Cellulose nanomaterials as additives for cementitious materials

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20.1 Introduction

Cementitious materials cover a very broad area of industries/products (buildings, streets and highways, water and waste management, and many others; see Fig. 20.1). Annual production of cements is on the order of 4 billion metric tons [2]. In general these industries want stronger, cheaper, more durable concrete, with faster setting times, faster rates of strength gain, and there is growing interest in advancing sustainability [3]. To achieve these improvements in properties, there are a wide range of additives such as supplementary cementitious materials (SCMs) [4], chemical admixtures [4], and fiber reinforcement [5,6]. Natural fibers have been used as a reinforcement phase in cementitious composites since ancient times and are seeing increased use in cementitious products such as nonstructural building materials (e.g., fiber cement boards for siding, cladding, and soffit panels). Though having lower reinforcement effectiveness than metallic reinforcements, natural fibers are increasingly being used as they are renewable, economical, and abundant compared with other commonly used fibers; additionally functionalized natural fibers are seeing utility in emerging applications as internal curing agents [7] and for control of shrinkage cracking [8].

Cellulose nanomaterials (CNs) are being investigated for new utility in cementitious materials. These nanosized cellulose-based particles fill a unique gap in the natural fiber and cellulose particle size spectrum. They have high surface area to volume ratio, giving the potential to increase chemical reactions, yet unlike molecular cellulose they can act as a stiff particle in suspensions and within composites; this differentiation allows CNs to do things that neither molecular cellulose nor macrosized plant fibers can do [9]. For cements, CN additions have been shown to alter rheology, setting times, and mechanical properties. Because of the small size of CNs, there seems to be limited applicability as a reinforcement phase in the traditional sense of crack-bridging mechanisms. Despite this, low-volume CN additions have been shown to alter the hydration reactions and increase mechanical properties (e.g., strength [10,11] and stiffness [11]). This mechanism may give a new capability for optimizing the hydration reaction kinetics and thereby achieving higher-strength cementitious

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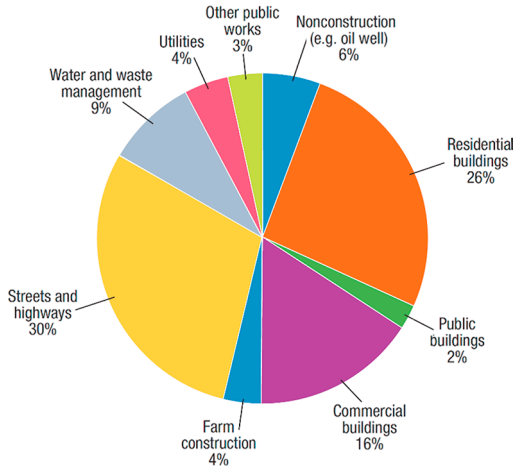

Figure 20.1 Estimated 2015 use of portland cement for several markets within United States. *Source*: Reprinted from PCA. U.S. cement industry annual yearbook. Skokie, IL: Portland Cement Association; 2015 [1], Copyright (2015), with permission from Portland Cement Association.

materials. Despite the promising work to date, commercial products are not yet on the market.

This section briefly describes cementitious materials, and how various types of cellulose-based particles (pulp fiber, microcrystalline cellulose, and CN) are used in cementitious materials for property enhancement. A more detailed summary is given on how CNs alter the rheology, and hydration reactions in cements. Finally, a brief summary is given on potential applications of CN in cementitious materials.

20.2 Cementitious materials

There exists a great volume of literature [12–16] on cementitious materials covering cement manufacture, the hydration reaction, and additives used in cementitious materials. This section provides an overview of cementitious materials relevant to understanding how CN would work in the system.

20.2.1 Cement manufacture

To manufacture portland cement, raw materials are combined and heated in a rotary kiln at approximately 1450°C to form hydraulic compounds that will harden in contact with water. The raw materials usually include one type of calcareous material (most commonly limestone or chalk), and one type of argillaceous material (most commonly clay or shale). The hydraulic compounds coming out of the kiln are

referred to as clinker. After the clinker is rapidly cooled, it is then finely ground with a small amount of calcium sulfate (most commonly gypsum) to regulate setting time. Limestone may also be added during this grinding stage to provide environmental benefits as well as performance improvements [17]. After grinding to pass through a 45-μm sieve, the resulting fine powder is the portland cement.

20.2.2 Hydration reactions and products

Portland cement contains five major compounds: tricalcium silicate (C_3S) also known as alite, tricalcium silicate (C_2S) also known as belite, tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C4AF), and gypsum ($C\$H_2$). Note following chemical abbreviations are used: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, \$ = SO_3, H = H_2O. When portland cement comes in contact with water, an exothermic chemical reaction occurs. The reaction is commonly referred to as hydration. More details about the reaction of different compounds are listed in Table 20.1. Fig. 20.2 shows a schematic of the general hydration reaction.

In general, two groups of reactions occur during cement hydration: aluminate hydration and silicate hydration. Being the most reactive phase in cement, C_3A reacts in the first several minutes and releases a large amount of heat. Gypsum is added to regulate the C_3A reaction and form rod-like crystals of ettringite, which contribute slightly to early-age strength development. Over time, this ettringite will react with remaining C_3A and form monosulfate at later age. In contrast, silicates (C_3S and C_2S) react in a slower fashion and form calcium silicate hydrates (C–S–H) and CH (calcium hydroxide). C–S–H consists 50%–60% (by mass) of total hydration product and is responsible for the majority of strength development. The dashes indicate that the composition of Si and Ca is not stoichiometric and can vary. Along with C–S–H, CH (calcium hydroxide) is also an important hydration product from silicate hydration. It should be noted that there are several minor additional reactions and there are also some trace chemical elements that can affect the reaction, which are not listed

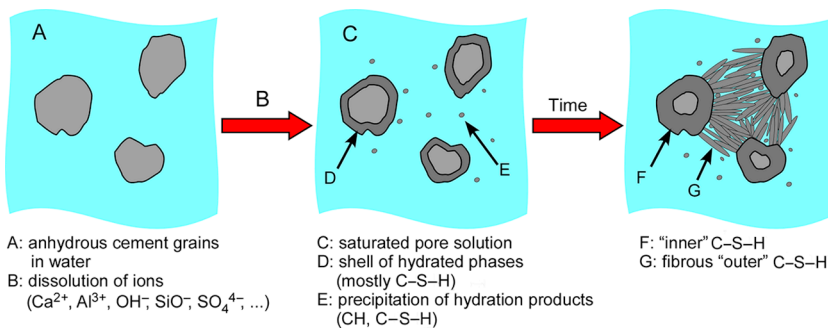

Figure 20.2 Schematic representation of hydration reaction.
Source: Adapted from Ridi F, Fratini E, Baglioni P. Cement: a two thousand year old nano-colloid. J Colloid Interface Sci 2011;357(2):255–64.

Table 20.1 Summary of portland cement hydration reactions

Reactants	Hydration products
C_3S[a] (tricalcium silicate) + water	C–S–H (calcium silicate hydrate), CH (calcium hydroxide)
C_2S (dicalcium silicate) + water	C–S–H (calcium silicate hydrate), CH (calcium hydroxide)
C_3A (tricalcium aluminate) + $C\$H_2$ (gypsum) + water	$C_6A\$_3H_{32}$ (ettringite)
C_3A (tricalcium aluminate) + $C_6A\$H_{32}$ (ettringite) + water	$C_4A\$H_{12}$ (monosulfate)
C_4AF (tetracalcium aluminoferrite) + CH (calcium hydroxide) + water	C_6AFH_{12} (calcium aluminoferrite hydrate)

[a]Cement chemists use the following chemical abbreviations: $\$ = SO_3$, $A = Al_2O_3$, $C = CaO$, $F = Fe_2O_3$, $H = H_2O$, $S = SiO_2$.

in Table 20.1. An extensive review on cement hydration mechanisms can be found in the literature [15].

20.2.3 Additives

Fundamentally, concrete is a mixture of aggregates (usually sand and stone) that are bound by paste (cementitious materials mixed with water). For decades a variety of "additives" have been used in the cementitious materials to achieve desired properties. These additives include SCMs, chemical admixtures, fibers, and more recently nanomaterials.

20.2.3.1 Supplementary cementitious materials

SCMs, also referred to as supplementary cementing materials, are materials (e.g., fly ash, silica fume, and natural pozzolans) that can be used alongside portland cement. When properly used, SCMs can improve cohesiveness, enhance workability, reduce temperature development, achieve improved strength, reduce permeability, and increase durability (resistance to sulfate attack, chloride penetration, alkali-aggregate reaction, and corrosion of embedded steel) [18]. In addition to improving concrete properties, there is also a great environmental benefit in using SCMs. Many SCMs are industrial by-products used by the concrete industry in hundreds of millions of tons per year that would otherwise end in landfills. Furthermore, SCMs reduce virgin cement demand by replacing a portion (5%–70%) of the cement, which helps to lower the overall embodied energy in concrete containing SCMs. In this section, several of the most common SCMs and their effect on cementitious materials are introduced.

Fly ash is a widely used SCM, and is a by-product of coal combustion power plants. This material is primarily silicate glass, which contains silica, iron, calcium, and alumina, with minor amounts of potassium, carbon, sodium, sulfur, and magnesium. The glassy particles are mainly solid plerospheres and some hollow cenospheres, and

range in size from less than 1 to 100 μm in diameter with the majority being under 20 μm. Compositions can be quite different between fly ashes due to different coal sources. In North America, fly ash is divided into two categories: (1) Class F, mostly pozzolanic with little or no hydraulic properties; and (2) Class C, pozzolanic as well as hydraulic. A typical amount of fly ash in concrete is between 15% and 40% of total cementitious materials.

Silica fume, also known as micro silica, is also a frequently used SCM. Derived from silicon metals and ferrosilicon alloys manufactured as a by-product, silica fume consists mainly of noncrystalline silica (>90%), thus is highly pozzolanic. It has very fine particle size (about 0.1 μm), which is approximately 100 times smaller than average cement particles. Due to the fine particle size, silica fume is particularly known to possess the "dense packing" effect, which can ensure a lower degree of permeability and higher strength. Typically, silica fume is used between 5% and 10% of the total cementitious materials.

Another group of SCMs are natural pozzolans, which are produced from natural siliceous and aluminous mineral deposits, including metakaolin (calcined clay), calcined shales, rice husk ash, diatomaceous earth, and volcanic ash. To work with cement, natural pozzolans are usually ground to an average particle size of about 1–2 μm, and used where low permeability or high strength is needed. Metakaolin is also known to be effective to control the alkali-silica reaction in concrete.

As discussed in Section 20.2.2, ordinary portland cement hydrates through hydraulic reactions (hydration). As a major product of hydration reaction, calcium silicate hydrate (C–S–H) significantly contributes to the strength. Portlandite (calcium hydroxide) is also formed during hydration, which has few cementitious properties and often considered as the weak link. For most SCMs, pozzolanic reactions happen when portlandite is present, which results in more calcium silicate hydrates. This contributes to higher strength and lower permeability in concrete with SCMs.

20.2.3.2 Chemical admixtures

Chemical admixtures are chemicals that are added during concrete mixing to achieve or alter specific properties in fresh and hardened concrete. Despite usually relative small quantities used in concrete mixtures comparing to other components, chemical admixtures have great impact on a variety of properties: workability, air content, accelerated or retarded hydration reaction, strength, corrosion resistance, drying shrinkage resistance, and durability. Among many types of chemical admixtures, air-entraining admixtures and water-reducing admixtures (WRAs) are commonly used in modern concrete.

Air-entraining admixtures encourage microscopic air bubbles (10–1000 μm in diameter) to form and stabilize these bubbles during the mixing of the fresh concrete. They significantly increase the resistance of the resulting concrete against freezing–thawing damage and deicing chemicals. Air-entraining admixtures act at the air–water interface to form a hydrophobic film due to their negatively charged hydrophilic head and hydrophobic "tail," which repels water (as shown in Fig. 20.3). A much more detailed explanation can be found in the literature [19].

WRAs are widely used to increase workability in the fresh concrete without increasing water content in a concrete mixture. The latest technology uses polycarboxylate

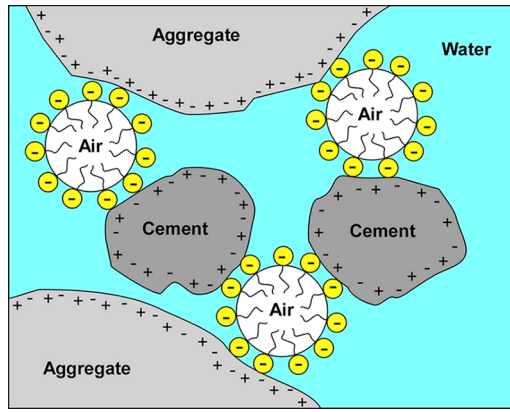

Figure 20.3 Schematic of air-entraining admixtures stabilize air bubble.
Source: Adapted from Thomas MDA, Wilson ML. Admixtures use in concrete. CD039. Skokie, IL: Portland Cement Association; 2002.

polymers comprising a main carbon chain with carboxylate groups and polyethylene oxide side chains. While the negatively charged backbone of the polymer is adsorbed at the cement–water interface, the long hydrophilic side chains prevent cement particles from agglomerating by steric repulsion on the order of 10 nm [20], which allows less water demand and a longer period of flowability in the fresh concrete.

20.2.3.3 Fiber reinforcement

Adding fibers in concrete has been in practice for decades [6,21,22]. In general, fiber reinforcements have high aspect ratio to improve flexural strength and toughness of cementitious materials. They come in many forms (steel fiber, glass fiber, synthetic fiber, and natural fiber) and size (microfiber and macrofiber). The majority of conventional fiber–cement composites benefit from the crack-bridging mechanism shown in Fig. 20.4, where fibers can delay or prevent crack propagation. Large fibers (macrofibers) bridge macroscale cracks, restricting further crack growth. Additionally, macrofibers absorb energy through plastic deformation, friction, and eventually pull-out to give a much higher toughness for fiber–cement composites (Fig. 20.4A). In contrast, microfibers are more effective at bridging microcracks, preventing these cracks from growing into macrocracks. The result is much higher tensile strength, and improved toughness (Fig. 20.4B). More information can be found in Section 20.3.1.

20.2.3.4 Nanosized materials

Adding nanosized materials to cementitious materials is quickly gaining popularity to achieve desired particle packing and improved properties. The high specific surface area (see Fig. 20.5) of nanosized particles can significantly increase chemical reactions, and provide nuclei for cement phases to promote degree of hydration (DOH)

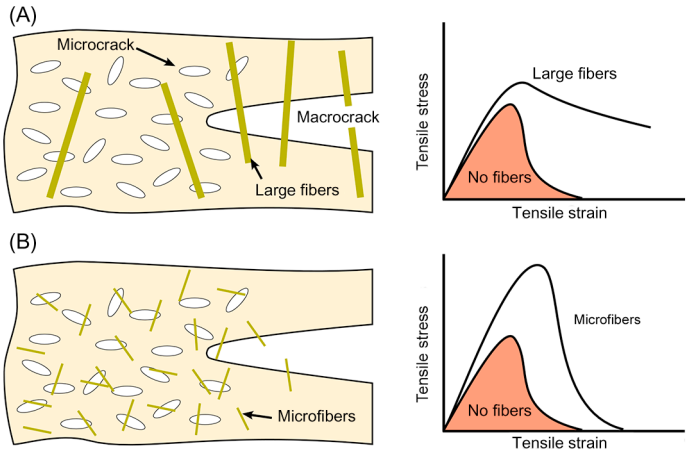

Figure 20.4 Schematic of fiber reinforcing mechanisms based on the fiber length (A) macrofibers and (B) microfibers.
Source: Adapted from Betterman LR, Ouyang C, Shah SP. Fiber-matrix interaction in microfiber-reinforced mortar. Adv Cem Based Mater 1995;2(2):53–61.

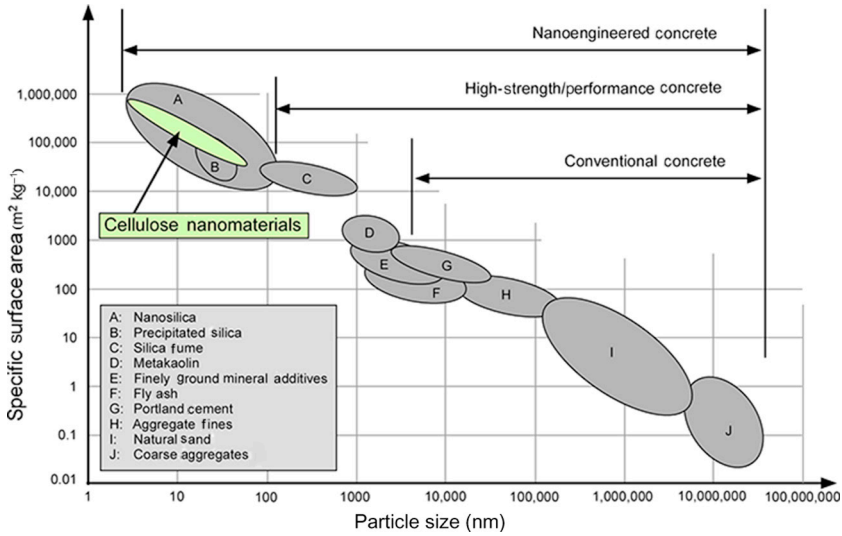

Figure 20.5 Materials in concrete, relationship between particle size and specific surface area.
Source: Adapted from Sobolev K, Gutiérrez MF. How nanotechnology can change the concrete world. Am Ceram Soc Bull 2005;84(10):14–17 [23].

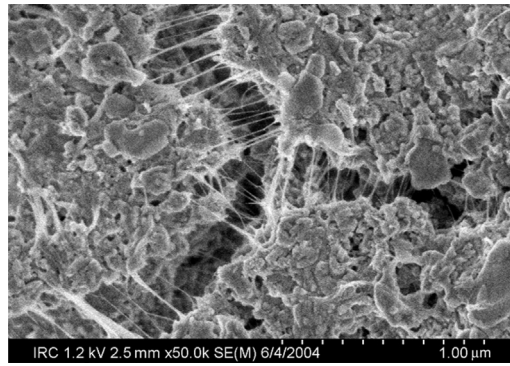

Figure 20.6 Crack bridging observed in a CNT/hydrated cement composites [27].

[24]. Some nanoparticles with high aspect ratio and high strength to moduli of elasticity ratio can be used as nanoreinforcement in cementitious materials.

Nanosilica (nano-SiO_2) is a great example of how nanoparticles can improve concrete mechanical properties [25] and impermeability [26] due to its highly reactive surface. The nanosilica added to the cementitious materials works as a nanofiller, which significantly enhances the interfacial transition zone (ITZ). Additionally, these are highly reactive pozzolanic materials. More specifically, the 28-day compressive strength was reported to increase by 10% and flexural strength by 25% [25], by adding a small amount (0.25%) of nanosilica.

Due to their high tensile strength and high moduli of elasticity along with high aspect ratios, carbon nanotubes/nanofibers (CNTs/CNFs) were found promising to work as nanoreinforcement in cementitious materials. Fig. 20.6 shows a SEM image of crack bridging observed in CNT–cement composites [27]. In addition, due to their unique electric and chemical properties, CNTs have been used as strain sensor for structural health monitoring [28,29].

A key in successfully using these nanomaterials is dispersion, since most nanoparticles tend to self-agglomerate even at low loading. Proper dispersion agent or procedures need to be in place to ensure the benefit of the small particle sizes and high surface area. If not properly dispersed, unreacted agglomeration (defects) can form and induce stress concentrations under loading conditions.

20.2.4 Sustainability

Cement is the dominant binder in concrete construction, and global cement production reached 4.0 billion metric ton consumption in 2013 [2], and it is estimated grow to 5 billion metric tons by 2030 [30]. Cement manufacture is energy intensive, consisting of 2%–3% global energy consumption and 5% total CO_2 emission [31]. Although concrete has a relatively low embodied energy comparing to many other construction materials [32], due to its vast product quantity, the construction industry is pressured to further mitigate environmental impact. One solution is to utilize a variety of waste

Table 20.2 Summary of reviewed research work

Type of cellulose	Authors
Cellulose fiber	Multiple authors [6,7,21,22,33–37]
Microcrystalline cellulose (MCC)	Hoyos et al. [38]
Cellulose microfibrils (CMFs)	Nilsson and Sargenius [39], Peters et al. [40]
Cellulose nanofibrils (CNFs)	Onuaguluchi et al. [41], Mejdoub et al. [42], Ardanuy et al. [11], Ferrara et al. [43] Dai et al. [44], Stephenson [45], Peters et al. [40]
Cellulose nanocrystals (CNCs)	Cao et al. [10,46,47]
Bacterial cellulose (BC)	Mohammadkazemi et al. [48]

materials in concrete such as fly ash, slag, and silica fume, which are by-products or waste from other industrial. In the meantime, the presence of these waste materials often enhances concrete performance and durability. As an emerging nanoadditive, CNs are potentially a product from the paper industry, with high volume production potential, low cost, and abundance sources. The CN–cement composite has the potential of enhanced mechanical properties, increased hydration reactions, and improved durability, making it a promising candidate to further increase cement sustainability.

20.3 Cellulose–cement composites

This section provides a brief review of how various types of cellulose-based particles are used in cementitious materials for property enhancement. These particles include cellulose fiber, microcrystalline cellulose (MCC), cellulose microfibrils (CMFs), cellulose nanofibrils (CNFs), cellulose nanocrystals (CNCs), and bacterial cellulose (BC). Table 20.2 gives a summary of reviewed research work in this section.

20.3.1 Cellulose fiber

Using natural fiber as an alternative to reinforce cementitious materials is nothing new [21,22,49,50]. A state-of-the-art report on natural fiber-reinforced concrete can be found in ACI C544 document [6]. During the last two decades, much research effort was given to cellulose fiber-reinforced cement composite. Wood fiber and plant fiber (e.g., pulp fiber) are mainly composed of cellulose (with low crystallinity of about 43%–65%), ranging in length from 10 μm to a few millimeters. These purified cellulose fibers have characteristics that have increased interest in their use with cementitious materials in the last two decades: (1) superior mechanical properties with low density (tensile strength up to 700 MPa); (2) high water retention (absorption capacity over 300%) for use as internal curing agent; and (3) environmentally friendly due to abundant resources, low cost, and fast renewability. By adding cellulose fibers

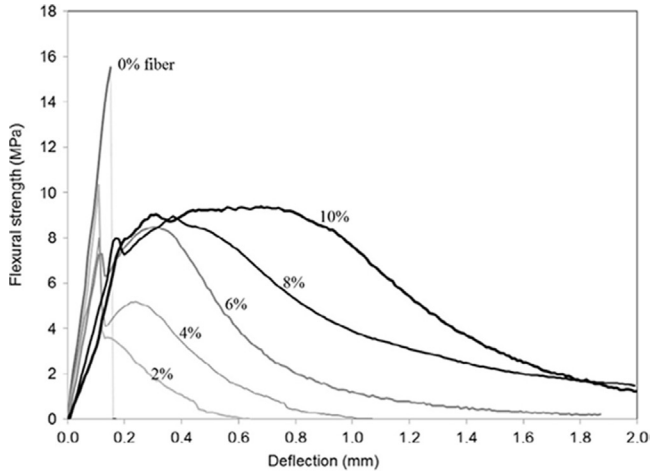

Figure 20.7 Typical stress–deflection curves of cellulose fiber-reinforced cement composites with various pulp fiber addition.
Source: Reprinted from Ardanuy M, Claramunt J, Toledo Filho RD. Cellulosic fiber reinforced cement-based composites: a review of recent research. Constr Build Mater 2015;79:115–28, Copyright (2015), with permission from Elsevier.

at 1–15 wt%, most reported improved toughness, ductility, flexural capacity, and crack resistance. A comprehensive review of the most recent work can be found in the literature [34]. Most research focused on the effect of randomly dispersed short or pulp cellulose fibers (less than a few millimeters) on flexural strength. As shown in Fig. 20.7 by Claramunt et al. [35], by adding more than 4 wt% cellulose fiber, the toughness and ductility of the cement composite was greatly improved according to the three-point bending test. Despite the improvement provided by the cellulose fiber, the long-term durability is a limiting factor for many applications. As discussed in Section 20.2.3.1, calcium hydroxide (portlandite) is one of the major hydration products in cementitious materials, and provides high alkalinity (pH > 13) in the pore solution. Under wetting/drying cycles, Mohr and coworkers [37] found fiber embrittlement due to portlandite precipitation in fiber lumen and/or fiber cell walls. Ardanuy and coworkers [33] also observed cement hydration compound deposits in the lumen and surface of the fibers. Two mitigation methods have been proposed to solve this issue: (1) physically and chemically modify fibers to increase resistance to degradation; and (2) reduce portlandite by adding pozzolanic compounds or inducing carbonation process.

Other research work investigated application of cellulose fiber as an internal curing agent in cementitious materials [7,36]. Since cellulose fibers have high absorption capacity, they can be introduced to hydrating cement paste and provide additional water for hydration reactions. This will significantly reduce autogenous shrinkage (self-desiccation), which is the major cause of early-age cracking and can be

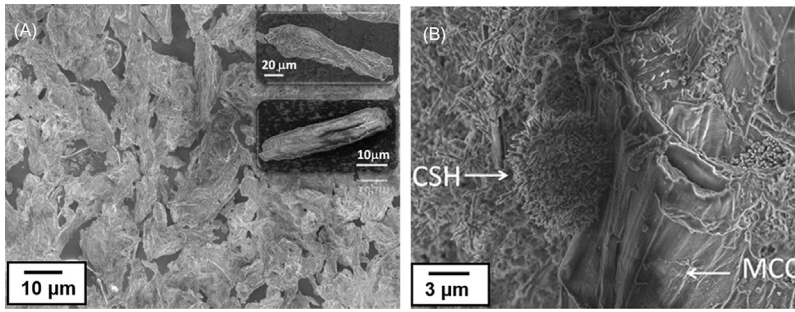

Figure 20.8 SEM image of (A) MCC particles, (B) MCC particles in hydrated cement paste. *Source*: Reprinted from Hoyos CG, Cristia E, Vázquez A. Effect of cellulose microcrystalline particles on properties of cement based composites. Mater Des 2013;51:810–18, Copyright (2013), with permission from Elsevier.

difficult to mitigate using traditional curing methods. Mezencevova and coworkers [7] reported that adding 1–1.5 wt% of dry cellulose fiber can significantly reduce autogenous shrinkage (45%–93%). Kawashima and Shah [36] also showed that in addition to the internal curing capability, cellulose fiber can also help to reduce cracking induced by drying shrinkage at later ages. However, using cellulose fibers effectively as internal curing agents require good dispersion, which can be achieved by using superplasticizer and by the presence of aggregate during mixing.

20.3.2 Microcrystalline cellulose

Microcrystalline cellulose (MCC) consists of mostly crystalline cellulose chains, prepared by acid hydrolysis of wood or vegetable fiber, back-neutralization with alkali, and spray-drying. The resulting MCC particles are 10 seconds of microns in size, highly hydrophilic, and have a high crystallinity (80%–85%), high water retention capability, and excellent mechanical properties [51,52]. MCC has been made commercially available for many applications in the pharmaceutical and food industries. There are very few research works on the application of MCC to cementitious materials.

Hoyos and coworkers studied the role of MCC additions to paste and mortar materials on fresh state rheology, mechanical properties, and heat evolution and hydration degree [38]. A commercially available MCC was used in this study at a loading of 3 wt% of cement. Fig. 20.8 shows SEM images of the MCC particles and MCC particles in cement paste. The results showed that the addition of MCC at 3 wt% showed slight reduction in flexural strength and modulus of elasticity (MOE). These results were also supported by semiadiabatic calorimetry (6°C lower peak temperature in MCC samples) and thermogravimetric analysis (TGA, less total weight loss in MCC samples). The authors attributed the lower DOH to the possible polysaccharides within the MCC used in this study, which has a known effect of delaying hydration.

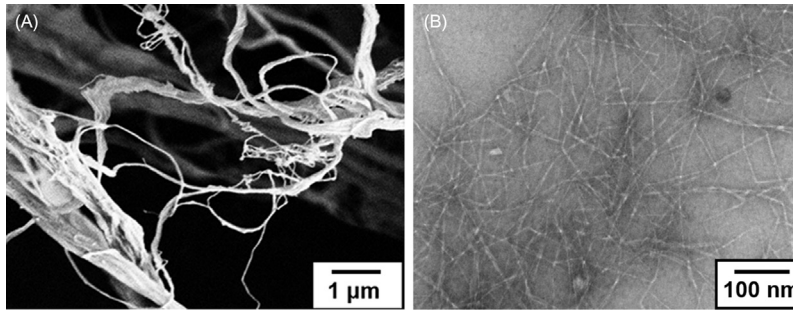

Figure 20.9 TEM image of (A) CMF produced from CMF pilot plant located at the Process Development Center at the University of Maine [17], (B) TEMPO-CNF produced from CNF pilot plant located at US Forest Service, Forest Products Laboratory.
Source: Reprinted from Moon RJ, Schueneman GT, Simonsen J. Overview of cellulose nanomaterials, their capabilities and applications. JOM 2016;68(9):2383–94, Copyright (2016), with permission from Springer.

However, if accelerated cured, samples showed very similar flexural strength with the control samples. The authors concluded that MCC–cement composite can be used in case of massive concrete to reduce thermal-induced cracking thanks to its lower MOE and lower heat generation during hydration. In addition, due to higher yield stress in fresh state, MCC can be added to concrete pavement mixtures where it required the mixture to maintain its shape before completely hardened.

Mohamed and coworkers [53] investigated the effects of MCC on mixture design, workability, and mechanical properties of self-compacting concrete (SCC) at six different fiber loadings, ranging from 14 to 138 vol% (based on a bulk density of 30 kg m^{-3}). The MCC used in this study was from recycled resinous origin cardboard treated with sulfate then bleached. It contained 80% cellulose and had an elastic modulus between 20 and 40 GPa and a tensile strength between 100 and 500 MPa, with an aspect ratio of 24.4 (mean length of 1.1 mm and mean diameter of 45 µm). The results showed at an optimum fiber content of 21 vol% for both mortar and concrete specimens in terms of increased compressive strength and reduced porosity.

20.3.3 Cellulose microfibrils/cellulose nanofibrils

Cellulose microfibrils (CMFs) and cellulose nanofibrils (CNFs) are both cellulose fibrils (about 100% cellulose) produced from mechanical refining of highly purified wood fiber and plant fiber pulps. In the literature, CMF and CNF are often used interchangeably. However, CNF processing incorporates an additional pretreatment step to the cellulose source, which facilitates fibrillation and results in a much finer sized particle (see Fig. 20.9). For CMFs, the particles are 10–100 nm wide and 0.5–10 µm in length, while the CNF particles are 4–20 nm wide and 0.5–2 µm in length [9]. In the last decade, several attempts to use CMF/CNF with cementitious materials have

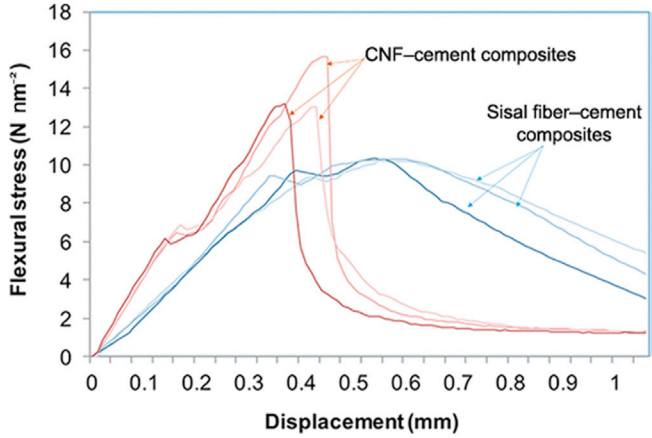

Figure 20.10 Flexural stress–displacement curves of the cement composites reinforced with CNF compared with sisal fiber (three specimen tested for each mix).
Source: Reprinted from Ardanuy M, Claramunt J, Arévalo R, Parés F, Aracri E, Vidal T. Nanofibrillated cellulose (NFC) as potential reinforcement for high performance cement moretar composites. BioResources 2012;7(3):3883–94, Copyright (2012), with permission from the corresponding author.

shown promising results in terms of improved strength [11,39,44], stiffness [11], toughness [40,43], and reduced porosities [39,44].

Nilsson and Sargenius [39] added CMF to mortar to evaluate the performance in terms of rheology, compressive strength, flexural strength, shrinkage and cracking resistance, and antiwashout resistance (underwater concrete). Two CMF types were extracted from pine kraft pulp, with one finer than the other due to extra homogenization. Three different loadings (1, 2, and 3 kg m^{-3}) were investigated. It was also reported that (1) plastic viscosity of fresh mortar was increased with higher CMF loading; (2) there were no significant differences in compressive strength and flexural strength; (3) restrained ring test showed high fiber loading increased the cracking resistance, however, only insignificantly; and (4) higher fiber loading increased water absorption resistance as a result of forming a more densified microstructure.

Ardanuy and coworkers [11] investigated the role of sisal fiber and CNF additions to the mechanical properties of cement composites. The CNFs used in the study were produced from a chemical-free mechanical treatment of the starting sisal fibers used in the study. The results showed that CNF–cement composite had a 40% increased flexural strength, and almost twice as high of flexural modulus comparing to sisal fiber–cement composites (see Fig. 20.10). However, the fracture toughness of CNF–cement composite was only about half of sisal fiber–cement composite. In general, due to the nanoscale size, CNF does not have crack bridging capability (see Section 20.2.3.3) as macrofibers do.

Onuaguluchi and coworkers [41] studied the effect of a CNF produced from mechanical defibrillation of bleached softwood pulp on general use limestone (GUL)

cement. The average length of the nanofibrils is 1.0–2.5 µm, and loadings were 0.05%, 0.1%, 0.2%, and 0.4% of cement weight. Significant delays in setting time, and significant increases in DOH, were observed in all CNF loadings. The authors attributed these alterations in hydration reaction to (1) possible organic acids and non-acidic products due to alkaline hydrolysis of cellulose resulted in significant delays in setting time; and (2) internal curing of CNF increased the total DOH in the later age. The mixture with 0.1% CNF showed optimum flexural strength increase, which was supported by microscopic evidence showing higher degree of fiber agglomeration in 0.4% loading.

Mejdoub and coworkers [42] recently conducted a comprehensive study on thermal, mechanical, and microstructural effects of CNF on portland cement. The CNF used in the research was produced by high-pressure homogenization from eucalyptus pulp, consisting of nanosized fibrils with width of 5–10 nm and length within the micron scale. The CNF was added at loadings of 0.01%, 0.05%, 0.1%, 0.2%, 0.3%, and 0.5% of cement weight. The results showed significant improvement in the thermal, mechanical, and microstructural properties of the CNF–cement composites. The optimum strength increase (43% comparing to the control specimen without CNF addition) was observed at 0.3%. The authors attributed these improvements to CNF's high hydrophilic potentials, high reactivity, and high specific surface area. Ferrara and coworkers [43] investigated the effects of CNF, eucalyptus microfiber, and sisal fiber on the autogenous and drying shrinkage of cement paste used for a typical high-performance fiber-reinforced cementitious composites (HPFRCCs). The results showed that CNF slightly decreased autogenous shrinkage and slightly increased total shrinkage. The results indicated that CNF unlikely has the internal curing capacity as conventional cellulose fibers due to its nanoscale size. The authors hypothesized that CNF could be a potential promoter of self-healing processes in cementitious composites due to its hydrophilic feature and the porous network that can be created inside the composites.

Dai and coworkers [44] researched the effects of CNF on the mechanical properties and hydration reaction on Type I cement paste. The CNFs used were procedure in the laboratory, and were 20–100 nm in diameter, 600–1700 nm in length, with high water retention (absorption capacity about 3700%) and high hydroxyl groups (1.85 mmol g^{-1}). It was observed that by adding 0.15 wt% CNFs to Type I cement paste of 0.50 w/c, the compressive and flexural strengths were increased by 20% and 15%, respectively. Isothermal calorimeter results showed a delay in the hydration reaction and an increase in the DOH. Mercury intrusion porosimetry (MIP) showed reduced porosity in CNF–cement composites with increased CNF loading. Dai and coworkers [44] attributed the enhanced properties of CNF–cement composite to (1) reactive hydroxyl groups that increase the interaction between CNF particles and cement compounds; and (2) microcracking bridging mechanism due to the dimension of the CNFs.

Peters et al. [40] and Stephenson [45] investigated fracture roughness of ultrahigh-performance concrete (UHPC) reinforced with CMF/CNF. Peters and coworkers [40] used 0, 1 wt%, and 3 wt%, 5 wt% of CMF and CNF respectively, and 1 wt% CMF combined with 1 wt% CNF as a hybrid mixture. It was reported that 5 wt% CMF

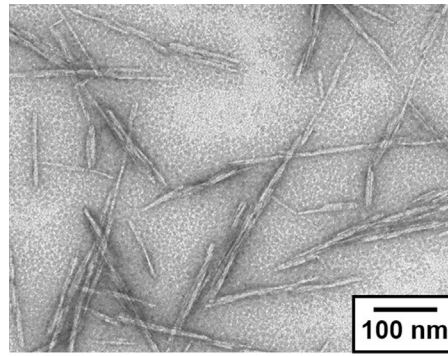

Figure 20.11 TEM image of wood CNC produced from the CNC pilot plant located at US Forest Service, Forest Products Laboratory.
Source: Reprinted from Moon RJ, Schueneman GT, Simonsen J. Overview of cellulose nanomaterials, their capabilities and applications. JOM 2016;68(9):2383–94, Copyright (2016), with permission from Springer.

loading was too high resulting in inconsistent workability and an increased superplasticizer demand. It was also found that the 3 wt% CMF mixture was most effective and increased fractured energy by 53% from three-point notched beam test. The hybrid mixture also increased fracture energy, but to a lesser degree, by 26% comparing to the control beam. In another study, Stephenson [45] investigated compressive strength, shrinkage behaviors, and fracture properties of UHPC incorporated with 0, 0.1, 0.5, and 1.0 wt% CNF. The results showed that at 0.5 wt% addition of CNF, early-age shrinkage was significantly reduced, which is contrary to the findings of Ferrara and coworkers [43].

20.3.4 Cellulose nanocrystals

Cellulose nanocrystals (CNCs) are rod-like nanofibrils that remain after acid hydrolysis of cellulose fibers. CNCs from wood/plant materials, typically have a spindle-like particle morphology (~3–20 nm wide and 50–500 nm in length; see Fig. 20.11), approximately 100% cellulose, high crystallinity, and have surface accessible hydroxyl groups that can be chemically modified to give additional functionalities.

Cao and coworkers [10] investigated the influence of CNCs on the performance of a Type V cement paste. By adding CNC (0.04%, 0.1%, 0.2%, 0.5%, 1.0%, and 1.5% in volume), improvements in several properties in the CNC–cement composites were observed: (1) the DOH was increased, measured by TGA and isothermal calorimeter, was increased with CNC loading (see Fig. 20.12); (2) flexural strength was increased by up to 20%–30% (Fig. 20.13) in comparison with cement paste without CNC, with an optimum loading for a normal mixing condition found to be 0.2 vol%; and (3) the CNC–cement composite also exhibited improved rheological properties (i.e., yield stress tests) and zeta potential. Fig. 20.13 also shows that the strength decreases as

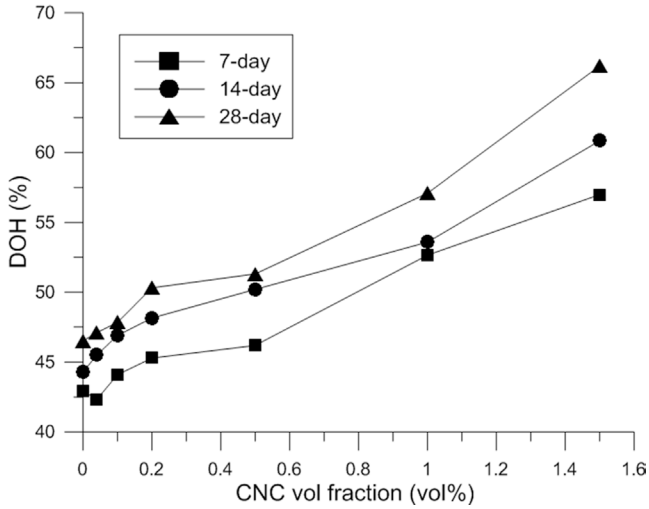

Figure 20.12 Degree of hydration (DOH) obtained from TGA at three ages.
Source: Reprinted from Cao Y, Zavattieri P, Youngblood J, Moon RJ, Weiss WJ. The influence of cellulose nanocrystal additions on the performance of cement paste. Cem Concr Compos 2015;56:73–83, Copyright (2015), with permission from Elsevier.

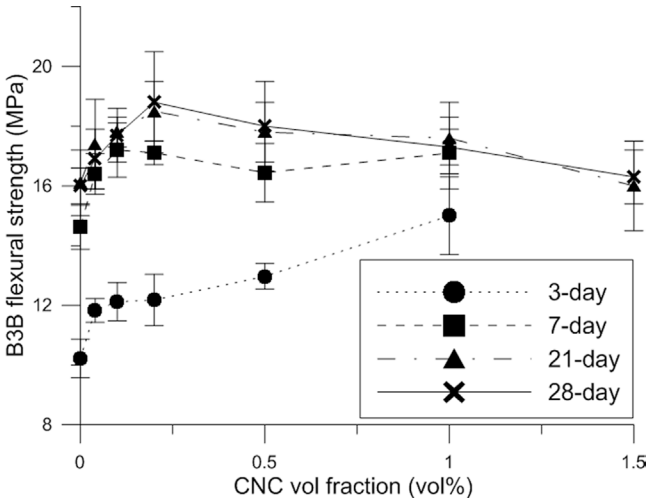

Figure 20.13 B3B flexural strength of CNC-reinforced cement paste with different CNC concentration at four ages.
Source: Reprinted from Cao Y, Zavattieri P, Youngblood J, Moon RJ, Weiss WJ. The influence of cellulose nanocrystal additions on the performance of cement paste. Cem Concr Compos 2015;56:73–83, Copyright (2015), with permission from Elsevier.

a function of CNC loading, which is likely due to agglomeration at higher loading. Cao and coworkers proposed two mechanisms responsible for the abovementioned enhancements: steric stabilization and short circuit diffusion. A more detailed explanation can be found in Section 20.4.3.

Cao and coworkers [46] also explored effective ways to disperse CNCs and studied the relationship between CNC dispersion and strength of CNC–cement composite. As discussed before, the key to a successful application of nanoscale materials is dispersion. By placing CNC in a simulated cement pore solution, the critical concentration to reach lowest yield stress was found to be 0.18 vol% based on rheological measurements (as shown in Fig. 20.15), which was close to the 0.2 vol% optimum loading reported in the previous research. When ultrasonication was used to reduce agglomeration, a critical concentration of 1.35 vol% was found, which is in agreement with the theoretical value of 1.38 vol% calculated from the percolation model. The results showed that after ultrasonication treatment, the flexural strength of CNC–cement composite was increased by up to 50%. This research provides insights into how to use CNC more efficiently with cementitious system for future applications. In addition, Cao [47] investigated how the sonication it modified the microstructures of the paste. Energy-dispersive X-ray (EDX) spectroscopy results showed (1) for CNC–cement composites that were not sonicated, CNC tends to concentrate along the interfacial regions between the cement particles and the paste; (2) for sonicated CNC–cement composites, more CNCs are dispersed into the paste. Nanoindentation results showed that regions of the cement paste that are rich in CNCs exhibited higher elastic modulus.

20.3.5 Bacterial cellulose

Bacterial cellulose (BC), also referred as microbial cellulose, is harvested from bacteria in growth medium, and usually has a high degree of crystallinity in the 65%–90% range [54,55], due to the highly crystalline nanosized cellulose. The morphology of BC depends on specific bacteria and culturing conditions [9]. Typically, BC has a high MOE and large aspect ratio (>50).

Mohammadkazemi and coworkers [48] investigated cement composites that incorporated BC as an additive or as a coating on pulp fibers. In this study, mechanical properties, as well as interaction between cement and fibers, were investigated on fiber–cement composites (FCCs). An unbleached bagasse pulp fiber (6% and 7% in weight) was used as the reinforcing fiber in FCC, with the average length and diameter of 1.13 mm and 29.5 μm. A BC harvested from bacterial strain *Gluconacetobacter xylinus* was used in three forms—powder, gel, and coated on bagasse fibers—with the same loading. The results showed that BC-coated FCC had the best mechanical performance, including the best modulus of rupture (MOR), MOE, internal bonding strength, and fracture toughness. Compared to the control FCC (no BC addition), BC-coated FCC showed 68% increase in MOR, 38% increase in MOE, about 40% increase in internal bonding strength, and about 70% increase in fracture toughness. Microstructural analysis using SEM and EDX spectroscopy revealed that the surface of BC-coated fibers was rich in hydration products (C–S–H). The researchers

concluded that there are two main reasons for enhanced mechanical properties of BC-coated FCC. The first one is mechanical interlocking due to extra accessible hydroxyl groups of BC enhanced the bonding between cement and fiber. Another main reason is that highly crystalline BC created a barrier at the interface of cement and bagasse fiber and reduced penetration of alkaline ions into the lumen, which is the major deterioration mechanism for cellulose-reinforced cement composites. This work provides new insight into how to use cellulose nanoparticles in cementitious materials.

20.4 Cellulose nanomaterial modification mechanisms

This section focuses on the potential mechanisms of CN when incorporating in the cementitious composites. Several prevalent hypotheses are introduced. It should be noted that the focus is nanosized cellulose particles, therefore some known working mechanisms for macroscale cellulose (e.g., pulp/natural fibers that typically have dimensions >20 μm in diameter and 1 mm in length) will not be discussed. Particular types of CN will be mentioned when each mechanism is explained.

20.4.1 Particle interactions

During the initial contact of water and cement particles, agglomerations tend to happen due to relatively large van der Waals forces of attraction. The range of this attraction is between 5 and 7 nm [14], entrapping water between particles. As discussed in Section 20.2.3.2, WRAs can be used to reduce this agglomeration by imparting a combination of electrostatic and steric repulsive forces between particles. CNs have high specific surface area, are rich in reactive hydroxyl groups, and exhibit high eletrosteric charges in solution.

Cao and coworkers [10] reported zeta potential of cement and CNC in a simulated pore solution (pH = 12.7) of freshly mixed cement paste. The results indicated that cement particles have a much stronger tendency to attract the CNCs at lower concentration. In other words, CNCs would tend to adhere to the surface of cement particles rather than agglomerate themselves. Cao and coworkers [10] also pointed out that CNC outperformed the WRA by achieving a higher DOH without significant segregation at higher loading (1.5 vol%). The steric stabilization effect was also supported by SEM imaging when comparing control mixtures to 1.5 vol% CNC–cement mixture. As shown in Fig. 20.14, the ring or shell structure around unhydrated cement particles can be explained by higher concentration of CNC particles in the area.

A delay in early-age hydration in some CN–cement composites were reported [10,38,44]. The delay is an indication of CN particles attached to the surface of cement particles, blocking the water access in the early ages. A similar observation can be frequently seen in cement paste with WRA [20], where early-age hydration is delayed while overall DOH is increased in the later age.

Other research also pointed out that the enhanced properties observed in CN–cement composites were related to large numbers of hydroxyl groups in CN

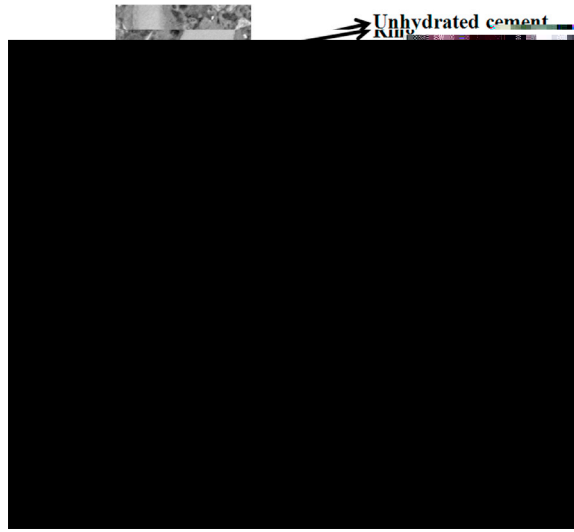

Figure 20.14 SEM image of 1.5 vol% Type V cement–CNC composites at 7-day age. *Source*: Reprinted from Cao Y, Zavattieri P, Youngblood J, Moon RJ, Weiss WJ. The influence of cellulose nanocrystal additions on the performance of cement paste. Cem Concr Compos 2015;56:73–83, Copyright (2015), with permission from Elsevier.

[38,43,44,48]. This is due to the high hydrophilic properties and high reactivity of hydroxyl groups, increasing the interactions between cellulose particles, cement particles, and cement hydration products.

20.4.2 Rheology modification

As CN interacts with cement particles in pore solution, the yield stress and viscosity of the cementitious mixture can be altered. Cao and coworkers [10] reported a trend of yield stress of freshly mixed CNC–cement pastes, as shown in Fig. 20.15. At low CNC loadings, eletrosteric stabilization was the most effective mechanism, liberating entrapped water molecules while lowering the yield stress. At higher CNC loadings, the yield stress increases linearly likely due to CNC agglomeration in the pore solution, which requires higher forces to break agglomeration. Based on a percolation model, the critical concentration in a pore solution was calculated to be 0.18 vol% [46].

Rheology modification by CN was also reported by other researchers [38,39,53]. Hoyos and coworkers [38] used mini slump test and yield stress test to evaluate rheology of MCC–cement composites. The results showed that at 3 wt% MCC loading, slump was slight reduced while yield stress of MCC–cement composites was found to be 2.6 times that of cement paste without MCC. Mohamed and coworkers [53] reported the effect of CMF loading on the rheology SCC, using tests specifically

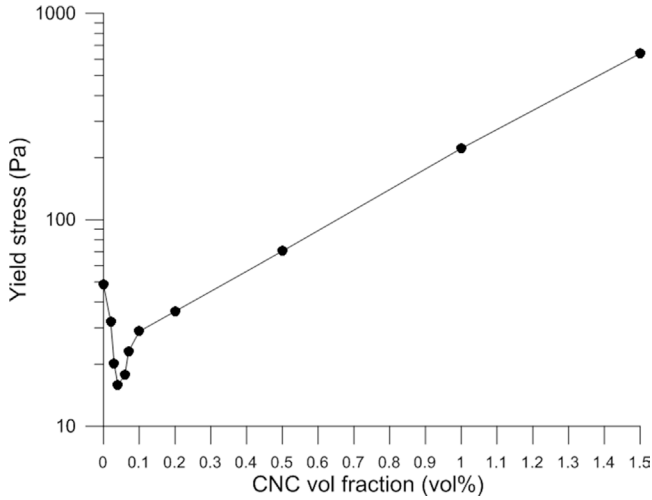

Figure 20.15 Yield stress of CNC–cement pastes with different concentrations. *Source*: Reprinted from Cao Y, Zavattieri P, Youngblood J, Moon RJ, Weiss WJ. The influence of cellulose nanocrystal additions on the performance of cement paste. Cem Concr Compos 2015;56:73–83, Copyright (2015), with permission from Elsevier.

designed for SCC, including concrete slump cone test (Abrams cone), L-box test, V-funnel test, and J-ring test. The results showed that the incorporation of CMF reduced superplasticizer demand to achieve the required workability. Nilsson and Sargenius [39] also reported that yield stress of MFC–cement composites increased as a function of MFC loading.

It is also worth mentioning that as a cementitious additive, the effect of rheology modification is an advantage of CN over inorganic carbon nanotube and carbon nanofiber. To properly disperse carbon nanotube and carbon nanofiber into cement paste is always a challenge, due to their high hydrophobicity and strong self-attraction. At lower loading, CN tends to improve the workability and reduce agglomeration during mixing. CN has been recognized as safe to use without adverse effect on health or the environment [23,56].

20.4.3 "Short-circuit diffusion"

Cao and coworkers [10] proposed a "short-circuit diffusion" (SCD) hypothesis to explain the increased DOH in the CNC–cement composites mentioned in Section 20.3.4. It is known that a dense shell of hydration products will form around the unhydrated cement particles, slowing down further hydration reaction by limiting water accessibility at early ages during the hydration process. When CNCs are introduced into the matrix, they tend to attach to the surface of the cement particle. As

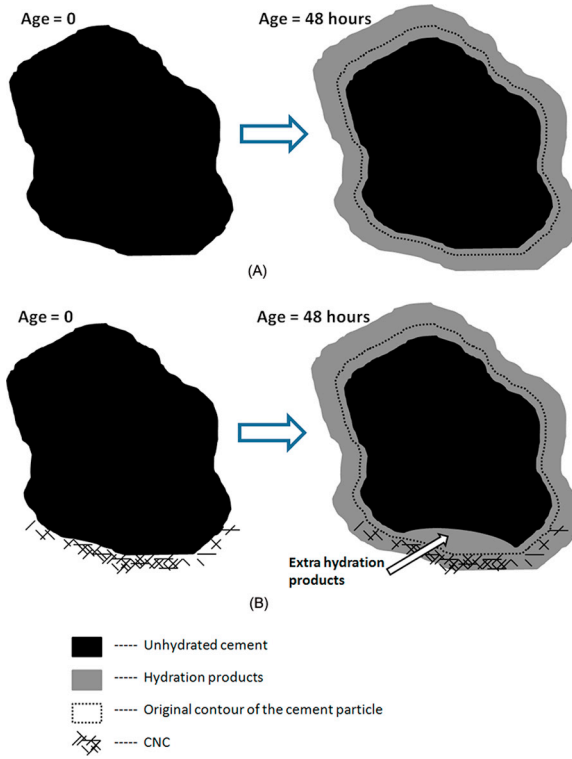

Figure 20.16 A schematic illustration of short-circuit diffusion: (A) plain cement paste, and (B) CNC–cement composites.
Source: Reprinted from Cao Y, Zavattieri P, Youngblood J, Moon RJ, Weiss WJ. The influence of cellulose nanocrystal additions on the performance of cement paste. Cem Concr Compos 2015;56:73–83, Copyright (2015), with permission from Elsevier.

the hydration products form, they appear to develop around the CNC network, which appears to allow water molecules to more easily diffuse through the hydration product to reach the unhydrated cement particle (as shown in Fig. 20.16). It is expected that water diffusion will happen faster in the CNC-rich region. Cao and coworkers [10] also pointed that there may be a critical CNC concentration at which SCD is triggered. This hypothesis was analyzed in terms of flexural strength and DOH.

Ferrara and coworkers [43] reported that autogenous shrinkage was slightly reduced by incorporating 0.2 vol% CNF in a representative paste of HPFRCC. The authors attributed the effect to additional moisture paths created by the CNF due to its porous structure, hydrophilic character, and water retention capability. However, the authors did not indicate how this moisture transport differs from that observed with micro- and macrocellulose fibers in which the pore spaces in the cellulose fibers (lumen and cell wall) can attract and transport water, as neither mechanism is available for CNF.

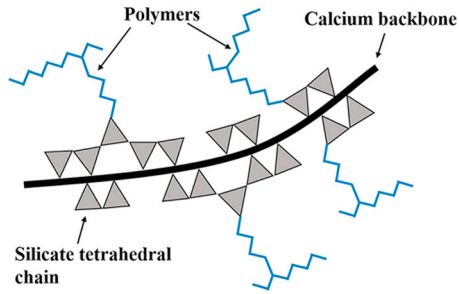

Figure 20.17 Schematic of polymer groups grafted at T-silicon sites.
Source: Adapted from Franceschini A, Abramson S, Mancini V, Bresson B, Chassenieux C, Lequeux N. New covalent bonded polymer-calcium silicate hydrate composites. J Mater Chem 2007;17(9):913–22 [60].

20.4.4 Other potential mechanisms

Raki and coworkers [27] gave a comprehensive summary of modification of C–S–H structures at nanoscale. Beaudoin and coworkers [57–59] showed that hexadecyltrimethylammonium (HTDMA), polyethylene glycol (PEG), and methylene blue dye can be attached to the sites where silicate tetrahedral is missing in C–S–H (See Fig. 20.17). Minet and coworkers [61] also demonstrated that nanosized organic groups can be directly linked to the silicate chains of C–S–H. Much research is still needed to study the C–S–H modification and its mechanism, mechanical properties, and durability. This could provide insights to understand cement hydration at fundamental levels and interactions between hydrated cement phases and chemical admixtures, nanosized fillers, and CN.

Most fiber–cement composites attribute strength and toughness improvement to crack bridging (see Section 20.2.3.3). It was observed that the presence of fibers can delay, and in some case even arrest, cracking propagation [6]. At the nanoscale, inorganic carbon nanotube and carbon nanofiber also demonstrated nanoreinforcement (See Fig. 20.6) due to extremely high mechanical properties (tensile strength in the range of GPa and MOE in the range of TPa), and large aspect ratio (of 1000 or more). However, the dispersion issue due to high hydrophobicity and strong self-attraction is really limiting their use in cementitious materials [25]. Despite only little evidence to date, it is likely that CN-reinforced cementitious materials can also take advantage of nanoreinforcement. Ardanuy and coworkers [11] observed an "embrittlement" in CNF–cement composite comparing to sisal fiber–cement composite, as shown in Fig. 20.10. Based on this observation, it was proposed that a CMF/CNF hybrid cement composite would be the ideal reinforcement system to cementitious materials, taking advantage of both "embrittlement" and toughness improvement.

In contrast, CNCs are even smaller in dimension, which render them too short (<200 nm) to bridge a microcrack as compared to CNF and CMF. The high MOE of CNC (e.g., 110–220 GPa in the axial direction) [9,62] is higher than that reported for

C–S–H (~20–30 GPa) [63], indicating that CNC could potential stiffen the C–S–H areas. The recent nanoindentation work by Cao and coworkers [47] showed that regions within the cement matrix rich in CNC exhibit higher elastic modulus, suggesting a nanoreinforcement effect of CNC.

20.5 Potential applications in cementitious materials

As a whole, research and development in CN is accelerating across many application areas, which is spurring an increased rate of CN-related patent application filings [64,65]. However, as the first commercial products containing CN are starting to hit the marketplace, none are for cementitious materials. One way to assess emerging application areas of materials is to explore the patent literature. Considering CN applications in cementitious materials, most effort has been related to CN as an additive in fiber–cement composites, and concrete.

20.5.1 Fiber-cement boards

Fiber–cement composites can be used in applications of siding, roofing, backer board, underlayment, and trim, which are generally composed of cement, silica sand, unbleached wood pulp, and various additives. The wood fiber is added to facilitate board manufacturing, and provides a level of impact resistance allowing some products to be nailed rather than by fixing through predrilled holes. Patents have focused on CN additions for tailoring internal curing [66], and on the methods for the incorporating fibrillated cellulose [62], or fibrillated carboxymethyl cellulose (e.g., type of CNF) in the admixture such that a fine dispersal of the CN is maintained in the final composite. The resulting composites had lower water adsorption [62], lower water wicking [62], increased elastic modulus [62], reduced internal shrinking that occurs while the cement sets [66], and increased durable toughness [63].

20.5.2 Concrete

Concrete is a construction material used to make pavements, architectural structures, foundations, motorways/roads, bridges/overpasses, parking structures, brick/block walls, and footings for gates, fences, and poles. Concrete is made of a mixture of cement, sand, stone, and water. As summarized in Section 20.3, there is a significant potential for CNs to improve the properties of cement and concrete. Patents have centered on CN as an additive to cement, for enhancing strength [44,67], for altering water retention as well as viscosity for various cementitious materials [68], and as a stabilization agent in SCC applications [69]. CNC additions to cement pastes can increase the extent of the hydration reaction, resulting in increased flexural strength (as described in Section 20.3.4) [67]. Likewise, CNF additions to cement pastes can increase the solidification delay time and maintain good liquidity, which helps discharge entrapped gas, reducing the porosity of cement paste, and subsequently improving the mechanical

properties of the cement slurry [44]. In SCC applications, CMFs can act as a stabilizing admixture [69], reducing water bleeding and aggregate settlement, resulting in increased concrete durability. Water bleeding is effectively prevented with the finest fibril additives. In cementitious materials applications (e.g., dry mortar, gypsum, gypsum compositions and/or lime, portland cement, iron portland cement, blast furnace cement, trass cement, or combinations thereof), CN additions have been shown to be a suitable alternative or additive to cellulose ethers (CEs), having good water retention properties, modified viscosity, and high mechanical strength [68].

20.5.3 Limitations

Advances over the past 10 years in the research, development, and larger volume processing of CN have enabled a viable exploration into various established industrial applications. CN shows potential as an additive in cementitious materials and drilling fluids, however, there are several limitations that must be overcome before industry acceptance, such as increased production volume of CN materials; need of multiple suppliers producing a similar product; development of standards, codes, and supporting metrology; and overcoming market/industry resistance. The immense scale of the industries associated with cementitious materials demands high CN production volumes to meet potential needs. For example, the approximate annual demand for cement is approximately 4 billion metric tons. The market potential for CN in cements [70,71] have recently been reported. An upper-end potential of CN in cements was 4.1 million metric tons (at 0.5 wt% loading and 25% market penetration). The estimate, though speculative, gives a sense of the CN volumes that may be needed. Note that currently the total annual production worldwide for CNC and CNF is 650 tons $year^{-1}$ and 1700 tons $year^{-1}$, respectively [72]. Industry will also require multiple CN producers that can make a similar CN product that can be used interchangeably. To date this has not been achieved, as most CN producers make a unique CN product (e.g., particle morphology, size, distribution, surface chemistry, surface charge, etc.). The development of supporting metrology is needed as precisely determining the size distribution of CN dispersion or length distribution is quite challenging. Along with this, the CN producer community and various cementitious communities will need to development materials standards and new codes to clearly reflect new property improvements as a result of CN additions (as compared to existing materials used to date); this will speed the adoption of CNs by these industries.

It is known that the loss of durability of cellulose–cement composites is significant due to degradation of cellulose fibers in high-alkali environment. To date there has been little or no research on the long-term durability of CN–cement composites, and such long-term durability studies are needed.

20.6 Concluding remarks

This review presents a survey of the research literature of CNs as additives in cementitious materials. The focus was how CNs will interact with the cement particles and

affect hydration process, rheological properties, and mechanical properties. In addition, potential working mechanisms responsible for the observed properties modification were introduced, hoping to provide insights into future research work on more efficient application of CN in cementitious materials.

Acknowledgments

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