3

Nanoparticles for high performance concrete (HPC)

F. PACHECO-TORGAL, University of Minho, Portugal, S. MIRALDO, University of Aveiro, Portugal, Y. DING, Dalian University of Technology, China and J. A. LABRINCHA, University of Aveiro & CICECO, Portugal

DOI: 10.1533/9780857098832.1.38

Abstract: According to the 2011 ERMCO statistics, only 11% of the production of ready-mixed concrete relates to the high performance concrete (HPC) target. This percentage has remained unchanged since at least 2001 and appears a strange choice on the part of the construction industry, as HPC offers several advantages over normal-strength concrete, specifically those of high strength and durability. It allows for concrete structures requiring less steel reinforcement and offers a longer serviceable life, both of which are crucial issues in the eco-efficiency of construction materials. Despite the growing importance of nanotechnology, investigations into the incorporation of nanoparticles into concrete are rare (100 out of 10,000 Scopus concrete-related articles published in the last decade). It therefore remains to be seen how research in this area will contribute to concrete eco-efficiency. This chapter summarizes the state of current knowledge in the field and considers the influence of nanoparticles on the mechanical properties of concrete and its durability. It also includes the control of calcium leaching. The problem of efficient dispersion of nanoparticles is analyzed.

Key words: Portland cement, nanoparticles, calcium leaching, concrete durability, high performance concrete (HPC).

3.1 Introduction

Concrete is the most widely used of all construction materials. Its production currently stands at around 10 km^3/year (Gartner and Macphee, 2011). For purposes of comparison, the amount of fired clay, timber, and steel used annually is around 2, 1.3 km^3 and 0.1 km^3, respectively (Flatt *et al.*, 2012). Portland cement, which acts as the main binder in concrete, represents almost 80% of the total CO_2 emissions associated with concrete, which contribute 6–7% of the planet's total CO_2 emissions (Shi *et al.*, 2011; Pacheco-Torgal *et al.*, 2012). This is of particular concern in the context of climate change.

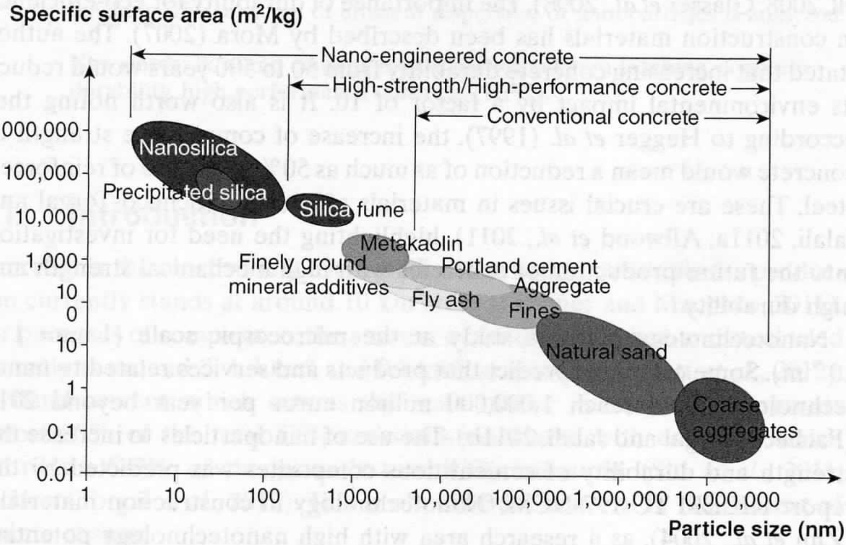
The demand for Portland cement is expected to increase by almost 200% over 2010 levels by 2050, reaching 6,000 million tons per year. According to the ERMCO 2011 statistics, ready-mixed concrete production lies essentially between C25/30 and C30/37. In addition, only 11% of the concrete production corresponds to the high performance concrete (HPC) strength class target. As ERMCO 2001 statistics showed a 10% figure for this type of concrete, it appears that high strength concrete demand has remained unchanged during the last decade. Normal strength concrete produces less durable structures which require frequent maintenance and conservation operations or even complete replacement, with the associated consumption of additional raw materials and energy. Many degraded concrete structures were built decades ago at a time when little attention was given to durability (Hollaway, 2011). It is not therefore surprising that worldwide concrete infrastructure rehabilitation costs are extremely high.

For example, in the USA, around 27% of all highway bridges are in need of repair or replacement. In addition, the cost of deterioration caused by deicing and sea salt is estimated at over US$150 billion (Davalos, 2012). In the European Union, nearly 84,000 reinforced and pre-stressed concrete bridges require maintenance, repair and strengthening. This results in an annual cost of £215 million, not including traffic management costs (Yan and Chouw, 2013). Beyond the durability problems caused by imperfect concrete placement and curing operations, the real problem with the durability of ordinary Portland cement concrete (OPC) is the intrinsic properties of the material which has a high degree of permeability. This allows the ingress of water and other aggressive elements, leading to carbonation and chloride ion attack, which ultimately result in corrosion (Bentur and Mitchell, 2008; Glasser *et al.*, 2008). The importance of durability for eco-efficiency in construction materials has been described by Mora (2007). The author stated that increasing concrete durability from 50 to 500 years would reduce its environmental impact by a factor of 10. It is also worth noting that according to Hegger *et al.* (1997), the increase of compressive strength in concrete would mean a reduction of as much as 50% in the use of reinforced steel. These are crucial issues in materials efficiency (Pacheco-Torgal and Jalali, 2011a; Allwood *et al.*, 2011), highlighting the need for investigation into the future production of concretes with high mechanical strength and high durability.

Nanotechnology involves study at the microcospic scale (1 nm= 1×10^{-9} m). Some estimates predict that products and services related to nanotechnology could reach 1,000,000 million euros per year beyond 2015 (Pacheco-Torgal and Jalali, 2011b). The use of nanoparticles to increase the strength and durability of cementitious composites was predicted by the report RILEM TC 197-NCM, 'Nanotechnology in construction materials' (Zhu *et al.*, 2004), as a research area with high nanotechnology potential. Since that time, several dozen papers have been published by the Society of Chemical Industry (SCI) in the field. However, the majority of these publications were written by materials science investigators and were principally concerned with materials performance with a lesser focus on civil engineering short-term commercial applications. For instance, the 'bottom-up' multiscale modeling approach (Pellenq *et al.*, 2009), could be an excellent strategy which 'has been spectacularly successful in fields ranging from metallurgy to medicine' (Jennings and Bullard, 2011) but, unfortunately, relies on tools that 'require years of training and considerable computational expense to operate', neither of which are traditionally associated with the construction industry. The importance of the present review lies in the need to redirect future investigations in this field to a precise target capable of serving a clear short-term civil engineering goal.

3.2 Concrete with nanoparticles

Nanoparticles may be obtained either through high milling energy (Sobolev and Ferrada-Gutierrez, 2005) or by chemical synthesis (Lee and Kriven, 2005). They have a high surface area to volume ratio (Fig. 3.1) which provides high chemical reactivity. Most investigations use nano-silica (nano-SiO_2), and nano-titanium oxide (nano-TiO_2), while a few use nano-Fe_2O_3 (Sanchez and Sobolev, 2010).



3.1 Particle size and specific surface area related to concrete materials (Sanchez and Sobolev, 2010).

3.2.1 Mechanical properties

Porro *et al.* (2005) refers to the use of nano-silica particles as increasing the compression strength of cement pastes. The same authors state that this phenomenon is not due to pozzolanic reaction, as the calcium hydroxide consumption is very low, but rather to the increase of silica compounds which contribute to a denser micro-structure.

According to Lin *et al.* (2008), the use of nano-silica on sludge/fly ash mortars, compensates for the negative effects associated with sludge incorporation in terms of the setting time and initial strength. Sobolev *et al.* (2008) reported that the addition of nano-silica produced an increase in strength of 15–20%. Other authors (Gaitero, 2008; Gaitero *et al.*, 2009) believe that nano-silica causes an increase in the C-S-H chain dimension and stiffness. Nasibulin *et al.* (2009) reported a twofold increase in strength. Chaipanich *et al.* (2010) records that 1% of carbon nano-fibers (by binder mass) can compensate for the strength reduction associated with the replacement of 20% fly ash. Konsta-Gdoutos *et al.* (2010a) also studied the effect of carbon nano-fibers on cement pastes (0.08% by binder mass) and observed an increase in strength.

Nazari and Riahi (2011a) used ZrO_2 nanoparticles with an average particle size of 15 nm and reported an improvement in the flexural strength of self-compacting concrete up to 4 wt%. Increasing the nanoparticle content caused a reduction in flexural strength because of the inadequate dispersion of nanoparticles within the concrete matrix. Givi *et al.* (2010) studied the effects of different particle sizes of nano-SiO_2 (15 and 80 nm) and reported that the optimal replacement level of nano-SiO_2 particles was gained at 1.0% and 1.5%, respectively. The effect of nanoparticle addition is threefold:

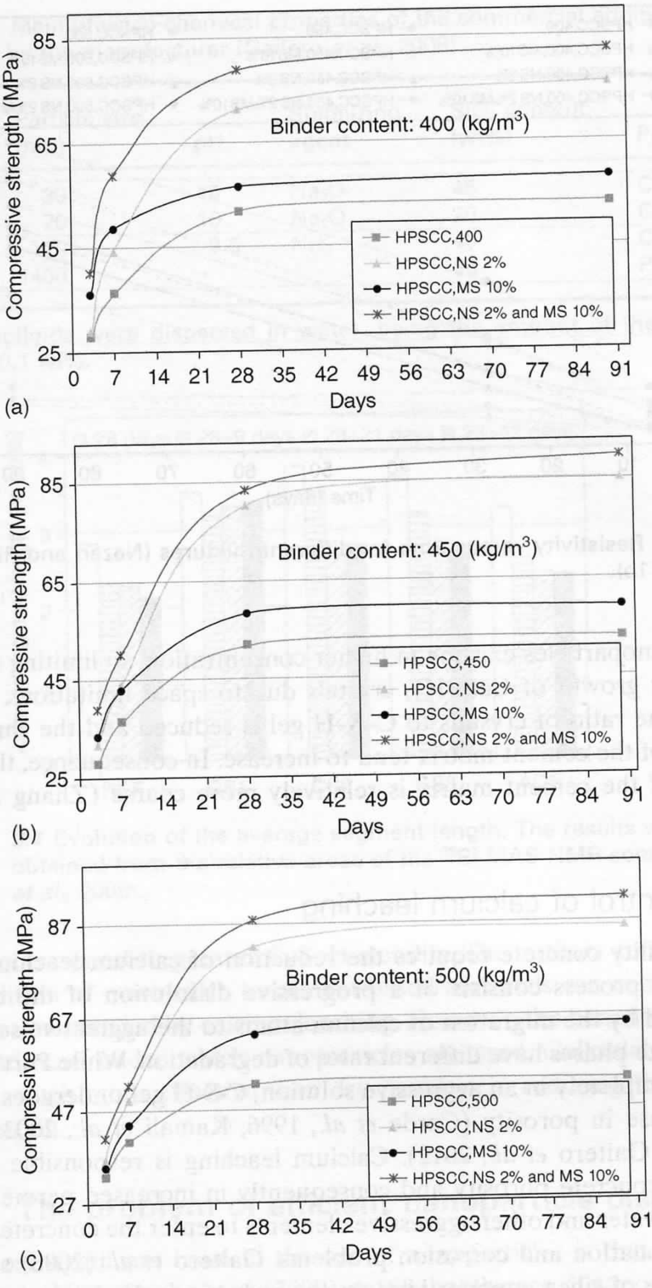
1. As the average diameter of C-S-H gel is approximately 10 nm, the nanoparticles fill the voids in the CHS structure, so producing a denser concrete.
2. The nanoparticles act as nucleation centers, contributing to the development of hydration in Portland cement.
3. Nanoparticles react with $Ca(OH)_2$ crystals and produce C-S-H gel. They also act as kernels in the cement paste which reduces the size of $Ca(OH)_2$ crystals.

3.2.2 Durability

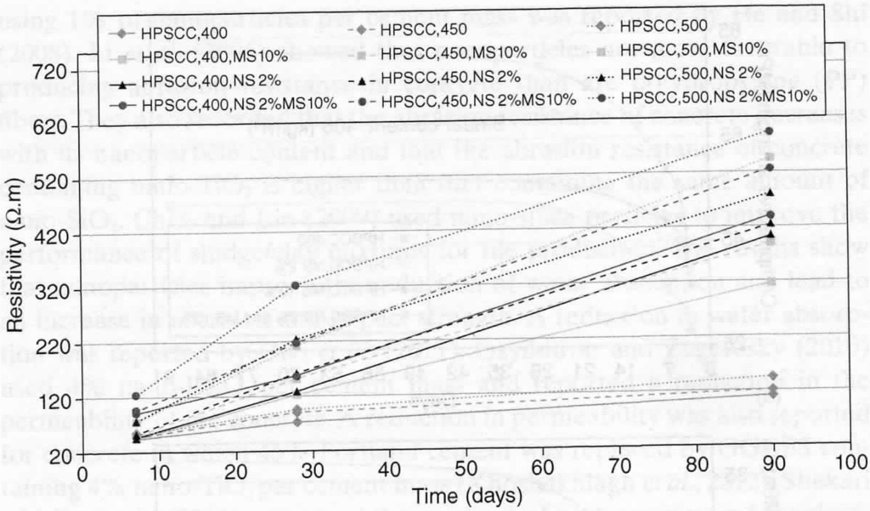
Investigations carried out by Ji (2005) showed that concrete containing nano-silica particles has lower water permeability. This is due to the reduction of the amount of $Ca(OH)_2$ which produces a denser inter-facial transition zone (ITZ). A reduction of chloride ion permeability as a result of using 1% of nanoparticles per cement mass was reported by He and Shi (2008). Li *et al.* (2006) showed that nanoparticles are more favorable to producing abrasion resistance in concrete than are polypropylene (PP) fibers. They also recorded that the abrasion resistance of concrete decreases with its nanoparticle content and that the abrasion resistance of concrete containing nano-TiO_2 is higher than that containing the same amount of nano-SiO_2. Chen and Lin (2009) used nano-silica particles to improve the performance of sludge/clay mixtures for tile production. The results show that nanoparticles improve the reduction of water absorption and lead to an increase in abrasion and impact strength. A reduction in water absorption was reported by Givi *et al.* (2011). Ozyildirim and Zegetosky (2010) used 4% nano-Fe_2O_3 per cement mass and reported a reduction in the permeability of the concrete. A reduction in permeability was also reported for concrete in which 45% Portland cement was replaced by GGBFS containing 4% nano-TiO_2 per cement mass (Khoshakhlagh *et al.*, 2012). Shekari and Razzaghi (2011) compared the mechanical performance and the durability of concretes containing 1.5% of distinct nanoparticles (nano-ZrO_2, nano-TiO_2, nano-Al_2O_3, nano-Fe_3O_4). They concluded that the nano-Al_2O_3 is the most effective, but offered no explanation for the finding.

Nazari and Riahi (2011b) studied the performance of concrete in which Portland cement was replaced by up to 2% nano-Al_2O_3, with an average particle size of 15 nm. They reported that the optimum level of nano-Al_2O_3 particle content was 1.0%. Jalal *et al.* (2012) showed that concretes containing 2% SiO_2 nanoparticles underperformed when compared to those prepared with a mixture of 2% SiO_2 nanoparticles with the addition of 10% micro-silica. This composition showed enhanced mechanical strength (Fig. 3.2) as well as improved durability. This was assessed by water absorption, capillary water absorption, Cl ion percentage and electric resistivity (Fig. 3.3). According to Zhang and Li (2011), the pore structure of concrete containing nano-TiO_2 is finer than that of concrete containing the same amount of nano-SiO_2. The resistance to chloride penetration of concretes containing nano-TiO_2 is higher than that of concretes containing the same amount of nano-SiO_2.

This is explained by the particle diameter of nano-SiO_2 being smaller than that of nano-TiO_2, and the specific surface area of nano-SiO_2 being much larger than that of nano-TiO_2. The water requirement of concrete containing nano-SiO_2 is therefore higher than that of concrete containing the same amount of nano-TiO_2. The authors also reported that the pore structure refinement increases with the content of nanoparticles (5% < 3% < 1%) while chloride penetration decreases (5% < 3% < 1%). These results partially confirm those previously obtained by Li *et al.* (2006). In their view, the increased content of nanoparticles weakens the refinement of the pore structure of concrete. This may be attributed to the reduction of the distance



3.2 Compressive strength of HPSCC samples with binder contents of (a) 400, (b) 450, and (c) 500 (Nazari and Riahi, 2011b).



3.3 Resistivity versus time for different mixtures (Nazari and Riahi, 2011b).

between nanoparticles existing in higher concentration, so limiting the formation and growth of $Ca(OH)_2$ crystals due to space limitations. In this situation, the ratio of crystals to C–S–H gel is reduced and the shrinkage and creep of the cement matrix tend to increase. In consequence, the pore structure of the cement matrix is relatively more coarse (Zhang and Li, 2011).

3.2.3 Control of calcium leaching

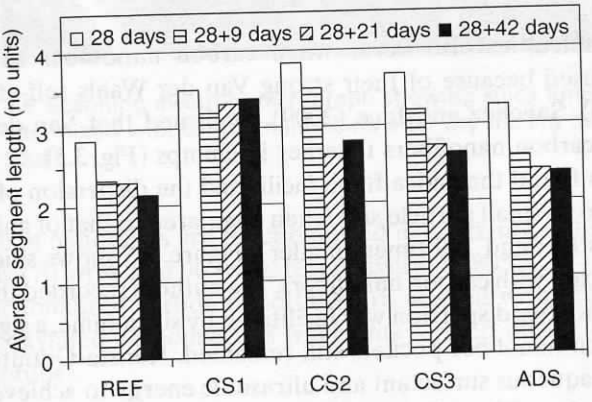
High durability concrete requires the reduction of calcium leaching. This degradation process consists of a progressive dissolution of the cement paste caused by the migration of calcium atoms to the aggressive solution. Cement paste phases have different rates of degradation. While Portlandite dissolves completely in an aggressive solution, C-S-H gel undergoes only a slight increase in porosity (Carde *et al.*, 1996; Kamali *et al.*, 2003; Haga *et al.*, 2005; Gaitero *et al.*, 2012). Calcium leaching is responsible for an increase in concrete porosity and consequently in increased permeability. This allows water and other aggressive elements to enter the concrete which causes carbonation and corrosion problems. Gaitero *et al.* (2008) studied the influence of silica nanoparticles on the reduction of calcium leaching. Concrete mixtures containing 6% (by weight of cement) of four different types of commercial silica nanoparticles (Table 3.1) were used.

Figure 3.4 shows that the addition of silica nanoparticles to the cement paste favors the growth of silicate chains. This is advantageous as longer

Table 3.1 Main physico-chemical properties of the commercial additions used as stated by the manufacturer (Gaitero *et al.*, 2008)

Name	Particle size (nm)	pH	Stabilizing agent	SiO_2 content (wt%)	Presentation
CS1	30	10	Na_2O	45	Colloid
CS2	20	10	Na_2O	20	Colloid
CS3	120	9.5	NH_3	40	Colloid
ADS	1400	–	–	95	Powder

All the colloids were dispersed in water, being the amount of the stabilizing agents <0.1 wt%.



3.4 Evolution of the average segment length. The results were obtained from the relative areas of the ^{29}Si MAS-NMR spectra (Gaitero *et al.*, 2008).

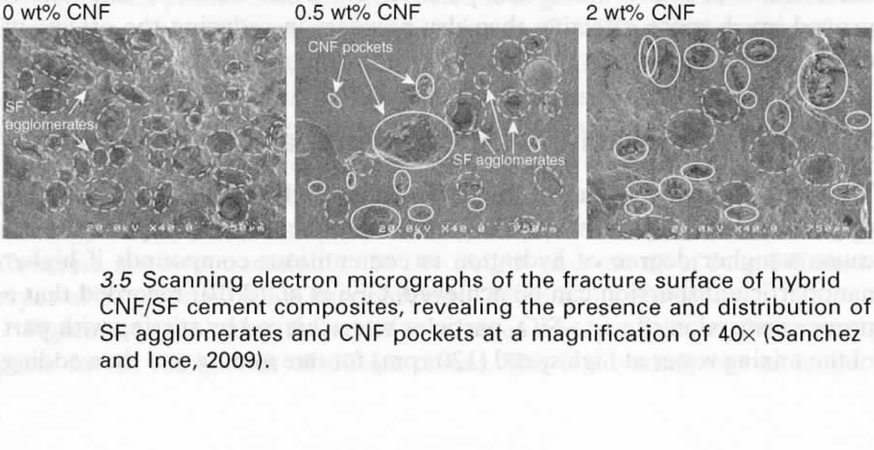
chains correspond to greater C–S–H stability. The authors concluded that the addition of nano-silica to cement-based materials can control C–S–H degradation induced by calcium leaching. However, the benefits depend on the conditions under which nanoparticles are used. Colloidal dispersions proved much more effective than dry powders in reducing the effects of degradation.

3.3 The problem of efficient nanoparticle dispersion

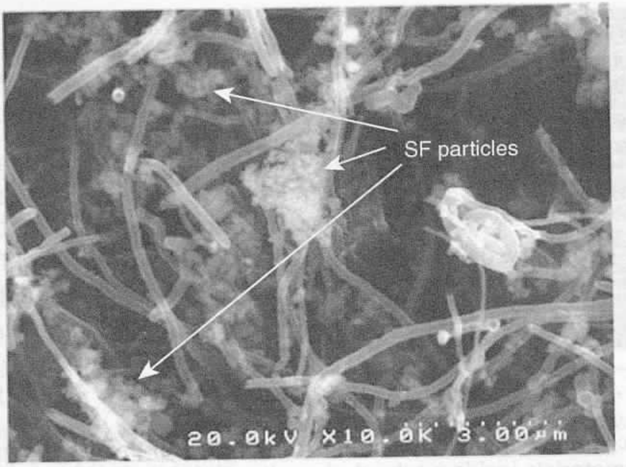
The most significant issue in the use of nanoparticles is that of effective dispersion. Vera-Agullo *et al.* (2009) stated that the use of nanoparticles will cause a higher degree of hydration in cementitious compounds if higher nanoparticle dispersion can be achieved. Givi *et al.* (2010) recorded that a proper dispersion of nano-SiO_2 particles was achieved by stirring with part of the mixing water at high speed (120 rpm) for one minute and then adding to the mixture. Zhang and Li (2011) used a water-reducing agent (UNF-5, a type of b-naphthalene sulfonic acid and formaldehyde condensates) to help disperse the nanoparticles in the cement paste and to achieve a good degree of workability in the concrete. A de-foamer (tributyl phosphate) was also used to decrease the number of air bubbles. To prepare concrete containing nanoparticles, a water-reducing agent was first mixed with water in a mortar mixer. The nanoparticles were then added and stirred at high speed for five minutes. A de-foamer was added during stirring. Following this, the cement, sand and coarse aggregate were mixed at low speed for two minutes in a centrifugal concrete blender. The mixture of water, water-reducing agent, nanoparticles, and de-foamer was then slowly added and stirred at low speed for a further two minutes to achieve good workability.

Dispersion difficulties also occur when carbon nanotubes or carbon nanofibers are used because of their strong Van der Waals self-attraction (Xie *et al.*, 2005). Sanchez and Ince (2009) confirmed that Van der Waals forces hold the carbon nanofibers together in clumps (Fig. 3.5).

These authors found that silica fume facilitated the dispersion of carbon nanofibers due to its small particle size when compared to that of anhydrous cement particles (around 100 times smaller). Figure 3.6 shows silica fume particles intermixed with carbon nanofibers. The authors recorded that even when carbon nanofiber dispersion was facilitated by silica fume, a significant number of carbon nanofiber pockets still remained. Konsta-Gdoutos *et al.* (2010b) used an aqueous surfactant and ultrasonic energy to achieve a high degree of carbon nanofiber dispersion. They found that a constant surfactant to carbon weight ratio of 4.0 achieved effective dispersion. Nochaiya and Chaipanich (2011) also found that homogeneous dispersion can be obtained if carbon nanotubes are mixed with water and then subjected to ultrasound for one hour. Nasibulina *et al.* (2012) suggest that high-quality dispersion of carbon nanotubes may be achieved by a two-step method:


0 wt% CNF 0.5 wt% CNF 2 wt% CNF

3.5 Scanning electron micrographs of the fracture surface of hybrid CNF/SF cement composites, revealing the presence and distribution of SF agglomerates and CNF pockets at a magnification of 40× (Sanchez and Ince, 2009).

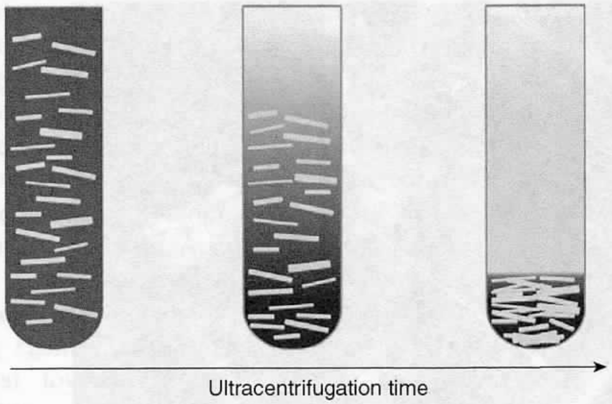


3.6 Scanning electron micrograph showing silica fume particles intermixed with carbon nanofibers after dry mixing (Sanchez and Ince, 2009).

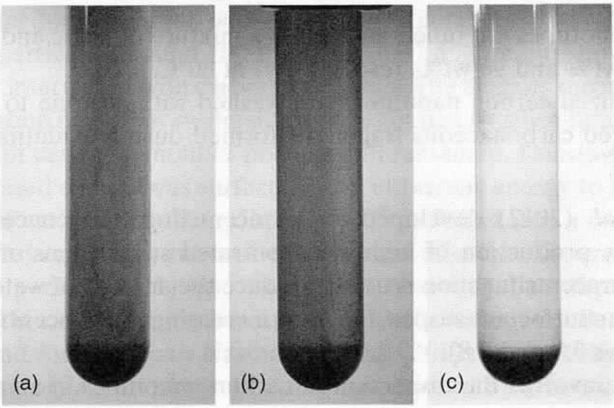
1. Carbon nanotubes are functionalized in a mixture of nitric and sulfuric acids (70 wt% and 96 wt%, respectively) at 80°C.
2. Functionalized carbon nanotubes are washed with acetone to remove carboxylated carbonaceous fragments formed during oxidation of the nanotubes.

Metaxa *et al.* (2012) developed an ultracentrifugation concentration process for the production of highly concentrated suspensions of carbon nanotubes. Ultracentrifugation is used to reduce the amount of water in the nanotube water/surfactant suspension, thus increasing the concentration of nanotubes (Figs 3.7 and 3.8).

The process involves the dispersion of carbon nanotubes in an aqueous surfactant solution by ultrasonication and ultracentrifugation of the suspension, followed by decantation and ultrasonication of the remaining suspension. Absorbance spectroscopy results confirmed a fivefold increase in the concentration of carbon nanotubes in the suspensions. Another important issue in the dispersion of nanoparticles is its quantitative characterization. To date, three common methods have been used to analyze the dispersion of CNTs or CNFs in aqueous solutions. These are optical microscopy, electron microscopy (using both scanning electron microscopes (SEM) and transmission electron microscopes (TEM)), and ultraviolet–visible (UV–Vis) spectroscopy (Tyson *et al.*, 2011). These authors developed a method for quantifying the dispersion and agglomeration of both carbon nanofibers and carbon nanotubes within an aqueous solution. The dispersion quantity, D, is measured by the free-path spacing between particles; the agglomera-



3.7 Schematic figure showing the progression of the sedimentation of nano-materials inside a tube during ultracentrifugation (Metaxa *et al.*, 2012).



3.8 Suspensions of carbon nanotubes ultracentrifuged for (a) 30 min, (b) 45 min and (c) 60 min (Metaxa *et al.*, 2012).

tion quantity, *A*, is measured by the particle size. The agglomeration percentage is critical because, in certain cases, dispersion between two images can be identical, although the agglomeration percentage will have changed. In both cases, a quantifiable percentage is calculated based on the statistical probability that either the free-path spacing or particle size will fall within a certain percentage above and below *l*, where *l* is either the mean spacing or the particle size. A high value of *D* indicates a better dispersion. A lower value of *A* indicates a reduction in agglomeration.

3.4 Conclusions

A review of the literature on the contribution of nanoparticles in HPC shows the following.

- Nanoparticles may contribute to a dramatic increase in the mechanical strength of cementitious composites, thus helping the production of HPC. The related mechanisms are as follows:
  - The filling of voids in the C-H-S structure, so enabling the production of concrete of greater density.
  - Acting as nucleation centres and contributing to the development of hydration in Portland cement.
  - Reaction with $Ca(OH)_2$ crystals to produce C–S–H gel. The nanoparticles also act as kernels in the cement paste and reduce the size of the $Ca(OH)_2$ crystals.
- The optimal quantity of nanoparticles will depend upon their type and average dimension.
- Further investigations are needed to determine which nanoparticles are most effective in enhancing concrete durability.
- Nano-silica appears to control calcium leaching. Colloidal dispersions are more effective in reducing the effects of degradation than dry dispersions.
- One of the most significant issues in the use of nanoparticles is that of effective dispersion. Different authors have used different methods in order to achieve a high dispersion. However, there is still a need to search for improved methods. The tools used to assess uniformity of distribution are largely quantitative (optical microscopy, electron microscopy and transmission electron microscopy). The validity of the methods used to date must therefore be confirmed using quantitative characterization tools.

3.5 References

Allwood J, Ashby M, Gutowski T, Worrell E (2011) Material efficiency: a white paper. *Resources, Conservation and Recycling* 55, 362–381.

Bentur A, Mitchell D (2008) Material performance lessons. *Cement and Concrete Research* 38, 259–272.

Carde C, Franqois R, Torrenti J (1996) Leaching of both calcium hydroxide and C–S–H from cement paste: modeling the mechanical behaviour. *Cement and Concrete Research* 26, 1257–1268.

Chaipanich A, Nochaya T, Wongkeo W, Torkittikul P (2010) Compressive strength and microstructure of carbon nanotubes-fly ash cement composites. *Materials Science and Engineering A* 527, 1063–1076.

Chen L, Lin D (2009) Applications of sewage sludge ash and nano-SiO_2 to manufacture tile as construction material. *Construction and Building Materials* 23, 3312–3320.

Davalos, JF (2012) Advanced materials for civil infrastructure rehabilitation and protection. Seminar at The City College of New York, New York.

ERMCO (2001) *European Ready-mixed Concrete Industry Statistics, Year 2000*. European Ready Mixed Concrete Organization, Brussels.

ERMCO (2011) *Ready-mixed Concrete Industry Statistics, Year 2010*. European Ready Mixed Concrete Organization, Brussels.

Flatt R, Roussel R, Cheeseman CR (2012) Concrete: an eco-material that needs to be improved. *Journal of the European Ceramic Society* 32, 2787–2798.

Gaitero J (2008) Multi-scale study of the fibre matrix interface and calcium leaching in high performance concrete. PhD Thesis, Centre for Nanomaterials Applications in Construction of Labein-Tecnalia, Spain.

Gaitero J, Campillo L, Guerrero A (2008) Reduction of the calcium leaching rate of cement paste by addition of silica nanoparticles. *Cement and Concrete Research*, 38 1112–1118.

Gaitero J, Zhu W, Campillo I (2009) Multi-scale study of calcium leaching in cement pastes with silica nanoparticles. *Nanotechnology in Construction 3*, Springer, Berlin Heidelberg.

Gaitero J, Dolado J, Neuen C, Heber F, Koenders E (2012) Computational 3D simulation of calcium leaching in cement matrices. INS Preprint No. 1203, Institut für Numerische Simulation, Rheinische Friedrich-Wilhelms-Universität Bonn.

Gartner E, Macphee D (2011) A physico-chemical basis for novel cementitious binders. *Cement and Concrete Research* 41, 736–749.

Givi A, Rashid S, Aziz F, Salleh M (2010) Experimental investigation of the size effects of SiO_2 nanoparticles on the mechanical properties of binary blended concrete. *Composites: Part B* 41, 673–677.

Givi A, Rashid S, Aziz F, Salleh M (2011) The effects of lime solution on the properties of SiO_2 nanoparticles binary blended concrete. *Composites: Part B* 42, 562–569.

Glasser F, Marchand J. Samson E (2008) Durability of concrete – degradation phenomena involving detrimental chemical reactions. *Cement and Concrete Research* 38, 226–246.

Haga K, Sutou S, Hironaga M, Tanaka S, Nagasaki S (2005) Effects of porosity on leaching of Ca from hardened ordinary Portland cement paste. *Cement and Concrete Research* 35, 1764–1775.

Hegger J, Nitsch A, Burkhardt J (1997) Höchleistungbeton im Fertigteilbau. *Betonwerk Fertigteil-Technik* 2, 81–90.

He X, Shi X (2008) Chloride permeability and microstructure of Portland cement mortars incorporating nanomaterials. *Transportation Research Record* 2070, 13–21.

Hollaway LC (2011) Key issues in the use of fibre reinforced polymer (FRP) composites in the rehabilitation and retrofitting of concrete structure. In Karbhari VM and Lee LS (eds), *Service Life Estimation and Extension of Civil Engineering Structures*. Woodhead Publishing, Cambridge.

Jalal M, Mansouri E, Sharifipour M, Pouladkhan A (2012) Mechanical, rheological, durability and microstructural properties of high performance self-compacting concrete containing SiO_2 micro and nanoparticles. *Materials and Design* 34, 389–400.

Jennings H, Bullard J (2011) From electrons to infrastructure: engineering concrete from the bottom up. *Cement and Concrete Research* 41, 727–735.

Ji T (2005) Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO_2. *Cement and Concrete Research* 35, 1943–1947.

Kamali S, Gerard B, Moranville M (2003) Modeling the leaching kinetics of cement based materials – influence of materials and environment. *Cement and Concrete Composites* 25, 451–458.

Khoshakhlagh A, Nazari A, Khalaj G (2012) Effects of Fe_2O_3 nanoparticles on water permeability and strength assessments of high strength self-compacting concrete. *Journal of Materials Science & Technology* 28, 73–82.

Konsta-Gdoutos M, Metaxa Z, Shah S (2010a) Highly dispersed carbon nanotube reinforced cement based materials. *Cement and Concrete Research* 40, 1052–1059.

Konsta-Gdoutos M, Metaxa Z, Shah S (2010b) Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites. *Cement and Concrete Composites* 32(2), 110–115.

Lee S, Kriven W (2005) Synthesis and hydration study of Portland cement components prepared by organic steric entrapment method. *Materials and Structures* 38, 87–92.

Li H, Zhang M-H, Ou J-P (2006) Abrasion resistance of concrete containing nanoparticles for pavement. *Wear* 260, 1262–1266.

Lin D, Lin K, Chang W, Luo H, Cai M (2008) Improvements of nano-SiO_2 on sludge/fly ash mortar. *Waste Management* 28, 1081–1087.

Metaxa Z, Seo J-W, Konsta-Gdoutos M, Hersam M, Shah S (2012) Highly concentrated carbon nanotube admixture for nano-fiber reinforced cementitious materials. *Cement and Concrete Composites* 34, 612–617.

Mora E (2007) Life cycle, sustainability and the transcendent quality of building materials. *Building and Environment* 42, 1329–1334.

Nasibulin A, Shandakov S, Nasibulina L, Cwirzen A, Mudimela P, Habermehl-Cwirzen K, Grishin D, Gavrilov Y, Malm J, Tapper U, Tian Y, Penttala V, Karppinen M, Kauppinen E (2009) A novel cement-based hybrid material. *New Journal of Physics* 11, 023013.

Nasibulina LI, Anoshkin IV, Nasibulin AG, Cwirzen A, Penttala V, Kauppinen EI (2012) Effect of carbon nanotube aqueous dispersion quality on mechanical properties of cement composite. *Journal of Nanomaterials* 2012, 169262.

Nazari A, Riahi S (2011a) The effects of zinc dioxide nanoparticles on flexural strength of self-compacting concrete. *Composites: Part B* 42, 167–175.

Nazari A, Riahi S (2011b) Al_2O_3 nanoparticles in concrete and different curing media. *Energy and Buildings* 43, 1480–1488.

Nochaiya T, Chaipanich A (2011) Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials. *Applied Surface Science* 257(6), 1941–1945.

Ozyildirim C, Zegetosky C (2010) Laboratory investigation of nanomaterials to improve the permeability and strength of concrete. Virginia Transportation Research Council, Final Report VTRC 10-R18.

Pacheco-Torgal F, Jalali S (2011a) *Eco-efficient Construction and Building Materials*. Springer Verlag, London.

Pacheco-Torgal F, Jalali S (2011b) Nanotechnology: advantages and drawbacks in the field of building materials. *Construction and Building Materials* 25, 582–590.

Pacheco-Torgal F, Jalali S, Labrincha J, John VM (2012) *Eco-efficient Concrete*. Woodhead Publishing, Cambridge.

Pellenq R, Kushima A, Shahsavari R, Vliet K, Buehler M, Yip S, Ulm F (2009) A realistic molecular model of cement hydrates. *Proceedings of the National Academy of Sciences* 106(38), 16102–16107.

Porro A, Dolado J, Campillo I, Erkizia E, de Miguel Y, de Ybarra Y, Ayuela A (2005) Effects of nanosilica additions on cement pastes. *Proc International Conference on Applications of Nanotechnology in Concrete Design*, 87–96.

Sanchez F, Ince C (2009) Microstructure and macroscopic properties of hybrid carbon nanofiber/silica fume cement composites. *Composites Science and Technology* 69, 1310–1318.

Sanchez F, Sobolev K (2010) Nanotechnology in concrete – a review. *Construction and Building Materials* 24, 2060–2071.

Shekari A, Razzaghi M (2011) Influence of nanoparticles on durability and mechanical properties of high performance concrete. *Procedia Enginnering* 14, 3036–3041.

Shi C, Fernández Jiménez A, Palomo A (2011) New cements for the 21st century: the pursuit of an alternative to Portland cement. *Cement and Concrete Research* 41, 750–763.

Sobolev K, Ferrada-Gutierrez M (2005) How nanotechnology can change the concrete world: Part 2. *American Ceramic Society Bulletin* 84, 16–19.

Sobolev K, Flores I, Hermosillo R, Torres-Martinez L (2008) Nanomaterials and nanotechnology for high-performance cement composites. *American Concrete Institute, ACI Special Publication* 254, 93–120.

Tyson B, Abu Al-Rub R, Yazdanbakhsh A, Grasley Z (2011) A quantitative method for analyzing the dispersion and agglomeration of nanoparticles in composite materials. *Composites Part B: Engineering* 42, 1395–1403.

Vera-Agullo J, Chozas-Ligero V, Portillo-Rico D, Garcia-Casas M, Gutierrez-Martinez A, Mieres-Royo J, Gravalos-Moreno J (2009) Mortar and concrete reinforced with nanomaterials. *Nanotechnology in Construction 3*, Springer, Berlin.

Xie X-L, Mai Y-W, Zhou X-P (2005) Dispersion and alignment of carbon nanotubes in polymer matrix: a review. *Mater Sci Eng R* 49, 89–112.

Yan L, Chouw N (2013) Behavior and analytical modeling of natural flax fibre reinforced polymer tube confined plain concrete and coir fibre reinforced concrete. *Journal of Composite Materials* (in press).

Zhang M-H, Li H (2011) Pore structure and chloride permeability of concrete containing nanoparticles for pavement. *Construction and Building Materials* 25, 608–616.

Zhu W, Bartos P, Porro A (2004) Application of nanotechnology in construction. Summary of a state-of-the-art report. RILEM TC 197-NCM. *Materials and Structures* 37, 649–658.