Nano Wonders in Concrete Technology: Mini Review

Anwar Khitab^{1*}, Sajjad Ahmad², Affan Jalil¹, Zain-Ul-Abdin¹

¹Department of Civil Engineering, Mirpur University of Science and Technology, Mirpur-10250, AJ&K, Pakistan

²Department of Building and Architectural Engineering, Bahauddin Zakariya University, Multan-60000, Pakistan

Keywords

Conventional concrete,
Drawbacks,
High performance,
Nano particles,
Nano concretes.

Abstract

Concrete is one of the most significant materials, man has produced. Conventionally, it is a mixture of cement, sand, coarse aggregates and water. It is versatile, and gains strength in a few weeks after its casting. It can withstand extreme weather conditions. However, traditional concrete also has some drawbacks. It has low tensile strength and develops cracks, which limit its usefulness. The performance of concrete can be enhanced by carefully selecting its ingredients and employing appropriate modern techniques. One such technique is the use of nano particles. Nano particles, due to their small size, possess very high surface area to volume ratio. They can be used as inert filler as well as chemically active ingredients in cementitious composites. Being filler, they can fill up very small voids in the matrix. As active ingredients, they can result in higher chemical reactivity. This work focuses on the wonders, nano particles have brought in concrete technology. The topics include self-healing, de-pollutant, de-icing and energy-saving concrete materials.

1. Introduction

Conventional concrete is a mixture of cement, fine aggregates or sand, coarse aggregates and water. Cement is used for binding purposes; it chemically reacts with water to form hydration products. The aggregates act as filler materials. Traditionally, concrete is a versatile material that can be used in a variety of residential, commercial and industrial applications. Ordinary concrete has a compressive strength of 20-25 MPa at maturity; however its tensile strength is only 8-10% of its compressive strength [1]. In the hardening process, cement particles chemically react with water to form binding compounds; the chemical process is known as hydration. Hydration initiates at the surface of the cement grains. Finer cement particles offer higher surface area, which leads to the rapid formation of the hydration products. The hydration products are mainly comprised of calcium silicate hydrate gel (CSH), calcium hydroxide (CH), and ettringite. These products are precipitated at the nucleation sites, forming the hard cement matrix, which is primarily responsible for the strength of the concrete. In conventional concrete, the size of the aggregate particles ranges from a fraction of millimeters to few centimeters. These particles due to their larger sizes deposit the cement hydration products inefficiently and result in a lower strength of the concrete [2, 3].

As discussed earlier, the aggregate particles are mere fillers and the classical aggregate sizes (from a fraction of a millimeter to a few centimeters) lead to the creation of voids. Nano fillers can accommodate inside the smaller voids obstructing the creation of nano cracks [4]. Owing to the fact that the nano sized particles might be very beneficial, nano materials made its ways inside the concrete technology. Nano concrete technology speaks of the synthesis and mixing of nano-sized particles in concrete in appropriate quantities, using suitable methods [5]. As such, concrete technology is just not limited to the ordinary concrete mixtures: A variety of concrete types have been developed for special purposes. Among such special concretes, include self-healing, self-cleaning, engineered cementitious composites (ECC) and many more [6-11].

Present work deals with the special concrete materials, which are developed by using nanotechnology. The materials like self-healing concrete, self-cleaning concrete, de-icing agents and Phase Change Materials (PCMs) are the focus of discussion.

2. Nano-mechanics

Nano-mechanics is defined as the mechanics of nano-particles and the nano-composites (Matrix plus nano-fillers) [12]. According to Strambeanu et al. (2014) a nanoparticle is defined as the one having its size in the interval 10^{-6} - 10^{-9} m [13]. Nanoparticles can be transformed both into loose-formed powder and stable-shaped nanomaterials. In loose form, their high surface to volume ratio, ensures high degree of adsorption, and increased reaction with other particles; Also their small size allows them to pass through extremely narrow passages [14]. For nanomaterials, the nano-particles are structured at molecule level (atom by atom), resulting in new or improved properties: This alteration or improvement in turn improves the properties of the composite material [15]. This bottom up approach led the scientists and engineers to synthesize and apply nano-particles in different domains of materials science and concrete technology is not an exception.

3. Self-healing concrete

3.1. Bio concrete

Ordinary concrete develops cracks due to numerous reasons like high ambient temperature, exothermic hydration reactions, applied loads, and freeze and thaw etc [16]. Self-healing concrete, also known as Bio-concrete or bacterial concrete, is a special type of concrete that repairs its cracks, when it comes in contact with air or water. It makes use of a special type of aerobic bacteria called *Bacillus*, which produces lime (CaCO_3) in the presence of Oxygen. The produced lime heals up the cracks. It was developed by Hendrik Jonkers, a microbiologist from Netherland [17]. Bacterial content is placed during the casting phase

*Corresponding Author: anwar.ce@must.edu.pk
(Anwar Khitab Orcid: 0000-0001-5264-5730)

Received 04 May 2020 Revised 09 May 2020 Accepted 09 May 2020
Cement Based Composites 1 (2020) 25-28
2717-9303 © 2019 ACA Publishing. All rights reserved.

<https://doi.org/10.36937/cebacom.2020.001.005>

and the can survive in alkaline environment developed during the hydration phase. Bacteria are coated with clay so that they do not mix with the cement particles. The bacteria are introduced with Calcium Lactate ($\text{Ca}(\text{C}_3\text{H}_5\text{O}_2)_2$) nutrient. The formation of CaCO_3 takes place in accordance with the following formula:

3.2 Nano-tailored self-healing concrete

Davies et al. (2018) have reported that one self-healing technique cannot be applied for all kind of damages and that a particular self-healing technique can be adapted keeping in view the specific damage mechanism [18]. Nano-tailored cementitious composites were developed to control the corrosion of reinforcing bars in concrete. Calcium containing polymeric nano-aggregates (PEO₁₁₃-b-PS₂₁₈ core-shell micelles and vesicles) were introduced in concrete mix. The concrete and steel material properties were investigated vis-à-vis the pore solution composition and steel/cement paste interface. It is reported that the nano-aggregates result in a reduction of porosity and water permeability. It has also been confirmed that the aggregates result in a more protective layer at the steel surface compared to ordinary concrete, increasing the corrosion resistance of the steel in an aggressive environment [19].

4. Self-cleaning concrete

Self-cleaning or photo-catalytic concrete is a concrete that employs the phenomena of photo-catalysis for the decomposition of the pollutants and contaminants present in air. When a photo-catalyst is introduced in concrete, it decomposes organic materials like dirt, mold, algae, bacteria, allergens, air pollutants, smoke, tobacco etc. in the presence of light. The harmful compounds decompose into Oxygen, Carbon dioxide, water, sulfates, nitrates, and other substances that are either beneficial or have a relatively minor effect on the environment [20].

Diagrammatically, the process of photo catalysis is shown in Figure 1. Sunlight consists of waves of different wavelengths. Nano Titania Particles (NTPs) absorb ultra-violet radiations from the sunlight. The excess energy received causes the transfer of its valence electrons to the conduction band creating an electron-hole pair. The chemical reaction is shown in Eq. 2 [21].

The positive hole decomposes water molecule into hydrogen gas and hydroxyl radical, whereas the electron reacts with oxygen molecule making superoxide radical. The hydroxyl and superoxide radicals have the power to decompose different contaminants/pollutants, which come in contact with the surface of the nano Titania particles.

Figure 1. Mechanism of Photo Catalysis

5. Self-heating concrete

De-icing agents or snow-removing machines are intended to remove snow, ice or frost from road surfaces to streamline traffic. Normally, high concentrations of Sodium Chloride (NaCl) are used as de-icing agents. NaCl decreases the freezing point of water. The decrease depends on the amount of salt. Nevertheless, the salts have found to be ineffective at temperatures below -16°C. Another problem with chlorides is that it promotes metallic corrosion. This affects both the vehicle parts and the steel reinforcement inside an RCC structural member [22].

An important alternate to de-icing agents is the self-heating concrete. The material consists of non-conductive Carbon Nano fibers integrated with an electric current [23]. The resistive material converts electrical current to heat. The heat is conducted to the road surface and melts the snow lying thereon. Self-heating concrete eliminates the use of corrosive de-icing agents or heavy machinery for removing snow. Diagrammatically, the process of self-heating concrete is shown in Figure 2.

Figure 2. Self-heating Concrete; redrawn from [23]

Normally, concrete is regarded as insulating material due to its non-homogeneous composition and voids. However, modern techniques can be used to enhance its thermal conductivity. One of such techniques is the use of a combination of silane and silica fume as admixtures. It is reported that the two admixtures together increase the thermal conductivity of the cement paste by 50%. The silane couples together the silica fume particles, which provides an easy flow of heat [24].

6. Energy storing concrete

In residential and commercial sectors, it is very important to provide thermal comfort to the occupants. With the passage of time, the thermal comfortability requirements and enhanced building services have increased the energy demand for heating and cooling applications. Traditionally, thermal insulation materials are being employed for reducing the energy losses through the building envelope. However, the increased insulation thickness leads to reduction in net useable space, complex building detailing and increased cost of construction. Literature indicates that the phase change materials (PCM), which can store heat or coolness are capable of reducing the energy demand for heating and cooling applications [25, 26]. The PCMs store energy in latent form, which is described as the amount of energy released or absorbed, while the material changes its phase i.e. from liquid phase to solid phase and vice versa. The latent heat for changing the material's phase is usually several times greater than their sensible heat: For example, the sensible heat for concrete is 1.0 kJ/kg K, whereas the latent heat of calcium chloride hexahydrate is 171 kJ/kg with melting temperature of 29.7 °C and for butyl stearate it is 140 kJ/kg with melting temperature from 18 to 23 °C [27]. This indicates that PCMs may offer their energy storage potential for controlling the indoor environment with reduced energy requirements for heating or cooling.

PCM are generally categorized in three groups i.e. (a) organic, (b) inorganic, and (c) eutectics. Organic PCM are generally stable, nontoxic and noncorrosive in nature. They exhibit high latent heat capacity but due to their poor thermal conductivity, they require fillers or admixtures for their effective utilization in the energy storage applications. Organic PCMs include paraffin wax and other

paraffin containing carbon atoms ranging from C14 to C50. Other non-paraffin based organic PCMs are polyglycols, dodecanol, biphenyl, HDPE, capric acid and lauric acid etc.

Inorganic PCMs are generally cheap with high latent heat capacity but they are corrosive and may undergo phase segregation. Phase segregation means that the inorganic PCMs e.g. salt hydrates decompose into lower salts thus reducing the effective amount of PCM and lowering the energy storage capacity. Common examples of hydrated salt based PCM are $\text{LiClO}_3 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ etc. The salt hydrates exhibit higher energy storage capacity but also require higher phase change temperature that may not fall in the comfortable range. Therefore, to modify the melting temperature, energy storage capacity, phase segregation and super-cooling tendency, two or more salt hydrates or other materials are mixed to form eutectics. Eutectics may be divided into three groups depending upon the types of PCMs mixed to form them e.g. (a) organic PCM mixed with other organic PCM, (b) inorganic PCM mixed with other inorganic PCM, and (c) organic PCM mixed with other inorganic PCM.

Mehling (2008) reported that the magnesium salt hydrates i.e. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ having melting points of 90°C and 117°C , respectively when mixed together as $58.7\%\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 41.3\%\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ bring down the melting temperature of the eutectic to 58°C [28]. A schematic view of the categories of PCMs is presented in Figure 3 below.

Figure 3. Categories of PCMs; redrawn from [29]

Generally, PCMs are incorporated by encapsulating them in suitable containers made up of metals, ceramics, and polymers. However, in building applications, the low heat transfer/thermal conductivity of PCM encapsulating materials, PCMs leakage and their volume changes associated with the phase changing may produce adverse effect on the physical/mechanical properties of PCM carrying materials. One of the solutions to these problems is to impregnate the PCMs directly in the construction materials.

Concrete is composed of 70–75% (by volume) of aggregates [30]. These are inert materials that can be employed for the impregnation of PCMs in concrete. Expanded clay and shale aggregates have been impregnated by Zheng et al. (2004) with butyl stearate [31]. They have reported that the PCM can occupy about 75% of the total pores of the aggregates and exhibit excellent thermal characteristics with no PCM leakage. The direct impregnation is an easy and effective method. However, the interaction between cement hydration products and PCM impregnated aggregates deteriorates the composite's mechanical strength [32, 33].

The direct inclusion of PCM in the cement composites has been investigated by Bao et al. (2017) [26]. They incorporated the paraffin modified with expanded graphite and graphene nano platelets, directly into the cement matrix. The paraffin was effectively held by the expanded graphite through capillary suction and surface tension, while the graphene nano platelets held the PCM on their surface due to van-der-Wall forces. The resulting composite exhibited no leakage of PCM with excellent thermal efficiency.

7. Conclusions

The bottom up approach i.e. controlling the characteristics of composites from nano and micro scale is very effective in engineering applications. In construction industry by exploiting the power of nano technology, tremendous enhancements in the functional capabilities of the resulting composites may be achieved. A lot of awareness and research is still needed to explore more benefits of nanotechnology for building materials. Some future ideas may include (but not limited to) the performance enhancement of the concrete containing recycled aggregates, reduction of carbon footprint due to cementitious materials, optimization of hydration reactions, concrete production under severe negative temperatures, and extraterrestrial construction.

The possible utilization of PCMs in cement and concrete for energy storage is very promising and may lead to enormous amounts of energy savings thus reducing the carbon foot prints of the construction industry. The direct incorporation, encapsulation and impregnation are the major and effective techniques for incorporating the PCMs in the cement and concrete composites. The PCMs may lead to reduction in strength of the cementitious composites however, this effect may be balanced by the utilization of nano/micro fibers, carbonaceous inerts or other high-performance materials.

Acknowledgement

This review was written as part of the project “Development and characterization of crack resistant environment friendly and sustainable cementitious composites with enhanced strength and ductility”, funded by Higher Education Commission (HEC), Government of Pakistan and Office of Research, Innovation and Commercialization (ORIC), Mirpur University of Science and Technology (MUST), Mirpur under the auspices of National Research Program for Universities (NRPU).

Declaration of Conflict of Interests

The authors declare that there is no conflict of interest.

References

- [1.] Khitab, A., Materials of Construction. Allied Books, (2012). https://scholar.google.com.pk/scholar?hl=en&as_sdt=0,5&cluster=1645605099361494451
- [2.] Ferro, G. A., Ahmad, S., Khushnood, R. A., et al., Improvements in self-consolidating cementitious composites by using micro carbonized aggregates, *Frattura ed Integrità Strutturale*, 30(2014) 75–83. <https://doi.org/10.3221/IGF-ESIS.30.11>
- [3.] Shamim, A., Ahmad, S., Khitab, A., et al., Applications of Nano Technology in Civil Engineering, *International Journal of Strategic Engineering*, 1(2018) 48–64. <https://doi.org/10.4018/IJoSE.2018010104>
- [4.] Ahmad, S., Khushnood, R. A., Jagdale, P., et al., High performance self-consolidating cementitious composites by using micro carbonized bamboo particles, *Materials & Design*, 76(2015) 223–229. <https://doi.org/10.1016/j.matdes.2015.03.048>
- [5.] Rao, N. V., Rajasekhar, M., Vijayalakshmi, K., Vamshykrishna, M., The Future of Civil Engineering with the Influence and Impact of Nanotechnology on Properties of Materials, *Procedia materials science*, 10(2015) 111–115. <https://doi.org/10.1016/j.mspro.2015.06.032>
- [6.] Gautam, B. R., Bacteria based self-healing concrete - A review, *International Journal of Engineering Science*, (2018) 57–61. <https://doi.org/10.1016/j.conbuildmat.2017.07.040>
- [7.] Benedix, R., Dehn, F., Quaas, J., Orgass, M., Application of titanium dioxide photocatalysis to create self-cleaning building materials, *Lacer*, 3(2000) 157–168.

- https://www.researchgate.net/publication/265540833_Applicati-on_of_Titanium_Dioxide_Photocatalysis_to_Create_Self-Cleaning_Building_Materials
- [8.] Li, V. C., Can concrete be bendable?: The notoriously brittle building material may yet stretch instead of breaking, *American Scientist*, 100(2012) 484–493. <https://doi.org/10.1511/2012.99.484>
 - [9.] Khitab, A., Alam, M., Riaz, H., Rauf, S., Smart Concretes: Review, *International Journal of Advances in Life Science and Technology*, 1(2014) 47–53. <https://doi.org/10.18488/journal.72/2014.1.2/72.2.47.53>
 - [10.] Khitab, A., Nadeem, M., Hussain, S., Use of flexible engineered cementitious composite in buildings, *Key Engineering Materials*, (2012) 591–596. <https://scholar.google.com.pk/scholar?oi=bibs&hl=en&cluster=15742999626438273177>
 - [11.] Khitab, A., Arshad, M. T., Nano construction materials: Review, *Reviews on Advanced Materials Science*, 38(2014) 181–189. <https://scholar.google.com.pk/scholar?oi=bibs&hl=en&cluster=13479574046563783682>
 - [12.] Guz, A., Rushchitskii, Y., Nanomaterials: on the Mechanics of Nanomaterials, *International Applied Mechanics*, 39(2003) 1271–1293. <https://doi.org/10.1023/B:INAM.0000015598.53063.26>
 - [13.] Strambeanu, N., Demetrovici, L., Dragos, D., Lungu, M., Nanoparticles: Definition, Classification and General Physical Properties, *Nanoparticles' Promises and Risks*, Springer International Publishing, Cham, (2015) 3–8. https://doi.org/10.1007/978-3-319-11728-7_1
 - [14.] Phosphorex Nanoparticles VS. Microspheres for Drug Delivery, *Micro & Nanoparticles*, (2014). <https://phosphorex.com/nanoparticles-vs-microspheres-for-drug-delivery.html>
 - [15.] Drexler, E., *Engines of Creation: The Coming Era of Nanotechnology*. Anchor, London, UK, (1987). <https://www.nanowerk.com/nanotechnology/reports/reportpdf/report47.pdf>
 - [16.] De Rooij, M., Van Tittelboom, K., De Belie, N., Schlangen, E., Self-Healing Phenomena in Cement-Based Materials. Springer Netherlands, Dordrecht (2013). <https://doi.org/10.1007/978-94-007-6624-2>
 - [17.] Jonkers, H., Schlangen, E., Development of a bacteria-based self healing concrete, In: *Tailor Made Concrete Structures*, (2008) 109–109. <https://doi.org/10.1007/978-94-007-6624-2>
 - [18.] Davies, R., Teall, O., Pilegis, M., et al., Large Scale Application of Self-Healing Concrete: Design, Construction, and Testing, *Frontiers in Materials*, 5(2018) 1–12. <https://doi.org/10.3389/fmats.2018.00051>
 - [19.] Hu, J., Koleva, D. A., Petrov, P., van Breugel, K., Polymeric vesicles for corrosion control in reinforced mortar: Electrochemical behavior, steel surface analysis and bulk matrix properties, *Corrosion Science*, 65(2012) 414–430. <https://doi.org/10.1016/j.corsci.2012.08.043>
 - [20.] Khitab, A., Anwar, W., Mansouri, I., et al., Future of civil engineering materials: A review from recent developments, *Reviews on Advanced Materials Science*, 42(2015). <https://scholar.google.com.pk/scholar?oi=bibs&hl=en&cluster=17080434772180993004>
 - [21.] Khitab, A., Ahmad, S., Munir, M. J., et al., Synthesis and applications of nano titania particles: A review, *Reviews on Advanced Materials Science*, 53(2018) 90–105. <https://doi.org/10.1515/rams-2018-0007>
 - [22.] Khitab, A., Modélisation des transferts ioniques dans les milieux poreux saturés: application à la pénétration des chlorures à travers les matériaux cimentaires, *Institut National des Science Appliquées de Toulouse*, (2005). <https://scholar.google.com.pk/scholar?oi=bibs&hl=en&cluster=14241165771659445169>
 - [23.] Chang, C., Ho, M., Song, G., et al., A feasibility study of self-heating concrete utilizing carbon nanofiber heating elements, *Smart Materials and Structures*, 18(2009). <https://doi.org/10.1088/0964-1726/18/12/127001>
 - [24.] Xu, Y., Chung, D. D. L., Cement of high specific heat and high thermal conductivity, obtained by using silane and silica fume as admixtures, *Cement and Concrete Research*, 30(2000) 1175–1178. [https://doi.org/10.1016/S0008-8846\(00\)00296-9](https://doi.org/10.1016/S0008-8846(00)00296-9)
 - [25.] Baetens, R., Jelle, B. P., Gustavsen, A., Phase change materials for building applications: A state-of-the-art review, *Energy and Buildings*, 42(2010) 1361–1368. <https://doi.org/10.1016/j.enbuild.2010.03.026>
 - [26.] Bao, X., Memon, S. A., Yang, H., et al., Thermal properties of cement-based composites for geothermal energy applications, *Materials (Basel)*, 10(2017) 11–13. <https://doi.org/10.3390/ma10050462>
 - [27.] Khudhair, A. M., Farid, M. M., A review on energy conservation in building applications with thermal storage by latent heat using phase change materials, *Energy Conversion and Management*, 45(2004) 263–275. [https://doi.org/10.1016/S0196-8904\(03\)00131-6](https://doi.org/10.1016/S0196-8904(03)00131-6)
 - [28.] Mehling, H., Cabeza, L. F., *Heat and cold storage with PCM*, Springer Berlin Heidelberg, Berlin, Heidelberg, (2008). <https://doi.org/10.1007/978-3-540-68557-9>
 - [29.] Kośny, J., *PCM-Enhanced Building Components*, Springer International Publishing, Cham, (2015). <https://doi.org/10.1007/978-3-319-14286-9>
 - [30.] Rizwan, S. A., Ahmad, S., Bier, T. A., Application of packing concepts to high performance self-consolidating mortar (SCM) systems, *American Concrete Institute, ACI Special Publication (SP 289)*, (2012) 299–315. <https://scholar.google.com.pk/scholar?oi=bibs&hl=en&cluster=16027104806223976097>
 - [31.] Zhang, D., Li, Z., Zhou, J., Wu, K., Development of thermal energy storage concrete, *Cement and Concrete Research*, 34(2004) 927–934. <https://doi.org/10.1016/j.cemconres.2003.10.022>
 - [32.] Ling, T.-C., Poon, C.-S., Use of phase change materials for thermal energy storage in concrete: An overview, *Construction and Building Materials*, 46(2013) 55–62. <https://doi.org/10.1016/j.conbuildmat.2013.04.031>
 - [33.] Li, H., Liu, X., Fang, G., Preparation and characteristics of n-nonadecane/cement composites as thermal energy storage materials in buildings, *Energy and Buildings* 42(2010) 1661–1665. <https://doi.org/10.1016/j.enbuild.2010.04.009>

How to Cite This Article

Anwar Khitab, A., Ahmad, S., Jalil, A., Abdin, Z., Nano Wonders in Concrete Technology: Mini Review, *Cement Based Composites*, 2(2020), 25–61. <https://doi.org/10.36937/cebacom.2020.001.005>