Chapter 6 Application of Nanomaterials in Civil Engineering

Md Daniyal, Ameer Azam and Sabih Akhtar

Abstract The potential use of carbon nanotubes, SiO_2 , TiO_2 , Fe_2O_3 , CuO, ZrO_2 , ZnO_2 , Al_2O_3 , $CaCO_3$, Cr_2O_3 and Ag nanoparticles in the civil engineering has been explored in this article. Most of the studies showed that addition of nanomaterials in appropriate quantity improved the strength and durability properties but decreased setting time as well as workability of cementitious composites. The other challenges include high cost, environmental and health risks associated with nanomaterials. That is why the comprehensive recommendations for the utilization of nanomaterials in day-to-day construction practice are still awaited. Also, a study to evaluate the corrosion behaviour of graphene and nano-TiO₂-incorporated steel-reinforced cementitious composite has been undertaken. The nanoadmixed composite showed lower corrosion rate compared to uninhibited specimens at early ages. However, more results are required involving fairly longer period of time to establish graphene and nano-TiO₂ as corrosion inhibitors.

Keywords Nanomaterials • Cementitious composites • Strength • Durability Civil engineering

M. Daniyal · S. Akhtar (⊠) Department of Civil Engineering, Aligarh Muslim University, Aligarh 202002, India e-mail: sabihced@yahoo.co.in

M. Daniyal e-mail: daniyalzhcet@gmail.com

A. Azam Department of Applied Physics, Aligarh Muslim University, Aligarh 202002, India e-mail: azam2288@gmail.com

© Springer Nature Singapore Pte Ltd. 2018 Z.H. Khan (ed.), *Nanomaterials and Their Applications*, Advanced Structured Materials 84, https://doi.org/10.1007/978-981-10-6214-8_6

6.1 Introduction

Nanotechnology was first introduced by physicist Richard P. Feynman in his famous lecture in a meeting of the American Physical Society at the California Institute of Technology in 1959 [1]. However, after two decades, it was defined as the manufacture of materials using sizes and accuracy of between 0.1 and 100 nm by Drexler [2]. Therefore, this is not a new science or technology but became a hot research topic in last two decades. Hence, nanotechnology refers to the development of devices, structures and systems by controlled manipulation of size and shape with at least one typical dimension measured in nanometres (atomic, molecular and macromolecular scale) [3]. In fact, the size of particles plays an important role in this technology because the properties of materials are significantly affected at nanometre level. This is because of the fact that at nanoscale. electrostatic forces and quantum effects begin to prevail over gravity. Also, as particles of matter turn into nanosized, the quantity of atoms on the surface relative to those inside increases and this leads to improve the properties. Moreover, nanomaterials may be obtained either through chemical synthesis or by high milling energy. These materials may be in the form of layers (if only one characteristics dimension in the nanoscale like surface coatings or thin films, graphene), nanowires or nanotubes (if two dimensions are in nanoscale) or particles (if all the dimensions are in nanoscale such as quantum dots, precipitates and colloids). The two most important factors which cause the properties (such as reactivity, strength and electrical characteristics) of nanomaterials to differ extensively from other materials are increased surface area to volume ratio and quantum effects [4, 5].

The use of nanomaterials is increasing in the various fields such as biomedicine, automobile, electronics, robotics, construction industry because of their unique mechanical, chemical, electronic and optical properties. However presently, use of nanotechnology and nanomaterials in civil engineering particularly in construction industry is very less [6-8]. This is mainly due to the lack of comprehensive information regarding the suitable construction nanomaterials, highly expensive and health risks associated with nanomaterials [9-21]. Therefore, in order to use the nanomaterials in the construction sector effectively, researches and investigations are required to find out various facts like performance of nanomaterials and their reactive mechanism with composite materials like cement, the preference of nanomaterials with possible use in construction, characteristics and behaviour of the building elements that have nanomaterials under different loading conditions. However, only few studies are reported in literature on the application of nanotechnology and nanomaterials in the area of construction. This article reviews the advancement made with the use of nanomaterials in civil engineering and particularly in construction field. Moreover, there is not any published study on the corrosion behaviour of steel in cementitious composite containing nanomaterials. Therefore, to fill this gap a proposal has been made in order to evaluate the corrosion behaviour of graphene and nano-TiO2-incorporated steel-reinforced cementitious composite.

6.2 Nanomaterials Used in Civil Engineering

After growing the use of nanotechnology in various fields such as biomedical sciences, automobile and electronic industries, recently construction industries also started to use nanomaterials in conventional construction materials. Currently, these materials are mainly used to give stronger structural composites, lighter structure, enhanced properties of cementitious materials, low maintenance coating, better pipe joining materials, better heat and sound insulation, improved reflectivity of glass, water repellents, self-cleaning and antifogging surfaces, ultraviolet light protector, nanosized sensors to monitor construction safety and structural health and solar cells. Hence, the application of some nanomaterials in civil engineering and their effects are listed in Table 6.1 [22–84].

6.2.1 Carbon Nanotubes (CNTs)

Carbon nanotubes are allotropes of carbon with a cylindrical tubular geometry of diameter that ranges from 1 to 100 nm and lengths up to a few millimetres. They can have single layer of graphene rolled in a cylindrical shape, called as single-wall carbon nanotube (SWCNT), or more than one layer, called as multiwall carbon nanotube (MWCNT). They are the strongest and stiffest material known to date and hold great promise for reinforcing cement-based composites [22–27]. They show unique electrical, thermal and mechanical properties because of their geometry and covalent sp^2 bonds formed between the individual carbon atoms. For instance, they have eight times the strength, 1/6th times the density and five times Young's modulus of elasticity of steel.

Some expected benefits of use of carbon nanotubes in concrete along with some dispersion agents includes enhancement in strength, durability and crack prevention in concrete, improvement in mechanical and thermal properties in ceramics and ability of real-time health assessment of structures [28]. Dispersion agents or techniques are used for deagglomeration and subsequent distribution of CNTs within matrices because they have strong tendency to agglomerate due to the presence of attractive forces (Van der Waals). Therefore, various researches have been conducted and highlighted the potential use of carbon nanotubes in cementitious matrix with different types of dispersion techniques as shown in Table 6.2.

Recently, sensors like nano- and microelectrical mechanical systems (MEMS) have been developed and used in concrete structures for accurate real-time health assessment of material or structures such as cracking, corrosion, wear and stress. These sensors could be easily fixed into the structures during the period of construction. Also smart aggregate (piezoceramic-based multifunctional device) has been used to observe properties of concrete at early age like temperature, moisture, strength and relative humidity [29, 30]. Further, CNT/polycarbonate nanocomposite provides an early warning on the probable structural health damage because it

Nanomaterials Base materials		Possible benefits	References	
Carbon nanotube (CNT)	Cement and concrete	Improvement in mechanical strengths and durability	[22–27, 33–42]	
	Ceramics	Enhancement in thermal and mechanical properties	[28]	
	Nanoelectrical mechanical systems	Real-time health assessment of structures	[29–31]	
	Solar cell	Efficient electron mediation	[32]	
Silicon dioxide	Cement and concrete	Enhancement in mechanical Strengths and durability	[43–54]	
(SiO_2)	Glass	Antireflective and heat isolation	[55]	
Titanium dioxide (TiO ₂)	Solar cell	Non-utility power production	[56]	
	Glass	Antifogging, hydrophilicity, fouling resistance	[57, 58]	
	Cement and concrete	Self-cleaning, rapid hydration and improvement in mechanical strengths	[57–61]	
Ferric oxide (Fe ₂ O ₃)	Cement and concrete	Improvement in mechanical strengths and durability	[62–65]	
Copper oxide (CuO)	Cement and concrete/steel	Improved mechanical strengths and durability, enhanced weldability and corrosion resistance of steel	[66–68]	
Aluminium oxide (Al ₂ O ₃)	Cement and concrete	Enhancement in mechanical strengths	[69–72]	
Zirconium oxide (ZrO ₂)	Cement and concrete	Improvement in mechanical strengths	[73–75]	
Zinc dioxide Cement and (ZnO ₂) Concrete		Improvement in mechanical strengths	[76, 77]	
Calcium Cement and carbonate concrete (CaCO ₃)		Enhancement in mechanical strengths	[78–81]	
Chromium oxide (Cr ₂ O ₃)			[82, 83]	
Silver (Ag)	Paints	Antimicrobial properties	[84]	

 Table 6.1
 Nanomaterials used in constructions with possible benefits

produces quick changes in the electrical resistance when the device senses strain inputs [31]. Furthermore, one of the most important applications of CNTs is to enhance the performance of fuel and solar cells that produce renewable energy because of its remarkable electron transfer properties [32].

Type and CNTs (wt%)	Dispersion techniques	Effects	References	
MWCNT (0.045)	Superplasticizer	Compressive and tensile strength increased by 26.69 and 66.3%, respectively	[26]	
SWCNT (0.06)	Superplasticizer	Compressive strength increased by 29.7%	[27]	
MWCNT (1.0)	Ultrasonication	Total porosity decreased by 16%	[33]	
SWCNT (1.0)	Ultrasonication	Compressive strength improved by 10%	[34]	
MWCNT (0.2)	Ultrasonication and Superplasticizer	Ductility and flexural strength improved by 81 and 26.9%, respectively	[35]	
MWCNT (0.08)	Ultrasonication and surfactant	Flexural strength and modulus of elasticity improved by 25 and 45%, respectively	[36]	
SWCNF (0.048)	Ultrasonication and surfactant	Flexural strength and Young's modulus improved by 50 and 75%, respectively	[37]	
MWCNT (0.5)	Ultrasonication and Solvent	Compressive strength improved by 11%	[38]	
MWCNT (0.2)	Ultrasonication, magnetic stirring and surfactant	Compressive and flexural strength improved by 29.5 and 35.4%, respectively	[39]	
MWCNT (0.5)	Ultrasonication, magnetic stirring and polycarboxylate	Compressive strength improved by 25%	[40]	
MWCNT (0.045)	Carboxylic acid, ultrasonication and polyacrylic acid	Compressive strength improved by 50%	[41]	
SWCNF (0.5)	Acetone, ultrasonication and surfactant	Load-carrying capacity and failure strain improved by 54 and 44%, respectively	[42]	

Table 6.2 Techniques used for CNT dispersion and their effects on composite

6.2.2 Silicon Dioxide (SiO₂) Nanoparticles

Silica fume or microsilica is a by-product of silicon and ferrosilicon alloys. This is a grey powder having surface area in the order of 20 m^2/g and particle sizes in the range of 100–200 nm. It has been observed that the addition of silica fume (by weight in the concrete mix) could increase compressive strength, tensile strength and abrasion resistance compared to the reference samples. These improvements are in fact due to the closed packing achieved in the cement paste system that reduces the overall porosity and improves the interfacial transition zone (ITZ). The reduction of porosity produces a concrete more durable and resistant to chemical

degradation processes like chloride ion diffusion, alkali silica reaction and calcium leaching, which preserves the material from mechanical degradation and protects reinforcing steel from corrosion [43]. Furthermore, several recent researchers report on the significant advantages of nano-SiO₂ (NS) as compared to silica fume (SF). The results of one such research are shown in Fig. 6.1 [44].

Therefore, it is evident from the results that the incorporation of nano-SiO₂ with silica fume or fly ash in the concrete could considerably enhance the mechanical strengths by filling the tiny pores between cement particles and silica fume/fly ash. It also reduces setting time of mortar, segregation and bleeding of concrete due to improved cohesiveness [45-48]. It was also observed that the addition of 3% nanosilica in cement mortar enhanced chloride ion diffusion resistance up to 43% whereas incorporation of silica fume improved 15% only [49]. However, most of the study reported that the addition of nanosilica alone up to 2% weight of cement enhanced the mechanical strengths and durability of cementitious composites [50-53]. Conversely, the flowing characteristics of fresh concrete may be affected due to the large surface area of nanosilica, which decreases the amount of lubricating water. Thus, it is essential to use some superplasticizers with nanosilica, so as to avoid air entraining in the fresh concrete and benefiting from the above-described performance [54]. Further, nanosilica can be used for the production of fire-protective glass. This is achieved by providing a layer of nanosilica in between two glass panels, which turns into a dense and rigid fire protector. Therefore, these glass panels control exterior light as an antireflection coating and hence conserve the energy (air conditioning) [55]. Hence, the microstructure of the cementitious composites can be enhanced with the aid of nanosilica and consequently producing more durable and sustainable materials.

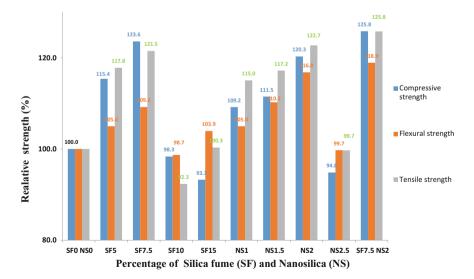


Fig. 6.1 Mechanical strengths of concrete containing silica fume and nanosilica

6.2.3 Titanium Dioxide (TiO₂) Nanoparticles

Recently, titanium dioxide nanoparticles have gained significant attention in the construction industry due to their self-cleaning properties and the ability to remove air pollutants through photocatalytic reactions. TiO_2 are semiconductors that act as photocatalysts when irradiated by ultraviolet (UV) light in the presence of gas or liquid [56]. When mixed with cement, it can photocatalytically degrade organic pollutants that are, after neutralization, washed away through the hydrophilic nature of the surface and hence maintaining the aesthetic characteristics of concrete structures, particularly those constructed with white cement [57]. Thus, TiO_2 nanoparticles are added to tiles, windows, cements, paints, etc., because of sterilizing and deodorizing properties and when included into outdoor construction materials can considerably decrease concentrations of airborne pollutants. Moreover, TiO_2 nanoparticles have proven very efficient in the removal of pollutants such as NOx, aromatics, aldehydes, ammonia and currently used in various infrastructure projects like pavements, tunnels, buildings [58].

Furthermore, it has been reported that TiO_2 nanoparticles can be used as a partial replacement of cement in the concrete mix. In one such research, it is found that the TiO_2 nanoparticles (up to 2.0%) could be advantageously used in place of cement, although the addition of TiO_2 nanoparticles not only increased the compressive, flexural and split tensile strength of concrete but also decreased its workability and setting time as shown in Fig. 6.2 [59, 60]. In another investigation, it was observed that the incorporation of 1% TiO₂ nanoparticles enhanced the compressive strength and durability performance of high-performance concrete [61]. Hence, TiO_2 nanoparticles can be advantageously used in construction industry.

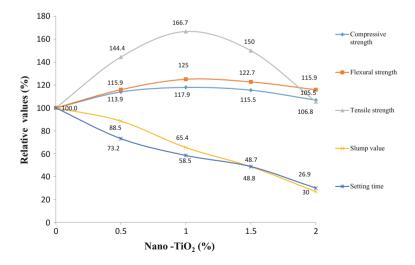


Fig. 6.2 Properties of 0.5-2% nano-TiO₂ incorporated cementitious composite relative to control composite

6.2.4 Ferric Oxide (Fe₂O₃) Nanoparticles

The use of Fe_2O_3 nanoparticles for enhancing the mechanical characteristics of cement and concrete has been carried out by few researchers. In one such investigation, it is observed that Fe_2O_3 nanoparticles could be used in concrete as a partial replacement of cement. The results of investigation show that the addition of Fe_2O_3 nanoparticles improved the strength properties of concrete but decreased its setting time and workability [62, 63]. The results of a similar study show that the properties of samples containing up to 3% Fe_2O_3 nanoparticles are desirable than the conventional cement mortar [64]. In another experiment, it was found that Fe_2O_3 nanoparticles could be advantageously used in high-performance self-compacting concrete as shown in Fig. 6.3 [65].

These increments in mechanical characteristics of concrete are due to the quick reaction between calcium hydroxide and Fe_2O_3 nanoparticles. Consequently, the hydration of cement is increased and larger amounts of reaction products are formed. However, some superplasticizer should be used while adding Fe_2O_3 nanoparticles for increasing the workability of fresh concrete.

6.2.5 Copper Oxide (CuO) Nanoparticles

The use of CuO nanoparticles in cement and concrete has been carried out by few investigators. It has been reported that CuO nanoparticles can be used in concrete as a partial replacement of cement. The results indicate that the addition of CuO nanoparticles improved the mechanical strengths and reduced the porosity of concrete as shown in Fig. 6.4 [66–68].

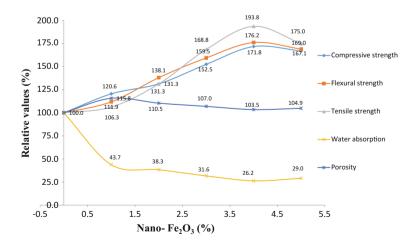


Fig. 6.3 Properties of 1-5% nano-Fe₂O₃ incorporated cementitious composite relative to control composite

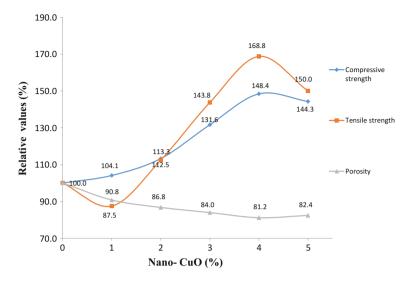


Fig. 6.4 Properties of 1-5% nano-CuO incorporated cementitious composite relative to control composite

This occurred mainly because of rapid reaction between CuO nanoparticles and calcium hydroxide. Consequently, the amount of crystalline $Ca(OH)_2$ at the early ages of hydration of cement is increased and larger amounts of calcium silicate hydrate (C-S-H gel) are formed. However, more than 4.0% addition of CuO nanoparticles reduced the mechanical strengths and increased the porosity of concrete. This may be due to inappropriate dispersion of CuO nanoparticles in the matrix that causes weak zones. Also, it may be due to the amount of CuO nanoparticles available in the concrete mix is more than the quantity needed to combine with the liberated Ca(OH)₂ during the hydration process.

6.2.6 Aluminium Oxide (Al_2O_3) Nanoparticles

The application of Al_2O_3 nanoparticles for enhancing the characteristics of cement and concrete has been carried out by few researchers. It has been reported that Al_2O_3 nanoparticles with average particles size of 15 nm can be used in the concrete as a partial replacement of cement. The results show that the Al_2O_3 nanoparticles could be advantageously used in place of cement although the addition of Al_2O_3 nanoparticles not only increased the compressive, flexural and split tensile strength of concrete but also decreased its workability and setting time as shown in Fig. 6.5 [69, 70].

These enhancements are mainly due to the rapid reaction between Al_2O_3 nanoparticles and calcium hydroxide, $Ca(OH)_2$ (formed during the hydration

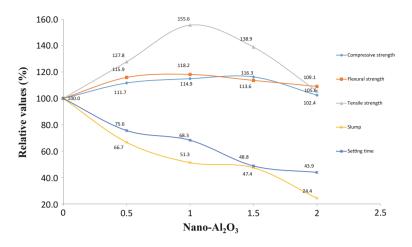


Fig. 6.5 Properties of 0.5–2% nano-Al $_2O_3$ incorporated cementitious composite relative to control specimen

cement). As a result, the hydration of cement is increased and larger amounts of reaction products (C-S-H gel) are formed. Moreover, the addition of Al_2O_3 nanoparticles improves the particle packing density of the mixed cement. Furthermore, the replacement of cement by Al_2O_3 nanoparticles decreased the workability of fresh concrete; thus, the use of some superplasticizer is essential [69–71]. The role of nanoalumina as a superfine aggregate was confirmed through SEM (scanning electron microscope) and EDS (energy-dispersive X-ray spectroscopy) studies, stating that the nano- Al_2O_3 fills the ITZ of cement, sand and some pores in the matrix, and hence, the compressive strength and elastic modulus of mortars is improved [72].

6.2.7 Zirconium Oxide (ZrO₂) Nanoparticles

The application of ZrO_2 nanoparticles for improving the properties of concrete and cement has been carried out only by a particular group of researchers. Possibility of enhancing mechanical characteristics of concrete by adding ZrO_2 nanoparticles as a partial replacement of cement is investigated. They reported that inclusion of ZrO_2 nanoparticles (up to 2.0% by weight) increased the compressive, flexural and split tensile strength of concrete but decreased its setting time and workability as shown in Fig. 6.6 [73–75]. These enhancements in mechanical characteristics of concrete are due to the rapid reaction between calcium hydroxide and ZrO_2 nanoparticles. As a result, the hydration of cement is increased and larger amounts of reaction products are formed. Moreover, the replacement of cement by ZrO_2 nanoparticles decreased the workability of fresh concrete, and therefore, some superplasticizer must be used.

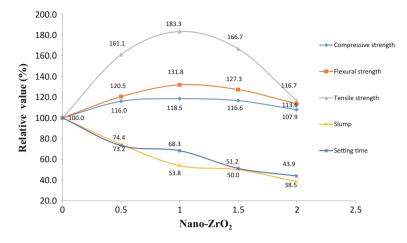


Fig. 6.6 Properties of 0.5-2% nano-ZrO₂ incorporated cementitious composite relative to control composite

6.2.8 Zinc Dioxide (ZnO₂) Nanoparticles

The use of ZnO_2 nanoparticles for influencing the properties of concrete and cement has been investigated by a particular group of researchers only. The results of a study indicate that ZnO_2 nanoparticles as a partial replacement of cement up to 4% are able to improve the flexural strength and pore structure of self-compacting concrete and recover the negative effects of polycarboxylate superplasticizer [76]. The results of another experiment indicate that the cement could be advantageously replaced with nano-ZnO₂ particles up to maximum limit of 2.0% as shown in Fig. 6.7 [77]. These enhancements in mechanical characteristics of concrete are due to the rapid reaction between calcium hydroxide and ZnO₂ nanoparticles. As a result, the hydration of cement is increased and larger amounts of reaction products are formed.

6.2.9 Calcium Carbonate (CaCO₃) Nanoparticles

The use of $CaCO_3$ nanoparticles for enhancing the characteristics of cement and concrete has been carried out by few researchers, though limestone (CaCO₃) powder is usually considered as inert and traditionally used as a filler material to improve rheological properties of concrete. However, current investigations have found that they can increase rate of hydration of ordinary Portland cement (OPC) when added as nanoparticles [78, 79]. The results of another research showed that CaCO₃ nanoparticles as a partial replacement of cement up to 5% could accelerate the rate of hydration, setting time and improve compressive

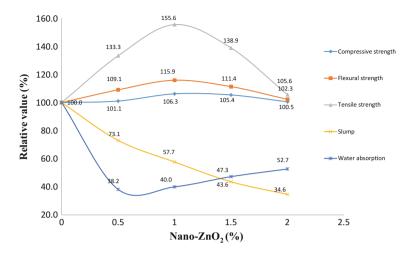


Fig. 6.7 Properties of 0.5-2% nano-ZnO₂ incorporated cementitious composite relative to control composite

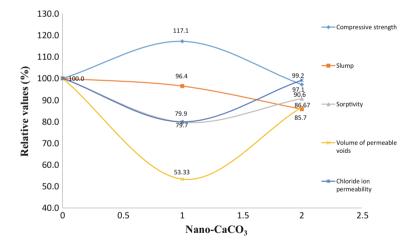


Fig. 6.8 Properties of 0.5-2% nano-CaCO₃ incorporated cementitious composite relative to control composite

strength [80]. In a similar study, the effects of $CaCO_3$ nanoparticles on the properties of concrete are shown in Fig. 6.8. The optimum content of nano-CaCO₃ is observed to be 1%. Also, it has been observed that the concrete containing 39% fly ash and 1% nano-CaCO₃ as a replacement of cement showed enhanced strength and durability properties compared to control concrete [81].

6.2.10 Chromium Oxide (Cr_2O_3) Nanoparticles

The utilization of Cr_2O_3 nanoparticles for influencing the properties of cementitious composites has been investigated by a particular group of researchers only. The results of a study showed that Cr_2O_3 nanoparticles as a partial replacement of cement up to 2% could improve the properties of concrete. Also, it has been found that the concrete cured in saturated lime water (LW) produced higher mechanical strength and durability properties compared to those cured in tap water (W) at all the ages; the 28-day properties are shown in Fig. 6.9. This may be due to the formation of excessive strengthening gel in the presence of saturated limewater in which the amount of nano- Cr_2O_3 particles (pozzolan) available in the composite is nearly equal to the quantity needed to combine with the liberated lime during the hydration process, thus lesser amount of silica leaching out compared to the specimens cured in water. Furthermore, the optimal level of cement replacement with nano- Cr_2O_3 particles was found to be 2% and 1% for the specimens cured in saturated limewater and water respectively [82, 83].

6.2.11 Silver (Ag) Nanoparticles

The silver nanoparticles can be used as an additive in paints to inactivate pathogenic microorganisms and give antimicrobial properties to the surfaces for instance hospital walls. This is because of the fact that the silver nanoparticles have inherent properties to reduce the growth and multiplication of fungi, viruses and bacteria, which causes itchiness, infection, odour and sore [84].

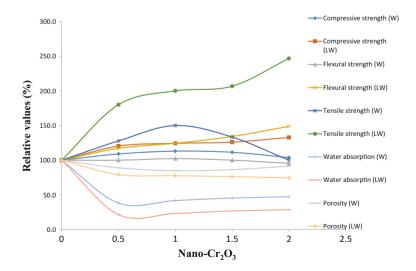


Fig. 6.9 Properties of 0.5–2% nano-Cr₂O₃ incorporated cementitious composite cured in water

6.3 Environmental and Economical Aspect

All the building and maintenance materials must be compatible to the natural environment, and their effects should not be harmful. Therefore, the consequence of different nanomaterials on the environment is discussed hotly in environmental and nanotechnology researches. Many recent investigations have focused on the ambiguity concerning the potential adverse impacts of nanomaterials. Some researches in this regard show that the unique properties that make nanomaterials in the construction sector so promising may also create unexpected human health and environmental problems. These possible problems may occur by releasing nanomaterials into air because of the production of dust, leaching of nanomaterials into the groundwater and exposing potentially hazardous materials at the time of construction and maintenance works. For example, both carbon nanotubes (SWNT and MWNT) can show antibacterial properties and pose a potential hazard because they exert side effects on the lungs, damage the cell membrane, slow down the respiratory functions, harm the mitochondrial deoxyribonucleic acid (DNA), etc. [9–12]. Similarly, TiO₂ nanoparticles irradiated through ultraviolet light or sunlight produce reactive oxygen species (ROS), which cause DNA damage, cytotoxicity and inflammation in mammals [13-15]. Likewise, SiO₂ nanoparticles have been reported to exert carcinogenic activity, harm the bacteria due to ROS productions and are toxic to marine algae, etc. [16, 17]. Also, the copper oxide or copper nanoparticles induce oxidative stress and DNA damage in human, algae, bacteria and yeasts cells [18–20]. Hence, the use of nanomaterials in civil engineering or construction industry becomes a double-edged sword. Therefore, more researches and investigations are required with well planned and designed so that building projects can be made environment-friendly and sustainable.

Currently, the cost of nanomaterials and nanotechnology equipments are quite high. This is essentially because of the novel technology and the complex equipments used for synthesis and characterization of the materials, although it is expected that cost of materials will reduce in due course with the upgradation of manufacturing technologies and equipments. However, recent view is that the nanotechnology and nanomaterials should be used in some special cases (e.g. for treating the complex problems) to give unique solutions with effective cost. In other cases, the conventional materials and methods may be used for treating the problems with effective cost. Therefore, it is a challenge to the construction or civil engineers and researchers to solve expenditure problems associated with nanomaterial-based constructions and give a service to the common public at a minimum cost [21].

6.4 Nanomaterials as Corrosion Inhibitors

Improvement in mechanical strength and durability properties of the concrete by the addition of nanomaterials is reported in literature. Yet another novel use of nanomaterial in controlling the corrosion of steel in concrete is proposed by the authors. A comprehensive study involving nanomaterials as corrosion inhibitors is under way. Some of the early results are included in this article. To compare the effectiveness of the chosen nanomaterials and their application methodology, one of the established chemical corrosion inhibitor, namely calcium nitrite, has also been included in this study.

The present investigation deals with the performance assessment of protective coatings on steel reinforcement. These coatings were made with plain cement slurry (SC), calcium nitrite (CN)-inhibited cement slurry, titanium dioxide (TO) and graphene (GP)-admixed cement slurry. Electrochemical tests were conducted on these specimens in normal and saline water (4% NaCl solution). Cyclic sweep tests using ACM (applied corrosion monitoring) potentiostat having inbuilt software for the data acquisition and post-processing was used for the study. Tafel plots for all these specimens in normal and saline water are shown in Figs. 6.10 and 6.11, respectively. Corrosion kinematic parameters were also obtained and are presented in Tables 6.3 and 6.4.

The results included here are observed at early stage of exposure. To establish the worthiness of the system in controlling and/or delaying reinforcement corrosion, longer duration exposure is required. Reduced corrosion current density and thereby very low corrosion rates were observed for all the systems investigated as compared

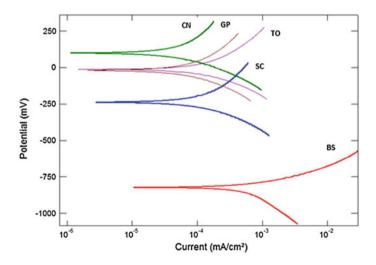


Fig. 6.10 Tafel plots of the specimens under normal exposure

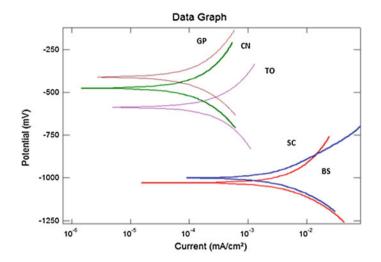


Fig. 6.11 Tafel plots of the specimens under saline exposure

System	Rest potential,	Anodic tafel constant, B _a	Cathodic tafel constant, B _c	Corrosion current, I _{corr}	Corrosion rate
	$R_{\rm P} ({\rm mV})$	(mV)	(mV)	(mA/cm^2)	(mm/year)
BS	-830.69	144.97	324.87	0.0020005	0.0231857
SC	-235.08	367.13	242.7	0.0001627	0.0018853
CN	101.56	444.91	192.85	0.0000847	0.0009817
ТО	-19.283	289.02	162.65	0.0001302	0.0015087
GP	-10.651	333.88	206.85	0.0000886	0.0010275

Table 6.3 Corrosion kinematic parameters for the specimens under normal exposure

Table 6.4 Corrosion kinematic parameters for the specimens under saline exposure

System	Rest potential, R _P (mV)	Anodic tafel constant, B _a (mV)	Cathodic tafel constant, B _c (mV)	Corrosion current, I _{corr} (mA/cm ²)	Corrosion rate (mm/year)
BS	-1030.3	387.09	236.78	0.0056604	0.0656045
SC	-998.4	184	157.79	0.0024881	0.0288372
CN	-473.94	304.16	268.05	0.0001291	0.0014958
ТО	-587.95	263.95	283.6	0.0002736	0.0031707
GP	-410.09	310.61	256.06	0.0001212	0.0014046

to the bare steel (BS) specimens both in normal and saline water. Results are quite comparable with the calcium nitrite-inhibited systems. In most of the systems, results comparable to that of the calcium nitrite were obtained.

6.5 Conclusions

The use of nanomaterials in civil engineering or construction industries presents numerous opportunities and challenges. The mechanism and function of various nanomaterials with the conventional building materials have been reviewed and discussed in detail. Further, the following conclusion may be drawn:

- (i) The addition of nanomaterials considerably reduced the initial setting time (IST) as well as final setting time (FST) of cementitious composite. This is due to its large specific surface areas, unambiguously more number of atoms on the surface, which are highly unstable and active, and consequently, speed up the cement hydration reaction and eventually reduces the setting time.
- (ii) The addition of nanomaterials considerably reduced the workability of cementitious composites. This may be because of the fact that the replacement of cement with nanoparticles increased the overall surface area and thus requires more lubricating water to wet the particles. However, this can be overcome with the use of superplasticizers and supplementary cementitious materials such as fly ash, silica fume, rice husk ash along with nanomaterials.
- (iii) The mechanical strengths and durability properties of cementitious composite are significantly improved with the use of appropriate amount of nanomaterials. This is mainly because of the fact that nanomaterials act as ultrafine aggregate which not only fills the tiny voids in the composite but also acts as kernel which reduces the size of $Ca(OH)_2$ and accelerate the hydration process resulting more consumption of $Ca(OH)_2$ and produced large quantity of C-S-H gel.
- (iv) The mechanical strengths and durability properties of cementitious composite were found to be decreased at higher dosages of nanomaterials. It may be because of the formation of weak zones due to inappropriate dispersion of nanoparticles.
- (v) Also, the suitable type and amount of nanomaterials to be added to the cementitious composite is still contradictory. Therefore, more researches and investigations are required in order to decide the appropriate quantity and type of nanomaterials to be used for a particular type of construction work.
- (vi) Furthermore, there are some other challenges to use nanomaterials in civil engineering like their impacts on human health and environment and high cost. All these issues seek attention from scientific community working in this area.
- (vii) A novel use of nanomaterials has been suggested by the authors. The results of the electrochemical tests clearly indicated the effectiveness of nanomaterials in controlling corrosion. The calcium nitrite-inhibited as well as graphene and nano-TiO₂-admixed cement slurry coating exhibited appreciable level of corrosion inhibition as compared to uninhibited systems. However, more tests are required involving fairly longer period of time to establish nanomaterials as corrosion inhibitors.

References

- 1. R. Feynman, There's plenty of room at the bottom (reprint from the speech given at the annual meeting of the west coast section of the American Physical Society). Eng. Sci. 23, 22–36 (1960)
- K. Drexler, Molecular engineering: An approach to the development of general capabilities for molecular manipulation. Proc. Natl. Acad. Sci. 78, 5275–5278 (1981)
- 3. W.A. Goddard, D.W. Brenner, S.E. Lyshevski, G.J. Iafrate, Handbook of nanoscience engineering and technology, second ed., CRC Press, (2007)
- 4. S. Lee, W. Kriven, Synthesis and hydration study of Portland cement components prepared by organic steric entrapment method. Mater. Struct. **38**, 87–92 (2005)
- K. Sobolev, M.F. Gutierrez, How nanotechnology can change the concrete world: Part 2. Am. Ceram. Soc. Bull. 84, 16–19 (2005)
- Z. Ge, Z. Gao, Applications of nanotechnology and nanomaterials in construction, *First International Conference on Construction in Developing Countries (ICCIDC-1), Advancing and Integrating Construction Education, Research & Practice,* (Karachi, Pakistan 2008), pp. 235–240
- G.Y. Li, Properties of high-volume fly ash concrete incorporating nano-SiO₂. Cem. Concr. Res. 34, 1043–1049 (2004)
- H. Irie, K. Sunada, K. Hashimoto, Recent developments in TiO₂ photocatalysis: Novel applications to interior ecology materials and energy saving systems. Electrochem. **72**, 807– 812 (2004)
- C.W. Lam, J.T. James, R. McCluskey, S. Arepalli, R.L. Hunter, A review of carbon nanotube toxicity and assessment of potential occupational and environmental health risks. Crit. Rev. Toxicol. 36, 189–217 (2006)
- L.H. Ding, J. Stilwell, T.T. Zhang, O. Elboudwarej, H.J. Jiang, J.P. Selegue, P.A. Cooke, J.W. Gray, F.Q.F. Chen, Molecular characterization of the cytotoxic mechanism of multiwall carbon nanotubes and nano-onions on human skin fibroblast. Nano Lett. 5, 2448–2464 (2005)
- 11. S. Kang, M. Pinault, L.D. Pfefferle, M. Elimelech, Single walled carbon nanotubes exhibit strong antimicrobial activity. Langmuir 23, 8670–8673 (2007)
- C. Blaise, F. Gagne, J.F. Ferard, P. Eullaffroy, Ecotoxicity of selected nano-materials to aquatic organisms. Environ. Toxicol. 23, 591–598 (2008)
- A. Rincon, C. Pulgarin, Bactericidal action of illuminated TiO₂ on pure escherichia coli and natural bacterial consortia: Post-irradiation events in the dark and assessment of the effective disinfection time. Appl. Catal. B 49, 99–112 (2004)
- E.J. Wolfrum, J. Huang, D.M. Blake, P.C. Maness, Z. Huang, J. Fiest, W.A. Jacoby, Photocatalytic oxidation of bacteria, bacterial and fungal spores, and model biofilm components to carbon dioxide on titanium dioxide coated surfaces. Environ. Sci. Technol. 36, 3412–3419 (2002)
- L.K. Adams, D.Y. Lyon, P.J.J. Alvarez, Comparative ecotoxicity of nanoscale TiO₂, SiO₂, and ZnO water suspensions. Water Res. 40, 3527–3532 (2006)
- K. Fujiwara, H. Suematsu, E. Kiyomiya, M. Aoki, M. Sato, N. Moritoki, Size dependent toxicity of silica nanoparticles to chlorella kessleri. J. Environ. Sci. Health A. 43, 1167–1173 (2008)
- D. Dutta, S.K. Sundaram, J.G. Teeguarden, B.J. Riley, L.S. Fifield, J.M. Jacobs, S.R. Addleman, G.A. Kaysen, B.M. Moudgil, T.J. Weber, Adsorbed proteins influence the biological activity and molecular targeting of nanomaterials. Toxicol. Sci. 100, 303–315 (2007)
- Z. Chen, H.A. Meng, G.M. Xing, C.Y. Chen, Y.L. Zhao, G.A. Jia, T.C. Wang, H. Yuan, C. Ye, F. Zhao, Z.F. Chai, C.F. Zhu, X.H. Fang, B.C. Ma, L.J. Wan, Acute toxicological effects of copper nanoparticles. Toxicol. Lett. 163, 109–120 (2006)

- 6 Application of Nanomaterials in Civil Engineering
- V. Aruoja, H.C. Dubourguier, K. Kasemets, A. Kahru, Toxicity of nanoparticles of CuO, ZnO and TiO₂ to microalgae *Pseudokirchneriella subcapitata*. Sci. Total Environ. **407**, 1461–1468 (2009)
- K. Kasemets, A. Ivask, H.C. Dubourguier, A. Kahru, Toxicity of nanoparticles of ZnO, CuO and TiO₂ to yeast *Saccharomyces cerevisiae*. Toxicol. Vitro. 23, 1116–112 (2009)
- M. Holman, Nanomaterial Forecast: Vols and applications, *ICON Nanomaterial* Environmental Health and Safety Research Needs Assessment, (Lux Research: Houston, TX, 2007)
- M.A. Ahmed, Y.A. Hassanean, K.A. Assaf, M.A. Shawkey, Fascinating improvement in mechanical properties of cement mortar using multiwall carbon nanotubes and ferrite nanoparticles. Int. J. Struct. Civ. Eng. Res. 4, 159–170 (2015)
- 23. S. Iijima, Carbon nanotubes: Past, present, and future. Phys. B 323, 1-5 (2002)
- 24. S. Kumar, P. Kolay, S. Malla, S. Mishra, Effect of multiwalled carbon nanotubes on mechanical strength of cement paste. J. Mater. Civ. Eng. **24**, 84–91 (2012)
- T. Manzur, N. Yazdani, Strength enhancement of cement mortar with carbon nanotubes: Early results and potential. Transp. Res. Record. 2142, 102–108 (2010)
- T.C. Madhavi, P. Pavithra, B.S. Sushmita, S.B. Vamsi, P. Surajit, Effect of multiwalled carbon nanotubes on mechanical properties of concrete. Int. J. Sci. Res. 2, 166–168 (2013)
- 27. L. Małgorzata, Carbon nanotubes influence on the compressive strength of cement composites. Tech. Trans. Civ. Eng. 1, 5–11 (2014)
- P.F. Becher, Microstructural design of toughened ceramics. J. Am. Ceram. Soc. 74, 255–269 (1991)
- 29. M. Saafi, P. Romine, Nano and micro technology. Concr. Int. 27, 28-34 (2005)
- G.B. Song, H.C. Gu, Y.L. Mo, Smart aggregates: Multifunctional sensors for concrete structures-A tutorial and a review. Smart Mater. Struct. 17, 1–17 (2008)
- W. Zhang, J. Suhr, N. Koratkar, Carbon nanotube/polycarbonate composites as multifunctional strain sensors. J. Nanosci. Nanotechnol. 6, 960–964 (2006)
- G. Girishkumar, M. Rettker, R. Underhile, D. Binz, K. Vinodgopal, P. McGinn, P. Kamat, Single-wall carbon nanotube based proton exchange membrane assembly for hydrogen fuel cells. Langmuir 21, 8487–8494 (2005)
- 33. T. Nochaiya, A. Chaipanich, Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement based materials. Appl. Surf. Sci. **257**, 1941–1945 (2011)
- A. Chaipanich, T. Nochaiya, W. Wongkeo, P. Torkittikul, Compressive strength and microstructure of carbon nanotubes-fly ash cement composites. Mater. Sci. Eng. 527, 1063– 1067 (2010)
- R.K.A. Al-Rub, A.I. Ashour, B.M. Tyson, On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites. Const. Build. Mater. 35, 647–655 (2012)
- M.S. Konsta-Gdoutos, Z.S. Metaxa, S.P. Shah, Highly dispersed carbon nanotube reinforced cement based materials. Cem. Concr. Res. 40, 1052–1059 (2010)
- Z.S. Metaxa, M.S. Konsta-Gdoutos, S.P. Shah, Carbon nanofiber cementitious composites: Effect of debulking procedure on dispersion and reinforcing efficiency. Cem. Concr. Compos. 36, 25–32 (2013)
- S. Musso, J.M. Tulliani, G. Ferro, A. Tagliaferro, Influence of carbon nanotubes structure on the mechanical behavior of cement composites. Compos. Sci. Technol. 69, 1985–1990 (2009)
- J. Luo, Z. Duan, H. Li, The influence of surfactants on the processing of multi-walled carbon nanotubes in reinforced cement matrix composites. Phys. Status Solidi A 206, 2783–2790 (2009)
- F. Collins, J. Lambert, W.H. Duan, The influences of admixtures on the dispersion, workability, and strength of carbon nanotube-OPC paste mixtures. Cem. Concr. Compos. 34, 201–207 (2012)
- A. Cwirzen, K. Habermehl-Cwirzen, V. Penttala, Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites. Adv. Cem. Res. 20, 65–73 (2008)

- 42. A.M. Hunashyal, S.J. Lohitha, S.S. Quadri, N.R. Banapurmath, Experimental investigation of the effect of carbon nanotubes and carbon fibres on the behaviour of plain cement composite beams. IES J. Part A: Civ. Struct. Eng. **4**, 29–36 (2011)
- 43. M.H. Zhang, H. Li, Pore structure and chloride permeability of concrete containing nano-particles for pavement. Constr. Build. Mater. **25**, 608–616 (2011)
- 44. S. Hussain, K. Sastry, Study of strength properties of concrete by using micro-silica and nano-silica. Int. J. Res. Eng. Technol. **3**, 103–108 (2014)
- Q. Ye, Z.N. Zhang, D.Y. Kong, R.S. Chen, Influence of nano-SiO₂ addition on properties of hardened cement paste as compared with silica fume. Constr. Build. Mater. 21, 539–545 (2007)
- L. Senff, D. Hotza, W.L. Repette, V.M. Ferreira, J.A. Labrinca, Mortars with nano-SiO₂ and micro-SiO₂ investigated by experimental design. Constr. Build. Mater. 24, 1432–1437 (2010)
- B.W. Jo, C.H. Kim, G.H. Tae, J.B. Park, Characteristics of cement mortar with nano-SiO₂ particles. Constr. Build. Mater. 21, 1351–1355 (2007)
- B. Hasan, S. Nihal, Comparative study of the characteristics of nanosilica, silicafume and fly-ash incorporated cement mortars. Mater. Res. 17, 570–582 (2014)
- L. Singh, S. Bhattacharyya, U. Sharma, G. Mishra, S. Ahalawat, Microstructure improvement of cementitious systems using nanomaterials: A key for enhancing the durability of concrete. Mechanical and Physics of Creep, Shrinkage and Durability of Concreate ASCE (2013) 293– 300
- 50. A. Boshehrian, P. Hosseini, Effect of nano-SiO₂ particles on properties of cement mortar applicable for ferrocement elements. Concr. Res. **2**, 167–180 (2011)
- H. Bahadori, P. Hosseini, Reduction of cement consumption by the aid of silica nanoparticles. J. Civil Eng. Manag. 18, 416–425 (2012)
- A. Heidari, D. Tavakoli, Properties of concrete incorporating silica fume and nano-SiO₂. Ind. J. Sci. Technol. 6, 108–112 (2013)
- P. Zhang, X. Dai, J. Gao, P. Wang, Effect of nano-SiO₂ particles on fracture properties of concrete composite containing fly ash. Curr. Sci. 108, 2035–2043 (2015)
- L. Senff, J.A. Labrinca, V.M. Ferreira, D. Hotza, W.L. Repette, Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. Constr. Build. Mater. 23, 2487– 2491 (2009)
- A.K. Rana, S.B. Rana, A. Kumari, V. Kiran, Significance of nanotechnology in construction engineering. Int. J. Recent Trends Eng. 1, 46–48 (2009)
- N. Serpone, E. Pelizzetti, *Photocatalysis: Fundamentals and applications* (Wiley, New York, 1989)
- B. Ruot, A. Plassais, F. Olive, L. Guillot, L. Bonafous, TiO₂-containing cement pastes and mortars: Measurements of the photocatalytic efficiency using a rhodamine B-based colourimetric test. Sol. Energy 83, 1794–1801 (2009)
- G.L. Guerrini, Photocatalytic performances in a city tunnel in Rome: NOx monitoring results. Constr. Build. Mater. 27, 165–175 (2012)
- A. Nazari, R. Shadi, R. Sharin, S.F. Shamekhi, A. Khademno, Improvement in the mechanical properties of the cementitious composite by using TiO₂ nanoparticles. J. Am. Sci. 6, 98–101 (2010)
- A. Nazari, R. Shadi, R. Sharin, S.F. Shamekhi, A. Khademno, Assessment of the effects of the cement paste composite in presence TiO₂ nanoparticles. J. Am. Sci. 6, 43–46 (2010)
- E. Mohseni, M. Ranjbar, K. Tsavdaridis, Durability properties of high-performance concrete incorporating nano-TiO₂ and fly ash. Am. J. Eng. Appl. Sci. 8, 519–526 (2015)
- A. Nazari, R. Shadi, R. Sharin, S.F. Shamekhi, A. Khademno, Benefits of Fe₂O₃ nanoparticles in concrete mixing matrix. J. Am. Sci. 6, 102–106 (2010)
- A. Nazari, R. Shadi, R. Sharin, S.F. Shamekhi, A. Khademno, The effects of incorporation Fe₂O₃ nanoparticles on tensile and flexural strength of concrete. J. Am. Sci. 6, 90–93 (2010)
- 64. N.A. Yazdi, M.R. Arefi, E. Mollaahmadi, B.A. Nejand, To study the effect of adding Fe_2O_3 nanoparticles on the morphology properties and microstructure of cement mortar. Life Sci. J. **8**, 550–554 (2011)

- 6 Application of Nanomaterials in Civil Engineering
- A. Khoshakhlagh, A. Nazari, G. Khalaj, Effects of Fe₂O₃ nanoparticles on water permeability and strength assessments of high strength self-compacting concrete. J. Mater. Sci. Technol. 28, 73–82 (2012)
- A. Nazari, R. Shadi, Effects of CuO nanoparticles on compressive strength of self-compacting concrete. Sadhana-Indian Academy Sci. 36, 371–391 (2011)
- A. Nazari, R. Shadi, Effects of CuO nanoparticles on microstructure, physical, mechanical and thermal properties of self-compacting cementitious composites. J. Mater. Sci. Technol. 27, 81–92 (2011)
- A. Nazari, M.H. Rafieipour, R. Shadi, The Effects of CuO Nanoparticles on properties of self compacting concrete with GGBFS as Binder. Mater. Res. 14, 307–316 (2011)
- A. Nazari, R. Shadi, R. Sharin, S.F. Shamekhi, A. Khademno, Influence of Al₂O₃ nanoparticles on the compressive strength and workability of blended concrete. J. Am. Sci. 6, 6–9 (2010)
- A. Nazari, R. Shadi, R. Sharin, S.F. Shamekhi, A. Khademno, Mechanical properties of cement mortar with Al₂O₃ nanoparticles. J. Am. Sci. 6, 94–97 (2010)
- M.R. Arefi, M.R. Javeri, E. Mollaahmadi, To study the effect of adding Al₂O₃ nanoparticles on the mechanical properties and microstructure of cement mortar. Life Sci. J. 8, 613–617 (2011)
- L. Zhenhua, W. Huafeng, H. Shan, L. Yang, W. Miao, Investigations on the preparation and mechanical properties of the nano-alumina reinforced cement composite. Mater. Lett. 60, 356–359 (2006)
- A. Nazari, R. Shadi, ZrO₂ nanoparticles effects on split tensile strength of self compacting concrete. Mater. Res. 13, 485–495 (2010)
- A. Nazari, R. Shadi, R. Shirin, F.S. Seyedeh, A. Khademno, An investigation on the strength and workability of cement based concrete performance by using ZrO₂ nanoparticles. J. Am. Sci. 6, 29–33 (2010)
- A. Nazari, R. Shadi, R. Shirin, F.S. Seyedeh, A. Khademno, Embedded ZrO₂ nanoparticles mechanical properties monitoring in cementitious composites. J. Am. Sci. 6, 86–89 (2010)
- A. Nazari, R. Shadi, The effects of zinc dioxide nanoparticles on flexural strength of self-compacting concrete. Compos. Part B: Eng. 42, 167–175 (2011)
- 77. A. Nazari, S. Riahi, The effects of ZnO_2 nanoparticles on strength assessments and water permeability of concrete in different curing media. Mater. Res. **14**, 178–188 (2011)
- T. Sato, J.J. Beaudoin, *The Effect Of Nano-Sized CaCO₃ Addition on the Hydration of OPC Containing High Volumes of Fly Ash.* Proceeding of the 12th International conference on the chemical of cement, Montreal, Canada, 1–12 (2006)
- T. Sato, F. Diallo, Seeding effect of nano-CaCO₃ on the hydration of tricalcium silicate. J. Transp. Res. Board. **2141**, 61–67 (2010)
- S. Kawashima, P. Hou, D.J. Corr, S.P. Shah, Modification of cement-based materials with nanoparticles. Cem. Concr. Compos. 36, 8–15 (2013)
- F.U.A. Shaikh, S.W.M. Supit, Mechanical and durability properties of high volume fly ash concrete containing calcium carbonate nanoparticles. Constr. Build. Mater. **70**, 309–321 (2014)
- A. Nazari, S. Riahi, Optimization mechanical properties of Cr₂O₃ nanoparticles binary blended cementitious composite. J. Compos. Mater. 45, 943–948 (2011)
- A. Nazari, S. Riahi, The effects of Cr₂O₃ nanoparticles on strength assessments and water permeability of concrete in different curing media. Mater. Sci. Eng. 528, 1173–1182 (2011)
- A. Kumar, P.K. Vemula, P.M. Ajayan, G. John, Silver nanoparticle-embedded antimicrobial paints based on vegetable oil. Nat. Mater. 7, 236–241 (2008)