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Title: A review of dispersion of nanoparticles in cementitious matrices:
nanoparticle geometry perspective

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Keywords: Dispersion; Nanoparticles; Cementitious; Geometry

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Abstract: In recent decades the dispersion of nanoparticles has been extensively investigated for the fabrication of cementitious nanocomposites, owing to their superior performance. In this review, studies related to dispersion of nanoparticles in cementitious matrices are reviewed in the context of the nanoparticle geometry, i.e. zero-, one-, and two-dimensional nanoparticles, leading to better understanding of the advantages and disadvantages of different methods to produce cementitious nanocomposites. The topics covered include different methods and mechanisms of nanoparticle dispersion in cementitious matrices and comparison of their effectiveness in the dispersion of nanoparticles with different geometrical configurations. It can be interpreted from our findings that a combination of methods to disperse and then stabilize would provide a desired state of dispersion. The technique used for each type vary from one nanoparticle to another. This paper provides insight into the application of nanoparticles in cementitious matrices and the efficient procedures for their dispersion.

MONASH University



June 25, 2017

Professor Masayasu Ohtsu,
Editor, Construction and Building Materials

Title: A review of dispersion of nanoparticles in cementitious matrices: nanoparticle geometry perspective

Authors: Asghar H. Korayem, Navid Tourani, Mohammad Zakertabrizi, Amir Mohammad Sabziparvar and Wen Hui Duan.

Dear Prof. Masayasu Ohtsu,

We received the reviewer's comments about our manuscript (Reference # CONBUILDMAT-D-16-05181R1) on 26 April 2017. We would like to thank reviewers for their valuable comments in improving the manuscript. We have responded to all comments and the manuscript has now been accordingly revised. Details of our responses to each comment are provided in a separate file. Please find enclosed a copy of responses to reviewer's comments and the revised manuscript file for your consideration to be published in Construction and Building Materials.

Thank you very much for your kind consideration.

Sincerely,

A handwritten signature in black ink, appearing to read 'Wenhui Duan'.

Wen Hui Duan

Professor
Department of Civil Engineering
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Ms. Ref. No.: CONBUILDMAT-D-16-05181

Title: A review of dispersion of nanoparticles in cementitious matrices: nanoparticle geometry perspective

Responses to Reviewer's Comments

The authors are grateful to the reviewers for their thorough, constructive and insightful comments and suggestions for improving the paper. Revisions made to the paper are summarized below.

Reviewer #1		
Reviewer Comment	Response	Amended Manuscript (highlighted in light blue)
English writing is to be revised.	The manuscript was reviewed and revised accordingly.	
Misusing information in the references [1], [5], [9], [37], [41], [45], [49], [53], [72], [93], [95], [96], [99], [100] and [153].	The references were checked and updated accordingly as follow: **It is necessary to mention that the numbers used to address the references highlighted by the reviewer are from the older version of the article. Which means that in the latest version, sent to the journal, the numbers might have changed.	
[1] Lu, S.-N., et al., <i>Applications of nanostructured carbon materials in constructions: the state of the art</i> . Journal of Nanomaterials. 2015 : p. 6.	Line 24, page 1: The mentioned article was used to establish the variety applications for nanoparticle composites, especially carbon-based nanoparticles among others which the 3 rd and 4 th references refer to.	
[5] Highway, K., <i>The aggregation status of nanosilicas and silica fume, used in cementitious mixtures</i> .	Reference has been removed due to the lack of credibility of the manuscript; journal version of the article has been used instead.	
[9] Parveen, S., S. Rana, and R. Figueiro, <i>A review on nanomaterial dispersion, microstructure, and mechanical properties of carbon nanotube and nanofiber reinforced cementitious composites</i> . Journal of Nanomaterials, 2013 : p. 80.	Line 41, page 2: The said article was used in preliminary introduction to previous works on nanoparticle dispersion. Line 14, page 5: it was replaced with: Abu Al-Rub, R.K., A.I. Ashour, and B.M. Tyson, On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of	

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	<p>cementitious nanocomposites. Construction and Building Materials, 2012. 35: p. 647-655.</p>	
<p>[37] Epaarachchi, J.A., et al., <i>CNT-cement based composites: fabrication, self-sensing properties, and prospective applications to structural health monitoring</i>. 2013. 8793: p. 87930V.</p>	<p>Line 15, page 5: removed</p> <p>Line 18 & 23, page 6 and Line 21, page 7: The citation has been corrected and replaced with following:</p> <p>Rainieri, C., Song, Y., Fabbrocino, G., Schulz, M. J., & Shanov, V. (2013, August). CNT-cement based composites: fabrication, self-sensing properties, and prospective applications to structural health monitoring. In Fourth International Conference on Smart Materials and Nanotechnology in Engineering (pp. 87930V-87930V). International Society for Optics and Photonics.</p> <p>Line 34, page 6: It was replaced with:</p> <p>Yu, J., Grossiord, N., Koning, C.E. and Loos, J., “Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution”, Carbon 45, 618–623 (2007)</p> <p>Line 22 ,page 6: it was replaced with reference:</p> <p>Zhu, J., Kim, J., Peng, H., Margrave, J., Khabashesku, V. and Barrera, E., “Improving the Dispersion and Integration of Single-Walled Carbon Nanotubes in Epoxy Composites through Functionalization”, Nano Letters3(8), 1107-1113 (2003).</p>	
<p>[41] Hielscher, T., <i>Ultrasonic production of nano-size dispersions and emulsions</i>. arXiv preprint arXiv:0708.1831, 2007.</p>	<p>Inappropriate Ref. (removed)</p> <p>Line 26, page 5: removed</p>	

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<p>[45] Williams Portal, N., et al., <i>Sustainable Potential of Textile-Reinforced Concrete</i>. Journal of Materials in Civil Engineering, 2014.</p>	<p>Inappropriate Ref. (removed) Line 28-31, Page 5: removed Line 5, Page 6: removed along with previous sentence</p>	
<p>[49] Kang, I., et al., <i>A carbon nanotube strain sensor for structural health monitoring</i>. Smart materials and structures, 2006. 15(3): p. 737.</p>	<p>Replaced with following Ref: Islam, M. F., Rojas, E., Bergey, D. M., Johnson, A. T., & Yodh, A. G. (2003). High weight fraction surfactant solubilization of single-wall carbon nanotubes in water. <i>Nano letters</i>, 3(2), 269-273.</p>	
<p>[53] Yu, X. and E. Kwon, <i>A carbon nanotube/cement composite with piezoresistive properties</i>. Smart Materials and Structures, 2009. 18(5): p. 055010.</p>	<p>The reference was removed.</p>	
<p>[72] Nasibulin, A.G., et al., <i>A novel cement-based hybrid material</i>. New Journal of Physics, 2009. 11(2): p. 023013.</p>	<p>This paper discusses a new CVD method by which CNT and CNF are directly grown on the surface of cement particles. In addition, it is mentioned that the compressive strength and electrical resistivity of the hardened paste have been enhanced dramatically.</p>	
<p>[93] Singh, A.P., et al., <i>Graphene oxide/ferrofluid/cement composites for electromagnetic interference shielding application</i>. Nanotechnology, 2011. 22(46): p. 465701.</p>	<p>Only the parts related to the subject were used in this article. Line 3, page 9: The ball milling step in fabricating concrete Lines 31 and 32, page 9: the paper clearly points to enhanced bonding and the lack of electro-conductivity in introduction.</p>	
<p>[95] Babak, F., et al., <i>Preparation and mechanical properties of graphene oxide: cement nanocomposites</i>. The Scientific World Journal, 2014.</p>	<p>Line 6, page 9: The authors specify using a rotary mixer while adding the cement into aqueous dispersion of GO, as a step in "dispersion of carbon structures within cement matrix".</p>	

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<p>[96] Gong, K., et al., <i>Reinforcing effects of graphene oxide on portland cement paste</i>. Journal of Materials in Civil Engineering, 2014.</p>	<p>Lines 6 and 11, page 9:</p> <p>The preparation process in this article were too complex to be mentioned thoroughly in our paper. So it was decided to only mention the general trend in their 4-step process which includes changing the mixing speed thorough steps while adding cement and etc. Also they mention using ultrasonication for dispersion, prior to high shear mixer as expressed in our paper.</p>	
<p>[99] Sedaghat, A., et al., Investigation of physical properties of graphene-cement composite for structural applications. Open Journal of Composite Materials, 2014.</p>	<p>Line 9, page 9:</p> <p>The sentence using this paper as reference was changed.</p>	<p>Line 16, page 9 was revised to: In another study, graphene-cement paste was used to achieve acceptable results.</p>
<p>[100] Yan, S., et al., Effect of reduced graphene oxide content on the microstructure and mechanical properties of graphene-geopolymer nanocomposites. Ceramics International, 2015.</p>	<p>Line 17, page 9:</p> <p>The article clearly specifies using ultrasonication to fabricate aqueous GO dispersion. This reference was used mainly to support the fact that using ultrasonication for producing graphene and its derivatives (i.e. GO) is effective and popular.</p>	
<p>[153] Fan, Y., et al., Effects of Nano-kaolinite Clay on the Freeze-thaw Resistance of Concrete. Cement and Concrete Composites, 2015.</p>	<p>Line 5, page 14:</p> <p>As the authors specify, the procedure they used to ensure effective dispersion was first to use ultrasonication followed by mechanical stirring with aggregates and completed according to the JTG E30-2005 method.</p> <p>Line 15, page 14:</p> <p>In the said paper, ultrasonication was used to effectively disperse the NMK particles into water. Their method has been elucidated in the “specimen</p>	<p>Line 4, page 14 was changed to: the general procedure begins with nanomaterials dispersed in water via ultrasonication, followed by mixing the dispersion with aggregates, and carry on the procedure according to the code previously chosen</p>

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	<p>preparation” section of the article.</p> <p>Table 2:</p> <p>As previously mentioned above, their main approach was categorized as ultrasonication.</p>	
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*Highlights

- Uniform dispersion of nanoparticles in cementitious matrices is a big challenge and thus requires more attention.
- Geometrical parameters play a key role to achieve proper dispersion.
- Dispersion of 1D nanoparticles is complex due to their bundling and entanglement.
- Dispersion of 2D nanosheets is more difficult due to their higher surface energy.

1 A review of dispersion of nanoparticles in cementitious 2 matrices: nanoparticle geometry perspective

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6 **Abstract**

7 In recent decades the dispersion of nanoparticles has been extensively investigated for the
8 fabrication of cementitious nanocomposites, owing to their superior performance. In this
9 review, studies related to dispersion of nanoparticles in cementitious matrices are reviewed in
10 the context of the nanoparticle geometry, i.e. zero-, one-, and two-dimensional nanoparticles,
11 leading to better understanding of the advantages and disadvantages of different methods to
12 produce cementitious nanocomposites. The topics covered include different methods and
13 mechanisms of nanoparticle dispersion in cementitious matrices and comparison of their
14 effectiveness in the dispersion of nanoparticles with different geometrical configurations. It
15 can be interpreted from our findings that a combination of methods to disperse and then
16 stabilize would provide a desired state of dispersion. The technique used for each type vary
17 from one nanoparticle to another. This paper provides insight into the application of
18 nanoparticles in cementitious matrices and the efficient procedures for their dispersion.

19 **Keywords:** Dispersion; Nanoparticles; Cementitious; Geometry.

20 **1. Introduction**

21 The use of different nanoparticle types, marvels of modern construction technology, has
22 become more industrial and common since their first appearance in recent decades. As is
23 known, nanoparticles have wide applications in modifying various aspects of concrete and
24 cementitious mixtures, such as mechanical properties, porosity, and frost resistance [1-4].
25 With these advantages known, the problem regarding nanomodification is dispersion
26 efficacy. Commercial nanoparticles, despite being produced and supplied in sizes below 100
27 nm, usually appear as large agglomerates with dimensions between 1 and 100 micrometres [5-
28 7]. Agglomeration reduces the specific surface area of nanoparticles, thereby hindering full
29 exploitation of these precious materials with the aim of improving desired properties of
30 concrete and other cement mixtures. Moreover, the formation and presence of these
31 agglomerates hampers proper dispersion of nanoparticles within cement mixtures, leading to
32 the creation of weak zones in the final product [5]. Therefore, ideal dispersion becomes a
33 goal of high importance and it is vital to investigate different aspects and factors that might
34 have a positive effect, even a minor one. The ideal dispersion can be described as the state in
35 which nanoparticles are completely separated from each other and no clusters or

*Corresponding author

1 agglomerates exist. Yet it is obvious that this objective is too high to achieve; therefore, as a
2 more pragmatic solution, we may focus on getting as close as possible.

3 In this article, we have chosen to investigate the influence of geometrical differences between
4 nanoparticles on their final dispersion. The dimensional ratio plays a major part in
5 categorizing nanoparticles as well as their performance in cementitious matrices. For this
6 aim, we classify nanoparticles as zero-dimensional (0D), one-dimensional (1D), and two-
7 dimensional (2D) nanoparticles. A 0D nanoparticle is defined as a particle with all its
8 dimensions subjected to nanoscale. For example, nano- SiO₂, TiO₂, ZnO, and CaCO₃
9 nanoparticles are categorized as 0D. A 1D nanoparticle can be described as having two
10 dimensions in nanoscale, with the other dimension reaching above nanoscale. Nanotubes
11 such as carbon nanotubes (CNTs) and halloysites belong to this category. A 2D nanoparticle
12 is originally a sheet with its thickness in the nanoscale and its sides spreading beyond the
13 'nano' criterion. This definition covers a considerably large area within nanomaterials,
14 involving nanoclay, graphene, and its derivatives such as graphene oxide (GO).

15 It is clear that there is a lack of knowledge in the efficient dispersion method of different
16 types of nanoparticles with zero, one and two dimensions in cementitious matrices, while the
17 correct method of mixing and dispersing added nanoparticles into cementitious matrix is
18 crucial for exploiting the potential of nanoparticles for the development of new cementitious
19 nanocomposites. To shed light on this problem, in this review we have gathered and surveyed
20 research regarding the dispersion of 0D, 1D and 2D nanoparticles in cementitious matrices.
21 The main discussion begins with a section elaborating on the dispersion of nanoparticles in
22 cementitious and aqueous environments and the differences between them, followed by a
23 brief introduction to the dispersion methods. Next, the dispersion of carbon-based
24 nanomaterials within cementitious mixtures is discussed. Subsequently, we investigate three
25 nanoparticles belonging to the family of silica-based nanomaterials, each pertaining to a
26 different dimensional category. The reason for reviewing these silica-based materials was to
27 confirm and complement our investigations of carbonic materials and to apply our
28 conclusions to more extensive types of nanoparticle. Furthermore, as the reviewed materials
29 each have different reactions to water, carbon-based particles being hydrophobic and silica-
30 based particles being hydrophilic, the study also compares the main objective, the
31 geometrical approach, alongside the reaction to water. Finally, the conclusion section of the
32 paper reviews the important findings and suggestions.

33 **2. Dispersion of nanoparticles in cementitious and aqueous environments**

34 Many of the experiments on the dispersion of nanoparticles have been performed in an
35 aqueous environment rather than in a cementitious context, contexts which are significantly
36 different, leaving behind many unanswered questions. In most situations, the quality of
37 dispersion is assumed based on the performance of the composite; improved properties have
38 been mostly translated into a better dispersion. However, there are cases in which the quality
39 of dispersion has been thoroughly assessed in the final matrix using various methods
40 including scanning electron microscopy (SEM) and transmission electron microscopy
41 (TEM). Thanks to Parveen et al. [8], who have provided a review on nanotube and nanofibre
42 dispersion in cementitious composites, and to others who have gathered information with
43 similar focus [9, 10], we have some data available, but a large part of it is sparse and
44 unorganized.

1 The cementitious environment, either paste or mortar, is filled with multiple ions including
2 sodium, potassium, calcium, sulphur and hydroxyl ions that are the main components, with
3 aluminium and silicon in lower concentrations [11]. The aforementioned ions do not maintain
4 a constant concentration, tending to fluctuate during the cement hydration. During the first
5 hours after fabrication of the dispersion, for instance, the concentration of calcium, sulphate
6 and hydroxyl remains almost stable. In contrast, the concentration of calcium and sulphate
7 ions decreases significantly in the time range of 6 to 24 hours after the beginning of the
8 hydration, while the concentration of the hydroxyl, Si, and Al undergoes an increment [12].
9 Furthermore, depending on the content of incorporated superplasticizer, this addition can also
10 increase the sodium and hydroxyl concentration [11]. In the context of the setting time of
11 cement, a focus on the concentration of each ion, the changing trends in that concentration,
12 and also whether the ions are monovalent or multivalent, all can be effective in finding a
13 proper treatment to achieve the desired dispersion. Apart from Van der Waals attractive
14 forces, the bridging influence of Ca^{2+} ions, resulting from the ionic nature of the cement, is
15 responsible for the agglomeration of nanoparticles when incorporated within ionic systems.
16 For instance, from a close look at nanosilica dispersion behaviour in a cementitious
17 environment, it seems that, due to the bridging effect of Ca^{2+} [13], the ionic composition of
18 cementitious systems is a significant limiting factor to the proper and uniform distribution of
19 nanosilica particles. Both the ionic composition of pore fluid of cement composites and the
20 high ion-adsorption tendency of silica nanoparticles in aqueous media affect the stability of
21 silica particles, causing significant agglomeration of these materials [13-15].

22 Besides the various factors already mentioned, the effect of pH can also be important in
23 dispersion. Mendoza et al. studied the effect of increasing pH on OH^- functionalized multi-
24 walled carbon nanotubes by using $\text{Ca}(\text{OH})_2$ powder. It was observed that with an increase in
25 pH value, the zeta potential decreases. This effect could be attributed to the interaction
26 between MWCNTs and $\text{Ca}(\text{OH})_2$, which eventually affected the stability of the dispersion
27 and caused re-agglomeration. Moreover, this phenomenon hindered the electrostatic repulsive
28 interaction between negative MWCNT functional groups and superplasticizer molecules,
29 ultimately translating into the dominance of Van der Waals forces [16].

30 **3. Dispersion methods**

31 The first step of proper dispersion of nanoparticles would be utilizing sufficient amounts of
32 energy in order to break down particle aggregates and agglomerates into smaller sizes and
33 even to their primary particle sizes if possible. After breaking down the agglomerates, the
34 next step would be stabilizing the fragments and preventing their re-agglomeration, with the
35 aid of proper mechanisms such as steric and electrostatic repulsion. Thus, to obtain the best
36 state of dispersion, utilizing a combination of mechanical dispersion methods in addition to
37 chemical modifications would be necessary.

38 To achieve a desirable level of nanoparticle dispersion within both aqueous solutions and
39 cement composites, different mechanical and chemical protocols can be used, either
40 separately or in conjunction. Mechanical methods, including high shear mixing [17],
41 mechanical stirring [18, 19], ultrasonication [5, 6, 19, 20], and ball milling [5], have been

1 widely used in order to carry out and facilitate the dispersion of nanoparticles through
2 aqueous solutions and composite mixtures. Further, physical surface modifications using
3 organic admixtures [21, 22] and different types of surfactant [23-26] alongside chemical
4 surface treatment of the nanoparticles using functionalization [27-29] have also been used
5 with the aim of nanoparticle dispersion. Mechanical methods work on the principle of
6 imparting high levels of locally focused shear energy to both present individual particles and
7 agglomerated nanoparticles in order to break down these materials into smaller sizes and
8 facilitate their dispersion into the incorporated solution. In contrast, physical and chemical
9 surface modifications contribute mainly to stabilizing the dispersed nanoparticles and
10 preventing re-agglomeration of these dispersed materials. Physical surface treatments work
11 through lowering the surface energy of the nanoparticles using steric and/or electrostatic
12 mechanisms, reducing the intensity of attractive Van der Waals forces on their surfaces [30,
13 31]. Using proper organic admixtures brings the advantage of solution stabilization via steric
14 hindrance and electrostatic repulsion, if the additive possesses at least an ionic functional
15 group. Physical surface modification is usually carried out using surface active agents, also
16 known as surfactants, such as different types of superplasticizers and other kinds of
17 dispersants. Surfactants usually consist of a hydrophilic head group and a hydrocarbon chain
18 (hydrophobic group) which is branched, linear or aromatic. According to the polarity of head-
19 groups, surfactants are either ionic or non-ionic. Ionic surfactants contain at least one type of
20 ionizable functional units such as carboxylic and sulphonic acid groups which in addition to
21 steric effect, produce an electrostatic repulsion. This combined action against Van der Waals
22 forces is referred to as electrosteric repulsion. The most common surfactants used in the
23 industry are superplasticizers which their application in producing high strength concretes is
24 indispensable.

25 Functionalization, then, is the process of attaching functional groups to the surface of
26 hydrophobic nanoparticles in order to improve the hydrophilic behaviour of these materials.

27 **4. Dispersion of carbon-based nanoparticles with zero, one, and two** 28 **dimensions**

29 Since the first observation of the CNT by Iijima in 1991 [32], much research has been
30 devoted to investigating this unique material as well as its carbon-based allotropes, which
31 came later. From fullerene to CNTs and graphene, geometrical insight could be truly assessed
32 when moving from fullerene as the 0D particle to CNTs and finally into graphene sheets as
33 the 2D member of the carbon family. Figure 1 shows TEM images of these nanoparticles. As
34 Figure 1(a) illustrates, fullerene is a 0D nanoparticle and appears under TEM observation like
35 a separate tiny black dot point. Figure 1(b) shows entanglement of CNTs due to their
36 flexibility and 1D structures. The irregular 2D plate shape of GO can clearly be observed in
37 Figure 1 (c).

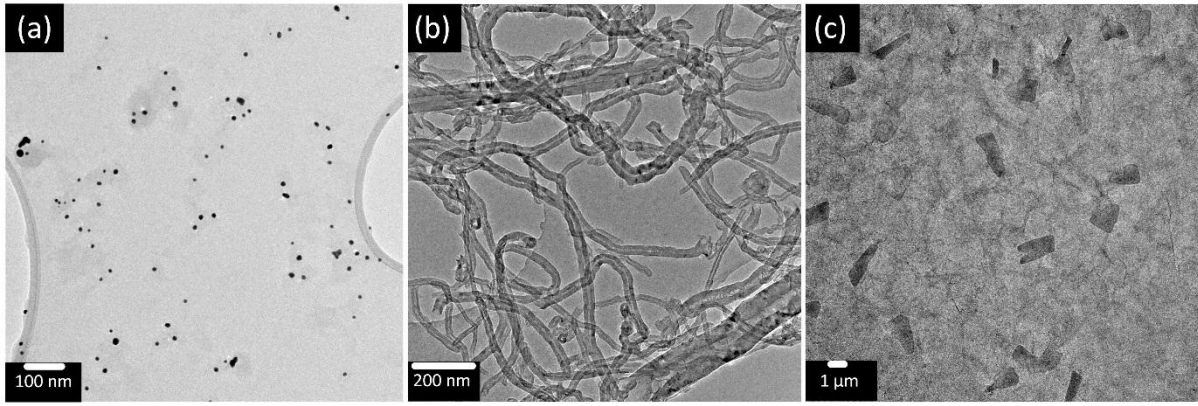


Figure 1 TEM images of (a) fullerene as 0D nanoparticles (b) CNTs as 1D nanoparticles and (c) GO as 2D nanoparticles

Sadly, there is no available research into the application of fullerene in concrete. To fill this gap, in Section 5 we provide a complementary section with the same geometrical perspective. The hydrophobic nature of this carbon-based materials is also another subject of comparison when adding the same geometrical perspective with the silica-based materials which are generally hydrophilic.

4.1 CNTs

Properties of ultra-high strength of about 60 Gpa, exceptional modulus of elasticity around 1 Tpa, an ultimate strain of 12% [33], and very high aspect ratios [4] make CNTs ideal reinforcing material for the production of nanocomposites [34]. CNTs can be categorized as single-walled (SWCNTs) and multi-walled (MWCNTs). SWCNTs are composed of a single graphene sheet rolled into a long hollow cylinder while MWCNTs are nested arrays of graphene [35]. Due to the higher surface area to volume ratio [36], SWCNTs are more effective in case of providing larger contact area between fibers and the surrounding matrix. Further, in the case of SWCNTs, achieving sufficient dispersion through a short route which causes less damage to the structure is more challenging because of their strong agglomeration tendency [25]. In most research, therefore, MWCNTs are selected due to their easier production and dispersion procedures accompanied by reasonable prices. However, they are less understood because of their greater complexity and variety and usually have more defects that can diminish their desirable properties [37, 38].

Different dispersion methods have been used for the distribution of CNTs in cementitious matrices including mechanical methods such as ultrasonication, magnetic stirring, and even hand mixing, as well as chemical methods (e.g. the use of surfactants and functionalization).

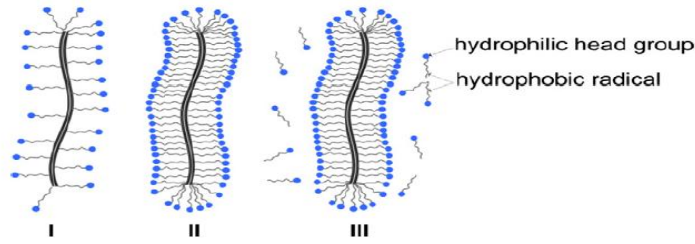
4.1.1 Mechanical methods

Ultrasonication is the most common physical technique for dispersing CNTs into host solutions [39], and in some studies magnetic stirring or hand mixing has also been utilized [25, 40]. Although a higher degree of dispersion can be achieved by increasing energy, ultrasonication can damage the structure of the particle, inducing defects such as dislocation, formation of amorphous carbon on the CNTs, shortening them, thereby decreasing their aspect ratio, and interrupting the cohesion between the tubes and the host matrix [41-43]. This

1 is why, recently, a novel method of using acoustic generator of the pulsating jet has been
2 proposed to disperse CNTs in the aqueous environment without damage or disintegration
3 [44]. Therefore, an optimal ultrasonication energy that balances desirable dispersion with
4 minimal induced damage has been proposed [27], which in turn depends on the CNT
5 concentration, diameter, length, and the solvent media [45, 46]. For instance, Islam et al. [47]
6 recommended a low power bath sonication to preserve the length and structure of CNTs,
7 Sabolkina et al. [42] concluded, based on UV-vis spectra, that sonication should last more
8 than 30 minutes to achieve satisfactory dispersion. On the other hand, sonication is reversible
9 in time due to re-agglomeration phenomena [14, 48]. Thus, other chemical methods such as
10 the use of surfactants and/or functionalization should be also incorporated for stable
11 dispersion and strong bonding with the cement matrix [9, 49]. It should be noted that these
12 objectives can be achieved by implementing other micro- or nanoparticles in addition to the
13 nanotubes [22, 50].

14 **4.1.2 Chemical methods**

15 Functionalization is a chemical treatment carried out by the means of neat acids, such as
16 H_2SO_4 and HNO_3 [51, 52], which results in a covalent bonding between hydroxyl or carboxyl
17 groups with the CNT surface as a result of oxidation. It is worth mentioning that in most such
18 studies, carboxyl functional groups have been selected for functionalizing the CNTs. Besides
19 the high production capacity of this method [53], chemical bonds between the $-COOH$
20 groups of the nanotubes and the C-S-H phase of the cement matrix can occur, improving the
21 transfer of loads [51, 54]. However, achieving functionalized CNTs could result in structural
22 defects and detrimental effects to graphitization of the nanotubes because of including several
23 steps, especially long acid treatment process [55]. It seems necessary to mention the efforts
24 made to overcome this problem by innovative plasma treatment [53]. Unlike
25 functionalization, surfactant does not affect electrical and mechanical properties of the
26 CNTs, but its amount has a strong influence on the final mechanical properties of the cement
27 composites [56]. As shown in Figure 2, based on the theory of micelle formation, three
28 possible states can be reached by increasing the surfactant concentration [42]. Before
29 reaching a critical concentration, surfactants are unable to coat the surface of CNTs entirely;
30 hence the Van der Waals forces dominate and agglomeration occurs. When a critical
31 concentration of surfactant is reached, it can completely coat CNT surfaces, forming a rod-
32 like micelle which blocks interaction between CNTs through their mutual electrostatic
33 repulsion or steric hindrance [42]. Further increasing the surfactant dosage above the critical
34 amount results in the formation of multilayer surfactant molecules, which cannot bring about
35 improvement in particle dispersion [42] and may even cause reduction in the repulsion forces
36 [39], while also encouraging CNT-flocculation [57] and negatively affecting hydration [39,
37 47, 58]. It is worth mentioning, based on observations of Korayem et al. [46], there is another
38 possible morphology for the adsorption of copolymers on the surface of the CNTs, called
39 hemi-micelle. The dispersion of CNTs with hemi-micelle coating is more stable than that of
40 random coating but not as efficient as cylindrical coating.



1

2 Figure 2 Schematic representation of the CNT surface state by increasing surfactant concentration I) low surfactant
 3 concentration, II) formation of rod-like micelles, III) formation of multilayer of surfactant molecules. Adapted from [42].

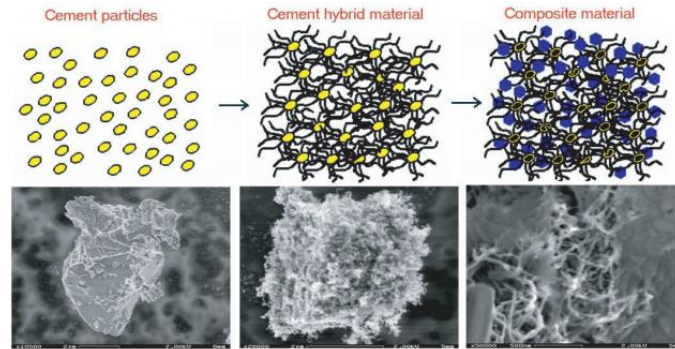
4 The most common additives used as agents for dispersing CNTs within cement matrix are
 5 polycarboxylate (-COOH) based superplasticizers [23, 51, 59-61], although, based on
 6 observations, they are not effective in the case of SWCNTs [62]. They improve bonding
 7 between CNTs and the cement matrix while reducing Van der Waals forces through attaching
 8 functional groups (-COOH) to the CNT surfaces [21]. It is worth mentioning that, although
 9 carboxylic groups cause electrostatic repulsion between CNTs, dispersion is achieved
 10 primarily due to the steric repulsion resulting from long lateral ether chains [63, 64].

11 Worthy of mention is the claim of Abu Al-Rub et al. [36] that, when a superplasticizer is
 12 added to a nano composite, around 75% of the superplasticizer is consumed during the
 13 dispersion process and the remaining 25% is consumed for workability enhancement.
 14 Therefore, to derive a logical comparison between the results obtained from reference
 15 samples and nanocomposite samples, lower amounts of superplasticizer should be used in
 16 plain cement specimens, otherwise less enhancement of mechanical properties should be
 17 expected compared with the reference sample [36].

18 Although choosing an appropriate method of dispersion significantly affects CNT dispersion,
 19 other factors which can improve dispersion include CNT length, diameter, and synthesis
 20 method. It has been stated that with the same dosage, longer CNTs are more effective in
 21 terms of enhancing strength, but their dispersion is harder to achieve [36, 53]. Additionally,
 22 according to previous studies, adding MWCNTs with an outer diameter below 20 nm resulted
 23 in higher strength properties compared to larger MWCNTs [65], although increasing the
 24 diameter of CNTs leads to easier dispersion in the matrix [45]. This could be a result of their
 25 higher potential for acting as a filler and also as nucleating sites for higher stiffness C-S-H
 26 phase formation [66].

27 In addition to the common procedures to modify carbon nanotubes surface, plasma treatment
 28 has been also considered as an efficient way to treat CNTs surface physically and chemically.
 29 Plasma treatment consists of a non-polluting and short process which is able to introduce
 30 wide variety of functional groups, especially oxygen containing groups, depending on plasma
 31 parameters such as used gases, treatment time etc. [67]. It was observed that by using 0.076%
 32 (by weight of cement) of plasma synthesized CNTs, flexural strength increased by 70%
 33 compared with control sample without CNTs. This new type of synthesized CNTs have also
 34 shown better dispersion and stability in comparison with CVD synthesized CNTs which are
 35 even treated through utilizing surfactants and ultrasonication [68].

1 As well as studies focused on producing nanocomposites containing CNTs using
2 conventional methods, some researchers have recently investigated novel synthesis methods
3 with the possibility of eliminating the dispersion step itself. For instance, Nasibulin et al. [69]
4 grew CNTs/CNFs directly on the surface of cement particles by a tailor-made and timeless
5 CVD method which resulted in a much stronger cement hybrid material, as shown in Figure
6 3.



7

8

Figure 3 General representation of CNTs/CNF direct growth on cement grains. Adapted from [69]

9 Sharma and Kothiyal [70] also studied the hybrid effect of spherical carbon nanoparticles and
10 CNTs as 0D and 1D entities, respectively, produced simultaneously by a novel CVD method
11 which achieved proper dispersions [70]. The implementation of 0D nanoparticles to disperse
12 nanotubes was also previously investigated by Sanchez and Ince [58], where silica fume
13 spherical particles contributed to the dispersion of CNTs [70]. Furthermore, because the
14 inclusion of multiple oxygen-rich functional groups makes GO highly soluble in water, this
15 2D nanomaterial was also introduced as an effective surfactant for dispersing CNTs, even
16 SWCNTs [71-73], in aqueous environments [74-76]. However, the ratio recommended
17 between CNTs and GO differed, depending on the study [77-79].

18 4.2 Graphene, Graphene Oxide and Reduced Graphene Oxide

19 Graphene, basically a layer made of hexagonal graphene, has been used to enhance some
20 aspects of cement, notably its strength, flexibility, durability, and barrier qualities among
21 many other properties. It has been explained that, due to its high specific surface area and 2D
22 features [80], the amount required to effect a notable improvement is significantly low
23 (around 0.05% of the cement weight) [81]. The main problem with using graphene is its
24 negligible dispersibility in water [82-84]. To solve this problem, we must exfoliate the
25 graphene sheets and then properly disperse them first into water and then in the matrix, to
26 ensure full graphene contribution to producing the desired properties [80]. Incomplete
27 exfoliation is harmful because, beyond a certain stress, the layers can slip on each other [85].

28 To further clarify the first problem, the exfoliation process breaks the parent graphite pieces
29 into much smaller 1-10 layers [86]. Direct exfoliation of graphene by ultrasonication helps to
30 preserve the basal plan of graphene flakes as well as preparing them prior to mixing.
31 However, excessive sonication can influence graphene size and shape, damaging the structure
32 [87, 88]. A notable point here is that the graphene, even exfoliated either by sonication or in
33 solvent, shows little dispersibility in water [83, 89]. Thus, even after the first barrier has been
34 surmounted, the main obstacle remains, namely the dispersal of graphene in cement matrices.

1 **4.2.1 Mechanical stirring**

2 Starting with the more simple method, mechanical stirring, whether using a Hobart mixer,
3 high shear mixer, hand mixer, or ball mill [90] disperses particles within the dry or moist
4 blend. In some studies, mechanical stirring was used as a preliminary step, preparing the raw
5 materials for supplementary steps such as ultrasonication [91], or after adding a dispersion
6 solution which has been prepared by ultrasonication [92-95].

7 Some of the observed results have shown homogeneity achieved in cement paste and mortar
8 samples modified by GO, resulting in a noticeable improvement in flexural strength [81, 82].

9 In another study, graphene-cement paste was used to achieve acceptable results [96]. There
10 are similar studies using mixers to blend GO into cement paste, but with a more complex
11 procedure, first adding the GO solution to water and then slowly adding cement powder [93].
12 Despite its simplicity and cheapness, this is not an accurate method and using it could
13 damage particles as well as leaving behind undisturbed agglomerations. However, it is fair to
14 say that this method is useful when dealing with low dosages [81].

15 **4.2.2 Ultrasonication**

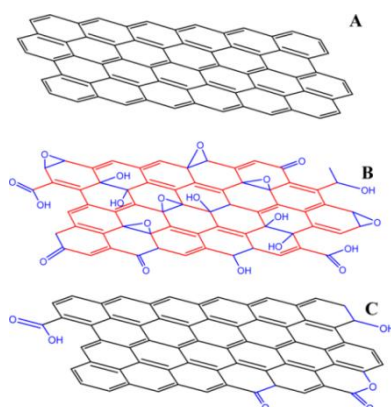
16 Many researchers have used ultrasonication as their principal approach to fabricating a cogent
17 aqueous dispersion of graphene or its derivatives [94, 97, 98]. Suggesting an optimum energy
18 for ultrasonication in terms of time and power is a difficult task, mainly because research in
19 this matter is widespread and generally incomplete. Furthermore, the use of superplasticizers
20 beside ultrasonication has been proved to be positive in terms of both time and quality.
21 Superplasticizers also combat a common side effect of the use of nanomaterials, which is
22 reduced workability resulting from their high specific area. Other research has confirming the
23 beneficial role of superplasticizers [99, 100], specifically pointing to their surface coating
24 ability. It seems necessary to say that well-dispersed graphene dispersions would still need re-
25 sonication in order to preserve homogeneity in the long term [101].

26 **4.2.3 Functionalization**

27 Due to the innate graphene attribute of hydrophobicity, chemical modification has been
28 suggested as a safe approach for achieving a consistent yet durable aqueous dispersion. One
29 common method is to oxidize graphene, changing it to hydrophilic as well as exfoliating it.
30 Although oxidizing graphene may help its dispersal in water and improve its bonding with
31 cement matrix [90, 100], GO loses some of its beneficial properties including electro-
32 conductivity [90]. GO consists of –COOH rich edges and –OH and =O covert basal plane,
33 which provides hydrophilicity, along with a basal plane of semi benzene rings [102-105]. It
34 has been established that these functional groups not only are likely to be interaction sites
35 with cement, but also can act as water reservoirs and water transport channels [98, 100]. The
36 oxidation process also wrinkles the sheets, improving the physical bonding potential [82,
37 100].

38 As mentioned earlier, the oxidation process highly alters the carbon network within the
39 graphene [106], weakening conductivity, an effect which is highly desirable in some fields.
40 To address this loss, scientists have proposed reducing the GO sheets to reduced-GO (RGO)
41 eradicating the oxygen-containing functional groups [107]. The reduction process
42 considerably decreases the oxygen ratio in GO, nearly restoring the once perfect carbon cycle

1 [43, 107] as shown in Figure 4, which can lead to aqueous dispersion either directly [108] or
2 to help obtaining a dispersion at the end. The reduction process involves a polymer, while the
3 whole system is ultrasonicated [106].



4
5 Figure 4 Graphene, GO and RGO graphene in aquatic environment. Adapted from [101].

6 Min et al. showed that the degree of reduction and pH of RGO dispersion can, in fact, affect
7 the final dispersion in aqueous environment [89, 109]. As mentioned before, preserving both
8 the sp^2 structure and dispersibility in water is a difficult goal to achieve, but in the latter
9 study, modifying pH and controlling the reduction progress proved to be effective; the higher
10 pH provided a higher zeta potential and a more stable solution besides the increased solubility
11 caused by a lower degree of reduction [109].

12 4.2.4 Dispersing agents

13 Covalent functionalization usually requires a reducing agent, hydrazine, and a polymer, along
14 with a specific amount of sonication ensuring a stable aqueous dispersion [106, 110]. In
15 contrast, the use of surfactants, particularly polymers, keeps the original structure intact while
16 providing spatial blockage or electrostatic repulsiveness to achieve proper dispersion. In the
17 surveyed works, graphene nanoplatelets (GNPs) were added to sodium cholate or sodium
18 deoxycholate [111] prior to ultrasonication. Superplasticizers, especially of the
19 polycarboxylate type, have been used as surfactants together with ultrasonication to ensure a
20 good GO or graphene dispersion [100, 112].

21 Considering cement as the main host, surfactants have been used as dispersion stabilizers
22 before adding cement to the mixture, after conducting ultrasonication [76, 98, 113]; yet, due
23 to the research being vague as to the dispersion process, our conclusions cannot venture
24 further. There are many influential factors, from the implemented energy to the surfactant
25 dosage, and even the process itself varies across every experiment.

26 4.3 Review

27 Table 1 tabulates some recent research studies with successful dispersion of carbon-based
28 nanoparticles in cementitious matrices. Overall consideration of the carbon-based particles
29 reveals that the geometrical point of view is an influential factor. In 1D particles (CNTs),
30 entanglement is a real threat to their application; clearly, entanglement only stems from the
31 geometry of the particle, as it does not affect 2D particles. Moreover, the elevation in
32 dimension also raises the specific surface area (from around $1200 \text{ m}^2/\text{g}$ [114] in SWCNTs to

1 2600 m²/g in GO [115]), which enhances the surface energy, increasing the tendency towards
 2 agglomeration.

3 Table 1. Dispersion methods for carbon-based nanoparticles

Ref.	Nanoparticle		Dispersion method
	Type	Percentage (wt.% of cement)	
[23, 116]	SWCNT/MWCNT	0.005 - 0.2	Physical coating
[21, 40, 117]	MWCNT	0.1 – 2	Ultrasonication in the presence of superplasticizer
[25, 27, 42, 118]	SWCNT/MWCNT	0.038 - 0.5	Functionalization followed by ultrasonication in the presence of superplasticizer
[100, 112, 113]	GO	0.01 – 1	Ultrasonication in the presence of superplasticizer
[119, 120]	GO	0.02 - 0.08	Ultrasonication
[111, 121]	GNP	0.05 - 0.1	Ultrasonic in the presence of superplasticizer

4

5 **5. Dispersion of 0D, 1D, and 2D silica-based nanoparticles**

6 In the carbon section, we remarked that there was no research on fullerene as the 0D member.
 7 To fully assess the pattern in the foregoing section, then, we have chosen nanosilica,
 8 halloysite, and nanoclay as silica-based nanoparticles with 0D, 1D, and 2D geometry,
 9 respectively. Their arrangement represents the basic insight of this study, which is
 10 investigation of the geometry factor in dispersion and also their hydrophilic quality opens
 11 another window for comparing dispersion of nanoparticles in cement matrices. Figure 5
 12 presents TEM micrographs of the nanoparticles investigated in this section. Figure 5 (a)
 13 presents nanosilica as a 0D nanoparticle with a tiny circle shape in which all dimensions are
 14 below 100 nanometres. Figure 5 (b) depicts halloysite as 1D nanoparticles with diameter of
 15 about a few 10s of nanometres and free length up to couple of microns. Figure 5 (c) shows
 16 nanoclay as 2D nanoparticles with flat plate shapes at micrometre scale. It worth noting that
 17 the halloysites look bar-shaped and are not entangled, unlike the CNTs which are rope-
 18 shaped and highly entangled. This feature could lead to easier dispersion of halloysite
 19 compared to CNTs.

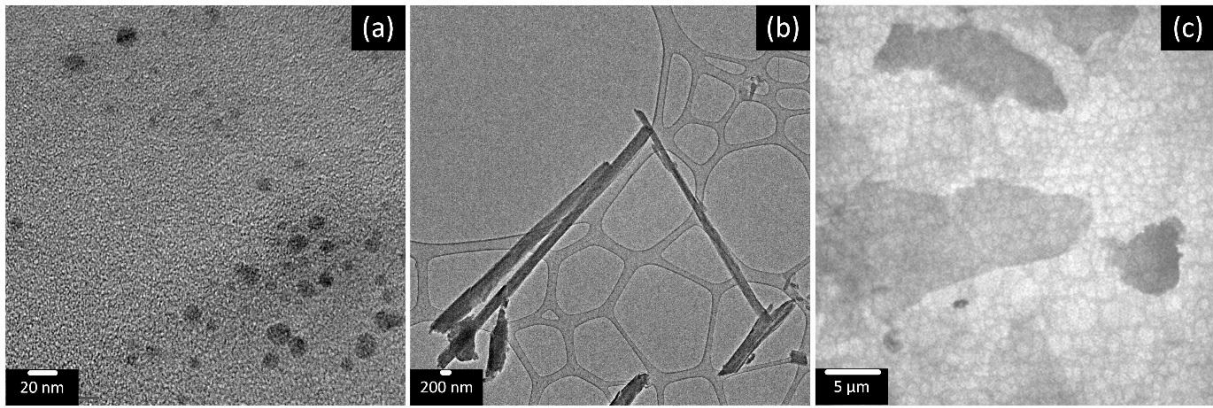


Figure 5 TEM image of (a) nano silica as 0D, (b) halloysite as 1D, and (c) nanoclay as 2D nanoparticles

5.1 SiO₂

Silica nanoparticles are incorporated either as colloidal suspensions or in dry powder form. Colloidal silica consists of small and mono dispersed amorphous SiO₂ particles which are insoluble in water, with a size distribution of 10-100 nm [122]. It has been observed that SiO₂ nanoparticles in the form of colloidal suspensions are more effective in their seeding and filling effect [123]. As-received dry nanosilica powders, as a result of their high specific surface area, are often in the form of large agglomerates (loosely-held clusters) and aggregates (firmly-held clusters) with dimensions greater than 1 micrometre to more than 100 micrometres [124-127].

The size of silica nanoparticles plays a vital role in their final dispersion and influence on the desired properties of the concrete. In small primary particle sizes such as 12 and 20 nm, the nanoparticles have a strong tendency to agglomerate and create large clusters. Consequently, particles with bigger primary particle sizes such as 40 nm, are better dispersed and have superior effects on the mechanical properties of cement pastes and mortars [128]. The process and method of synthesis of nanoparticles is an important factor which affects the final particle size and extent of particle agglomeration. As mentioned already, commercial nanopowders, despite being designed for primary particle sizes in the nanometre range, usually consist of large clusters and agglomerates with micrometre dimensions [6, 7]. Various methods have been used for synthesis of nanoparticles [129]. The sol gel method, one of the most widely used, has the advantage of controlling the size and morphology of desired nanoparticles by modifying and changing the reaction conditions and parameters such as temperature, type of catalyst, and reagent concentrations [7, 129].

With the aim of nanosilica dispersion, methods such as ultrasonication, mechanical stirring, and high shear mixing [126-128, 130-132] alongside incorporating different superplasticizers, have been proposed and utilized by several researchers [125, 133-135].

5.1.1 Superplasticizers

Superplasticizers, among the most influential additives found in common methods of dispersion, are also amid the most used dispersing agents in the application of 0D nanoparticles. Various kinds of superplasticizer, such as polycarboxylic and naphthalene-

1 based superplasticizers, are utilized in almost every relevant research. It has been suggested
2 to use a superplasticizer as a dispersing agent to facilitate the distribution of nano-SiO₂
3 particles [136]. Using silica nanoparticles within cement paste without a superplasticizer
4 leads to an increase in viscosity of the fresh mixture and the addition of extra air bubbles to
5 the matrix[131], which is detrimental to the pore structure. It is known, however, that
6 superplasticizers have a retardation effect if applied in high dosages; as a result, the hydration
7 would slow down and heat treatment would be indispensable for accelerating the hydration
8 and pozzolanic reaction [131].

9 **5.1.2 Ultrasonication**

10 Ultrasonication can be utilized with either water or other kinds of solution to facilitate the
11 dispersion of nanoparticles. The use of acetone for implementation of nanoparticles within
12 cement paste and drying the product in the oven has been reported [134, 137]. Horszczaruk et
13 al. [134] concluded that the use of acetone as dispersant is more effective and results in
14 higher compressive and flexural strength than those of cement with water. Zhang et al.[127]
15 stated that, for the dispersion of silica nanoparticles, ultrasonication is probably superior to
16 common mechanical mixing methods. Common methods of mixing nanosilica powders with
17 water using low shear mixers such as conventional concrete mixers does not result in the
18 desired dispersion of silica nanoparticles [125].

19 To facilitate the dispersion and avoid the agglomeration of nano-additives which results from
20 their high specific surface area, small amounts are usually used. Amounts below 2% are
21 usually sufficient to cover cement particles with nanoparticles [138]. Higher dosages can
22 cause particle agglomeration, with adverse effects on the workability and mechanical
23 properties of the cement pastes. When small amounts are added to cement paste, even poor
24 dispersions and agglomerated particles do not have adverse effects on the strength properties
25 of the samples [139].

26 **5.2 Halloysites**

27 One of the least recorded 1D nanoparticles is halloysite, which is categorized with nanoclays
28 due to the similarity in composition to kaolin. A halloysite tube is a sheet consisting of
29 Al₂Si₂O₅(OH)₄.2H₂O units wrapped in two layers, with the outer surface covered with SiO₂
30 and the inner part with Al₂O₃ [140]. The presence of silica enables nearby floating calcium
31 ions to form C-S-H, and the detachment of aluminate ions in pore solution along with
32 aforementioned calcium may form calcium aluminosilicates [141, 142]. The amount of
33 research reported on halloysites is severely limited, so it is almost impossible to comment on
34 their dispersion. A few methods that have been used include surfactants with mixer [143], dry
35 mixing with cement [141], mechanical stirring in slurry state [144], and ultrasonication[145].
36 It has been suggested that the optimum percentage for halloysites should be less than 10%,
37 closer to 5.5% of the cement weight when used with surfactants and mixer [143] and 3% of
38 the cement weight when used with dry mixing [141].

39 **5.3 Nanoclay**

40 Regarding nanoclay (NC) as an additive for mortar and cement paste, many experiments have
41 shown promising results from the addition of a small percentage, usually up to 10% of

1 cement weight. With reference to the main subject, dispersion of the NC particles, researchers
2 have used mechanical stirring to disperse the NC particles in dry state [146], reporting good
3 results obtained with 5% NC. In some cases it has been noted that other methods (mainly
4 ultrasonication) [147, 148] were superior; the general procedure begins with nanomaterials
5 dispersed in water via ultrasonication, followed by mixing the dispersion with aggregates,
6 and carry on the procedure according to the code previously chosen [149]. However, too
7 much NC can be fatal to both compressive and flexural strength, causing a considerable
8 decrease. This outcome has been attributed to the agglomeration phenomenon resulting in
9 weak spots and hindering the hydration process [146, 150, 151].

10 Two of the most widely used NC types are nano metakaolin (NMK) and nano
11 montmorillonite (NMMT). NMK acts as a complementary element to the mixture, added
12 mainly to strengthen the bonds between fibres and cementitious matrices [152, 153]. In
13 various research, NMK has been used in cementitious matrices alongside other additives
14 including fly ash [154], natural fibre [155], and CNTs [156], each using a different approach
15 in dispersing nanoparticles. There has been research into pastes, mortars, and concrete
16 samples containing NMK dispersed by ultrasonication in water [148, 149], dry state mixing
17 [146, 155], or using a dispersant solution for exfoliation and dispersion [156].

18 Basically, most NMMT particles used in research programs have been Cloisite 30B, an
19 industrially-produced modified natural montmorillonite. The modification is done to separate
20 layers from each other, preparing the particles for dispersion in the host matrix. For organic
21 modifiers, the resultant would be organomodified and hydrophobic [157], while Papatzani
22 and Payne [157] showed that the addition of inorganic montmorillonite had better effects on
23 concrete than organomodified MMT (OMMT), a finding which the authors traced back to the
24 OMMT being hydrophobic, agglomerating, and shaping clusters, resulting in weak spots in
25 the samples. For the hydrophobicity problem, in order to disperse OMMT particles properly,
26 the need for a surfactant arises which, according to Papatzani and Payne, would make the
27 product much more complex and expensive. It is worth noting that this particular approach
28 (using surfactants) can easily be used to exfoliate NC, obviating the need for modification in
29 the first place. Finally, due to the discrete yet vast area of reported experiments (mostly on
30 hybrid additives), we have a limited foundation on which to form our conclusions; yet it is
31 possible to point to some of the experiments and their dispersion methods. For example, dry
32 mixing (using a Hobart mixer) [158] was suggested for Cloisite 30B along with hemp fabric,
33 and for another experiment on waste-glass cement mortars, the addition of a suspension
34 solution of Cloisite 30B was used [159].

35 **5.4 Review**

36 Ignoring 1D particles due to lack of information, the effects of differences in the specific
37 surface area is more evident in this section. Moving from 320 m²/g in SiO₂ [160] to 750 m²/g
38 in Cloisite 30B [161], the effect of surface energy as a derivative of particle geometry is
39 obvious. A greater surface area means higher surface energy and greater agglomeration
40 tendency, which implies a more complex dispersion. Some recent research studies with
41 successful dispersion of silica-based nanoparticles in cementitious matrices are selected and
42 summarized in Table 2.

43

1 Table 2. Dispersion methods for silica-based nanoparticles

Ref.	Nanoparticle		Dispersion method
	type	Percentage (wt.% of cement)	
[126-128, 131, 132, 162]	SiO ₂	0.5 - 12	Mechanical stirring in the presence of superplasticizer
[127, 134]	SiO ₂	0.5 - 3	Ultrasonication
[146]	Nano kaolinite	5	Dry mixing
[148, 149]	Nano kaolinite	0.75 - 3	Ultrasonication
[158, 163]	NMMT	1	Dry mixing
[151, 159]	NMMT	0.0625 – 2.5	Mechanical stirring

2

3 Conclusions

4 In this review we have highlighted the most recent trends in the field of dispersion of
 5 nanoparticles in cementitious matrices for the production of cementitious nanocomposites in
 6 a wide range of technical applications. Nanoparticles geometry has been emphasized;
 7 Geometrical parameters play a major part in the agglomeration process, and obviously these
 8 parameters are also influential in achieving proper dispersion both in water and cementitious
 9 matrices. Because of their much lower complexity than 1D and 2D nanomaterials, 0D
 10 nanoparticles, are more easily dispersed in cementitious matrices. Dispersion of 1D
 11 nanomaterials, as a result of their geometrical complexity which contributes to bundling and
 12 entanglement of the nanotubes, is more difficult and thus requires more attention. Dispersion
 13 of 2D nanosheets, because of their higher surface energy, is even more complicated and they
 14 show a stronger tendency to agglomeration. Moreover, 1D and 2D nanoparticles can
 15 introduce additional failure modes to the material; for instance, they may slip on each other in
 16 the bundles. Thus, as the geometry of the incorporated nanoparticles becomes more complex,
 17 the procedure for obtaining a desirable dispersion becomes more complicated.

18 For each type of particle there is a preferred method, and for each method there are certain
 19 conditions and terms to be met which result in the best dispersion possible. A desirable
 20 dispersion can be obtained by performing a two-phase procedure involving several steps. The
 21 first phase of a good dispersion consists of breaking particle agglomerates that form during
 22 and after the synthesis process or agglomerates that are prone to formation during dispersion.
 23 For this aim, various mechanical methods can be utilized, the effectiveness of which depends
 24 highly on the extent of the agglomeration in addition to the bonding strength. Consensus is
 25 lacking as to the optimal values of power, irradiation time, amplitude, and other parameters
 26 of this method, which vary for different nanoparticles under different conditions. The second
 27 phase of a good dispersion is the use of surface modification methods to stabilize the
 28 dispersed solution, preventing re-agglomeration of nanoparticles and maintaining the
 29 obtained dispersion. Generally speaking, polycarboxylate superplasticizers are believed to be
 30 superior to other kinds of dispersing agent and have shown far better results than any other
 31 surfactant for 0D, 1D, and 2D nanoparticles. Further investigation is needed to determine the
 32 effectiveness of common surfactants on different nanoparticles.

1 What can be drawn from the context of this investigation, given current knowledge, points to
2 a combination of methods, using mechanical energy, for instance, ultrasonication, or a high
3 shear mixer for primary dispersion, followed by chemical functionalization or physical
4 coating to stabilize the obtained dispersion in cement based materials. To determine better
5 dispersal methods in terms of time, energy, and quality, there is still a need for more
6 concentrated research. Current literature on the issue of dispersion relies mostly on describing
7 the quality of the dispersion by descriptive words such as ‘good’, ‘sufficient’, ‘adequate’,
8 which does not lead to precise and consensual interpretation by different researchers.
9 Attention should therefore be directed to defining new quantitative standards and indices for
10 analysing dispersion or agglomeration of nanoparticles in the host matrix.
11 While a notable proportion of research into dispersion has focused on gaining proper
12 dispersion in water or other solvents, there is no guarantee that agglomeration will not occur
13 after pouring the solution into the mix. For this problem, more in-depth research is needed
14 into nanoparticle dispersion in the latter stages of producing concrete.
15 Finally, little is known about the application of fullerene and halloysite and specifically their
16 dispersion in cementitious materials. Because of this gap in knowledge, it is difficult to
17 deduct a definite pattern. It is up to future researchers to further explore this field and bridge
18 this gap.

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