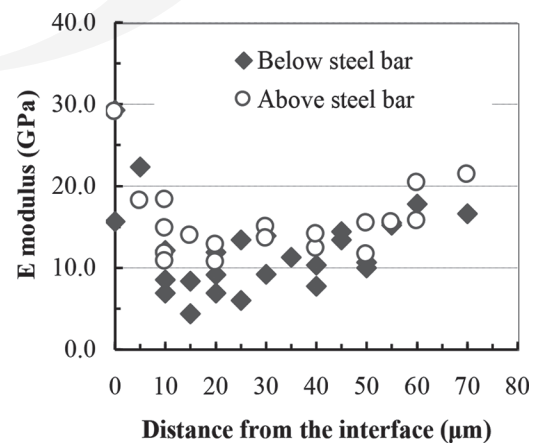


Fig. 3.2.1c—Profiles of Young's (E) modulus in interfacial transition zone (ITZ) at top and bottom of steel bar (Sonebi 2008).

include measuring nanocreeep using the nanoindentation test method or the continuous compliance method. In nanoindentation test, the load is ramped up to its maximum value and the maximum load is kept constant for dwell time so creep takes place. The nanoindentation depth will increase during dwell time and this change in nanoindentation depth can be used to calculate nanocreeep compliance. Creep

calculations shall account for the fact that the increase in nanoindentation will change the indentation imprint area and, thus, creep takes place under decreasing stress (Begaye et al. 2013). Nanocrep experiments of C-S-H showed significant influence of water on the mechanical behavior of C-S-H (Reda Taha et al. 2008). Wet and dry measurements were performed as shown in Fig. 3.2.2, where it is obvious that significant additional creep takes place in C-S-H when measured under wet conditions. An alternative method to measure nanocrep is known as continuous compliance measurements. This method of measurement is based on the fact that the contact stiffness (S), or compliance, can be measured during the loading portion of the nanoindentation test using the continuous stiffness measurement (CSM) technique described by Li and Bhushan (2002). This is done by imposing a harmonic force that is added to the nomi-

nally increasing load P on the indenter. The displacement response of the indenter at the excitation frequency and the phase angle between the indenter load and the specimen response are measured continuously as a function of depth. Solving for the in-phase and out-of-phase portions of the response yields an explicit determination of contact stiffness S as a function of the indentation depth. Creep compliance of C-S-H measured using continuous compliance method has also been reported (Reda Taha et al. 2008).

3.2.3 Ultrasonic atomic force microscopy (AFM)—

Another approach for direct measurement is offered by ultrasonic atomic force microscopy (AFM). In general, for an AFM probe cantilever shown in Fig. 3.2.3(c), and idealized in Fig. 3.2.3(d), the equation of motion is expressed in Eq. (3.2.3) as

$$\frac{k^*}{k} = \frac{1}{3}(\lambda^* L)^3 \frac{1 + \cosh \lambda^* L \cos \lambda^* L}{\sinh \lambda^* L \cos \lambda^* L - \cosh \lambda^* L \sin \lambda^* L} \quad (3.2.3)$$

where k is the stiffness of the probe cantilever ($k = 3EI/L^3$), as defined in Fig. 3.2.3(d). The notation k^* is contact stiffness, which is the stiffness of the surface that the AFM probe is in contact with, with L as the probe cantilever length. By changing the frequency of the PZT actuator supporting the sample, the contact stiffness of the sample can be identified when resonance is achieved. The resonant frequency is used to determine the eigenvalue (λ^*), which in turn is used to determine the contact stiffness k^* from Eq. (3.2.3). Like the nanoindentation analysis, which is based on the Hertz contact theory, the reduced modulus and Young's modulus of cement paste are calculated from the measured contact stiffness. Because spatial resolution is governed by indenting or contact cross-sectional area, the ultrasonic AFM produces a comparatively small size of the contact—generally approximately 20 nm diameter—which is identical to that for a contact-mode AFM. Therefore, this technique is applicable for a more delicate, localized measurement (Kolosov and Yamanaka 1993; Dinelli et al. 2000; Cuberes et al. 2001; Rabe et al. 2000, 2002; Hurley et al. 2005; Huey 2007).

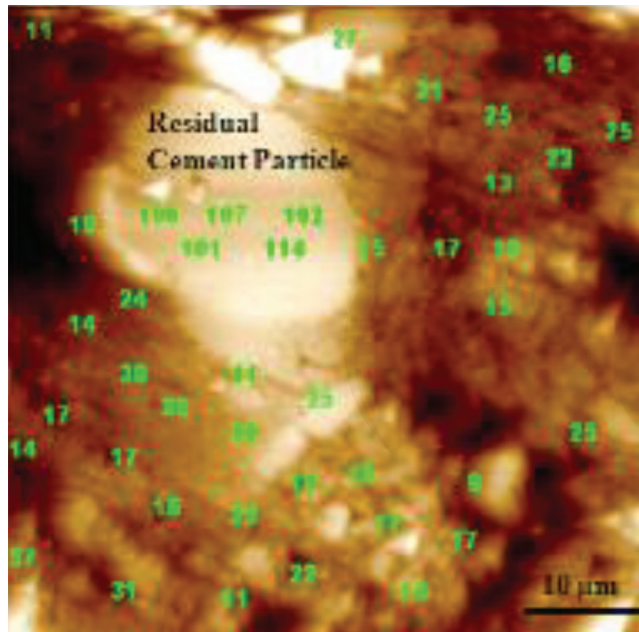
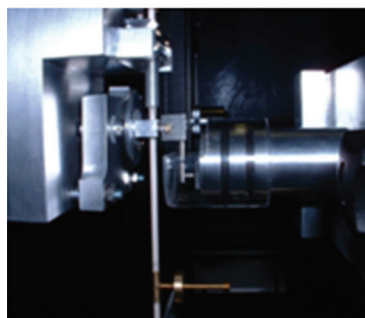
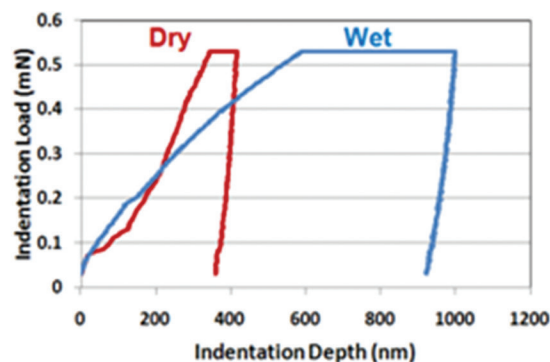


Fig. 3.2.1d—Image of gel with unhydrated particle, indicating the location of indents and E values (GPa) (Mondal et al. 2007).

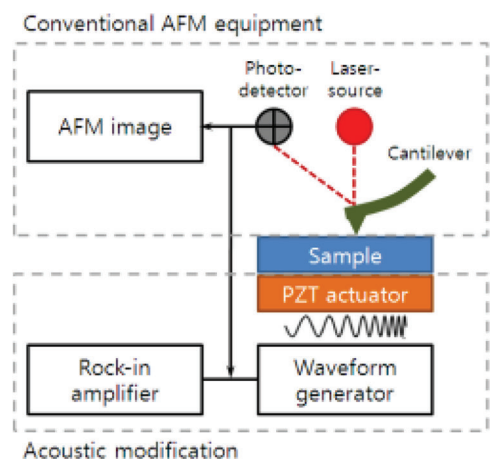


(a)

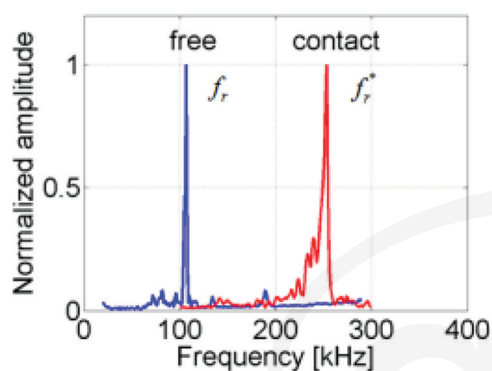


(b)

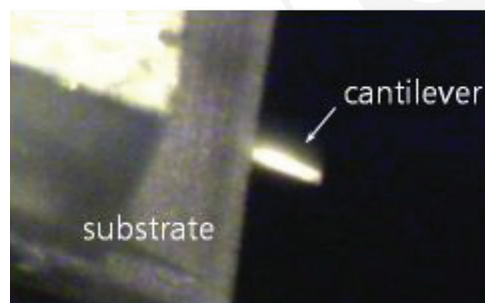
Fig. 3.2.2—(a) Examining significance of drying on nanoindentation of cement paste (wet and dry stage in nanoindentation); and (b) load-indentation curves of cement paste under wet and dry conditions (Reda Taha et al. 2008).



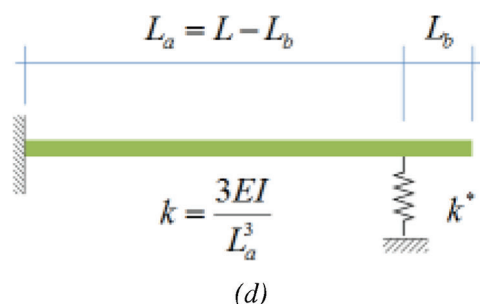
(a)



(b)



(c)



(d)

Fig. 3.2.3—Atomic force acoustic microscopy (AFAM): (a) schematics of experimental setup; (b) measured spectrum; (c) probe cantilever used; and (d) idealized model for cantilever resonance (Kim et al. 2010a,b).

Kim et al. (2010a,b) applied atomic force acoustic microscopy (AFAM), one of the ultrasonic AFM techniques, for investigation of hydrated cement paste. AFAM employs the resonant frequency of the cantilever contacted with a sample, where the contact-resonant frequency depends on the sample stiffness. Figure 3.2.3(a) through 3.2.3(d) provides a schematic of the experimental setup and measured spectrum. While the AFM probe is in contact with the sample, a piezo transducer-actuated frequency-modulated vibration and the corresponding dynamic motion of the AFM probe are analyzed with the use of a lock-in amplifier. The contact-resonant frequency of the AFM probe cantilever, approximately 250 kHz in the figure, depends on the contact stiffness k^* . Results by ultrasonic AFM were comparable to that obtained by nanoindentation and the hydrates have the similar range of Young's elastic modulus, 10 to 35 GPa (Kim et al. 2010a,b).

3.2.4 Other characterization techniques—X-ray diffraction techniques can provide only a very limited indication of C-S-H nanostructure. The XRD peaks of synthetic C-S-H are better defined and employed to study the crystalline structure of these materials. Some analytical tools, such as nuclear magnetic resonance (NMR) spectroscopy, do not require a long-range order and can probe the local environment near the atoms at the nanolevel. One example is Si MAS NMR spectroscopy, which provides the evidence of silicate connectivity/polymerization and, therefore, is used to study the significance of different admixtures or environments on cement hydration. Si MAS NMR is the most widely employed method to study the silicate structure of C-S-H (Nonat 2004; Begaye et al. 2013).

3.3—Modeling of cementitious nanostructures

Molecular dynamics have been used to model C-S-H (Gmira et al. 2008). Molecular dynamic models based on free energy minimization techniques have been used to theoretically estimate the elastic properties of C-S-H. In Pellenq et al. (2007), it was demonstrated that the average Young's modulus E increases with the increase in the C/S ratio of the C-S-H. The C/S ratio is not the only governing parameter in determining E , as other factors such as molecular arrangements and extent of water within the nanostructure of C-S-H could play an important role (Manzano et al. 2007). The bulk modulus of tobermorite was computed in two separate studies to be approximately 70 GPa (Gmira et al. 2008; Reinhardt et al. 2009). The discrepancy between the modeling simulations and the experimental results was attributed to the nanostructural defects in the silicate structure of tobermorite-like materials. Moreover, the finite element method was successfully used to model the nanoindentation response of cementitious materials (Reinhardt et al. 2009).

CHAPTER 4—NANOASSEMBLY AND BIOMIMETICS IN CEMENT-BASED MATERIAL

Looking to nature for inspiration for effective engineering design is a novel approach related to nanotechnology. Biomimetics, which is also known as "biomimicry" and