

NANOPARTICLES IN CEMENT BASED MATERIALS: A REVIEW

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Abstract. Portland cement is the major chemical product processed in the world, more than 3.6 Bton at 2011, causing important environmental impacts. Several nano-particles have been tested in cement based materials in order to improve their performance and durability leading to an eco-efficiency use for this binder. Published researches for nano-particles in cement based materials have been demonstrated optimum volumetric contents considering the relative strength gain, directly related with packing and nucleation effect observed for nano-particles, and a pozzolanic reaction is observed for nano-SiO₂.

1. INTRODUCTION

Portland cement based materials like concrete, mortar, fiber reinforcement and others are widely used building materials, according with CEMBUREAU [1] about 3.6 Bton of Portland cement was produced at 2011 and a continuous demanding could be needed, increasing the environmental impacts related with this worldwide industry. Nano-engineered cement based materials is actual trends which could play an important role for efficient use of this binder, recently many oxide nano-particles like nano-SiO₂, nano-TiO₂, nano-Fe₂O₃, nano-Al₂O₃, nano-CaCO₃, nano-ZnO₂, nano-cement particles of C₂S (alita) and C₃S (belite), nano-clays and Carbon Nanotubes have been tested, those improve the cement based materials performance. Although, nano-particles have a unitary coast 100 to 1000 times bigger than the Portland cement or others conventional raw-materials employed for cement based materials production, an important economic aspect for material design, Fig. 1a. [2-8].

But a structural efficiency, estimated by the relative strength gain and nano-particles volume con-

tent ratio, indicates a better efficiency for low nano-particles volume content, illustrated by Fig. 1b considering compressive strength of cement based materials containing nano-SiO₂ and nano-TiO₂. So in order to study the nano-particles in cement based materials, this paper objective is a review for different nano-particles effects for cement based materials, discussing their mechanical and durability properties, microstructural and rheological aspects published in the last years.

2. OXIDE NANO-PARTICLES

Nano-SiO₂ is the main studied oxide nano-particles for cement based materials that could be delivered in powdered or liquid suspensions. The nano-SiO₂ real density, about 2.25-2.54 g/cm³ [3,9], leads to the cheapest cost x volume relationship for the oxide nano-particles and the pozzolanic reaction directly related with its high surface area, between 50 to 750 m²/g [3,9] depending on the nano-particles size distribution, are two important issues for cement based materials design, those could explain this bigger effort for nano-SiO₂ researches.

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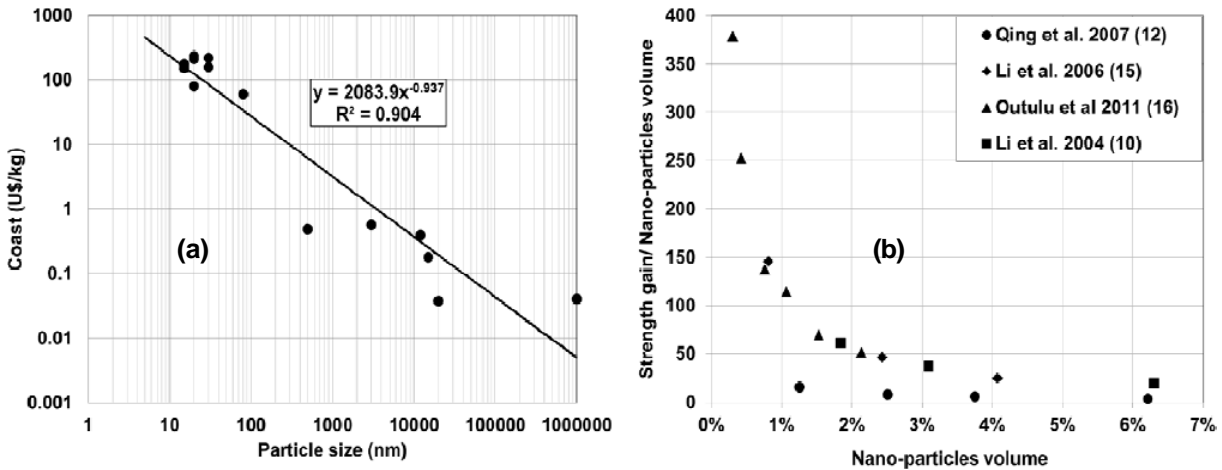


Fig. 1. (a) Raw-material coast of cement based materials [2-8]; (b) Nano-particles Efficiency [10,12,15,16].

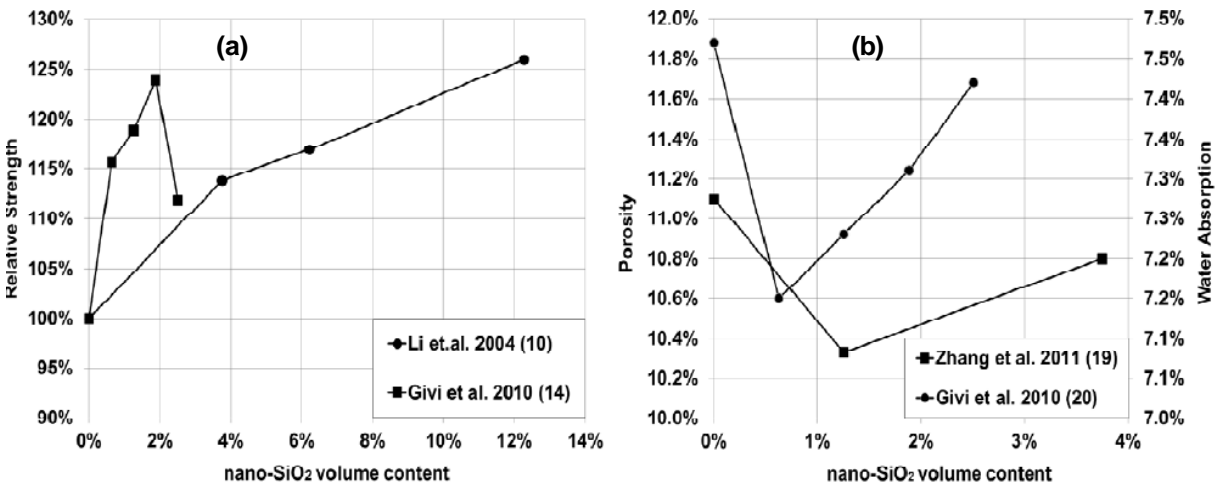


Fig. 2. (a) Nano-SiO₂ volume content x relative compressive strength [10,14]; (b) Nano-SiO₂ packing effect [19,20].

Nano-SiO₂ particles present a direct effect in cement based materials properties and durability, for large nano-SiO₂ volume content Li et al. (2004) [10] has demonstrated that the compressive strength increases, according with published results of Jo et al. (2007) [11], Qing et al. (2007) [12] and Litfi et al. (2011) [13], Fig. 2a. Although, for low nano-SiO₂ volume content, Givi et al. (2011) [14], Li et al. (2006) [15] and Oltulu et al. (2011) [16] published results indicate optimum nano-SiO₂ volume content about 2% and the compressive strength decreases after this point, Fig. 2a. Permeability, an important durability feature of cement based materials, present a reduction about 45% for a concrete containing 3 wt.% of nano-SiO₂ as demonstrated by Ji (2005) [17] and consequently carbonation velocity and chloride diffusion coefficient reductions according with Collepari et al. (2002) [18] and Zhang et al. (2011) [19] published results for concretes containing 1, 2, and 3 wt.% of nano-SiO₂.

These properties and durability enhancement caused by the nano-SiO₂ could be related with two important microstructural aspects of cement based materials: the packing effect and pozzolanic reaction of nano-SiO₂ particles. Fig. 2b shows Zhang et al. (2011) [19] results of porosity determined by Mercury Intrusion Porosimetry (MIP) for concretes with 1 and 3 wt.% of nano-SiO₂, similar results published by Givi et al. (2010) [20] considering the water absorption for cement based materials with 0.5, 1, 1.5, and 2 wt.% of nano-SiO₂ with two different nano-particles diameters 15 and 80 nm. These results indicate a characteristic curve for packing effect of nano-SiO₂ in cement based materials considering nano-SiO₂ volume content and particle size.

Pozzolanic reaction has been observed by Senff et al. (2010) [21] using thermogravimetric analysis (TGA) Fig. 3a considering the higher mass loss peak for C-S-H hydrated products and the peak reduction of Ca(OH)₂, Fig. 3b, due the consumption in

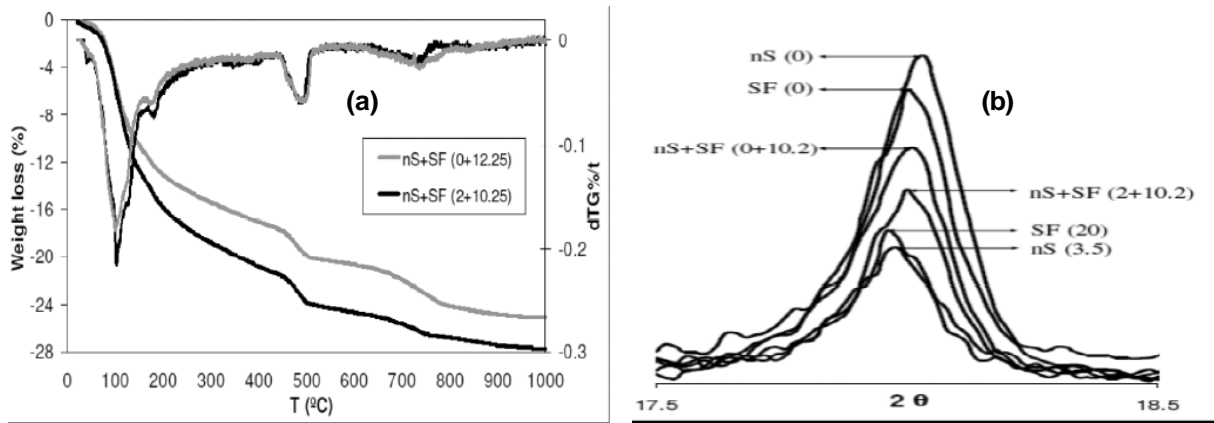


Fig. 3. (a) Thermogravimetric analysis results for cement pastes containing nano-SiO₂, (b) DRX of Ca(OH)₂ peaks, reprinted with permission from L. Senff, D. Hotza, W.L. Repette, V. Ferreira and J.A. Labrincha // *Advances in Applied Ceramics* **109** (2010) 104, (c) 2010 Maney.

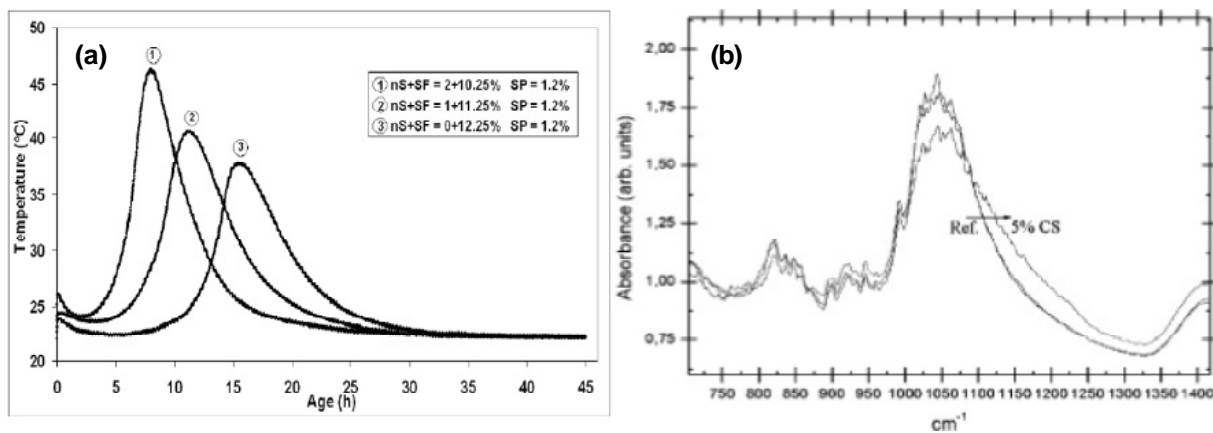


Fig. 4. Adiabatic Calorimetry of cement pastes with 0, 1, and 2% of nano-SiO₂, reprinted with permission from L. Senff, D. Hotza, W.L. Repette, V. Ferreira and J.A. Labrincha // *Advances in Applied Ceramics* **109** (2010) 104, (c) 2010 Maney.

pozzolanic reaction with nano-SiO₂. The nano-SiO₂ plays an important role in reaction kinetics accelerating the cement hydrated products formation; Fig. 4 shows this effect for cement pastes with 0, 1, and 2 wt.% of nano-SiO₂ measured by Senff et al. (2009) [22] using adiabatic calorimetry. Similar results has been published by Bjornstrom et al. (2004) [23] considering the tobermorite (C-S-H) characteristic absorption band (1200 cm⁻¹), measured by Infrared Spectroscopy (FTIR) for cement pastes after 12 hours containing 0, 1 and 5% of nano-SiO₂.

The cement based materials processing is directly affected by nano-SiO₂, reducing the concrete bleeding for self-compact concretes as demonstrated by Collepardi et al. (2002) [18], but increasing suspensions yield stress and viscosity leading to a setting time (Senff, 2009) [24] and slump reduction Li et al. (2006) [15], two important rheological properties for casting. Drying shrinkage results published by Collepardi et al. (2002) [18] for self-compact concrete containing 0, 1, and 2 wt.% indi-

cates that self-compact concretes containing nano-SiO₂ has the same order of magnitude of drying shrinkage of self-concretes without nano-SiO₂.

Nano-TiO₂ particles is second nano-oxide particles most used for cement based materials, rutile photo-catalysis effect is an important auto-clean feature needed for nano-engineered building materials. Nano-TiO₂ high density about 3.9 g/cm³ and consequently its higher hardness has a direct impact on cement based properties and durability, Fig. 5a shows the negative effect of nano-TiO₂ on compressive strength for large volume content published by Meng et al. (2012) [25] for cement based materials containing 0, 5, and 10 wt.% of nano-TiO₂. Chen et al. 2012 [26] published results shows a compressive strength gains about 10 and 20% results for cement based materials containing 0, 5, and 10 wt.% of rutile and anatase nano-particles. For small nano-TiO₂ volume content an optimum value, about 1% in volume, is observed by Zhang et al. (2011) [19] considering the compressive strength (Fig. 5a);

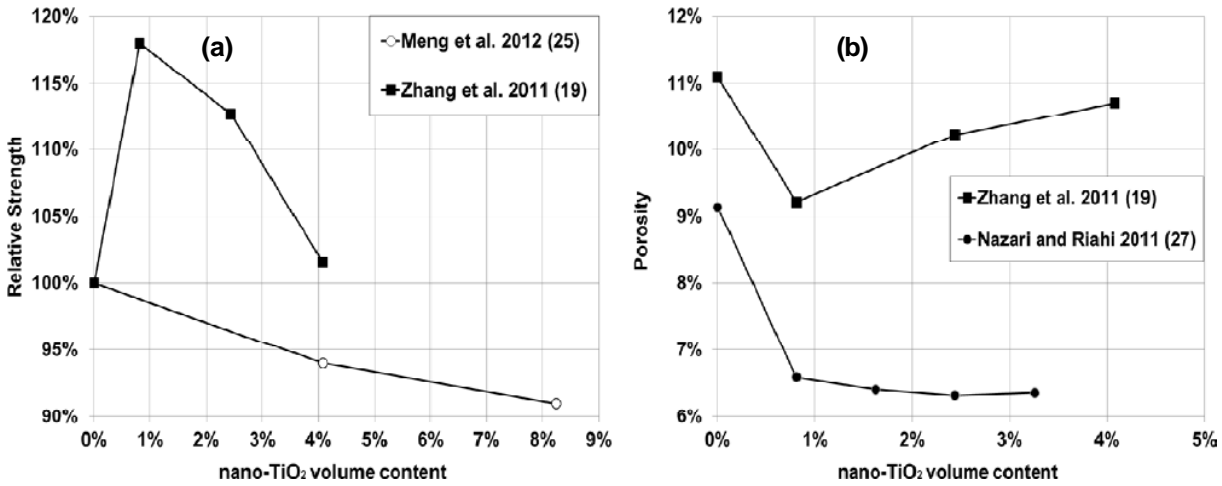


Fig. 5. (a) Nano-TiO₂ volume content x relative compressive strength [19,25]; (b) Nano-TiO₂ packing effect [19,27].

and concrete porosity (Fig. 5b) measured by Mercury Intrusion Porosimetry for cement based materials with 0, 1, 2, 3, 4, and 5 wt.% of nano-TiO₂, as published by Zhang et al. (2011) [19], Nazari and Riahi (2011) [27]. These results indicates a similar packing effect of nano-TiO₂ particles in cement based materials reducing materials permeability and consequently the chloride diffusion coefficient as demonstrated by Zhang et al. (2011) [19].

Thermogravimetric analysis (TGA) between 110-650 °C for cement hydrates products C-S-H and Ca(OH)₂, shows that nano-TiO₂ content increases total mass lost for this temperature range, as published by Nazari and Riahi (2011) [27] according with published results of Meng et al. (2012) [25] considering the C₃S peaks reduction and Ca(OH)₂ peaks increases determined by X-Ray Diffraction for cement based materials containing 0, 5, and 10 wt.% of nano-TiO₂ after 28 days of curing. Cement reaction kinetics is directly affected by nano-TiO₂

content, calorimetry results published by Chen et al. 2012 [26] and Senff et al. (2012) [28], show that nano-TiO₂ accelerates the cement hydration and increases the reaction total heat indicating a nucleation effect of nano-TiO₂, according with Nazari and Riahi (2011) [27] results considering the X-Ray diffraction peaks related to formation of the hydrated products Ca(OH)₂ and C-S-H at early ages. Nano-TiO₂ has a direct effect on materials based materials rheological properties, Senff et al. (2012) [28] results show that the nano-TiO₂ content increases the suspensions yield stress and viscosity, reducing the mortars fluidity and concretes slump as published by T. Meng et al., 2012) [25] and Li et al. (2006) [15], respectively.

Many other nano-oxides particles have been tested in cement based materials nano-Fe₂O₃, nano-Al₂O₃, nano-ZnO₂, nano-CuO₂, and nano-CaCO₃, which present a direct effect on materials properties and durability. Fig.6a shows a volume content

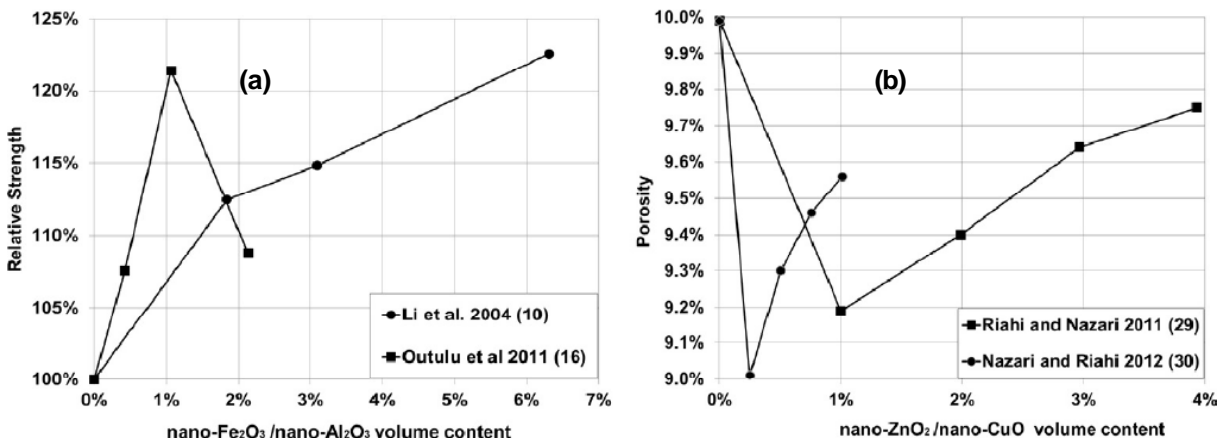


Fig. 6. (a) Nano-Fe₂O₃/Al₂O₃ volume content x relative compressive strength [10,16]; (b) Nano-ZnO₂/CuO Packing effect [29,30].

effect of nano-oxides particles on compressive strength, for small volume content of nano- Al_2O_3 and Fe_2O_3 an optimum volume could be observed based on compressive strength results published by Oltulu et al. (2011) [16], for cement based materials containing 0.5, 1.25, and 2.5% of these nano-particles oxides. Similar results have been published by Riahi and Nazari (2011) [29], Nazari and Riahi (2012) [30] and Xianoyan et al. (2012) [31] for cement based materials containing small quantities of nano- ZnO_2 and nano- CuO and nano- CaCO_3 . For large volume content, Li et al. (2004) [10] present a positive effect on the compressive strength for cement based materials containing 3, 5, and 10 wt.% of nano- Al_2O_3 , according with published results of Sato and Beaudoin (2011) [32] considering the micro-hardness and elastic modulus of cement based materials containing 10 and 20 wt.% of nano- CaCO_3 .

Packing effect could be identified for small volume of nano-oxides particles; Fig. 6b shows mercury intrusion porosimetry results published by Riahi and Nazari (2011) [29] and Nazari and Riahi (2012) [30] for cement based materials containing 0.5, 1, 1.5, and 2% wt.% of nano- ZnO_2 and nano- CuO . Oltulu et al. (2011) [16] has demonstrated an important effect of nano-oxide particles for cement based materials durability, considering the capillary permeability reduction for concretes containing nano- Al_2O_3 and nano- Fe_2O_3 .

A nucleation effect has been identified by Riahi and Nazari (2011) [29] and Nazari and Riahi (2012) [30] for cement based materials containing 0.5, 1, 1.5, and 2% nano- ZiO_2 and nano- CuO , considering the higher mass lost determined by thermogravimetric analysis between 110 and 650 °C; the accelerate effect of nano-oxides in hydrated products kinetics and reaction total heat measured using an adiabatic calorimeter; and XDR peaks intensity for hydrated products $\text{Ca}(\text{OH})_2$ and CSH at early ages. Similar results about nucleation effect were published by Sato and Beaudoin (2011) [32] for cement based materials containing 10 and 20% of nano- CaCO_3 , considering adiabatic calorimetry and X-ray diffraction (XRD), carboaluminate peaks were not identified. Rheological properties are directly affected by nano-oxides particles, slump, initial and final setting time decreases for concretes containing nano- ZiO_2 [29] and nano- CaCO_3 [31].

3. CEMENT NANO-PARTICLES

Binder nano-particles of C_2S , C_3S , C_3A , and C_4AF compounds obtained by sol-gel processing and heating treated by flame spray reactor and oven

heating have been tested by Halim et al. (2007) [33] and Huang (2006) [34], respectively; nano- C_2S (alita) and nano- C_3S (belite) particles obtained by sol-gel processing and submitted to oven heating treatment at 900 and 1400 °C has been analyzed by Perera et al. (2007) [35]; and sonochemical fabricated nano-pozzolan particles have been studied by A. Askarinejad et al. (2012) [36].

The high surface area of synthesized nano-binder particles leads to a considerable water demanding and consequently a higher water/binder ratio and porosity, reducing the compressive strength and micro-hardness of pure nano-cement based materials as demonstrated by Halim et al. (2007) [33] and Huang et al. (2006) [34]. Ultrasonic treatment for nano-pozzolan particles present a positive impact on compressive strength as compared nano-pozzolan particles without a sonochemical treatment like demonstrated by Askarinejad et al. (2012) [36]. The surface area of nano-cement has an important impact on reaction kinetics considering accelerating effect and the bigger total heat of nano-cement chemical reaction as published by Halim et al. (2007) [33] and Huang et al. (2006) [34].

4. CARBON NANO TUBES

Cement based nano-composites of carbon nanotubes (CNT) have been widely studied, mainly due the positive impact of carbon nanotubes on important composites properties like compressive and flexural strength. Fig. 7a shows the effect of carbon nanotubes on composites compressive strength, for very low volume content, published results by Morsy et al. 2011 [37] show an optimum value for cement based materials containing 0.005, 0.02, 0.05, and 0.1 wt.% of CNT. Considering another volume content of carbon nanotubes studied by Melo (2009) [38], an optimum value about 0.3 wt.% has been achieved for cement based nano-composites containing 0.3, 0.5, and 0.75 wt.% of carbon nanotubes, similar results has been published by Manzur (2011) [39].

Fig. 7b shows the effect of carbon nanotubes on flexural strength of cement based nano-composites, for very low volume content, results published by Cwirzen et al. (2008) [40] show a positive impact for volume content lower than 0.01% of carbon nanotubes, similar results has been published by Konsta-Gdoutos et al. (2010) [41]. For carbon nanotube volume content higher than 0.5%, results published by Li et al. (2005) [42] and Musso et al. (2009) [43] show a positive impact on cement based nano-composite's flexural strength. For high carbon

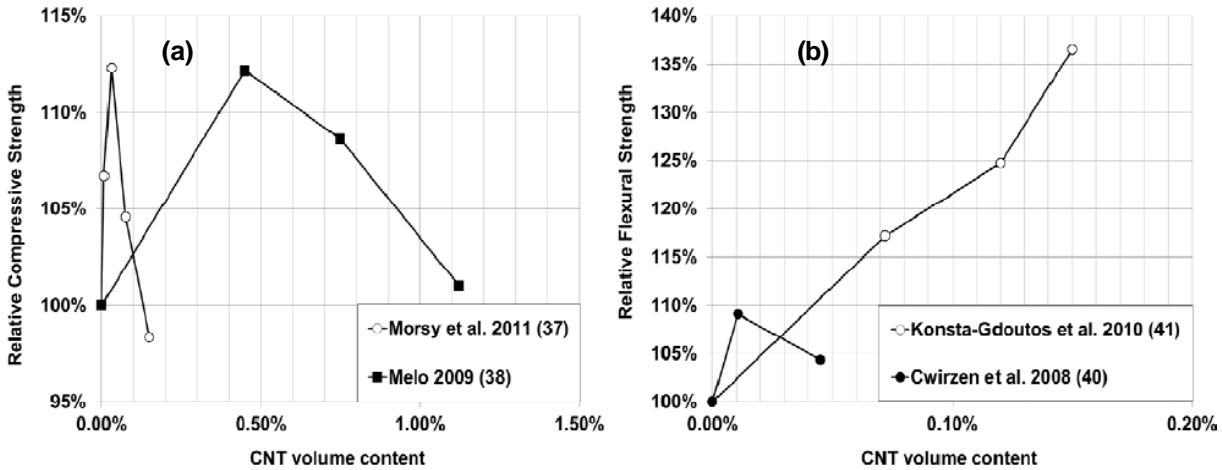


Fig. 7. (a) Carbon nanotube volume content x relative compressive strength [37,38]; (b) Carbon nanotube volume content x relative flexural strength [40,41].

nanotubes content, splitting tensile strength results published by Ince (2008) [44] for cement based nano-composites containing 2 wt.% of carbon nanofibers (CNF) present approximately the same value for cement paste without carbon nanotubes.

These cement based nano-composites properties improvement could be related with a total porosity reduction as demonstrated by Nochaiya and Chaipanich (2011) [45] applying Mercury Intrusion Porosimetry (MIP) technique for mixtures containing 0.5 and 1% of carbon nanotubes, similar results has been published by Li et al. (2005) [42] for batches containing by 0.5% of CNT, Fig. 8a; and a carbon nanotube specific surface effect on materials strength as published by Manzur (2011) [39] for cement based nanocomposites containing 0.1, 0.2, 0.3 wt.% of Multi-Walled Carbon Nanotubes, 10-30 mm length and diameter varying between 8 and 30 nm resulting on specific surface areas of 40, 233,

and 500 m²/g, Fig. 8b shows this positive effect of carbon nanotubes specific surface on materials compressive strength. Surface chemical treatment of carbon nanotubes allows a possible interaction between COOH or C-OH groups of treated CNT and CSH cement phase as demonstrated by Li et al. (2005) [42] applying Infrared Spectroscopy (FTIR) technique.

A nucleation effect of Single Walled CNT has been verified by Makar and Chan (2009) [46] for cement nano-composites containing nanotubes, allowing a C-S-H hydration products growth on carbon nanotubes surface as published by Makar and Chan (2009) [46] considering micrographs obtained by Scanning Electron Microscopy. Ca(OH)₂ mass loss measured using thermogravimetric analysis and adiabatic calorimetry published results by Makar and Chan (2009) [46] for cement pastes containing SWCNT, confirm the SWCNT nucleation effect. Ara-

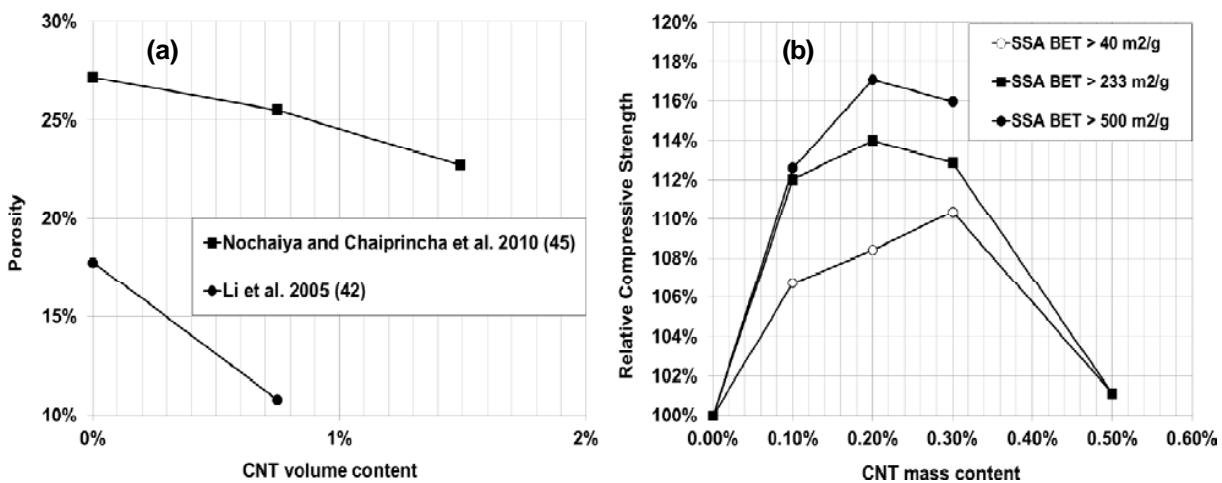


Fig. 8. (a) Carbon nanotube packing effect [42,45]; (b) Multi-walled Carbon Nanotubes Specific Surface Area x relative compressive strength [39].

gonite XRD peaks has been identified by Musso et al. (2009) [43] for cement pastes containing chemical treated carbon nanotubes. Cement based nanocomposites rheological behavior is directly affected by carbon nanotubes presence, as demonstrated by Konsta-Gdoutos et al. (2010) [47] considering the suspension viscosity increases for cement pastes containing MWCNT. A new technique for carbon nanotubes and nanofibers production called Carbon HedgeHog (CHH) allows growing the CNTs/CNFs from Fe catalyst particles naturally occurring in Portland cement, applying a chemical vapor deposition. Published results of Cwirzen et al. (2009) [48] for cement based carbon hedgehog nanocomposites has demonstrated a positive impact of these CNT/CNF on materials strength and electrical resistivity.

5. CONCLUSIONS

Mechanical performance, mainly compressive and flexural strengths, of cement based materials is improved by nano-particles use, reaching an optimum volume content for all nano-oxides studied. Carbon nanotubes, present a very small optimum volume content; and carbon nanotubes surface area present an important bonding effect on compressive strength.

These mechanical improvements are directly related with two important microstructural aspects of cement pastes containing nano-particles: the packing and nucleation effects observed for all nano-oxides and carbon nanotubes studied. For nano-SiO₂, pozzolanic reaction has been observed and lead to a mechanical improvement for large volumes contents.

Cement nano-particles does not present a mechanical improvement due high water demand and large porosity. Kinetic reaction is directly affected due the high surface area of nano-particles modifying the suspensions rheological behavior: setting time, yield stress and viscosity, and consequently the flowability and blending of concretes and mortars.

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