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1 Characterization of Adhesion Strength between Carbon Nanotubes and Cementitious Materials

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12 Abstract

2

Multi-walled carbon nanotube (MWCNT) and carbon nanofiber (CNF) additions increase the elastic 13 14 modulus, flexural strength, and toughness of Portland cement concrete. However, the interaction mechanism between cement constituents and these nanomaterials is not fully understood. A modified 15 16 MWCNT-coated atomic force microscopy (AFM) probe is developed by coating a silica particle with 17 oxidized MWCNT through layer-by-layer assembly and adhering it to a tipless AFM cantilever. The probe allows measurement of adhesion between MWCNT and the substrate with a force control procedure. SEM-18 EDS is acquired in the same region as AFM measurements through a benchmarking scheme to correlate 19 chemistry with the measured adhesion. Statistical deconvolution shows C-S-H regions have lower adhesion 20 21 to MWCNT than intermixed regions (C-S-H/Clinker). Furthermore, in C-S-H regions, the normalized 22 adhesion strength increases with calcium concentration. This result is due to the higher interaction between 23 the oxygen functional groups in the MWCNT surface and the calcium in the substrate. 24 Keywords: Carbon nanotube, Cementitious composite, Adhesion interaction, Chemical correlation, Concrete reinforcement

25 1. Introduction

Although numerous studies [1-5] have clearly established the benefits that well-dispersed multi-walled 26

27 carbon nanotubes (MWCNT) and carbon nanofibers (CNF) provide to the mechanical properties of

- hardened Portland cement concrete, the effects are out of proportion to the composite effect of the 28
- 29 nanomaterials themselves, and are also not adequately explained with the characteristics of mesoscale

fiber reinforcement behavior. There must therefore be an alteration to the chemical or physical structure or behavior of the cement matrix in the presence of carbon nanomaterials – this phenomenon is not yet well understood, and is the focus of this study. A phenomenon that can help explain nanoscale interactions, elastic properties, and crack formation and propagation is the adhesion between the various constituents of hardened cement paste and the nanoscale additions to the material. In this study, the methodologies described below will help answer whether differences in chemical composition of the cementitious composite changes the interaction between the carbon nanoreinforcement and the matrix.

37 1.1. Concrete Mechanical Enhancement using Carbon Nanomodification

38 Prior researchers show that well-dispersed MWCNT or CNF additions enhance Young's modulus,

39 flexural strength, and flexural toughness of cementitious composites [1-5]. In these experiments,

40 specimens are prepared by premixing (dispersing) the nanomaterials in the required mixing water, which

41 is then mixed with the Portland cement. The greatest successes have been seen in aqueous solutions

42 prepared for small additions (0.05 - 0.15%) by weight of cement) of MWCNT or CNF, which are pre-

43 dispersed in the mixing water with a superplasticizer (SP)-to-MWCNT/CNF ratio of 4, and with

44 additional mechanical agitation to break agglomerates [1–5]. High-range water reducers (HRWR) or SP,

45 are dispersing agents for Portland cement particles, but in this application they graft onto the

46 MWCNT/CNF surface, and change nanomaterials from hydrophobic to hydrophilic [6].

In this study, dispersion will be achieved with horn sonication providing the mechanical agitation in conjunction with the superplasticizers - this dispersion technique has been studied and explained with further detail within previous work [1–5]. This technique is the key component into obtaining a welldisperse system of MWCNT/CNF in the cementitious matrix. Figure 1 shows a confocal microscope image of a polished Portland cement paste sample of w/c = 0.5 and 0.1 wt.% by cement of CNF, showing the effectiveness of the dispersion method in randomly distributing CNF within the hardened matrix.



Figure 1. Carbon nanofibers distributed in hardened cement paste obtained from Olympus Laser Confocal Microscope.

Figure 2 shows that nanomodified concrete with 0.1 wt.% by cement of MWCNT/CNF can generate a 30% increase in the Young's modulus compared to conventional concrete. The conventional approach to achieve concrete with higher stiffness in concrete is to increase the compressive strength (f_c') by lowering water-to-cement ratio (w/c), and densifying the matrix with higher packing density with the addition of supplementary cementitious materials. In contrast, the measured increase in Young's modulus with MWCNT/CNF addition occurs without significant change in the compressive strength compared to conventional concrete counterpart [1,2,4].

As observed in Figure 2 there is a decoupling effect between stiffness and compressive strength due to MWCNT and CNF addition. The ACI 363 [7] equation shown in Figure 2 cannot be used to predict the stiffness of the nanomodified composite. Furthermore, the change in the mechanical property does not follow the rule of mixture. Since, the nano inclusions occupy very small volume of the composite which does not generate a significant change in the modulus just by the rule of mixtures. This implies that a chemical or physical change is occurring in the cementitious system.

53



Figure 2. Decoupling effect of 0.1 wt.% CNF in the Young's modulus of concrete with respect to compressive strength in
comparison with ACI 363 [7] curve for high strength concrete and ultra-high performance concrete (UHPC) [1,2].

73

69 70

74 Additionally, nanoreinforced concrete of w/c = 0.5 achieves a Young's modulus comparable to the lower 75 end of ultra-high performance concrete (UHPC) as shown in Figure 2. The cost of UHPC mix is around 76 20 times than conventional concrete according to USA Federal Highway Administration (FHWA) [8]. In contrast, the estimated cost increase of nanomodification is one and half to three times compared to 77 conventional and nanomodified concrete[9]. Additionally, UHPC contains two to three times more 78 79 cement content, and higher mixing energy due to a dense matrix and higher steel fiber content compared to the conventional concrete. These design properties of UHPC generate higher carbon footprint due to 80 the CO_2 byproduct of the cement calcination process, and higher fuel consumption in both the cement kiln 81 82 and for thee mixing energy [10]. Thus, nanomodification with MWCNT/CNF provides a potential path 83 for sustainable concrete in a performance-based design framework where Young's modulus is valued. 84 1.2. Mechanisms for the Nanocomposite Enhancement 85 Previous research shows a 30 % increase in the bulk Young's modulus of nanomodified concrete, which

86 is correlated to a 50 % increase in the contact modulus of the interfacial transition zone (ITZ) using

87 Atomic Force Microscopy - PeakForce Quantitative Nanomechanical Mapping (AFM-QNM) [1,2]. In

88	addition, a chemical composition analysis with Scanning Electron Microscope - Energy Dispersive X-ray
89	Spectroscopy (SEM-EDS) indicates that CNF addition creates an uniform microstructure in the ITZ
90	region compared to control samples [2]. The results show tighter distribution of calcium-to-silica (Ca/Si)
91	under 2.5 which corresponds to Calcium-Silicate-Hydrate (C-S-H) region [2]. This supports the
92	hypothesis that MWCNT and CNF serve as nucleation site for C-S-H growth [11] which increases the C-
93	S-H content and the structural homogeneity within the ITZ. These changes in matrix properties due to the
94	nanofibers are not observed with macro- and micro- scale fibers addition which leads to studying the
95	fundamentals of the interaction between the nanofibers and the components of the cement matrix.
96	The second mechanism which can produce enhancement is that MWCNT/CNF could be behaving as
97	nanoscale crack bridges during the fracture process. The crack bridging effect theory comes from three
98	sources: (1) the geometrical similarity (cylindrical tubes) to mesoscale fiber reinforcement, (2) the
99	random distribution, shown in Figure 1, in the cementitious composite, and (3) presence of
100	MWCNT/CNF on crack surfaces after fracture. The line of thought is that the MWCNT/CNF nanofibers
101	behave in a similar way to micro- and meso-scale fibers, only on a different scale.
102	The main mechanism observed in fiber reinforced concrete (FRC) or Engineering Cementitious
103	Composite (ECC) is the crack bridging effect of micro- and macro- fibers [12–16]. The crack bridging
104	enhances fracture energy, flexural strength, and lower the autogenous shrinkage cracking in FRC or ECC
105	due to the fiber-matrix interaction [12-16]. The enhancements in these mechanical properties are also
106	observed in MWCNT/CNF modified cementitious composites [1–5], however this increment might come
107	from the matrix enhancement rather than from nanofiber bridging effects due to the smaller embedded
108	length of the carbon nanofiber materials in comparison with the crack sizes.
109	A pathway to model and understand FRC's fracture is to use the Lattice Discrete Particle Model for Fiber
110	reinforced concrete (LDPM-F) [15,16]. LDPM-F applies the fiber-bridging constitutive law from Yang, et
111	al., [13] which describes the relationship between the fiber bridging stress transferred across a crack and
112	the opening of this crack. The LDPM-F response depends on (1) LDPM material parameter which govern

113 plain concrete behavior, and (2) governing parameters of the fiber-matrix interaction constitutive law 114 [13]. The bond fracture energy (G_d) , and the frictional stress (τ_0) are important for the fiber-matrix 115 interaction constitutive law. These parameters control the embedded fiber bonding phase, pulling phase, 116 and the onset between bonding – pulling phase from the matrix. Usually, fiber-matrix interaction 117 parameters are measured through statistical pull-out test [13–15] of fibers with different embedded 118 lengths. The pull-out test consists in casting concrete sample surrounding a fiber or rebar and then 119 applying a displacement control procedure which pulls the fiber or rebar from the composite while 120 measuring the pull-out force. This experimental setup for carbon nanoreinforcements (MWCNT/CNF) 121 from concrete is challenging to perform due to the size of the fibers which diameter is in nanometers and 122 lengths in micrometers. Furthermore, the cementitious composite chemical heterogeneity which will be in 123 the same scale of the interaction with the surface of the nanofibers will generate dispersion in the measurements. This problem opens the idea of using Atomic Force Microscopy (AFM) as a pathway to 124 measure the interaction between MWCNT and different cementitious substrates. 125

126 1.3. Atomic Force Microscopy of Portland Cement Concrete

127 AFM has been used to measure the local contact properties of many materials with a high spatial 128 resolution [17–25]. The use of AFM for the heterogeneous cementitious composite, which changes in the micro- and nano- scale, produces phase-specific measurements which cannot be gathered with 129 130 nanoindentation, pull-out test, or contact between large surfaces (such as a tape pulling force test). The AFM gathers data on the contact force between the AFM probe and the surface of contact through the 131 132 deflection of a cantilever. AFM can gather data on surface topography and contact force, from which surface features, contact modulus, adhesion force, energy dissipation, and other properties can be 133 134 obtained.

AFM topographical measurements from Peled, et.al. has shown that C-S-H regions are composed of
clusters of grains (globules) which range in sizes in the hundred of nanometers, and CH crystal regions
have smaller (nanometers) size grains, and the topography can show a stacked hexagonal shape using

lateral force microscopy (LFM) [17]. The globules formation is a characteristic shape of C-S-H
agglomerates which was observed by Nonat [18]. Trtik, et.al. [19], Jones, et.al. [20], and Mondal, et.al.
[21], all of which demonstrate that AFM can be used to map the elastic modulus of the distinct phases of
the heterogenous cementitious microstructure with lateral resolution comparable to low keV electron
microscopy. Lomboy, et.al. obtained measurements of the adhesion force between a silicon nitride AFM
probe and different cementitious materials to determine the work of adhesion and Hamaker constant,
which describes the van der Waals force between two particles or between a particle and a substrate [22].

145 The results show lower interaction forces for samples in air than samples in wet condition due to the

146 double layer effect of submerged surfaces [22]. These tests are obtained through standard AFM probe, but

147 the technique shows that contact forces can be measured with AFM procedure.

For graphite, epoxy, and polyimide substrate, a AFM peeling test of a single multiwalled carbon nanotube attached onto a AFM tipless cantilever was used to measure work of adhesion between the two materials by Strus, et.al. [26]. However, the cementitious composite needs a smaller area of interaction due to the large changes in chemical composition at the nano- and micro- scale compared to the three substrates mention before.

This paper will discuss an AFM-QNM approach developed to obtain measurements of the interaction 153 between MWCNT and different concrete constituents. The conceptual idea comes from the dry adhesive 154 155 tapes design field. The field studies ways to mimic the attaching behavior to different surfaces of the 156 gecko's setae and spatula structures within gecko feet [27-29]. To study the interaction between a tape (material 1) and surface (material 2), adhesion is obtained by dividing the force needed to dettach the tape 157 158 from the surface by the tape area, in adisplacement controlled experiment. The maximum force needed to 159 dettach two materials by the contact area defines the adhesion strength. The experiments show average adhesion strengths are: 3 N/cm² for polyimide hairs, 10 N/cm² for gecko's setae and spatula, 1.7 N/cm² 160 for ant (crematogaster), and 11.7 N/cm² for vertically aligned MWCNT tapes onto silicon oxide wafer 161 162 (glass) [27]. This idea comes from a similar procedure used for the characterization of interfacial adhesion

- and shear strength between graphene oxide and graphene oxide interface performed previously by Soler-
- 164 Crespo, et.al. [30]. In where the AFM tip is coated with graphene oxide and the AFM probe is used to
- 165 measure the interaction forces during the force control procedure.
- 166 *1.4. Research Motivation*
- 167 The prior sections have summarized results that show MWCNT/CNF nanomodification have notable
- 168 effects on concrete properies, while also showing that the mechanisms of those effects are not well
- understood. This leads to the overall objective of understanding how the MWCNT interact with the
- 170 heterogenous cementitous matrix through adhesion measurements. Thus, this paper tasks will focus on:
- 171 (1) development of a modified AFM probe to measure the adhesion interaction between MWCNT and
- different concrete constituents using AFM-QNM with a nano-/micro- scale spatial resolution, and (2)
- 173 correlating the adhesion strength and chemical composition analysis (SEM-EDS) between the
- 174 heterogeneous cement bulk paste and MWCNT.
- 175 2. Materials and Methodology
- 176 2.1. Materials, Substrate Preparation, and Benchmarking Procedure
- 177 2.1.1. Substrate Materials
- 178 The adhesion measurements are performed onto the following substrate materials: (1) silicon oxide wafer,
- (2) limestone, (3) sand, (4) type I/II Portland cement paste, (5) tricalcium silicate (C3S) paste, and (6)
- 180 benchmarked type I/II Portland cement paste.
- 181 The silicon oxide wafer (substrate (1)) is cleaned with ethanol, acetone, isopropyl alcohol, and DI water
- using a sonication bath with each step for 5 minutes. To finish, the silicon oxide wafer is further cleaned
- in the oxygen plasma chamber. The limestone (2) and sand (3) substrates are acquired from concrete
- samples with water-to-cement (w/c) = 0.5, and sand-to-cement (s/c) = 2.75 with included limestone
- 185 coarse aggregates. Type I/II Portland cement paste (4) with w/c = 0.5, and C3S paste (5) with water-to-
- 186 C3S (w/C3S) = 0.42 specimens are cured for 7 days at 100% relative humidity and 23°C.

187	For substrate (6)), another sample	of Type I/II Portland	l cement paste with	w/c = 0.5, and 0.4 wt. % by	y
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- 188 cement of Sika®Viscocrete®-2100 superplasticizer is cast and cured for 16 days. After, this sample is
- 189 submitted to the polishing procedure and localization benchmarking scheme that will be described in
- 190 section 2.1.2 and 2.1.3, respectively.
- 191 In general, the cement paste, mortar or concrete are prepared with the procedure from Table 1 with a
- 192 small Hobart mixer following ASTM C192/C192 M [31], and cast into 2 cm x 2 cm x 8 cm molds. After
- 193 24 hours, the samples are demolded and cured for the remaining time at 100 % relative humidity and
- 23°C. 194
- 195

196 Table 1. 197

Cement	naste mortar	and concrete	sample mixing	procedure
Comon	paste, mortan	, and concrete	sample mining	procedure

Table 1. Cement paste, mor	tar, and concrete sample mixing procedure	
Specimen type	Mixing Procedure	198
Cement paste	 Add water/SP solution to cement. Mix for 30 seconds at around 50 rpm. Mix for two minutes at around 90 rpm 	199
	 Cast the samples into molds 	200
Mortar	 Add 1/3 of mix water/SP solution to sand and mix for 1 minute at 50 rpm. Add Portland cement powder and mix for 30 seconds at 50 rpm. Add the remaining of mixing water or solution and mix for 1 minutes at 90 rpm. 	201
	Scrape the bowl.Mix for 2 minutes at 90 rpm.	202
Concrete	Follow the same procedure indicated in mortar mixing.Hand-mix the limestone into the mortar mix (due to small size of the mix)	203
		204

205 2.1.2. Sample Surface Preparation

206 Samples are cut with a Tech Cut 5 diamond blade and placed in ethanol for 15 minutes to stop hydration.

For the grinding and polishing procedure, the cut samples are either glued to a precast hot pressure 207

208 Durofast epoxy disk with ethyl cyanoacrylate, or they are embedded within DuroFast epoxy using hot

209 pressure mounting. Table 2 shows the automatic EcoMet 250 grinder/polisher procedure used for grinding

210 and polishing the samples surface.

212	
213	

Table 2.

Gridding and Polishing procedure for cementitious substrate surface preparation

Time (min)	Griding and Polishing	Platen/Head Speed (rpm)	Applied Force (N)
5	P400 (35 μm)	110/60	22
5	P800 (22 μm)	110/60	22
5	P1200 (15 μm)	110/60	22
5	P1500 (13 μm)	110/60	18
10	6 μm Diamond Suspension MicroCloth	150/60	22
10	$3 \mu m$ Diamond Suspension MicroCloth	150/60	22
10 + 10 (if needed)	$1 \mu m$ Diamond Suspension MicroCloth	150/60	22
10 + 10 (if needed)	0.05 μm Alumina Suspension MicroCloth	150/60	22

214

An Olympus 3D Laser Confocal Microscope (confocal microscope) and AFM Tapping mode are used to 215 216 measure the roughness of the substrate after finishing the grinding and polishing procedure. The aim is to accomplish a replicable surface roughness lower than 100 nm (around 40 - 70 nm) which corresponds to 217 218 roughness values used in previous study for nanoindentation in cementitious substrates [32-34]. The requirement for nanoindentation is to achieve a root mean square roughness (R_a) around one fifth of the 219 minimum nanoindentation depth [32–34]. The time for the final polishing steps (1 μm diamond 220 221 suspension and 0.05 μm alumina suspension) is tuned by randomly checking the samples surface 222 roughness (R_a) with the confocal microscope.

223 2.1.3. Sample Localization Benchmarking

224 The adhesion test data are collected at locations of interest on the substrate surface. For a heterogenous 225 substrate, the adhesion force measurement varies depending on the phase where the test is conducted. 226 Accordingly, the substrates studied can be divided into two groups: (1) mostly homogenous substrates 227 such as silicon oxide wafer, limestone, and sand, or (2) heterogenous substrates such as Portland cement, 228 and C3S paste. For the heterogenous substrates, the composition can include different hydration products, 229 clinker, and voids, and it is desirable to know the phase in which an adhesion measurement is taken. For 230 this reason, an asymmetric microindentation grid, as shown in Figure 3a, is marked onto a hardened 231 cement paste sample using the Struers Duramin 5 Vickers microhardness tester. This benchmark is the

key to spatially orient two characterization techniques: the adhesion interaction with the AFM-QNM, and

the chemical composition with the SEM-EDS. After the sample is marked, the roughness around each

indent is measured with the confocal microscope as shown in Figure 3b. For this roughness, the

- indentation edge with lowest roughness (R_q) (less than 100 nm) is selected as the region of interest to
- perform the measurements by AFM-QNM and SEM-EDS.
- 237





Figure 3. (a) Vickers microindentation benchmarks in hydrated cement paste, and (b) surface topography obtained from Olympus Laser Confocal Microscope ($R_q = 44$ nm depicts the regions of interest for AFM adhesion test and SEM-EDS).

241 2.2. SEM-EDS Instrumentation and Data Acquisition

The chemical composition of the cementitious samples is obtained using a Hitachi S3400N-II SEM with a
beam voltage of 15 kV. SEM-EDS information of Ca, Si, Al, Fe, Mg, K, Na, O, C, and S are acquired
through the Back-Scatter Energy (BSE) in low vacuum mode with the ESED II detector. The beam
voltage of 15 kV is used since it is at least two times the EDS characteristic X-ray (keV) Kα of Iron (Fe)
is 6.4 keV. For the cementitious materials, the low vacuum mode is needed since it inserts air into the
chamber which decreases the charge accumulation in the matrix, a potential issue since surface coating is
not possible due to the adhesion measurements.

249 The Hitachi S3400N-II SEM is used for characterization of the polished cementitious substrates. This

analysis is conducted with straight lines of chemical data collected with the Aztec software in the regions

of interest as identified from the location of the AFM-QNM adhesion test measurements via the
benchmarking technique. Each line gathers data for 500 spatial points within 5 minutes, which minimizes
the noise of the data acquisition.

Another use of SEM-EDS will be to evaluate the modified AFM-QNM tip which will be discussed in

254

subsections 2.3 and 2.4. This analysis is completed with the Hitachi SU8030 and Hitachi S4800-II cFEG SEMs, which have higher spatial resolution than Hitachi S3400N-II SEM because imaging of the AFM cantilever and tip can be conducted in high vacuum conditions. SEM images with the Hitachi S8030 at a beam voltage of 2 kV are used to visually track the changes of the layer-by-layer coating procedure which will be presented in section 2.4 and Figure 5. Hitachi S4800-II cFEG is used to obtain images from the coated AFM modified tip and determine the successful attachment of the tip to the cantilever which will be further discussed in section 2.4 and Figure 6.

262 2.3. Atomic Force Microscopy – Tapping mode and PeakForce Quantitative Nanomechanical Mapping

263 The Atomic Force Microscopy (AFM) maps properties in a sample surface by measuring interactions 264 with an approaching mechanical probe [17-25]. The main capabilities used are topographic surface mapping (Tapping mode) and force measurement (PeakForce – Quantitative Nanomechanical Mapping 265 (QNM)). Tapping mode is a non – contact procedure which acquires surface topography by noting 266 267 changes in the oscillating AFM probe due to interacting forces between tip and samples [23]. The AFM-268 QNM is a contact procedure used to measure the force between probe tip and sample as function of the distance between them [23–25]. Force applied to the tip causes deflection in the probe (cantilever) which 269 270 changes the reflected incoming laser beam position in the photodiode detector as shown in Figure 4a. Figure 4b is the schematic of the force versus tip separation which is obtained from the force control 271 272 procedure [23,24]. Our research will focus on studying the interaction using the adhesion force and indentation depth data. 273





- 280 2.4. Modified MWCNT coated AFM Probe
- The modified AFM probe is developed by attaching a MWCNT-coated silica particle to a tipless AFM probe (cantilever) as shown on Figure 4a. The first step in this procedure is to coat the colloidal silica microparticles with MWCNT following the layer-by-layer procedure developed by Correa-Duarte, et.al. [35]. Polydiallyldimethylammonium chloride (PDDA), Polystyrene sulfonate (PSS), and oxidized MWCNT/NaCl solutions, as shown in Table 3, are used as coating layers as shown in Figure 5.

286

287

Table 3.

274

Layer-by-layer assembly coating materials description

Material	Original Product	Solution Procedure [35]	Coating solution
PDDA	PDDA(M_w 400,000 – 500,000) in 20 wt.% H_2O	- Dilute PDDA solution in Milli-Q water and add NaCl to achieve 0.5 M	PDDA 1 mg/mL 0.5 M NaCl
PSS	PSS ($M_w \sim 70,000$) powder	- Dilute PSS solution in Milli-Q water and add NaCl to achieve 0.5 M	PSS 1 mg/mL 0.5 M NaCl
Oxidized MWCNT	MWCNT bulk powder	 Add 10 mg of MWCNT to 10 mL of H₂SO₄/HNO₃ 3:1 (7.5 mL H₂SO₄ and 2.5 mL HNO₃) Sonicate solution for 2 hours Wash with NaOH solution Disperse in the pellet in 25 mL of Milli-Q water 	Oxidized MWCNT dispersed in water
NaCl	NaCl	- Prepare 0.2 M NaCl	0.2 M NaCl

- Figure 5 shows the schematics of the layer-by-layer assembly procedure steps for coating the silica
- 290 microparticles with MWCNT. Table 4 show the description of the steps and the waiting period for each
- coating layer. For steps 2-6 in Table 4, the substrate with the deposited particles is placed in a
- disposable glass container and the solution is poured into the container.





Figure 5. (a) Silicon oxide particle drop deposition, (b) 1st layer deposition: PDDA, (c) 2nd layer: PSS, (d) 3rd layer: PDDA, (e)
 4th layer: MWCNT/NaCl solution, and for additional layers of MWCNT, return to step (d) [35]. Inset SEM images show (f) plain
 silica microparticle, (g) silica microparticle coated with PDDA/PSS/PDDA layers, and (h) Silica particle coated with 4 layers of
 oxidized MWCNT.

298 299 300	Table 4. Colloidal silica microparticle MWCNT layer-by-layer coating procedure			
300	Step	Dropped Solution	Waiting period	
301	1 (Figure 5a)	10 μ L Colloidal silica microparticles in ethanol drop onto silicon oxide wafer	Ethanol dries	
501	2 (Figure 5b)	1 mL PDDA solution	20 min	
302	3 (Figure 5c)	1 mL PSS solution	20 min	
502	4 (Figure 5d)	1 mL PDDA solution	20 min	
303	5 (Figure 5e)	0.5 mL Oxidized MWCNT + 0.5 mL NaCl 0.2M	30 min	
505	6	Add more MWCNT layers by repeating 4 and 5		

The coated silica particle is adhered with epoxy to the AFM tipless probe using a micromanipulator under an optical microscope. Figure 6 shows the Hitachi S4800-II cFEG SEM image of the attached particle onto the AFM Tipless cantilever. Also, Figure 6 shows chemical analysis points which show carbon (C) concentration around 90 % at the tip of the coated microparticle, and in the epoxy region around 50 %

308 carbon (C) and 30 % silicon (Si). These weight percentages are obtained by point chemical analysis of the





310

Figure 6. MWCNT-coated microparticle attached to AFM tipless probe. EDS results of MWCNT coating and epoxy regions.

312 2.5. Adhesion Strength Data Acquisition and Processing

The PeakForce - QNM procedure [25] is performed in square regions of different sizes. During each
session (typically once per day), the deflection sensitivity analysis and cantilever spring constant
measurements of the probe are performed following the PeakForce QNM User Guide [25] for calibration.
All experiments were collected with a set peak force of 10 nN which was selected according to the
adhesion test measurements onto a silicon oxide wafer substrate (control sample). The QNM analysis is
set to gather the contact information in a raster composed of 256 x 256 (65,536 loading and unloading
curves per samples).

One challenge in interpreting the AFM data will be that the measured adhesion force will be dependent on the indentation depth, because there is a larger contact area when indentation is deeper. An analytical normalization scheme is used to normalize measure adhesion force by the contact area of interaction which defines the adhesion strength (F_{adh}/A_{surf}). The derivation of the normalization scheme is presented in the appendix A. For each point in the mapping, the contact surface area (A_{surf}) between the tip and substrate is calculated by a numerical surface integration method. This integral is a function of the measured indentation depth and tip geometry.

327 While within the study there are homogenous substrate, the primary focus of this study is measurement of 328 adhesion properties in the highly heterogenous cement paste matrix. To achieve this, during post-329 processing, the AFM-QNM topographical image will be superimposed to a series of individual BSE image obtained by the Hitachi S3400N-II SEM. These BSE images include the location of the chemical 330 331 acquisition lines described in 2.2. Then, each point in the chemical analysis lines which lie inside the region of the AFM-ONM measurements are mapped to the reference system of the normalized adhesion 332 strength raster. Finally, the chemical composition is coupled to the nearest normalized adhesion strength 333 value within the AFM test raster. 334

335 A gaussian deconvolution scheme will be used to further understand the distribution of adhesion strength 336 and chemical composition of the heterogeneous substrates obtained from the two instruments: AFM, and SEM. Due to the spatial chemical heterogeneity of cement paste, the spectrum of measured normalized 337 338 adhesion strengths will be the summation of the distributions of the adhesion strengths of the different 339 phases in the substrate. To acquire the distinct phase adhesion properties, it is assumed to have the 340 substrate divided into different phases with distinct Gaussian distribution [34] within the acquisition area. A Gaussian deconvolution optimization scheme is performed by a nonlinear multivariable constraint 341 342 optimization scheme using the MATLAB Optimization Tool to acquire the best fit of the cumulative 343 density function (CDF) for the normalized adhesion strength data for each sample. This follows the 344 approach developed by Ulm, et. al. [34]. The Gaussian deconvolution optimization determines the 345 number of distinct phases $\{n\}$ (for j = 1 to n) with distinct surface fraction $\{f_i\}$, mean $\{\mu_i\}$ and standard deviation $\{s_i\}$ for a given spatial distributed property through minimum square error minimization 346 between the experimental CDF and theoretical CDF. Equation 1 defines the experimental CDF, where X_i 347 348 is the sorted array of normalized adhesion strength values from the AFM mapping. Each of these values 349 are given a corresponding D_x which is a function of N the total number of tests. For the 256 x 256 grid 350 mapping, N = 65,536 for each data collection region. Equation 2 is the theoretical CDF equation for one 351 distinct Gaussian distributed phase. Equation 3 is the minimum square error formula between the

- experimental CDFs and the theoretical weighted model-phase CDF [34] to obtain the best fitting curve.
- Equation 4 constraints the sum of surface fraction to be 1, and Equation 5 is a constraint which does not

permit overlap between two neighboring Gaussian distributions [34].

355
$$D_X(X_i) = \frac{i}{N} - \frac{1}{2N} \text{ for } i \in [1, N]$$
 (1)

356
$$D(X_i; \mu_j; s_j) = \frac{1}{s_j \sqrt{2\pi}} * \int_{-\infty}^{X_i} exp\left(\frac{-(u-\mu_j)^2}{2(s_j)^2}\right) du$$
 (2)

357
$$\min \sum_{i=1}^{N} \left(\sum_{j=1}^{n} f_j D(X_i; \mu_j; s_j) - D(X_i) \right)^2$$
 (3)

358
$$\sum_{j=1}^{n} f_i = 1$$
 (4)

359
$$\mu_j + s_j \le \mu_{j+1} + s_{j+1}; \mu_j + s_j \le \mu_{j+1} - s_{j+1}$$
 (5)

360 3. Results and Discussion

The results are presented for three set of measurements acquisition substrates: (1) silicon oxide wafer, (2)
concrete constituent substrates without localization benchmarking, and (3) cementitious substrate with

363 localization benchmarking a correlation with chemical composition.

364 *3.1. Adhesion test on silicon oxide wafer*

- 365 The silicon oxide wafer is the heterogenous control sample to test the MWCNT-modified AFM probe in
- the process of acquisition adhesion forces. Figure 7 shows the adhesion force and indentation depth raster
- 367 measured from the interaction between the MWCNT-coated AFM tip surface in a $10 \,\mu m \, x \, 10 \,\mu m$ region
- 368 of the silicon oxide wafer. The measurements of the silicon oxide wafer topography show a low surface

369 roughness of $R_q \sim 0.5 nm$.



Figure 7. Adhesion force (left) and indentation depth raster for the interaction of a silicon oxide wafer/MWCNT coated AFM tip.
The horizontal line visible in both graphs is not a MWCNT - it is a discontinuity in the adhesion force and indentation depth
detected by the probe in one of the 256 lines of passing. This does not affect the measurement above and under this line.

374 The strong correlation in the two graphs of Figure 7 indicate that adhesion force is dependent on the indentation depth in where location of higher indentation depth will measure higher adhesion force. This 375 376 is expected due to an increase in contact area between the tip and the sample when the indentation depth 377 increases. A linear relation between the adhesion force and the indentation depth can be observed as 378 shown in Figure 8a of the same data plotted in adhesion force versus indentation depth. This linear 379 relation from Figure 8a collpases to a constant value shown in Figure 8b which distribution is 8.37 \pm $0.05 \ N/cm^2$ (the notation used throughout this paper is mean value \pm standard deviation) using the 380 381 adhesion strength normalization procedure from Appendix A. These data agree well with the adhesion strengths available in the literature that were discussed in section 1.3. The control specimen measurments 382 383 show that the technique is able to measure normalized adhesion strengths comparable to these previous 384 studies.

385

370



Figure 8. (a) Adhesion force and (b) Normalized adhesion strength vs. indentation depth for MWCNT and silicon oxide wafer.
 3.2. Adhesion test on limestone, sand, hydrated Portland cement and hydrated C3S

386

A 2^{nd} set of experiments examined the behavior between the MWCNT-modified AFM probe and the following substrates: embedded limestone, embedded sand particle, 7-day hydrated Portland cement type I/II paste (w/c = 0.5), and 7-day hydrated C3S (w/C3A = 0.42). Figure 9 shows the summary of mean and standard deviation of the normalized adhesion strength distribution for the different substates. The limestone, sand, cement paste and C3S paste showed a lower normalized adhesion strength interaction with the tip relative to the silicon oxide wafer within the same conditions of testing.

The 10 $\mu m x$ 10 μm limestone regions show two distinct distributions with normalized adhesion strength 395 $3 \pm 0.42 N/cm^2$ ($R_q = 21$ nm) for limestone 1, and $2 \pm 0.42 N/cm^2$ ($R_q = 8$ nm) for limestone 2. Even 396 397 when the limestone is mostly calcium carbonate, the difference could arise from performing the test in 398 two different chemical composition or within the junction between two crystals. However, the benchmarking procedure was not implemented on limestone so the regions of AFM-QNM acquisition 399 400 was not investigated through SEM. The two 10 $\mu m \times 10 \mu m$ sand samples show similar behavior with $2.53 \pm 0.67 \ N/cm^2$ ($R_q = 34 \text{ nm}$), and $2.56 \pm 0.61 \ N/cm^2$ ($R_q = 15 \text{ nm}$). Finally, the values observed 401 for both hydrated cementitious samples showed similar behavior. The 5 $\mu m x$ 5 μm C3S samples shows a 402 $2.12 \pm 0.80 \ N/cm^2$ ($R_q = 74 \text{ nm}$), and the 10 $\mu m x$ 10 μm Portland cement type I/II sample 2.09 \pm 403

404 0.80 N/cm^2 ($R_q = 33$ nm). According to AFM measurements, the roughness did not generate an effect in



405 the adhesion force and indentation depth measured by the probe within similar constituent samples.

407 Figure 9. Mean and standard deviation of normalized adhesion strength between MWCNT and Substrate.

406

408 The C3S sample shows different regions with distinct interaction with MWCNT as shown in the contour 409 plot obtained from the AFM-QNM shown in Figure 10a. Gaussian deconvolution is used to determine the 410 distinct phases which contribute to the measurement results, shown in Figures 10b and 10c. Figure 10b 411 shows the experimental cumulative density function, the fitted theoretical cumulative density function 412 (CDF), and the individual CDF curves for each phase obtained by the gaussian deconvolution. Figure 10c 413 shows the probability density function (PDF) of the measured data, the theoretical gaussian PDF, the PDF of the two distinct phases, and the results of the optimization for surface fraction $\{f_i\}$, mean $\{\mu_i\}$, and 414 standard deviation $\{s_i\}$ of the two gaussian distributed phases are shown within figure 10c. The analysis 415 416 shows lower relative adhesion strength within regions with globule formations within the hydrated C3S. According to previous research, these globule formations are a characteristic shape of calcium-silicate-417 418 hydrate (C-S-H) agglomerated nanoparticles [18]. This led to the hypothesis that the regions within the 419 globules are intermixed regions (C-S-H plus other phases) which might have higher interaction adhesion 420 strength with the tip. This hypothesis will be further studied in section 3.3.





Figure 10. (a) Normalized adhesion strength of C3S sample, (b) CDF curve fitting with the phases delineated in red, and (c) PDF
of data/ theoretical curve with the phases delineated in blue.

424 *3.3. Adhesion Test on Vickers Microindentation Benchmarked sample*

425 A 3^{rd} set of experimental data was obtained from (w/c = 0.5) Portland cement type I/II sample cured for 426 16-day at 100% RH. Figure 11 shows a collection of the normalized adhesion strength for cement paste 427 w/c = 0.5 for different sizes within the same region demarked by the Vickers localization benchmark.

428 The acquisition sizes are $1 \mu m x 1 \mu m$, $5 \mu m x 5 \mu m$, $10 \mu m x 10 \mu m$, and $25 \mu m x 25 \mu m$. Data is 429 gathered for a constant grid size of 256 x 256 which means the AFM point spacing is approximately 4 430 nm, 20 nm, 40 nm, and 98 nm, respectively. The first image in each row (a, b, c, and d) of Figure 11 shows the topographical surface for each size with their respective roughness R_q . The root means square 431 roughness (R_q) ranges from 27 nm to 106 nm for $1 \mu m$ to 25 μm sizes, respectively. These R_q values are 432 433 calculated for the entire area, and it is affected by differences in the relative heights within different 434 regions of the image. From the topography, two surface morphologies are observed: globules, and relatively flat surfaces. Samples of R_q were taken from smaller portions of the image in the individual 435 regions' globules and flat areas. These regions to have an average individual roughness $R_a = 17.7 \pm 8.6$ 436 437 nm for globules and 5.6 \pm 2.3 nm, for flat areas. This shows that the difference in the roughness from 27 438 nm to 106 nm is due to an increase in the overall height range. The AFM can adjust the initial position of 439 the acquisition during the measuring process and the roughness which is encountered by the tip is located.

The adjustment to the surface topography accomplishes adhesion strength measurements within the samemagnitude in all the acquisition size and shows comparable measurements within each distinct phase.

442 The data analysis shows points with relative lower normalized adhesion strength are predominantly

- localized in regions were the topography map shows globule formations and higher adhesion strength in
- regions with flat topography. As stated in the previous section, the globule regions are characteristics of
- 445 C-S-H formation [17,18].
- 446 The last image in each row of Figure 11 shows the index of the phase $\{j\}$, the surface fraction $\{f_i\}$,
- 447 Gaussian distribution mean $\{\mu_i\}$, and Gaussian distribution standard deviation (s_i) results from the

448 deconvolution of the different size. The $1 \mu m x 1 \mu m$ cement region contains three phases and the other

sizes $(5 \ \mu m, 10 \ \mu m, and 25 \ \mu m)$ presented only two distinct phases. In the $1 \ \mu m \ x \ 1 \ \mu m$ region, the

450 phases are divided into three distinct regions: (1) 50.1 % of surface with $5.52 \pm 0.50 N/cm^2$, (2) 44.9 %

451 with $6.34 \pm 0.31 N/cm^2$, and (3) 5 % with 8.07 $\pm 1.42 N/cm^2$.

452 There is an effect of the acquisition grid size observed by a shift on the normalized adhesion strength 453 distribution. However, this shift occurs mainly due size of the acquisition grid and the region in which the samples is being tested. Due to the small size, the 1 μm normalized adhesion strength distribution is 454 location-dependent. The data acquisition for this size is mainly in the region of flat topography which 455 skew the normalized adhesion strength to a relatively high value. The 5 μm and 10 μm give similar 456 457 distributions in terms of the normal distribution mean and standard deviation localization for both phases 458 detected. The change in the PDF is mainly due to a decrease from 25 % to 15 % of the second phase surface fraction within the acquisition region between 5 and 10 μm . Due to the grid size of approximately 459 100 nm, the 25 μ m region probability density function is mostly given by the globule phase which has 460 461 higher occurrence in larger areas. The decrease in higher relative adhesion strength comes from a decrease in probability of acquiring data in small flat regions due to a coarser grid. 462



464 Figure 11. Topography (left), normalized adhesion strength (center), and PDF (right) of (a) 1 μ m, (b) 5 μ m, (c) 10 μ m, and (d) **465** 25 μ m scans obtained from 16 days Portland cement paste (w/c = 0.5) with benchmarking. Note: The faded white square region **466** within each topography indicates the previous size's acquisition region.

Figure 12a shows the superposition of the 25 $\mu m x 25 \mu m$ AFM topography (brown image) onto the confocal microscope surface (RGB image). The center image of Figure 12 is the blowout image of the demarked faded black rectangle (this is the 25 by 25 μm region from AFM). Figure 12b shows the 12 kV Hitachi S3400N-II SEM image of the region of interest and the post-processing superposition of the 25 $\mu m x 25 \mu m$ AFM-QNM. Various chemical analysis lines were acquired with the SEM around the interest region aiming to have points which lay within the previously acquired AFM region.



474 Figure 12. Superposition between (a) confocal microscope (left) and AFM Topography (center), and (b) SEM-BSE (right) and
475 AFM Topography (center) obtained from 16 days Portland cement paste (w/c = 0.5) with benchmarking. Confocal microscope
476 and SEM-BES image show around 90-degree rotation between them, but the area demarked in the center is the same.

- 477 The chemical analysis noise is decreased by applying a five data points moving average. Then, the cement
- 478 classification for the different phases [2,36] which states that rich C-S-H regions shows $0.8 \le Ca/Si \le$
- 479 2.5; $(AL + Fe)/Ca \le 0.2$, Calcium Hydroxide (CH) rich: $Ca/Si \ge 10$; $(Al + Fe)/Ca \le 0.4$; $S/Ca \le 0.4$
- 480 0.04, and monosulfate (AFm) rich $Ca/Si \ge 4.0$; (Al + Fe)/Ca > 0.40; S/Ca > 0.15 is used to
- 481 identified the presence of cement constituents within the AFM region. In addition, stoichiometric oxides
- 482 totals ratios are used to identify C-S-H + CH intermixed regions $(0.68 < Ca, Si \ Oxides \ ratio < 0.76)$,
- 483 hydrates region (*Ca*, *Si* Oxides ratio < 0.76) and clinker + hydrates region (*Ca*, *Si* Oxides ratio >
- 484 0.76) as described by [37].

473

485 Afterwards, the correlation of both AFM normalized adhesion strength and SEM-EDS chemical 486 composition is done through mapping as stated in section 2.5. Figure 13a and 13b show the chemical analysis lines classified by the Ca/Si ratio and their distribution of normalized adhesion strength for the 487 488 respective classification. Red marks show C-S-H rich acquisition regions with normalized adhesion strength $3.56 \pm 1.06 N/cm^2$. Distinct regions of CH rich and AFm rich are not predominant in the 489 490 studied region. Black marks in Figure 13b shows acquisition points with 2.5 < Ca/Si < 10 which 491 defines an intermix between clinker/hydrated phases or hydrated/hydrated phases. The intermix region shows a $4.15 \pm 1.58 N/cm^2$ distribution. CaO and SiO₂ stochiometric oxides ratio from total oxides 492 were calculated and shown in Figure 13c and 13d. This image shows that hydrates with oxide ratio under 493 0.76 corresponds to 67 % of the points and they cover regions distributed in the entire analysis area. 494 495 However, clinker + hydrates with oxides ratio over 0.76 correspond to 33 % of the points and they are mostly present in the right-side of the 25 $\mu m x$ 25 μm region where relative flat surfaces are observed. 496 Performing deconvolutions to the Figure 13c histogram shows a bimodal distribution with first peak 497 occurs at $3.58 \pm 1.00 \ N/cm^2$ ($f_1 = 82\%$) and the second peak at $5.28 \pm 0.71 \ N/cm^2$ ($f_2 = 18\%$). 498 Figure 13d shows a distinct bimodal distribution with first peak at $3.55 \pm 0.97 N/cm^2$ ($f_1 = 72\%$) and 499 second peak at 5.46 \pm 0.61 N/cm² ($f_2 = 28\%$). 500



Figure 13. (a) C-S-H rich region and (b) intermix region classified by Ca/Si from SEM-EDS and their respective normalized adhesion strength distribution; (c) hydrates region and (d) clinker + hydrate regions classified by CaO, SiO₂ Oxides ratio from SEM-EDS and respective normalized adhesion strength distribution.

501

- 505 Figure 14 shows 2D histograms which include red markers which indicate the average normalized
- adhesion strength for each the bin range as a function of Ca/Si (Figure 14a), oxides ratios (Figure 14b), or
- 507 (Al + Fe)/Ca (Figure 14c). The following conclusions can be stated from the plots of Figure 14:
- 508 (1) In C-S-H rich regions the average adhesion strength increases with Ca/Si ratio (Figure 14a).

509	(2) For Ca/Si ratio larger than 2.5, the adhesion strength reaches a relative plateau at around $4 N/cm^2$
510	due to the coexistence of both clinker/hydrated phases in the acquisition region (Figure 14a).
511	(3) The predominant Ca/Si ratio is around 3 which might indicate the presence of anhydrate alite (C3S)
512	phase surrounded by hydrates.
513	(4) Adhesion strength increases for Ca and Si oxides ratio above 0.76 which is linked to higher content of
514	clinker in the region (Figure 14b).
515	(5) An increase is also observed in normalized adhesion strength at Ca and Si oxides ratios less than 0.68
516	in Figure 14b due to the increase in Al + Fe content shown in Figure 14c.
517	(6) Higher content of Al + Fe in Figure 14c generates an increase in the measured adhesion strength. This
518	increase might be due to the presence of tricalcium aluminate $[Ca_3Al_2O_6 (C3A) \rightarrow (Al + Fe)/Ca =$
519	0.66)] intermixed with C3S or traces of AFm/C3S.
520	(7) Overall, the presence of higher concentrations of Ca, Al, and Fe generates higher normalized
521	adhesion strength with the MWCNT.
522	
523	



525 Figure 14. 2D histograms of (a) normalized adhesion strength vs. Ca/Si, (b) oxides ratios, and (c) (Al+Fe)/Ca with red markers 526 of average adhesion strength on each bin range; (d) 2D histogram showing increase in aluminum content for lower oxides ratio. Results show a decrease in calcium (Ca⁺²) of C-S-H rich regions leads to a lower average normalized 527 adhesion strength to the MWCNT. This decrease in adhesion with lower amount of calcium cations (Ca^{+2}) 528 529 is observed using molecular dynamics for a different interaction system between two different C-S-H 530 (OPC [Ca/Si = 1.65] and UHPC [Ca/Si = 2.1]), and graphene oxide (GO) with oxygen – containing 531 functional groups (carboxyl (O_{C-O-I}), hydroxyl (O_{C-O-I}), and epoxy (O_{C-O-C})) [38]. The oxidation treatment used in the layer-by-layer assembly generates surface oxygen-containing functional groups in MWCNT, 532 mainly carboxyl and hydroxyl [35,39], which generates a similar trend in the behavior of the MWCNT/C-533 S-H interaction as the GO/C-S-H interaction. 534

524

535 Another question arises in terms of the effect of water-to-cement ratio in this interaction behavior: does

the attraction between the MWCNT and C-S-H phases increase or decrease due to water content? Brown

et. al. [40] showed that the calcium anion (Ca^{+2}) content in solution decreases with the dilution ratio 537 538 (higher w/c ratio) in studies of the aqueous solution of early hydration of C3S. Bazzoni [41] and Muller 539 et. al. [42] showed the diluted systems tend to generate C-S-H with lower Ca/Si ratio. This is due to 540 Portlandite and C-S-H reaching a thermal equilibrium point when the Ca/Si ratio for C-S-H is 1.5. Higher 541 diluted systems tend toward this equilibrium due to a higher degree of reaction. It is expected that samples 542 with water-to-cement ratio lower than 0.5 will generate C-S-H with higher Ca/Si ratio which interact more with the MWCNT with oxygen - containing functional groups. This means that concrete with lower 543 544 w/c ratio is expected to have similar or higher percent increase in elastic modulus compared to w/c = 0.5with the addition of the carbon nanoreinforcement. This finding agrees with previous studies [43], where 545 a 40% increase in the Young's modulus is observed for high strength concrete (w/c = 0.32) by using 0.1 546 wt.% MWCNT and CNF. While this value did not reach the 56 % increase measured for conventional 547 548 concrete (w/c = 0.5), this may be due to using the same 0.1 wt. % CNF by cement addition which means 549 there is a higher concentration of MWCNT in the water which might lead to dispersion challenges and nanomaterial agglomeration. 550

551 4. Conclusion

552 Overall, this study shows the development of Atomic Force Microscopy procedure that was able to 553 achieve measurements from the interaction between the MWCNT and different substrates which are 554 present in the carbon nanomodified cementitious composites. The following conclusion can be obtained 555 from this experimental campaign:

556 (1) A modified AFM MWCNT probe was successfully developed by coating MWCNT on a silica 557 particle, using a layer-by-layer assembly procedure, and employed to generate adhesion maps, 558 which enable interpretation of MWCNT-cement interactions that were not previously possible. 559 (2) Data acquisition and analysis showed that the normalized adhesion strength between MWCNT 560 and a silicon oxide surface is $8.37 N/cm^2$, which is similar to previous literature reports of dry

561 adhesion [27–29].

562 (3)	The modified AFM probe was employed to characterize adhesion with concrete constituents by
563	simply changing the substrate. For the case of hydrated Portland cement and C3S, two peaks in
564	the normalized adhesion strength distribution are observed using a Gaussian Deconvolution
565	technique.
566 (4)	Lower adhesion is measured in regions containing C-S-H agglomerate nanoparticles, which
567	exhibits a characteristic globular shape, while higher levels of adhesion were identified within
568	clinker + hydrate intermixed regions defined by $2.5 < Ca/Si < 10$ and Ca, Si oxide ratios >
569	0.76.
570 (5)	The size of the AFM-QNM acquisition area affected the distribution of normalized adhesion
571	strength, which is mainly due to the grid size and location dependency of the test region.
572 (6)	Using a benchmark microindentation mark, a correlation between the chemical composition,
573	measured using SEM-EDS, and adhesion strength, obtained with AFM-QNM, was achieved.
574 (7)	The analysis revealed that C-S-H rich regions (Ca/Si < 2.5) tend to have a lower normalized
575	adhesion strength than intermixed region. Within the C-S-H region, the higher the calcium (Ca ⁺²)
576	content, the higher the average normalized adhesion strength is, which can be attributed to the
577	interaction of oxygen-containing functional groups present on the surface of oxidized MWCNT.
578 5. Ap	pendix

579 A. Adhesion Strength Normalization

The particle's geometry is approximated by a triaxial ellipsoid for analytical calculations. The SEM image in Figure 5 is used to calculate the major and minor axis of the particles using ImageJ as shown in Figure A.1. The modified tip is characterized with the AFM Tapping mode shown in Figure A.1 to determine the height of the tip (surface topography). The major axis length (2 * a) used is the largest diagonal of around 8.88 μ m and the minor axis length (2 * b) is around 4.72 μ m. The AFM topography shows that the maximum height of the modified tip (2 * c) is around 4.52 μ m.



586

587 Figure A.1. SEM minor and major axis of coated silica particle and AFM surface topography.

588 The particle geometry is described by the equation (A.1). The equation (A.2) to (A.4) shows the analytical

representation of the surface area integral of the triaxial ellipsoid.

590
$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$$
 (A.1)

591
$$S = \iint \sqrt{\left[f(x,y)_x\right]^2 + \left[f(x,y)_y\right]^2 + 1 \, dA} \quad ; \quad f(x,y)_x = \frac{\partial f(x,y)}{\partial x} = \frac{\partial z}{\partial x} \quad ; \quad f(x,y)_y = \frac{\partial f(x,y)}{\partial y} = \frac{\partial z}{\partial y} \quad (A.2)$$

592
$$S = \iint \sqrt{\frac{c^4 x^2}{a^4 z^2} + \frac{c^4 y^2}{b^4 z^2} + 1} \, dy dx = \iint \sqrt{\frac{a^4 b^4 z^2 + b^4 c^4 x^2 + a^4 c^4 y^2}{a^4 b^4 z^2}} \, dy dx \tag{A.3}$$

593
$$S = \iint \sqrt{\frac{a^4 b^4 \left(c^2 \left(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2}\right)\right) + b^4 c^4 x^2 + a^4 c^4 y^2}{a^4 b^4 \left(c^2 \left(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2}\right)\right)}} \, dy dx \, ; z^2 = c^2 \left(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2}\right)}$$
(A.4)

594 Figure A.2 is a schematic showing the integration limits of the surface area double integrals.



595

596 Figure A.2. Schematic of the integral limits for the surface area calculation.

The indentation depth is measured along the z axis direction. For a given indentation depth $d \ll c$, the part of the triaxial ellipsoid in contact with the substrate will be constrained until the x-y plane z = c - d, where c is the half-length in the z – direction and d is the indentation depth. Therefore, the limits in x and y axis will be function of the indentation depth d. The equation (A.5) and (A.6) shows the limits of the x and y integral.

602
$$x \text{ integral limits} \rightarrow 0 \text{ to } x_1 = \sqrt{a^2 * \left(1 - \frac{(c-d)^2}{c^2}\right)}$$
 (A.5)

603
$$y \text{ integral limits} \rightarrow 0 \text{ to } y_1 = \sqrt{b^2 * \left(1 - \frac{(c-d)^2}{c^2}\right)}$$
 (A.6)

604 Only one quadrant of the ellipsoid is used to calculate the surface area by numerical integration using the605 Simpson's 2D method shown in equation (A.7) and (A.8).

606
$$I = \int_{a_y}^{b_y} \int_{a_x}^{b_x} f(x, y) \, dx \, dy = \left(\frac{h_x h_y}{9}\right) \sum_{m=1}^{N_{sim}} \sum_{n=1}^{N_{sim}} (S_{mn} F_{mn}) \tag{A.7}$$

607
$$d_x \equiv h_x = \frac{b_x - a_x}{N_{sim} - 1}$$
; $d_y \equiv h_y = \frac{b_y - a_y}{N_{sim} - 1}$ (A.8)

608 N_{sim} equal to 5 is used for the subdivisions of the integral. The S_{mn} (Two – dimensional Simpson's 609 coefficient matrix) which correspond to a set of multiplication factor is constructed for $N_{sim} = 5$ shown 610 in equation (A.9).

611
$$N_5 = \begin{bmatrix} 1 & 4 & 2 & 4 & 1 \\ 4 & 16 & 8 & 16 & 4 \\ 2 & 8 & 4 & 8 & 2 \\ 4 & 16 & 8 & 16 & 4 \\ 1 & 4 & 2 & 4 & 1 \end{bmatrix}$$
 (A.9)

The F_{mn} is the matrix built from the evaluation of f(x, y) in a grid in the x-y plane within the range of integration. Finally, the integral will be multiplied by 4 which give the contact surface area. The normalized adhesion strength is obtained by dividing the adhesion force by the surface contact area calculated from the indentation depth.

616 B. Supplementary data

- 617 Supplementary data associated with this article can be found, in the online version, at Marrero Rosa, Raul
- 618 (2021), "Adhesion Strength-Chemical Composition of Carbon Nanotubes and Cement", Mendeley Data,
- 619 V1, doi: 10.17632/2fm3bxctrx.1

620 **Declaration of interest**

- 621 The authors declare that they have no known competing financial interests or personal relationship that
- 622 could have appeared to influence the work reported in this paper.

623 CRediT authorship contribution statement

- 624 Raúl E. Marrero Rosa: Conceptualization, Methodology, Formal analysis, Investigation, Data Curation,
- 625 Writing Original Draft, Review & Editing, Visualization, Funding acquisition, Project administration,
- 626 Data analysis MatLab Coding; David J. Corr: Conceptualization, Supervision, Funding acquisition,

627 Writing – Review; Horacio D. Espinosa: Resources, Writing – Review; Surendra P. Shah:

628 Conceptualization, Supervision, Writing – Review, Funding acquisition.

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Highlights:

- A MWCNT-coated atomic force microscopy probe is developed
- Adhesion between multiwall carbon nanotubes (MWCNT) and concrete constituents is measured
- A benchmarked localization method is developed to correlate SEM and AFM measurements
- Lower adhesion strength is measured in C-S-H-rich regions
- Higher calcium content in the C-S-H produces larger adhesion forces with MWCNT

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: