# Evaluation of modified-graphite nanomaterials in concrete nanocomposite based on packing density principles

Libya Ahmed Sbia [a], Amirpasha Peyvandi [b,*], Parviz Soroushian [a], Anagi M. Balachandra [c], Konstantin Sobolev [d]

[a] Dept. of Civil and Environmental Engineering, Michigan State Univ., 3546 Engineering Building, E. Lansing, MI 48824-1226, USA
[b] Bridge Dep., HNTB Corporation, 10000 Perkins Rowe, Suite#640, Baton Rouge, LA 70810, USA
[c] Metna Co., 1926 Turner St., Lansing, MI 48906, USA
[d] Dept. of Civil Engineering and Mechanics, University of Wisconsin-Milwaukee, 3200 North Cramer Street, Milwaukee, WI 53211, USA

## HIGHLIGHTS

- The Compaction Packing Model was employed to calculate the packing densities of concrete.
- Nanomaterials extends the size range of particulate matter in fresh concrete.
- CNF at 0.04 vol.% of concrete account for 9% of the packing density of UHPC.

## ARTICLE INFO

## ABSTRACT

Fresh concrete is a dispersion of particulate matter with a broad size distribution in water. Addition of graphite nanomaterials extends the size range of particulate matter well into nano-scale dimensions, which could benefit the packing of particles in fresh concrete and the engineering properties of hardened concrete materials. In order to test this hypothesis, five classes of concrete (normal-strength, high-strength, ultra-high-performance, self-consolidating normal strength, and self-consolidating ultra-high performance concrete) with different packing densities were evaluated. The Compaction Packing Model was used to calculate the packing densities of various examples of these five categories of concrete materials. The packing density was observed to be lowest for normal-strength concrete and highest for ultra-high-performance concrete. In the case of self-consolidating concrete materials, finer particulate matter was found to make a greater contribution towards raising the packing density with increasing compressive strength. In self-consolidating ultra-high-performance concrete, the effect of micro-scale fibers on improving the packing density was found to be about half that of non-self-consolidating ultra-high-performance concrete. A key finding of the analytical investigations was that graphite nanomaterials (carbon nanofibers) at very low dosages (0.04 vol.% of concrete) account for 9% of the packing density improvement in ultra-high-performance concrete nanocomposites. This notable contribution at such low concentration can be attributed to the fine geometry of the nanomaterials. Experimental results were used to validate the correlation between the contributions of graphite nanomaterials to concrete material properties and the corresponding effects on the packing density of the particulate matter in fresh concrete. These correlations indicated that the Compaction Packing Model provides a viable basis for design of concrete nanocomposites.

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## 1. Introduction

Graphite nanomaterials such as carbon nanotubes (CNT), carbon nanofibers (CNF), and graphite nanoplatelets (GnP) provide a large specific surface area available for interacting with cement hydrates [1–3]. Their nano-scale cross-sectional dimensions (diameter or thickness) and micro-scale length or planar dimensions, however, could compromise the effective interactions with the porous structure of cementitious paste [4,5]. The relatively high capillary porosity (typically more than 10 vol.%) of cementitious paste, with a large fraction of the pores approaching micro-scale dimensions, and also the relatively strong presence (∼35 vol.%) of micro-scale crystals (calcium hydroxide, calcium

aluminate hydrate, calcium monosulfate aluminate hydrate), which cannot effectively interact with nanomaterials, could hinder the effective interactions of graphite nanomaterials with (and thus their beneficial effects on) cementitious matrices. Only the nano-structured calcium silicate hydrate (C-S-H) offers the potential for the development of massive (partly primary) bonds with properly modified graphite nanomaterials [6]. Neither capillary (and larger) pores nor micro-scale crystals match this capability of C-S-H. Fig. 1a schematically depicts a graphite nanomaterial which occurs largely outside the C-S-H phase (with effective binding qualities) within the capillary pores and in contact with micro-scale crystals; this nanomaterial cannot effectively interact with the cementitious paste. It may still produce physical benefits (e.g., towards enhancement of the diffusion resistance and conductivity of the cementitious matrix), but would not effectively contribute to the mechanical properties of the matrix. One can overcome this drawback by employing some commonly used practices in conventional and high-performance concrete mix design. The porosity and volume fraction of micro-scale crystalline constituents of concrete can be reduced, and the capillary pores can be shifted towards the nanometer scale for effective interactions with nanomaterials (Fig. 1b) through: (i) maximizing the packing density of the particulate matter in concrete while retaining the desired level of fresh mix workability [7]; (ii) inducing pozzolanic reactions that replace micro-scale crystalline products of cement hydration with C-S-H of reduced density, which effectively fills capillary pores and bonds to nanomaterials [8]; and (iii) lowering the water/cementitious paste ratio through the effective use of high-range water reducers, which lower the size and content of capillary pores and also benefit the dispersion of nanomaterials.

The use of water-reducers (and high-range water-reducers in the case of higher-performance concrete), which is a common practice in concrete technology, is highly beneficial towards effective use of graphite nanomaterials with very high specific surface area. Refined concrete mix designs incorporating high-range water-reducers enable development of concrete nanocomposites that realize valuable gains in engineering properties. Such properties can thus be effectively improved using graphite nanomaterials without refinement of the concrete mix design.

Fresh concrete comprises of the particulate constituents of different dimensions, including centimeter- to millimeter-scale aggregates, micrometer-scale cement particles, and occasionally nano-scale silica fume particles. The addition of graphite nanomaterials extends this size range into nano-scale dimensions [9,10]. Adjustment of particle size distribution for increasing the packing density in a fresh state (in an aqueous medium) using different consolidation efforts has been an important consideration in the development of concrete materials. The desire to maximize the packing density to reduce porosity and thus improve the engineering properties of concrete is generally constrained by the need to produce workable fresh concrete mixtures that are compatible with conventional construction practices.

## 2. Packing density

Given a unit volume filled with particles, packing density (or degree of packing) is defined as the volume of solids in a unit volume and is equal to one minus the volume occupied by the voids. The packing density gives an indication of how efficiently particles fill a certain volume. If a high volume of aggregates are packed in a certain volume, the need for binder, which is usually much more expensive, to fill the voids and bind the particles will be decreased. Packing density ($\varphi$) can be expressed as follows:

$$\varphi = V_s/V_t = V_s/(V_s + V_e) = 1 - e \tag{1}$$

where $V_s$ = volume of solids; $V_e$ = volume of voids; $V_t$ = total volume (volume of solids plus volume of voids); and $e$ = porosity ($V_e/V_t$).

The particulate matter of uniform grain size cannot realize very high packing densities. Spherical grains of similar size can reach packing densities of only 0.52 and 0.74 in cubic and tetrahedral packing structures (Fig. 2). Packing density can be increased through the use of particles of different dimensions, with finer particles filling the space between coarser particles (Fig. 3) [11]. Increased packing of the particulate matter in concrete without compromising fresh mix workability could be used to reduce of the required cementitious paste content and thus the cost of concrete materials; the dimensional stability, durability and heat build up in young concrete due to exothermic hydration reactions are also among the benefits of reducing the cementitious paste content of concrete [12]. Various methods are available for measuring the maximum and loose packing densities of various particulate matter and concrete aggregates; use of representative aqueous media and water-reducers can help obtain more representative values of packing density because they produce strong surface forces which influence packing conditions.

Packing density is a function of the combined effects of the shape, texture and grading of particles. Besides particle size distribution (grading), shape factor and convexity ratio are other major factors affecting packing density. The significance of the effects of surface texture depends upon the particular system. Packing density also depends upon the compaction method and the dimensions of the container. Measurement of packing density can be performed in air (dry packing) or in water (or other liquids). For cementitious materials and fine aggregates (<75 μm particle size),
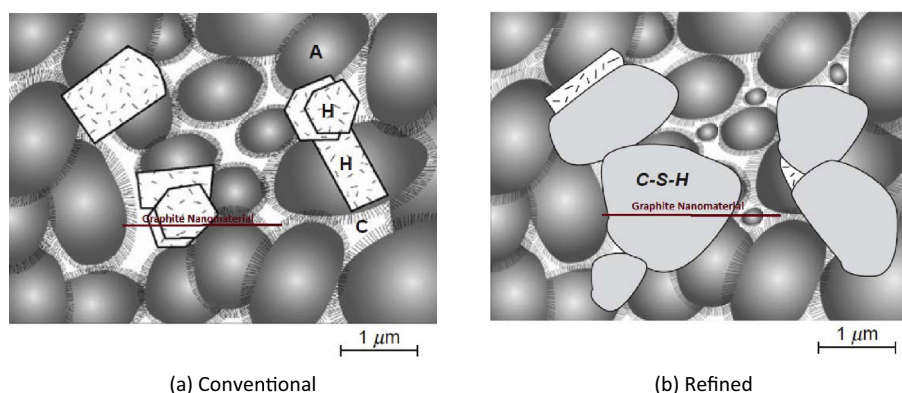


(a) Conventional　　　　　　　　　　　　　(b) Refined

**Fig. 1.** Schematic depiction of (a) the conventional and (b) refined microstructures of cementitious matrices incorporating a graphite nanomaterial (C = capillary pores; H = micro-scale crystalline products; A = calcium silicate hydrate).