

Short Communication

Nanoscience and Nano Engineering in Concrete Advances A Review

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Abstract

This paper reviews some progressive studies and innovations in cement and concrete materials in nano field. Due to the widespread acceptance of the special properties of nano materials and using them for engineering concrete performance, understanding and directing their properties are not achievable without instructing concepts and investigating interactions among components. Due to achievement of different properties of matters at the nanoscale, evaluating their physical and chemical effects on micro and macro scales in concrete and understanding the mechanisms that govern the interactions of nanoscale materials with appropriate characterization are essential. Advanced characterization techniques should be used for concrete to distinguish components of concrete multiphase composite. The other aim of this study was to better understand the importance of probably future advanced techniques and how they can be used as valuable tools to study the nanostructure and microstructure of cement and cement hydration products.

Keywords: Nano, Concrete, Structure, Characterization, Engineering.

1. INTRODUCTION

Concrete is considered to be the most widely used construction material. Nowadays consumption rate of concrete is estimated to be around 20000 million metric tons per year [1]. It is a nanostructured multiphase composite material [2]. Concrete in definitions is composed of an amorphous phase, nanometer- to micrometer-size crystals, and bound water. The properties of concrete exist in according the degradation mechanisms occur across, multiple length scales (nano-micro-macro) where the properties of each scale derive from smaller one [3]. Due to the complex structure of concrete and its heterogeneity at all length scales, and the recent

innovations in nanotechnology, nano-modification of cement-based materials has generated much research interest [4].

The main hydration product of ordinary Portland cement is a calcium-silicate hydrate (C-S-H) having a pseudotobermoritic like crystal chemistry. C-S-H is a slightly crystalline and nanoscale phase formed from the reaction of the calcium-silicate phases with water. Its colloidal-like behavior and self-organization into an interconnected network convey cohesive properties to the cement paste. The other hydration products are Ca(OH)₂ (portlandite) and an hydrous sulfo-aluminate (ettringite). Ettringite has a major influence on the early stage

rheology, but it has a negligible effect on determining the mechanical properties in long term [10]. The mechanical behavior of concrete materials depends to a great extent on structural elements and adventure that affect micro and nano scale reactions [5-6].

An analysis of new and published solubility data for C-S-H, illustrates an unrecognized family of solubility curves in the CaO-SiO₂-H₂O system at room temperature and observed differences in solubility arise from systematic variations in Ca/Si ratio, silicate structure and Ca-OH content [7]. This has significant impact on the performance of concrete because the structure is sensitive to moisture movement, during hydration. This may result in shrinkage and consequent crack [8]. Thus, nanotechnology may have the potential to engineer concrete with arised properties through the optimizing behavior of material and performance is required to intensively improve mechanical performance, durability and sustainability [7-14].

The properties and procedures that occurring at the nanoscale define the interactions that occur between particles and phases at the microscale and the effects of working loads and the surrounding environment at the macroscale [15-17].

It goes without saying that nanotechnology-based development in concrete materials requires a multidisciplinary approach, consisting some expert teams of concrete materials, civil engineers, chemists, physicists and materials scientists.

2. NANOTECHNOLOGY- BASED RESEARCH IN CONCRETE TO DATE

2.1. High performance properties

Scientists could mostly achieve improvement in performance, durability and sustainability of concrete until now. Although these studies goes to create a huge evolution in concrete industry, some

unknown and effective elements in micro and nano scale could not be recognized to obtain better and directed results till now.

For instance, the addition of nanofine particles could improve the properties of concrete due to the effect that increased surface area has on reactivity and through filling the nanopores of the cement paste. Nanosilica and nanotitanium dioxide have been the most reported additives used in nanomodified concrete [18-26]. Nanomaterials also could improve the compressive strength and ductility of concrete [21]. Carbon nanotubes or nanofibers (CNT-CNF) have also been used to modify strength, modulus and ductility of concretes. Durability of concretes could also be improved through reduced permeability and improved shrinkage properties. These effects could be obtained through nano modified cements or the use of nano developed additives to the paste [18].

Utilization of nanomaterials into the cement matrix to improve its mechanical properties reputedly has appeared as a promising research field. A few studies on incorporation of nanoiron, nanoalumina and nanoclay particles have also been reported [18- 23].

When a small quantity of nanoparticles is uniformly dispersed in a cement paste, the hydrated products of cement deposit on the nanoparticles due to their higher surface energy. Thus nanopaticles act as nucleation sites for lattice growth. Nucleation of hydration products on nanoparticles further promotes and accelerates cement hydration. It has been reported that adding colloidal nano silica causes acceleration of C₃S dissolution and rapid formation of C-S-H phase in cement paste [18].

The second mechanisms for improving the performance are that: (a) nanoparticles fill the nanosize pores of the cement paste and (b) nano-SiO₂ reacts with Ca(OH)₂ (i.e., pozzolanic reaction) and generates additional C-S-H [3]. Both processes are influenced by the particle size and the

proper dispersion of the nanoparticles within the cement paste, with colloidal dispersions being more effective than the powder. A reduction in $\text{Ca}(\text{OH})_2$ content and increase in C-S-H content in cement mortar as a result of nano- SiO_2 addition was noticed through Differential Thermal Analysis (DTA) and X-Ray Diffraction (XRD) testing. With the addition of 3 wt% of nano- SiO_2 , significant improvement of early-age interfacial transition zone (ITZ) structure with respect to reduction in content, crystal orientation degree and crystal size of portlandite crystals was obtained. In another study, it is reported that the improvement in strength due to nanosilica addition was not related to pozzolanic reaction, but due to the formation of denser microstructures through growth of silica chains in C-S-H [21]. According to the study done by Raiees Ghasemi et al. in 2010, applying mixture of colloidal Nano SiO_2 with 50 wt% of solid content which contains 0.75 wt% nano- SiO_2 and 3 wt% silica fume has shown better performance of compressive strength on 7th, 28th, 91th and 180th day respectively. Review of compressive strength, RCPT and DWPT results, shows the influence of NS on improvement of concrete properties, both are due to filling ability (Filler) and the Pozzolanic activity, but based on the results of RCPT, it is expected that nano SiO_2 behaves more as a filler [20].

Only the nanostructured calcium silicate hydrate (C-S-H) offers the potential for the development of massive (partly primary) bonds with properly modified graphite nanomaterials [6]. Sbia et al. in 2015 reported, neither capillary (and larger) pores nor micro-scale crystals match this capability of CSH. Figure 1 schematically depicts a graphite nanomaterial which occurs largely outside the C-S-H phase

(with effective binding qualities) within the capillary pores and in contact with microscale crystals; this nanomaterial cannot effectively interact with the cementitious paste. It may still produce physical benefits, but would not effectively contribute to the mechanical properties of the matrix [14].

The particulate matter of uniform grain size cannot realize very high packing densities. Spherical grains of similar size can reach packing densities of only 0.52 and 0.74 in cubic and tetrahedral packing structures respectively. Sbia et al. reported packing density can be increased through the use of particles of different dimensions accompanied by finer particles filling the space between coarser particles [14].

The effect of the debulking procedure on the dispersion and the reinforcing efficiency of carbon nanofibers, was studied by Zoi et al in 2013. They illustrated lower ultrasonic energies could not effectively disperse the CNFs, while higher ultrasonic energies possibly reduced the aspect ratio of the nanofibers, which in turn decreased their reinforcing efficiency in the cementitious matrix. The addition of CNF to cement paste was found to mainly increase flexural strength and stiffness, and crack control at the nanoscale. SEM analysis also confirmed the results of the mechanical testing; nanoimaging showed that good bonding existed between all types of carbon nanofibers and the matrix. At early ages of hydration, CNFs with an outer layer of multiwall graphene tubes (CVD layer) improved the mechanical performance of the matrix, possibly acting like high stiffness fillers.

At later ages, the use of a CNF with a rougher surface consisting of conically shaped graphite planes was found to be more efficient for improving the mechanical performance of the matrix. These graphite planes improved the bonding of the CNFs with the cement hydration products, resulting higher load transfer efficiency between the fibers and the matrix, the key element that determines

the mechanical response of the nanofiber nanocomposites [27].

It seems that studies in nano and micro scales in hydrated cement by detail with suitable measurement in nano field and accurate analysis based on nano phenomena could confirm these results and suggest progressive decisions for concrete technology.

2.2. Micro structural studies on concrete

Thomas et al. in 2009 reported that a relatively small amount (1-4 wt%) of well-dispersed calcium silicate hydrate (C-S-H), a pure form of the main hydration product, significantly increased both the early hydration rate and the total amount of hydration during the early nucleation and growth period (the first 24 h), as measured by calorimetry. The seeding effect of C-S-H also provides a new explanation of the hydration-accelerating effects of various forms of reactive silica because these additives form C-S-H by reacting with aqueous calcium ions released by cement dissolution. Experiments involving sucrose, a hydration retarder, confirmed that sucrose interferes with the normal

nucleation process on the particle surface. The retarding effects of sucrose can be negated by adding C-S-H seed at the time of mixing and can be reversed by adding C-S-H later, after the retarding effect has already been established. This confirms that sucrose has retarded by preventing the nucleation of C-S-H gel on the particle surfaces and the addition of C-S-H seed provides an alternate pathway for the hydration process [12].

The generally accepted model for C-S-H formation is based on the heterogeneous nucleation of C-S-H nuclei onto the surface of the dissolving cement particles. The branching outward of the C-S-H aggregates forms a percolated network and induces the development of mechanical properties in the hardened material. Any chemical or physical modification of the starting mixture induces substantial changes in the hydration reactions and consequently significant modifications of the microstructure of the hydrating cement paste, originating from the modified spatial relationships among the phases.

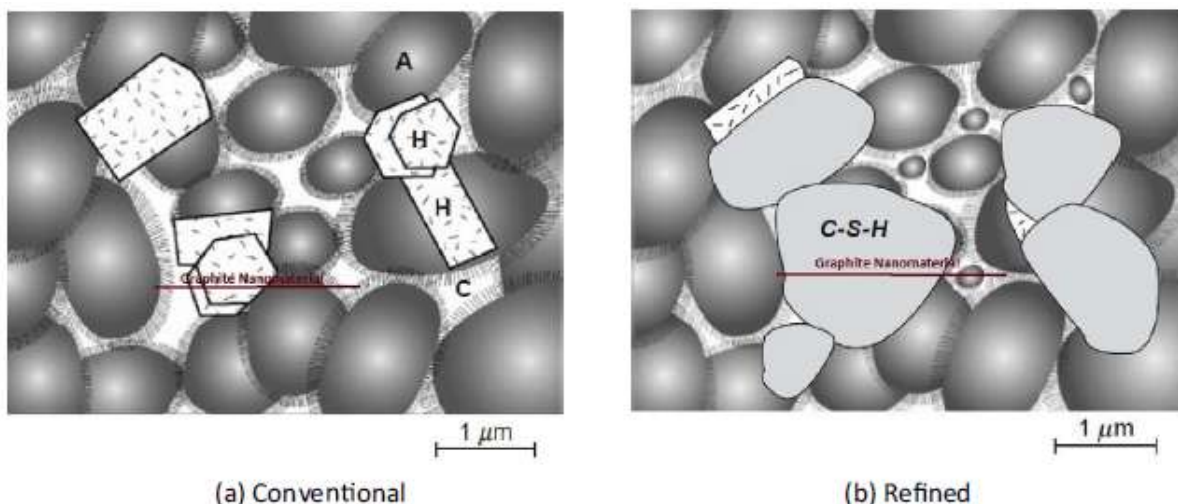
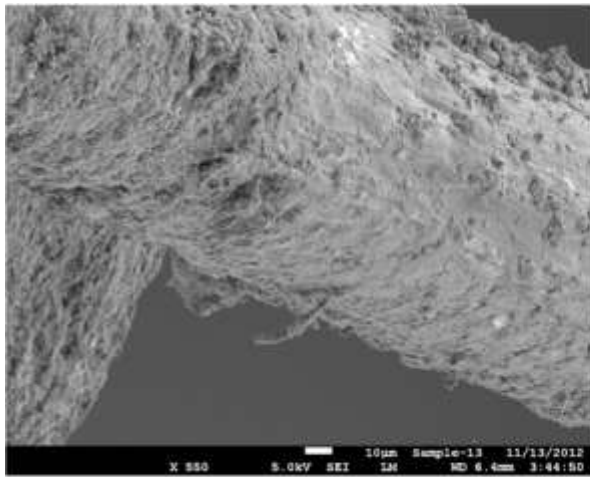
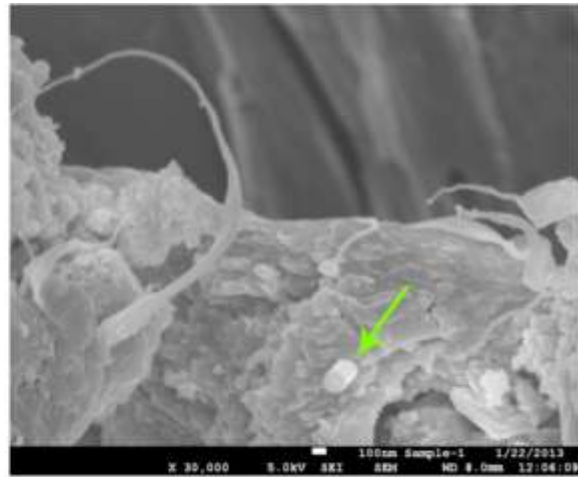


Figure 1. Schematic depiction of (a) the conventional and (b) refined microstructures of cementitious matrices incorporating a graphite nanomaterial (C=capillary pores; H = micro-scale crystalline products; A = calcium silicate hydrate), Sbia et al., 2015 [14].



(a)



(b)

Figure 2. SEM images at different magnifications of high-performance concrete reinforced with PVA fiber and CNF; (a) Low magnification image of a pulled-out PVA fiber; (b) High-magnification image depicting the presence of CNF in the interface of cementitious paste with PVA fiber, Peyvandi et al., 2014 [30].

For instance, the addition of nucleation seeds, especially in the form of synthetic C–S–H nanoparticles, seems to trigger the autocatalytic precipitation of C–S–H throughout the pore solution. Changes in both habit and nucleation density of the product phases have also been observed in cement pastes hydrating in the presence of superplasticizing polymers [12].

A switch to homogeneous nucleation may be due to the inhibiting effect on C–S–H heterogeneous nucleation of the PCE (polycarboxylate-ether based superplasticizers) adsorbed onto the surface of the cement particles. The higher degree of super-saturation is required for C–S–H homogeneous nucleation to occur, compared with heterogeneous nucleation. This phenomenon may cause contribution to slow the rate of dissolution down, by reducing the driving force for the dissolution of the calcium-silicate phases. Specific interaction between C–S–H and PCE occurring in the pore solution may also inhibit C–S–H nucleation and subsequently further reduce the overall rate of hydration [10].

Kong et al. in 2012 investigated the influence of nano-silica agglomeration on microstructure and properties of the hardened cement-based materials by using

precipitated silica (PS) with very large agglomerates and fumed silica (FS) with much smaller ones as nanoscale additives. Through BET measurement, it was found that a great deal of nano-pores existed in the agglomerates. The most probable pore diameter was about 200–400 nm for PS and 100–200 nm for FS, and the specific surface area was 157.8 and 142.9 m²/g, respectively. Through SEM observation, an obvious microstructure improvement of the HCP (hardened cement paste) and the ITZ in mortar was found by adding nano-silica, regardless of its agglomerate size. Nevertheless, addition of FS with much smaller agglomerates showed a more significant improvement than that of PS with much larger agglomerates. It was observed even in presence of ITZ between the large reacted agglomerates and the bulk paste while adding both PS and FS. The SEM observations implied that the microstructure improvement of the HCP with nano-silica may have nothing to do with the seeding effect, but resulted from the water-absorbing, filling and pozzolanic effects of the small agglomerates in nano-silica. The nano-indentation test results revealed that the pozzolanic C–S–H gels from reacted agglomerates showed nearly the same properties as the LD C–S–H gels

from cement hydration. Nevertheless, the agglomerates might partially react in peripheral regions. The outer layer of C–S–H appeared to impede further reaction of the agglomerates with CH [24].

Another research by Kong et al. in 2013 compared the influence of nano-silica agglomeration on fresh properties of the cement paste by using precipitated nano-silica (PS) with very large agglomerates, fumed nano-silica (FS) and much smaller ones as nano-strengthening admixtures. The specific surface areas of PS and FS measured through BET method were 157.8 and 142.9 m²/g, respectively. The TEM photograph showed that the primary particles of both PS and FS were in nano-scale, with size of about 20–30 nm for PS and 5–10 nm for FS, but tended to aggregate and agglomerate together. The SEM observation shown in this study indicated that the agglomerates in PS reach were as large as more than 100 μm in size, but those in FS were just several micrometers. The pore size distributions detected through BET measurement revealed that there were a great number of nano-pores in both powders. The most probable pore diameters were about 20–40 nm for PS and 10–20 nm for FS [29].

Peyvandi et al. worked on synergistic actions of carbon nanofibers and polyvinyl alcohol (PVA) fibers in high-performance concrete. Carbon nanofiber surfaces were modified by introduction of hydrophilic groups in order to improve their dispersion and interfacial interactions in cementitious matrices. The low magnification SEM image of Fig. 2(a) shows strong bonding of cement hydrates to PVA fiber; the high-magnification SEM image of Fig. 2(b) shows the presence of CNF within the interface of cementitious paste at PVA fiber (at fractured surface) where nanofibers are expected to render reinforcing effects [30].

They have hypothesized that, among cement hydrates, calcium silicate hydrate with nano-scale morphology provides the ability to bind to graphite nanomaterials.

Crystalline structures such as calcium hydroxide, on the other hand, cannot effectively interact with nanomaterials. Their experimental results verified that optimum reinforcement systems were comprised of both carbon nanofiber and (microscale) PVA fiber. To obtain engineered properties in concrete, optimizing in both nano- and micro-scale will be required and could not be provided by each nano- or micro-scale reinforcement alone.

This finding supports the hypothesis that nano- and micro-scale reinforcement plays complementary/ synergistic roles in concrete by providing reinforcing effects at different scales and are also due to the benefits rendered by nanomaterials towards interfacial stress transfer and pull-out behavior of fibers [30].

It can be understood from the recent studies, the growth of C–S–H lattice which is the main parameter for hardening of concrete in long terms by contribution of C₃S and other composition like C₂S and Ettringate, effect on early age hardening and setting time, obey nano sciences and rules governing them. For understanding these phenomena, we should got to know concepts like physical chemistry of solid surface, chemical potential, electrostatic, steric stabilization and other beneficial terms to manage the growth rate and formation of homogenous or heterogenous growth. Also, with knowing the main parameters influencing the interaction of two or more particles in nano scale, like attraction and repulsion, growth control methods and nano synthesis methods, we can decide to fabricate new nano-engineered materials or improve the properties of ordinary concrete.

3. ADVANCED TECHNIQUES FOR CHARACTERIZATION OF CONCRETE

Nanoindentation includes a variety of indentation hardness tests applied to small volumes. Indentation is perhaps the most commonly applied means of testing the

mechanical properties of materials. Small loads and tip sizes are used, so the indentation area may only be a few square micrometers or even nanometers. Typically, an indenter with a geometry known to high precision is used. During the course of the indentation process, a record of the depth of penetration is made, and then the area of the indent is determined using the known geometry of the indentation tip. While indenting, various parameters such as load and depth of penetration can be measured. A record of these values can be used to extract mechanical properties of the material (Poon et al., 2008) [31].

The ability to conduct nanoindentation studies with nanometer depth, and sub nano-newton force resolution is also possible using a standard AFM setup. AFM is a type of scanning probe microscopy where the sample is scanned under the probe by a piezoelectric translator in order to get information on surface properties. The probe has a very sharp tip, often less than 50Å; when the tip is approached to the sample surface, interaction forces between the tip and the surface causes a deflection of the cantilever. This deflection is detected by an optical lever technique. The AFM allows for nanomechanical studies to be conducted alongside topographic analyses, without the use of dedicated instruments. Load-displacement curves can be collected similarly for a variety of materials, and mechanical properties can be directly calculated from these curves (e.g., Kurland et al., 2011) [32].

Measuring of mechanical properties of cementitious materials at the nanoscale is still an emerging science. Considering the sizes of ITZ and capillary pores, a spatial resolution of about 1 µm, which is thought to be the minimum for nanoindentation, is required (Kim et al., 2010). Acoustic AFM (AFAM) is used to characterize the cement paste in order to achieve this resolution. AFAM gives a more concentrated probability of the modulus than

nanoindentation. Considering the contact and indent sizes, AFAM is a more promising means of measuring mechanical properties at the nanoscale [33].

The influence of internal curing by water filled lightweight aggregates (LWAs) on the microstructure of mortars was studied by scanning AFM and SEM (Peled et al., 2010). The differences and similarities that exist at both the microscale and nanoscale of conventionally cured mortars and internally cured mortars were studied. It was found that LWAs can be used for internal curing to provide a greater degree of hydration in a small region around the aggregate interface, which results in a microstructure that is denser, more homogeneous and that contains less CH [34].

TEM and SEM studies have revealed the presence of nanosized hydration products embedded in a cross-linked polymer matrix (Bortzmeyer et al., 1995). The nanoscale composite structure of the cement is thought to play an important part in the mechanical properties [35]. TEM studies of C-S-H gels in portland cement indicated large fluctuations in the local calcium-silicon ratio (Viehland et al., 1996) [36]. Lattice imaging studies have revealed the presence of nanocrystalline regions within an amorphous matrix. The local composition within the nanocrystalline regions is believed to be homogeneous. Optical diffractograms taken from individual nanocrystalline regions demonstrated the coexistence of both jennite and 1.4 nm tobermorite structural elements, supporting the essential features of the Taylor nanophasic model (Taylor, 1993) [37].

NMR spectroscopy [cross-polarization (CP) technique in combination with MAS] was used to investigate the hydration of alkali-activated slag (Wang and Scrivener, 2003) [38]. The NMR study provides information on the polymerization of silicates, the role of aluminates in cement hydration and the nanostructure of C-S-H gel. Recent progress in experimental and

theoretical nanomechanics opens new venues in materials science for the nanoengineering of cement-based composites. Some recent results obtained by nanoindentation technique have been reviewed (Constantinides, Ulm, and Van Vliet, 2003), which reveal that the C-S-H gel exists in two different forms: a low-density form and a high-density form. These two C-S-H types have different mean stiffness and hardness values and different volume fractions. While the volume fractions of the two phases depend on mix proportions, the mean stiffness and hardness values do not change from one cement-based material to another; instead they are intrinsic properties of the C-S-H gel [39].

Peled et al. in 2013 used atomic force microscopy (AFM) and lateral force microscopy (LFM) techniques to understand the nanostructure and microstructure of cement and cement hydration products. According to their investigations, AFM and LFM techniques were used on mortar samples to distinguish between CSH, CH, and unhydrated cement particles. As shown in figure 3 the LFM technique appears to be more sensitive to topographic changes than conventional AFM and it can more clearly distinguish between the different phases at high magnification (low scan range) [40].

Silva et al. in 2014 developed a methodology applied for determination of macro-scale elastic properties of high performance cementitious composites (HPCC) based on nanoindentation measurements. Their results indicate that the presented methodology allows a reliable advanced prediction of HPCC elastic properties, which is promising for the concrete industry since it would allow for reducing the number of large scale experiments and producing of a more predictable composite in an easier and experimentally less expensive way [41].

4. CONCLUSION

This study reviewed the current state of nanotechnology in concrete performance. The capability of nanotechnology to improve the performance of concrete to novel, sustainable and advanced cement based composites has developed these years. The advances in instruments have enabled scientists and engineers to obtain unpredicted information about concrete from the atomic scale and the role of nanoscale structures on performance and durability. This information is vital for predicting the service life of concrete and providing new idea on how it can be improved.

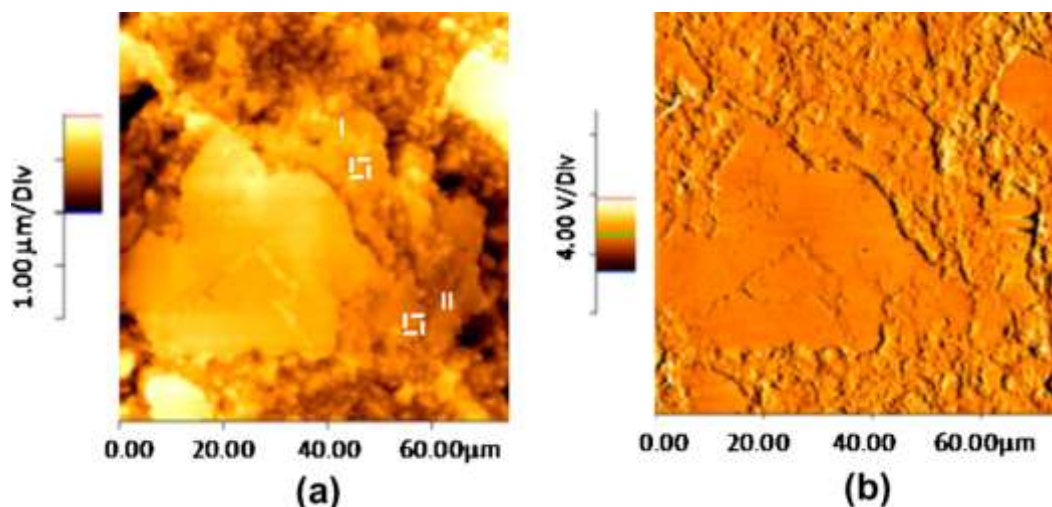


Figure 3: An overview observation, same zone using the: (a) AFM, and (b) LFM techniques, Peled et al., 2013 [40].

New developments have taken place in the modification of cement and concrete; however, some difficulties should be solved before the achievement of full potential of nanotechnology in concrete applications. These challenges include proper dispersion, compatibility of the nanomaterials in cement, processing, manufacturing, safety, and handling issues, scale-up and cost.

From this point of view and considering the fact that nanotechnology could change the properties of materials, to attain improvement in concrete, we should characterize the changes in micro and nanostructure in hydrating gel, ITZ area and other effects of nanomaterials on chemical reaction competition of component on cement paste and concrete microstructure.

Nanosilicate is the mostly used material produced by grinding which requires a large amount of energy. Thus, nanosilicate can be produced through chemical processing of clays or using of natural pozzolans as precursor to minimize the use of energy. It should be noted that nanostructure recognition of multiphase in concrete composite and rules governing the process by nano could maximize the nanoparticle admixture and nanomodify performance of engineered materials.

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