## CONTRIBUTIONS AND MECHANISMS OF ACTION OF GRAPHITE NANOMATERIALS IN ULTRA HIGH PERFORMANCE CONCRETE

By

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#### ABSTRACT

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Ultra-high performance concrete (UHPC) reaches high strength and impermeability levels by using a relatively large volume fraction of a dense binder with fine microstructure in combination with high-quality aggregates of relatively small particle size, and reinforcing fibers. The dense microstructure of the cementitions binder is achieved by raising the packing density of the particulate matter, which covers sizes ranging from few hundred nanometers to few millimeters. The fine microstructure of binder in UHPC is realized by effective use of pozzolans to largely eliminate the coarse crystalline particles which exist among cement hydrates. UHPC incorporates (steel) fibers to overcome the brittleness of its dense, finely structured cementitious binder. The main thrust of this research is to evaluate the benefits of nanmaterials in UHPC. The dense, finely structure cementitious binder as well as the large volume fraction of the binder in UHPC benefit the dispersion of nanomaterials, and their interfacial interactions. The relatively close spacing of nanomaterials within the cementitious binder of UHPC enables them to render local reinforcement effects in critically stressed regions such as those in the vicinity of steel reinforcement and prestressing strands as well as fibers. Nanomaterials can also raise the density of the binder in UHPC by extending the particle size distribution down to the few nanometers range. Comprehensive experimental studies supported by theoretical investigations were undertake in order to optimize the use of nanomaterials in UHPC, identity the UHPC (mechanical) properties which benefit from the introduction of nanomaterials, and define the mechanisms of action of nanomaterials in UHPC. Carbon nanofiber was the primary

nanomaterial used in this investigation. Some work was also conducted with graphite nanoplates. The key hypotheses of the project were as follows: (i) nanomaterials can make important contributions to the packing density of the particulate matter in UHPC by extending the particle size distribution down to the few nanometers range; (ii) there are synergistic reinforcing actions of steel fibers and graphite nanomaterials in UHPC, which can be explained by their complementary spacing and also the benefit of nanomaterials to the interfacial bonding and pullout behavior of steel fibers; and (iii) nanomaterials make important contributions to the bonding and pullout behavior of prestressing strands and deformed bars in concrete, which can be attributed to the close spacing of nanomaterials within the highly stressed interfacial regions occurring in the vicinity of strands and reinforcing bars; steel fibers are loss effective in this regard due to the disturbance of their distribution and orientation in the vicinity of strands and bars. These hypotheses were successfully verified through the experimental and theoretical investigations conducted in this research.

This dissertation is dedicated to my dad, my mom, my husband, my brothers and sister for their support, patience and understanding in the past few years.

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## TABLE OF CONTENTS

LIST OF TABLES	ix
LIST OF FIGURES	xi
CHAPTER 1	1
INTRODUCTION	1
1.1 Statement of the Problem / Opportunity	1
1.2 Hypotheses	9
1.3 Objectives	10
1.4 Work Plan	11
1.5 Organization of the Research	12
CHAPTER 2	14
LITERATURE REVIEW	14
2.1 Introduction	14
2.2 Use of Nanomaterials in Concrete	15
2.3 Ultra-High-Performance Concrete	37
2.3 Pullout Behavior of Steel Fibers, and Reinforcing and Prestressing Steel	41
CHAPTER 3	44
DEVELOPMENT OF A FRAMEWORK FOR MIX DESIGN OF CON	CRETE
NANOCOMPOSITES BASED ON PACKING DENSITY PRINCIPLES	44
3.1 Introduction	44
3.2 Packing Density: Basic Principles	48
3.3 Packing Models	53
3.3.1 Theory of Particle Mixtures (TPM)	53
3.3.2 Compressible Packing Model (CPM):	55
3.3.2 Europack	59
3.4 Equivalent Diameter of Fibers	60
3.5 Applications of Compressible Packing Model (CPM) to Different Classes of Concre	ete 61
3.6 Development of UHPC Mix Design Procedures	83
3.6.1 Packing Density of UHPC	83
3.6.2 Selection of Particulate Components	85
3.6.3 Contributions of Nanomaterial towards Total Packing Density	88
3.7 Approach to UHPC Mix Proportioning	89
3.8 Discussion	90
CHAPTER 4	
MATERIAL SELECTION, OPTIMIZATION. AND CHARACTERIZATION OF U	JLTRA-
HIGH-PERFORMANCE CONCRETE	
4.1 Introduction	
4.2 Selection of Materials	92

4.2.1 Cement	92
4.2.2 Aggregates	92
4.2.2.1 Experimental Evaluation of Aggregates	95
4.2.2.1.1 Micro-Deval Abrasion Test Result for Fine aggregate	95
4.2.2.1.2 Los Angeles Abrasion Test Results for Coarse aggregate	97
4.2.3 Carbon Nanofiber (CNF)	101
4.2.4 Steel Fiber (SF)	102
4.2.5 Polyvinyl Alcohol Fiber (PVA)	103
4.3 Experimental Optimization of Carbon Nanofiber Use in Ultra-High-Performance C	oncrete
in Combination with Steel Fiber	104
4.3.1 Experimental Program	105
4.3.2 Carbon Nanofiber Surface Modification	107
4.3.3 Carbon Nanofiber Dispersion Method	108
4.3.4 Concrete Preparation	109
4.3.5 Test Methods	110
4.3.6 Experimental Results and Discussion	113
4.3.7 Characterization of Optimum UHPC Nanocomposite with Unmodified and M	odified
Carbon Nanofibers	131
4.4 Experimental Optimization of Carbon Nanofiber Use in Ultra-High-Performance C	oncrete
in Combination with PVA Fibers	133
4.4.1 Experimental program	134
4.4.2 Experimental Results	135
4.5 Comparison of Optimum Reinforcement Systems Incorporating Steel Versus PVA	A Fiber
	154
4.6 Characterization of Optimized Ultra-High-Performance Concrete Nanocomposites	160
4.6.1 Experimental Program.	160
4.6.2 Experimental Results	161
4.6.2.1 Slump and Slump Flow	161
4.6.2.2 Flexure	164
4.6.2.3 Split Tension	172
4.6.2.4 Direct Tension	174
4.6.2.5 Impact Resistance	180
4.6.2.6 Length Change	188
4.6.2.7 Moisture Sorption.	191
4.6.2.8 Thermal Conductivity and Specific Heat	193
4.7 Discussion	198
CHAPTER 5	202
THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF SINGLE FIBER PUL	
BEHAVIOR IN ULTRA-HIGH-PERFORMANCE CONCRETE NANOCOMPESTES	202
5.1 Introduction	202
5.2 Theoretical Modeling of Single Fiber Pullout Behavior	204
5.2.1 Overview of theoretical nullout models	, 204 204
5.2.1 Overview of incordical purious models	∠04 rmance
Concrete	200
5 3 Experimental Results and Discussion	209
5.5 Experimental Results and Discussion	212

CHAPTER 6	246
CONTRIBUTIONS OF NANOMATERIALS TO THE PULLOUT BEHAVIO	R OF
DEFORMED BARS AND STRANDS FROM ULTRA-HIGH PERFORMANCE CONC	RETE
NANOCOMPESTES	246
6.1 Introduction	246
6.2 Analysis of The Deformed Bar and Strand Pullout Behavior	251
6.3 Experimental Program and Test Results	252
6.3.1 Deformed Bars	252
6.3.2 Prestressing Strand	268
6.3.2.1 Strand Embedded in Ultra-High-Performance Concrete	268
6.3.2.2 Strand Embedded in High-Strength Concrete	279
6.4 Theoretical Treatment of the nanomaterial Spacing and Concentration	285
6.5 Discussion	288
CHAPTER 7	290
CONCLUSIONS, AND RECOMMENDATIONS FOR FUTURE RESEARCH	290
7.1 Conclusions	290
7.2 Recommendations for Future Research	292
REFERENCES	295

### LIST OF TABLES

Table 3.1 Spacing factors (m)	55
Table 3.2 Empirical coefficients (kint and kp)	55
Table 3.3 Values of the compaction factor (index) for different compaction methods	58
Table 3.4 Ultra-high-performance concrete.	63
Table 3.5 Ultra-high-performance concrete.	64
Table 3.6 Ultra-high-performance concrete.	65
Table 3.7 High strength concrete.	66
Table 3.8 High strength concrete	67
Table 3.9 High strength concrete.	68
Table 3.10 Normal strength concrete	69
Table 3.11 Normal strength concrete	70
Table 3.12 Normal strength concrete	71
Table 3.13 Self-consolidating normal-strength concrete.	72
Table 3.14 Self-consolidating normal-strength concrete	73
Table 3.15 Self-consolidating normal-strength concrete.	74
Table 3.16 UHPCSCC concrete mixes.	75
Table 3.17 Self-consolidating ultra-high-performance concrete	76
Table 3.18 Self-consolidating ultra-high-performance concrete	77
Table 3.19 Initial UHPC mix designs (kg/m3) and their predicted packing densities	87
Table 4.1 Composition of the Type I Portland cement	92
Table 4.2 Fine aggregate gradation for Micro-Deval test.	95

Table 4.3 Physical and mechanical properties of local aggregates	101
Table 4.4 Volume fractions with respect to anhydrous cementitious materials (concrete) of steel fiber and carbon nanofiber used in the optimization experimental program	106
Table 4.5 Ultra-high-performance concrete mix design	107
Table 4.6 Mean values of material properties for plain and optimally reinforced ultra- high-performance concrete (UHPC) materials, and UHPC with a relatively high steel fiber content.	133
Table 4.7 Volume percent with respects to anhydrous cementitious materials (concrete) of PVA fiber and carbon nanofiber used in the optimization experimental program	135
Table 4.8 Optimum nano- and micro-scale reinforcement systems in UHPC- and micro-scale reinforcement systems	155
Table 5.1 The model parameters for ultra-high performance concrete	229
Table 6.1 Summary of pullout test result for uncoated #4 steel bars	266
Table 6.2 Summary of pullout test result for epoxy-coated #4 steel bars	267
Table 6.3 Summary of strand pullout test result	277
Table 6.4 High strength concrete mix design	280
Table 6.5 Summary of pullout test result for high strength concrete without and with         graphite nanoplatelet (NP) reinforcement.	284
Table 6.6 Bond strengths of uncoated #4 deformed bars normalized with respects to the UHPC split tensile strength	289
Table 6.7 Bond strengths of prestressing strand normalized with respects total UHPC         split tensile strength	289

## LIST OF FIGURES

Figure 1.1 (a) UHP versus steel beams with similar structural qualities, and prestressed and reinforced UHPC beams; (b) Normal concrete versus equivalent UHPC pipe [2]	2
Figure 1.2 Flexural load-deflection curves of plain versus steel fiber reinforced concrete	4
Figure 1.3 Scanning electron micrographs of carbon nanofiber	6
Figure 2.1TEM image of clusters of C-S-H (top), and the molecular model of C-S-H (bottom) [36]	17
Figure 2.2 Schematic representation of single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) [44]	18
Figure 2.3 TEM image of CNF showing a single layer [46]	19
Figure 2.4 SEM image of CNT/cement paste after hydration (a) 100x of magnification (b) 1800x of magnification [47]	21
Figure 2.5 Dispersion of MWCNT within cementitious nanocomposites prepared using different surfactant-t-MWCNT weight ratio: (a) no surfactant (b) very low surfactant content, (c) low (near-optimum) surfactant content, and (d) optimum surfactant content [50]	23
Figure 2.6 Dispersion of CNF in cementitious nanocomposites [48]	24
Figure 2.7 TEM image of MWCNTs showing (a) the presence of acrylic acid polymer on the surface at magnifications of 13000x and (b) 800000x [51]	26
Figure 2.8 TEM image of (a)MWCNT dispersion in water without any treatment and (b) with acrylic acid polymer and sonication [51]	27
Figure 2.9 SEM images of cement nanocomposites with ((a), (b)) untreated CNTs and ((c), (d) acid-treated CNTs [101]	30
Figure 2.10 SEM micrographs at different magnifications of 1 wt. % CNT/cement paste after 28 days of hydration [54]	31
Figure 2.11 An example of UHPC bridge applications in the United States [7]	39
Figure 2.12 Improved packing density resulting from the blending of particles of different size	41

Figure 2.13 Fiber bending across crack, and spalling of the cementitious matrix at the fiber exit point.	43
Figure 3.1 Dimensional ranges of voids and solid in hydrated cementitious paste [91]	46
Figure 3.2 Schematic depiction of the conventional and refined microstructures of cementitious matrix incorporating a graphite nanomateiral ( $C = capillary pores; H = micro-scale crystalline products; A = calcium silicate hydrate)$ [93]	47
Figure 3.3 Cubic and tetrahedral packing structures of spherical particles of similar size [91]	49
Figure 3.4 Dense packing of particles of different dimensions [94]	49
Figure 3.5 Voids ratio diagram [98]	54
Figure 3.6 Wall and loosening effects in a binary blend of particulate matter [102]	58
Figure 3.7- Compaction index (K) versus packing density (φ) [98]	59
Figure 3.8 Typical outcome of Europack [98]	60
Figure 3.9 Contribution of different content materials in Table 3.4 to the packing density Ultra-high-performance concrete	63
Figure 3.10 Contribution of different content materials in Table 3.5 to the packing density Ultra-high-performance concrete	64
Figure 3.11 Contribution of different content materials in Table 3.6 to the packing density Ultra-high-performance concrete	65
Figure 3.12 Contribution of different content materials in Table 3.7 to the packing density high-strength concrete	66
Figure 3.13 Contribution of different content materials in Table 3.8 to the packing density high-strength concrete.	67
Figure 3.14 Contribution of different content materials in Table 3.9 to the packing density high-strength concrete.	68
Figure 3.15 Contribution of different content materials in Table 3.10 to the packing density normal-strength concrete	69
Figure 3.16 Contribution of different content materials in Table 3.11 to the packing density normal-strength concrete	70

Figure 3.17 Contribution of different content materials in Table 3.12 to the packing density normal-strength concrete	71
Figure 3.18 Contribution of different content materials in Table 3.13 to the packing density self-consolidating normal-strength concrete	72
Figure 3.19 Contribution of different content materials in Table 3.14 to the packing density self-consolidating normal-strength concrete	73
Figure 3.20 Contribution of different content materials in Table 3.15 to the packing density self-consolidating normal-strength concrete	74
Figure 3.21 Contributions of different constituent materials in Table 3.16 to the packing density of self-consolidating ultra-high performance concrete	75
Figure 3.22 Contributions of different constituent materials in Table 3.17 to the packing density of self-consolidating normal-strength concrete	76
Figure 3.23 Contributions of different constituent materials in Table 3.18 to the packing density of self-consolidating ultra-high performance concrete	77
Figure 3.24 Packing densities of normal strength concrete (NSC), high strength concrete (HSC) and ultra-high performance concrete (UHPC) materials with normal fresh mix workability (means & standard errors).	78
Figure 3.25 Packing densities of self-consolidating normal strength concrete (SCCNSC) and self-consolidating ultra-high performance concrete (SCC UHPC) (means & standard errors).	79
Figure 3.26 Relative contributions of different particulate constituents towards packing of self-consolidating normal strength concrete (SCC NSC) and self-consolidation ultra-high performance concrete (SCC UHPC) (means & standard errors)	80
Figure 3.27 Relative contributions of different particulate constituents towards packing of self-consolidating normal strength concrete (SCC NSC) and self-consolidation ultra-high performance concrete (SCC UHPC) (means & standard errors)	81
Figure 3.28 Relative contributions of different particulate constituents towards packing of self-consolidating normal strength concrete (SCC NSC) and self-consolidation ultra-high performance concrete (SCC UHPC) (means & standard errors)	82
Figure 3.29 Typical size distributions of the particulate matter used in UHPC [123]	84
Figure 3.30 Particle size distributions of aggregates, cement, slag, silica fume, and quartz powder.	85

Figure 3.31 Measured packing densities of the various particulate constituents used in UHPC	86
Figure 3.32 Contributions of carbon nanofiber towards total packing density of UHPC	88
Figure 3.33 Flowchart outlining the approach to UHPC mix design	89
Figure 4.1 The Classification map of the United States for aggregates [131]	94
Figure 4.2 The drum and steel balls used in Micro-Deval test	96
Figure 4.3 Percent weight losses of fine aggregates	97
Figure 4.4 Los Angeles abrasion test equipment and steel balls	98
Figure 4.5 Los Angeles abrasion losses of coarse aggregates	99
Figure 4.6 Reported values of Los Angeles abrasion loss for different coarse aggregates [135]	100
Figure 4.7 Transmission electron microscope image of carbon nanofiber	102
Figure 4.8 Fibers used in UHPC mixture	103
Figure 4.9 Dispersion of nanomaterials in the mixing water incorporating the superplasticizer.	109
Figure 4.10 Steam curing chamber	110
Figure 4.11 Experimental setups	111
Figure 4.12 Flow table test for ultra-high performance concrete with and without different volume fractions of nano- and/ or micro-scale reinforcement systems (a) Static flow. (b) Dynamic flow.	114
Figure 4.13 Effects of steel fiber and carbon nanofiber volume fraction (with respect to anhydrous cementitious materials) on fresh mix static and dynamic flow (regression lines and 95% confidence intervals)	116
Figure 4.14 Results of experiments results on hardened ultra-high-performance concrete material properties (means & standard errors)	119
Figure 4.15 Response surfaces developed based on the test data products for ultra-high- performance concrete materials	125

Figure 4.16 Flow table test for ultra-high performance concrete with and without different

volume fractions of nano- and/ or micro-scale reinforcement systems (a) Static flow. (b) Dynamic flow	136
Figure 4.17 Effects of PVA fiber and carbon nanofiber volume fraction (with respect to anhydrous cementitious materials) on fresh mix static and dynamic flow (regression lines and 95% confidence intervals )	138
Figure 4.18 Typical flexural load-deflection curves of ultra-high-performance concrete materials with carbon nanofiber and/or PVA fiber reinforcement	141
Figure 4.19 Experimental results on hardened ultra-high-performance concrete material properties (means & standard errors)	142
Figure 4.20 Response surfaces developed based on the test data products for ultra-high- performance concrete materials with PVA and/or carbon nanofiber reinforcement	148
Figure 4.21 SEM images of steel fiber (a) and PVA fiber (b) at the fractured surfaces of ultra-high-performance (UHPC)	157
Figure 4.22 (a) High-magnification image of carbon nanofiber (CNF) at a fractured surface of ultra-high-performance concrete (UHPC) near a PVA fiber, (b) SEM image at a fractured surface of UHPC, depicting pullout of uniformly dispersed nanofibers	159
Figure 4.23 (a) Slump and (b) slump flow tests	162
Figure 4.24 Slump test results for UHPC with steel fiber and carbon nanofiber reinforcement.	163
Figure 4.25 Slump flow test results for UHPC with steel fiber and carbon nanofiber reinforcement.	164
Figure 4.26 Flexure test setup	165
Figure 4.26 Flexure test setup.      Figure 4.27 Failed plain and fiber reinforced UHPC specimens tested in flexure.	165 167
Figure 4.26 Flexure test setup.Figure 4.27 Failed plain and fiber reinforced UHPC specimens tested in flexure.Figure 4.28 Flexure test results for selected UHPC materials with different discrete reinforcement conditions.	165 167 169
<ul> <li>Figure 4.26 Flexure test setup.</li> <li>Figure 4.27 Failed plain and fiber reinforced UHPC specimens tested in flexure.</li> <li>Figure 4.28 Flexure test results for selected UHPC materials with different discrete reinforcement conditions.</li> <li>Figure 4.29 A typical fiber reinforced UHPC specimen after failure in split tension test</li> </ul>	<ul><li>165</li><li>167</li><li>169</li><li>173</li></ul>
<ul> <li>Figure 4.26 Flexure test setup.</li> <li>Figure 4.27 Failed plain and fiber reinforced UHPC specimens tested in flexure.</li> <li>Figure 4.28 Flexure test results for selected UHPC materials with different discrete reinforcement conditions.</li> <li>Figure 4.29 A typical fiber reinforced UHPC specimen after failure in split tension test</li> <li>Figure 4.30 Split tensile strength test results (means &amp; standard errors.</li> </ul>	<ol> <li>165</li> <li>167</li> <li>169</li> <li>173</li> <li>174</li> </ol>
<ul> <li>Figure 4.26 Flexure test setup</li> <li>Figure 4.27 Failed plain and fiber reinforced UHPC specimens tested in flexure</li> <li>Figure 4.28 Flexure test results for selected UHPC materials with different discrete reinforcement conditions</li> <li>Figure 4.29 A typical fiber reinforced UHPC specimen after failure in split tension test</li> <li>Figure 4.30 Split tensile strength test results (means &amp; standard errors</li> <li>Figure 4.31 Tension test setup</li> </ul>	<ol> <li>165</li> <li>167</li> <li>169</li> <li>173</li> <li>174</li> <li>175</li> </ol>

Figure 4.33 Cracked section of (a) plain UHPC and (b) fiber reinforced UHPC, both exhibiting a prevalence of aggregate rupture	176
Figure 4.34 Bridging of a crack by fibers in fiber reinforced UHPC	177
Figure 4.35 Direct tension test results for UHPC materials with different discrete reinforcement systems	179
Figure 4.36 Impact test setup	181
Figure 4.37 Processing of the impact test results	183
Figure 4.38 Impact damage in plain (a) and fiber reinforced (b) UHPC specimens	184
Figure 4.39 Impact load time-histories of UHPC with different discrete reinforcement systems.	186
Figure 4.40 Time-histories of the impact energy absorption of UHPC with different discrete reinforcement systems	187
Figure 4.41 Total absorbed energy of UHPC with different discrete reinforcement systems	188
Figure 4.42 UHPC specimen placed in comparator for measurement of length	190
Figure 4.43 Length change (autogeneous shrinkage) test results for the UHPC mix with different discrete reinforcement conditions	191
Figure 4.44 Moisture sorption test setup	192
Figure 4.45 Total moisture sorption of UHPC with different discrete reinforcement conditions	193
Figure 4.46 The hot disc test equipment used for measurement of the thermal conductivity and specific heat of UHPC	195
Figure 4.47 Thermal conductivity test results UHPC (mean & standard error)	197
Figure 4.48 Specific heat test results UHPC (mean & standard error)	198
Figure 5.1 Schematics of single fiber bond and pullout test with fiber aligned with the loading direction. (a) pre-critical load; (b) partial debonding (c) full debonding and pullout [149]	203
Figure 5.2 Micromechanisms involved in pullout of an inclined fiber from concrete [24, 150]	204

Figure 5.3 Bond shear stress versus slip relationship [88]	206
Figure 5.4 Free-body diagram of steel fiber during pullout [88]	206
Figure 5.5 Schematic description of the micromechanical model	209
Figure 5.6 Modeling of the embedded segment 2 of fiber	210
Figure 5.7 Modeling of segment: deformation of the tow-beams system and reaction loads generated by the application of	211
Figure 5.8 Single fiber pullout test setup	213
Figure 5.9 Typical fiber pullout load–slip curv	213
Figure 5.10 Pullout load-slip behaviors of fibers with inclination angle of 00 from plain UHPC	214
Figure 5.11 Pullout load-slip behaviors of fibers with inclination angle of 300 from plain UHPC	215
Figure 5.12 Pullout load-slip behaviors of fibers with inclination angle of 450 from plain UHPC	216
Figure 5.13 Pullout load-slip behaviors of fibers with inclination angle of 600 from plain UHPC.	217
Figure 5.14 Average pullout load-slip behavior of fibers with different inclination angles from plain UHPC	218
Figure 5.15 Pullout load-slip behavior of steel fiber with inclination angle of 00 from UHPC reinforced with 0.04 vol. % carbon nanofiber	220
Figure 5.16 Pullout load-slip behavior of steel fiber with inclination angle of 300 from UHPC reinforced with 0.04 vol. % carbon nanofiber	221
Figure 5.17 Pullout load-slip behavior of steel fiber with inclination angle of 450 from UHPC reinforced with 0.04 vol. % carbon nanofiber	222
Figure 5.18 Pullout load-slip behavior of steel fiber with inclination angle of 600 from UHPC reinforced with 0.04 vol. % carbon nanofiber	223
Figure 5.19 Average pullout load-slip behavior of steel fiber with different inclination angles from UHPC reinforced with 0.04 vol. % carbon nanofiber	224
Figure 5.20 Pullout behavior of steel fiber from plain UHPC versus UHPC reinforced with	

carbon nanofiber for different fiber inclination angles	225
Figure 5.21 Theoretical vs. experimental values of average critical pullout load for ultra- high-performance concrete with and without carbon nanofiber	232
Figure 5.22 Theoretical vs. experimental values of average peak pullout load for ultra- high-performance concrete with and without carbon nanofiber	233
Figure 5.23 Theoretical vs. experimental values of average debonding pullout load for ultra-high-performance concrete with and without carbon nanofiber	234
Figure 5.24 Theoretical vs. experimental values of average displacement at peak pullout load for ultra-high-performance concrete with and without carbon nanofiber	235
Figure 5.25 SEM image of pulled-out steel fiber in ultra-high-performance concrete without carbon nanofiber	236
Figure 5.26 High-magnification SEM image of pulled-out steel fiber in ultra-high- performance concrete without carbon nanofiber	237
Figure 5.27 SEM image of the hole left after pullout of steel fiber in UHPC without carbon nanofiber	238
Figure 5.28 SEM image of pulled-out steel fiber in ultra-high-performance concrete with carbon nanofiber	239
Figure 5.29 High-magnification SEM image of pulled-out steel fiber in ultra-high- performance concrete with carbon nanofiber	240
Figure 5.30 SEM image of the hole left after pullout of steel fiber in ultra-high- performance concrete with carbon nanofiber	241
Figure 5.31 Spalled parts of UHPC at fiber exit point	242
Figure 5.32 Spalled parts of UHPC at exit points of fibers with inclination angles of (a) $30^{\circ}$ , (b) $45^{\circ}$ , (c) $60^{\circ}$	243
Figure 5.33 (a) SEM images at different magnifications of carbon nanofibers on fractured surfaces of UHPC with carbon nanofiber	245
Figure 6.1 (a) Pull-out force applied to an embedded bar; (b) Inclined cracking of concrete caused by slippage of deformed reinforcing bar	247
Figure 6.2 Split cracking of ultra-high-performance concrete caused by slippage of deformed reinforcing bar	248

Figure 6.3 Sheared segment of ultra-high-performance concrete in pullout tests performed on deformed bars and prestressing strands	249
Figure 6.4 Typical pullout load-displacement curve	251
Figure 6.5 Pullout test specimen	253
Figure 6.6 Pullout test setup	254
Figure 6.7 (a) Pullout test specimen, and (b) uncoated (left) and epoxy-coated (right) steel reinforcing bars	255
Figure 6.8 Individual pullout load–slip test results for uncoated deformed steel bar in plain UHPC	256
Figure 6.9 Individual pullout load-slip test results for uncoated deformed steel bar in UHPC with 1 vol. % steel fiber	257
Figure 6.10 Individual pullout load–slip test results for uncoated deformed steel bar in UHPC with 0.04 vol. % carbon nanofibe	258
Figure 6.11 Individual pullout load–slip test results for uncoated deformed steel bar in UHPC with 0.04 vol. % carbon nanofiber and 1 vol.% steel fiber	259
Figure 6.12 Mean pullout load–slip test result for uncoated deformed steel bar in UHPC with different discrete reinforcement systems	260
Figure 6.13 Individual pullout load–slip test results for epoxy-coated deformed steel bar in plain UHPC.	261
Figure 6.14 Pullout load–slip test results for epoxy-coated deformed steel bar in UHPC with 1 vol.% steel fiber	262
Figure 6.15 Individual pullout load–slip test results for epoxy-coated deformed steel bar in UHPC with with 0.04 vol. % carbon nanofiber	263
Figure 6.16 Pullout load–slip test results for epoxy-coated deformed steel bar in UHPC with 0.04 vol.% carbon nanofiber and 1 vol.% steel fiber	264
Figure 6.17 Mean pullout load-slip test results for epoxy-coated deformed steel bar in UHPC with different discrete reinforcement systems	265
Figure 5.18 Shearing failure modes of UHPC in deformed steel bars (uncoated and epoxy- coated) embedded in ultra-high-performance concrete without (a) and with (b) carbon nanofiber.	267

Figure 6.19 Seven-wire strand with 12.7 mm (0.5 in.) diameter	270
Figure 6.20 Strand pullout test setup	270
Figure 6.21 Pullout load – slip behaviors of UHPC with different discrete reinforcement conditions.	272
Figure 6.22 Pullout load – slip behaviors of UHPC with 0.21% graphite nanoplate	273
Figure 6.23 Pullout load – slip behaviors of UHPC with 0.04% carbon nanofiber	274
Figure 6.24 Pullout load – slip behaviors of UHPC with 1.1% steel fiber	275
Figure 6.25 Pullout load – slip behaviors of UHPC with different discrete reinforcement conditions.	276
Figure 6.26 Optic microscopy Olympus C100	278
Figure 6.27 Optic microscope images of the bonded segment of prestressing strand after pullout from UHPC with (a) and without (b) carbon nanofiber	278
Figure 6.28 Pullout load-slip behavior of prestressing strand in high-strength concrete without rainforcement	281
Figure 6.29 Pullout load-slip behavior of prestressing strand in high-strength concrete with graphite nanoplatelet reinforcement	282
Figure 6.30 Average Pullout load-slip behavior of prestressing strand in high-strength concrete without and with graphite nanoplatelet reinforcement	283
Figure 6.31 X-ray images for steel fiber reinforced UHPC incorporating a steel bar	285
Figure 6.32 Calculated values of average spacing versus volume fraction for carbon nanofiber, graphite nanoplatelet, and steel fiber	286
Figure 6.33 Calculated values of the number per unit cross-sectional area versus volume Fraction for carbon nanofiber, graphite nanoplatelet, and let steel fiber	287

#### **CHAPTER 1**

#### INTRODUCTION

#### 1.1 Statement of the Problem / Opportunity

Ultra-High Performance Concrete (UHPC) refers to concrete materials with very low waterbinder ratios, and fine gradation and dense packing of particulate matter; UHPC materials provide compressive strength exceeding 150 MPa (22 Ksi). Ultra-high-performance concrete generally incorporates discrete reinforcement (fibers) to avoid brittle modes of failure, and to encourage strain hardening behavior in tension. The high compressive and tensile strengths of UHPC enable design of more efficient structures with reduced weight and material consumption. The high density of UHPC makes it highly resistant against sorption of moisture and diffusion of aggressive ions (chloride, sulfate, etc.), rendering excellent durability characteristics. These attributes greatly benefit the life cycle economy of infrastructure system made with ultra-high performance concrete [1, 2]. Moreover, the high tensile strength and ductility of UHPC enable reduction of the size of structural elements and the required amounts of steel reinforcement (Figure 1.1). Ultra-high performance concrete can also reduce the formwork, labor, and maintenance costs, and raise the speed of construction and the service life of infrastructure systems. Applications of UHPC include bridge girders and decks, solid and perforated wall panels/facades, pipes, and marine structures. Ultra-high-performance concrete can also compete with steel and ceramics in applications traditionally dominated by these materials. Currently, UHPC is produced using specialty materials and mixers, employing long mixing periods and curing at elevated temperatures. These requirements reduce the market appeal of UHPC.

The high early strength of UHPC enables pretensioning of prestressed concrete elements at an early age. This feature combined with the benefits of thermal curing to UHPC suit applications to precast and prestressed structural elements [2]. The high binder content of UHPC facilitates thorough dispersion of fibers, which enhances their reinforcement efficiency [3].

UHPC is characterized by a high packing density of the particulate matter, which is achieved through optimization of grain size distribution of aggregates, micro-scale fillers, cementations materials, and nano-scale silica fume [4].



Figure 1.1 (a) UHP versus steel beams with similar structural qualities, and prestressed and reinforced UHPC beams; (b) Normal concrete versus equivalent UHPC pipe [2].

Ultra-high-performance concrete experiences relatively large autogenece shrinkage (due to loss of capillary water to the hydration process). The relatively high cementitious paste content in UHPC could feasibility produce relatively large temperature rise due to the heat of hydration. Internal or external restraint of the autogeneous and thermal shrinkage could produce relatively large tensile stresses in UHPC, causing crack formation [5]. Cracking and failure of cementbased materials is a multi-scale process. Under initial loading, short and discontinuous microcracks form in a distributed manner. These microcracks coalesce to form large macroscopic cracks, known as macrocracks [6]. The relatively low water content, high fine content, and the presence of fibers at relatively large volume fractions influence the rheology of fresh UHPC mixtures, complicating their processing. Existing UHPC mixture also require thermal curing to mobilize the chemical potentials of their relatively high contents of pozeolans and fines [2]. If viewed solely based on the cost per cubic yard of material, the cost of UHPC can be about ten times greater than the cost of normal-strength concrete [7], which is due to the high contents of cementations materials, fines, fibers and superplasterizer [1].

Fibers are used in UHPC at relatively high dosages to overcome the problems with brittleness of UHPC and its susceptibility to restrained shrinkage cracking [8]. Fibers provide UHPC with improved ductility, toughness, and crack resistance (Figure 1. 2); they could also reduce the need for secondary and some primary conventional (e.g., shear) steel reinforcement in concrete structures [9]. UHPC materials generally incorporate 1.5 to 3.0% by volume of steel fibers with 0.15-0.2 mm diameter and tensile strengths up 3500 MPa (508 Ksi) to realize improved ductility and toughness [10]. The aspect ratio of fibers and their bond strength to the cement-based matrix are among factors governing the reinforcement efficiency of fibers in concrete [11]. Improved bonding of fibers to matrix benefits stress transfer from matrix to fibers, and thus mobilizes the tensile load-carrying capacity of fibers more effectively. In addition, the friction between fibers and cement-based materials provides for energy dissipation during fiber pull-out. Pull-out tests performed on fibers embedded in concrete help characterize the bond strength and frictional pull-out behavior of fibers. Interactions of fibers with cracks developing in concrete are impotent considerations in fiber reinforced concrete.

Cracks form in concrete at different scales ranging in spacing from nanometer to millimeter and larger. This rationalizes multi-scale discrete reinforcement of concrete by employing nanofibers which occur at nanometer-scale spacing, and coarser fibers at micrometer- and millimeter-scale spacing. Multi-scale discrete reinforcement effectively mitigates crack propagation at different scales. For the purpose of energy dissipation and ductility via frictional fiber pull-out, longer fibers with micrometer, and millimeter-scale diameters are preferred [6].



Deflection

Figure 1.2 Flexural load-deflection curves of plain versus steel fiber reinforced concrete.

Higher fiber volume fractions increase the likelihood of fibers interacting with each other and with aggregates during mixing, causing fiber balling and reduced workability of fresh concrete [8]. These phenomena impose maximum limits on the fiber volume fraction, which depend upon the fiber type, the concrete mix design, and the mixing procedure [12]. Another consideration is the high cost of steel fibers in UHPC [1].

This research considers nanomaterials as complements to fibers for multi-scale reinforcement of UHPC. Nanomaterials could actually benefit the fresh mix workability by improving the packing density of solids in concrete. The rise in packing density reduces the volume of voids that need to be filled with concrete, thus making more water available to lubricate particles and improve the fresh mix workability. The complementary and synergistic actions of nanomaterials with microscale fibers could help lower the required fiber volume fraction, thus benefiting the fresh mix workability and potentially the cost of UHPC. The term complementary action refers to those aspects of nano- and micro-scale reinforcement that are additive and complement each other. The term synergistic action refers to the beneficial effects of nanomaterials and the reinforcement efficiency of micro-scale fibers, which make their combined contributions more than additive. Carbon nanofibers (CNFs) are discontinuous, highly graphitic nanomaterials. Figure 1.3 shows scanning electron micrographs of carbon nanofibers. They have excellent mechanical properties, and high electrical and thermal conductivity [13, 14], which can benefit the mechanical and conductivity attributes of UHPC. Carbon nanofibers also have unique surface characteristics, which facilitates their functionalization and bonding to cementitious matrix. Carbon nanofibers (CNFs) provide high level of specific strength and chemical resistance for use in cement-based matrices [15]. They have been found to increase the strengths of cementations materials [16], and control cracking by bridging across fine cracks [17]. Carbon nanofibers (CNFs) are different from carbon nanotubes in that they have more active sites on their surfaces, which enable more effective functionalization for improved interfacial bonding. Carbon nanofibers are assemblies of graphene cones; secondary bonding of these cones compromise the tensile properties of carbon nanofibers when compared with carbon nanotubes. The cost of preparing carbon nanofibers is less than that of carbon nanotubes due to the synthesis techniques used [13].



Figure 1. 3 Scanning electron micrographs of carbon nanofiber.

The experience with the use of CNFs in cement-based materials is limited. Poor dispersion of nanomaterials in cementitious matrices is a probable reason for the modest effects of CNFs on the mechanical performance of cementitious materials occasionally reported in the literature [13, 18]. Dispersion of nanomaterials in cement-based matrices can be improved by taking measures such as surface modification of nanomaterials, use of surfactants, and ultrasonication of nanomaterials in solution [18].

The relatively large concentrations of nano-scale silica fume particles as well as the relatively high dosages of superplasticizers used in UHPC can enhance the dispersion of carbon nanofibers (CNF) within cementitious matrices [19], and benefit their bond strength. Silica fume also benefits the dispersion and bonding of micro-scale fibers in concrete [20].

A key hypothesis of this research is that nanomaterials benefit the reinforcing action of fibers in concrete. The load-bearing mechanism of fibers after cracking primarily involves development of interfacial shear stresses between fibers and matrix. In order to analyze the effectiveness of fiber reinforcement, the properties of fiber and matrix constituents as well as those of fibermatrix interface should be known. The properties of fibers and matrix have been studied extensively, whereas those of the interfaces are more difficult to measure directly. Therefore, some assumptions have to be made when estimating the interfacial or bond properties between fiber and matrix. The bond properties are usually derived indirectly from a fiber pullout test, using theoretical models. Many analytical models assume a relationship between the shear stress and the local relative displacement between fiber and matrix. Stang et al. (1990) modeled the matrix as a shear lag with a linear shear stiffness on a rigid support [21]. Modeling the effect of the hook on steel fibers was advanced by Van Gysel by assuming that the hook geometry is a sum of straight and curved segments. Using the principle of energy conservation, the procedure was based both on theoretical and experimental considerations, and accounted for fiber debonding, plastic deformations and additional frictional forces due to incomplete straightening of the hook. An alternative approach was proposed by Alwan et al. using the concept of a frictional pulley along with two plastic hinges to simulate the hook action. The model consists of a two-step procedure, and considers the contribution of two hinges at the first stage and one hinge superposition accounting for the frictional and mechanical components. Subsequently, a

model was proposed based on the concept of nonlinear springs to resemble the effect of the hook [22]. Applying an iterative procedure over the geometry of the mechanical anchorage, the approach superposes the effect of the spring on previous pullout models for straight fibers [23]. An experimental investigation of the pull-out response of both straight and hooked-end steel fibers produced test data, based on which a semi-analytical model was developed to predict the fiber pull- out behavior. The ability of the model to deal with different geometric and mechanical characteristics of fibers as well as the influence of orientation, embedment length and matrix compressive strength, reflect upon its overall quality [24]. Nanomaterials could benefit the reinforcing action of fibers in concrete by improving the tensile strength of the cementitious matrix, rendering microcrack control attributes by bridging across finer cracks, and improving the bonding and frictional pull-out behavior of fibers in concrete. These effects of nanomaterials enable more effective use of fibers in cementitions materials. A primary focus of this research is on verifying these beneficial effects of nanomaterials on the reinforcing actions of fibers in concrete.

The closely spaced nanomaterials are imminently present throughout the cement past volume, including the critical, highly stressed locations. Fibers, on the other hand, would not exhibit uniform dispersion and random orientation as they encounter solid obstructions such as steel reinforcing bars and prestressing strands. Hence, nanomaterial, may be more effective than fibers in the vicinity of deformed bars and prestressing strands, which tend to experience large local stresses, and could be the weak links determining the performance limits of large structural systems.

Ultra-high-performance concrete materials rely upon a high packing density of particulate matter (cementations powder, and fine and coarse aggregates) to realize improved engineering

8

properties. Nanomaterials could benefit the packing density of UHPC by extending the size distribution of particulate matter into the nano-scale range. They would fill the gaps between finer (cement, silica fume, etc.) particles, and benefit the density, engineering properties and bonding attributes of UHPC.

This research project undertook extensive experimental studies complemented with theoretical investigations towards effective use of nanomaterials in ultra-high-performance concrete using the principle outlined below.

#### **1.2 Hypotheses**

The Primary hypotheses of the research are:

1. Nano-scale reinforcement can be used to benefit the packing density and the fresh mix workability of ultra-high-performance concrete, thereby improving the hardened material properties.

2. Micro-and nano-scale reinforcement of ultra-high-performance concrete make complementary contributions towards enhancement of material properties by rendering reinforcing effects at different scales.

3. There are synergistic actions of nano- and micro-scale reinforcement in ultra-highperformance concrete because nanomaterials improve the bonding and pullout behavior of micro-scale fibers.

4. Optimum discrete reinforcement systems for concrete comprise both nanomaterials and microscale fibers.

9

5. Nanomaterials can provide improvements in the pull-out behavior of deformed bars and prestressing strands from concrete through effective control of localized microcracks, which cannot be matched by conventional microfibers.

#### **1.3 Objectives**

The main thrust of this research is to enhance the mechanical properties and bonding attributes of ultra-high-performance concrete throiugh optimum use of carbon nanofibers and micro-scale reinforcement (steel or PVA fibers), and to develop a theoretical basis for assessing the contributions of nanomatirals to the bonding and pullout behavior of steel fibers in ultra-high-performance concrete. The specific objectives accomplished in the project are presented below together with an overview of the approach devised for meeting each objective.

#### Objective 1 Select Materials, and Develop Mix Design and Production Procedures for

#### Ultra-High-Performance Concrete Nanocomposites.

Mix proportioning methods were developed based on packing density principles for design of UHPC nanocomposite mixtures with readily available raw materials. The potential to enhance the packing density of UHPC with nanomaterials was verified.

## Objective 2 Optimize the Nano- and Micro-scale Reinforcement System in Ultra-High-Performance Concrete Nanocomposites.

The complementary and synergistic reinforcing actions of nano- and micro-scale reinforcement in UHPC were evaluated. Optimization experimental programs were implemented in order to identify multi-scale reinforcement systems which bring about balanced gains in key engineering properties of UHPC.

# Objective 3 Thoroughly Characterize the Optimum Ultra-High-Performance Concrete Nanocomposites.

Selected UHPC materials with optimum nano- and micro scale reinforcement systems were thoroughly characterized. Fresh mix workability and hardened material mechanical, thermal, sorption, abrasion, and free and restrained shrinkage tests were performed in order to verify and quantify the performance gains of UHPC realized by nano- and micro-scale reinforcement.

## Objective 4 Develop and Experimentally Validate a Theoretical Model for the synergistic Actions of Nanomaterials and Micro-scale fibers in Ultra-High-Performance Concrete Nanocomposites.

A theoretical model was developed to explain the contributions of nanomaterials towards enhancement of the fiber bonding and pullout behavior in UHPC. Fiber pullout tests were conducted in order to produce inputs to the model for prediction of the pullout behavior of steel fibers.

## Objective 5 Determine the effects of nanomaterials and steel fibers on the interfacial bond strength and pullout behavior deformed steel bars and prestressing strands in UHPC.

An experimental study was conducted in order to determine the effectiveness of nanomatirials and steel fibers in enhancing the bonding and pullout behaviors of deformed steel bars and prestrssing strands in UHPC.

#### 1.4 Work Plan

#### Task Outline

The tasks performed for achieving the project objectives are listed below.

**Task 1** Develop mix design procedures based on the packing density principles for ultra-highperformance concrete (UHPC) nanocomposites, and evaluate the contributions of nanomaterials to the packing density of UHPC. **Task 2** Design UHPC nanocomposite mixtures with selected readily available materials, and conduct trial and adjustment experimental studies to refine the initial mix designs.

Task 3 Devise optimized nano- and micro-scale reinforcement systems for UHPC.

**Task 4** Thoroughly characterize UHPC nanocomposites, and quantify the benefits of nanomaterials to different material properties.

**Task 5** Develop and experimentally verify a theoretical basis to explain the synergistic actions of nano- and micro-scale reinforcement in UHPC.

**Task 6 Evaluate** the contribution of nanomaterials and / or steel fibers to the bond strength and pullout behavior of deformed steel bars and prestressing strands in UHPC.

#### **1.5 Organization of the Research**

The dissertation has been organized into the following chapters.

Chapter 2 presents a literature review.

Chapter 3 reviews the packing density model used in mix deign of ultra-high-performance concrete.

**Chapter 4** covers optimization of nano- and micro-scale reinforcement for UHPC, and presents the experimental results conducted for thorough characterization UHPC nanocomposites.

**Chapter 5** presents the theoretical model developed for steel fiber pullout behavior, and reviews the fiber pullout test results which explain the synergistic actions of nano- and micro-scale reinforcement towards enhancing the mechanical properties of UHPC.

**Chapter 6** presents experimental results on the contributions of nanomaterials and/or steel fibers towards the bond strength pullout behavior of deformed steel bars and prestressing strands in ultra-high-performance concrete.

12

Chapter 7 presents the conclusions of the research, and presents recommendations for future research in the field.

#### **CHAPTER 2**

#### LITERATURE REVIEW

#### **2.1 Introduction**

Ultra-high performance concrete (UHPC) offers compressive strengths exceeding 150 MPa (22 ksi), complemented with highly desired impermeability and durability characteristics. These desired engineering properties are generally realized by avoiding coarse aggregates, use of distinctly high cementitions materials contents, proper selection of the cementitious binder composition, size distribution of the particulate matter to realize high density levels, use of distinctly low water/binder ration enabled by introduction of high superplasticizer dosages, and use of relatively high fiber volume fractions [25-27]. The highly desired balance of mechanical, impermeability and durability characteristics offered by UHPC can be used to design structural systems with reduced material consumption, weight, energy demand, carbon footprint, maintenance requirements and life-cycle cost [28]. The research reported here emphasizes enhancement of UHPC through introduction of nanomaterials. The focus of this work in on the mechanical properties of UHPC, effects of nanmaterials on fiber pullout behavior, and contribution of nanomaterials and fibers towards the pullout behavior of steel reinforcing bars and prestressing strands in UHPC. The contributions of nanomaterials, to the packing density of UHPC are also emphasized in this research.

#### 2.2 Use of Nanomaterials in Concrete

Cementitious materials are characterized by their quasi-brittle behavior, and are susceptible to cracking. The cracking process within concrete begins with isolated nanocracks, which then join to form microcracks and then macrocracks. Reinforcement is required because

of this brittle nature of concrete. Steel and polymeric fibers as well as glass and carbon fibers have been used in concrete since 1970s [29]. Recently, the use of microfiber reinforcements has led to significant improvements in the mechanical properties of cement-based materials by delaying the transformation of microcracks into macrocracks, but they could not stop the crack growth. This fact has encouraged the use of nanomaterials as concrete reinforcement [30]. Nanoparticle addition to cement paste was found to improve mechanical, chemical, and thermal properties of cementitious matrix. There are various types of nanoparticles, especially SiO<sub>2</sub> and  $Fe_2O_3$ , which when incorporated into cement lead to considerable improvement in compressive strength [31, 32]. Nano-sized TiO<sub>2</sub> has been added to accelerate the rate of hydration and increase the degree of hydration [33].

Carbon nanomaterials cover a large variety of nanomaterials with exceptional mechanical and physical characteristics. Extensive research projects conducted in recent years have demonstrated the potential of various carbon nanomaterials, including carbon nanotube (CNT) and carbon nanofiber (CNF), in polymeric matrices. This fact has encouraged the use of these nanomaterials in concrete [34, 35]. The nanometer length scale of CNTs and CNFs offer the possibility to restrict the formation and growth of fine (nano- and micro-scale) cracks within concrete. However, there exists a large difference in the structure and chemistry of polymeric and cementitious, matrices; therefore, a great deal of research has been directed towards understanding the interactions between these nanomaterials and cementitious matrices.

Portland cement is composed of 63% calcium oxide, 20% silica, 6% alumina, 3% iron oxide, and small amounts of other compounds (including some impurities). These materials, when reacted with water, produce an exothermic reaction forming a mineral glue (known as "C-S-H" gel), calcium hydroxide, ettringite, monosulfate, unhydrated particles, and air voids. The molecular structure of CS-H gel was not fully understood until recently; some researchers [36] have proposed a structure where cement hydrates consist of long chain silica tetrahedral and calcium oxide in long-range distances, with water causing intralayer distortions in otherwise regular geometry (Figure 2.1). The distortion in structure due to the addition of water makes the cement hydrate robust. The density of C-S-H has been determined to be 2.6 g/cc [37], and the elastic modulus of different cementitious phases were determined as follows[38]: 35 MPa for the Ca(OH)2 phase, 26 and 16 MPa for high- and low-stiffness C-S-H, respectively, and 10 MPa for the porous phase. One of the major drawbacks of cement structure is its susceptibility to crack formation and degradation. The amorphous phase of cement, that is the C-S-H gel, is itself a nanomaterial; therefore, the degradation mechanisms within concrete start at nano-scale, spreading then to micro- and macro-scales. Degradation of concrete can be due to physical reasons such as abrasion and erosion, freeze-thaw cycles, leaching and efflorescence, drying shrinkage, etc., or chemical reasons such as the aggregate-paste reaction, sulfate and acid attack, carbonation, etc. [39, 40].


Figure 2.1 TEM image of clusters of C-S-H (top), and the molecular model of C-S-H (bottom) [36].

After the discovery of buckyball (a ball-like molecule made of pure carbon atoms) in 1985 by Kroto et al. [41], a tubular form of carbon was reported by Iijima [42] in 1991 and named carbon nanotube (CNT). These nanotubes (called multiwalled carbon nanotubes or MWCNTs) consisted of up to tens of graphitic shells with adjacent shell separation of ~0.34 nm, diameters of a few nanometers, and high length-to-diameter ratio. About two years later, he reported the

observations of single-walled carbon nanotubes (SWCNTs), which consist of a single graphite sheet seamlessly wrapped into a cylindrical tube [43], as shown in Figure 2.2.



Figure 2.2 Schematic representation of single-walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT). [44]

CNTs possess outstanding properties such as distinctly high Young's modulus (1.4 TPa), tensile strength (above 100 GPa), and thermal conductivity (above 3000 W/mK). Additionally, CNTs are flexible and have high breaking elongation. Vapour-grown carbon nanofibers (CNFs) are another type of carbon nanomaterial which was first explored in 1889 by Hughes and Chambers [45], and their hollow graphitic structure was first revealed in the early 1950s by Radushkevich and Lukyanovich [36]. Because of their low production cost and higher availability as compared to CNTs, and excellent properties (although lower than CNTs), CNFs have received growing attention in recent times. The dimension and structure of CNF are highly dependent on the manufacturing and post-treatment methods [44]. CNFs are hollow core nanofibers comprising either a single layer as shown in Figure 2.3 [46]or double layer of graphite planes [45].The

graphite planes can be stacked parallel or at a certain angle from the fiber axis, and nested with each other to form different structures [46-49].



Figure 2.3 TEM image of CNF showing a single layer [46].

Dispersion of CNTs and CNFs is a key factor that strongly influences the properties of nanocomposites incorporating them. These nanomaterials exhibit a strong tendency to agglomerate due to presence of attractive (van der Waals) forces over their large specific surface areas. Infiltration of agglomerates is very difficult for any matrix, and their presence is therefore the source of potential defects in nanocomposites. The process of deagglomeration and subsequent distribution of nanomaterials within matrices or solvents is called dispersion. Dispersion can occur either due to abrupt splitting up of agglomerates into small fragments under high stress (rupture) or due to continuous detachment of small fragments at a comparatively lower stress (erosion). The dispersion behavior of CNF and CNT depends on a few critical factors such as length of nanomaterials, their entanglement density, volume fraction, matrix viscosity, and attractive forces. Different chemical methods have been tried for homogeneous dispersion of carbon nanomaterials in water and various polymers; these methods employ solvents [50], surfactants [51-54], functionalization with acids [55], amines [56], fluorines [57],

plasma [58, 59], microwave [60] and matrix moieties [61], noncovalent functionalization [62], using block polymers [63, 64], wrapping conjugated polymers [65], and other techniques [66, 67]. On the other hand, the basic physical technique used for carbon nanomaterial dispersion is ultra-sonication, which is often used in combination with other methods mentioned above [68-

74].

Dispersion of carbon nanomaterials in cementitious matrices is also a critical issue which strongly influences the properties of cement-based nanocomposites. Dispersion of CNF/CNT directly within cement paste during mixing is not feasible, as the thickening of cement paste begins within a short period after addition of water [75]. The mixing process using a conventional mixers cannot ensure proper dispersion of CNT within the cementitious matrix, resulting in large CNT clusters in the hydrated paste (Figure 2.4) [47]. To avoid this situation, the strategy commonly employed for mixing CNTs/CNFs in cementitious matrices is to disperse these nanomaterials first in water, followed by mixing of nanomaterial/water dispersion with cementitious materials using a conventional mixer. However, the methods of dispersing nanomaterials in water should be carefully selected so that they do not interfere with the hydration and processing of cement nanocomposites. Many surfactants that are successfully used to disperse carbon nanomaterials in polymeric matrices have been reported to create problems in cement hydration, entrap air in the cement paste or react with the water-reducing admixtures [77].



Figure 2.4 SEM image of CNT/cement paste after hydration (a) 100x of magnification (b) 1800x of magnification [47].

Dispersion of CNF/CNT in cement is even more difficult as compared to the polymeric matrices. One of the reasons for poor dispersion may be the size of cement grains. As CNFs or CNTs are separated by the cement grains, the presence of grains larger than the average particle size leads to the absence of CNFs/CNTs in some areas, whereas they can be present in higher quantities in other areas where cement grains are much smaller in size [78]. Although reduction of cement particle size by ball milling can improve nanomaterial dispersion, small-grain cement has some disadvantages such as high water consumption, thermal cracking, and larger chemical and autogenous shrinkage [79]. However, it should be noted that the various chemical routes (such as using surfactants, polymers, or functionalization) cannot directly disperse nanomaterials in water; instead, they help in the dispersion process by wetting the nanomaterials with water and improving the dispersion stability. Therefore, these chemical routes are always used in combination with the physical routes (such as ultrasonication) which can directly disperse the nanomaterials. The chemical method using Surfactants can improve aqueous dispersion of nanomaterials by reducing surface tension of water and, moreover, yield a stable dispersion as a result of electrostatic and/or steric repulsions between the surfactant molecules adsorbed on the nanomaterial surfaces. However, the dispersion capability of surfactants strongly depends on their concentration, and an optimum surfactant-to-nanomaterial ratio should be used for preparing cementitious nanocomposites. The dispersion homogeneity tends to be preserved in the presence of nanomaterials, with only individual nanotubes observed at the fractured surfaces of nanocomposites (Figure 2.5). Lower than optimum surfactant-to-CNT ratios, however, could not disperse CNTs as well, leading to the presence of large CNT clusters within the composites. Similarly, CNFs can be dispersed homogeneously (Figure 2.6) using a proper surfactant-to-CNF ratio [48].

Besides concentration, it has been observed that the type and structure of surfactant also have significant effects on the dispersion of carbon nanomaterials in water and subsequently within cementitious nanocomposites. Among various available surfactants such as Sodium dodecylben-zenesulfonate (SDBS), sodium deoxycholate (NaDC), Triton X-100 (TX10), Gum Arabic (GA), and cetyl trimethyl ammonium bromide (CTAB), the anionic one (e.g., SDBS) have provided better aqueous dispersion of MWCNTs (prepared using optimum surfactant concentration and magnetic stirring for 10 min at 300 rpm combined with ultrasonication using a tip sonicator), which was stable after 70 minutes of ultracentrifugation and 60 days of storage [49].



Figure 2.5 Dispersion of MWCNT within cementitious nanocomposites prepared using different surfactant-t-MWCNT weight ratio: (a) no surfactant (b) very low surfactant content, (c) low (near-optimum) surfactant content, and (d) optimum surfactant content [50].



Figure 2.6 Dispersion of CNF in cementitious nanocomposites [48].

The result was even better when SDBS was used in combination with Triton X-100 (nonionic) in a specific weight ratio. The better stabilization in case of SDBS was attributed to the benzene ring in the hydrophobic chain, smaller charged  $SO_3^{2^-}$  head group, and relatively long alkyl hydrophobic chain [84]. The dispersion ability of various surfactants was found in the following order: SDBS and TX10 > SDBS > NaDC and TX10 > NaDC > AG > TX10 > CTAB. The cationic surfactant CTAB showed the lowest dispersion capability because of the absence of benzene ring on the long chain and the positive charge which might have neutralized the negative charge of MWCNTs in aqueous solution. The fracture surfaces of cement nanocomposites containing 0.2 wt.% MWCNT dispersed using SDBS/TX10 showed a very uniform distribution of CNTs. Sodium dodecyl sulfate (SDS) has also been reported as an effective anionic surfactant for fabricating CNT/cement nanocomposites [85]. However, one drawback of using surfactants as nanomaterial dispersant is the lack of connectivity of nanomaterials within the cementitious matrix due to blocking by surfactant moleculesand this affects the conductivity of nanocomposites [85]. Surface modification of carbon nanomaterials using polymeric surfactants has been reported to introduce steric repulsion between the nanomaterials, leading to their homogeneous dispersion. The surfaces of MWCNTs could be covered with acrylic acid polymer through ultrasonication in water, as can be seen in Figure 2.7 [51], and this led to very good aqueous dispersion of CNT (Figure 2.8). Methylcellulose is another polymer which has been used to prepare highly stable aqueous dispersions of CNTs for fabricating cementitious nanocomposites [87].



Figure 2.7 TEM image of MWCNTs showing (a) the presence of acrylic acid polymer on the surface at magnifications of 13000x and (b) 800000x [51]



(a)



Figure 2.8 TEM image of (a)MWCNT dispersion in water without any treatment and (b) with acrylic acid polymer and sonication [51]

Polycarboxylate, which is commonly used as a superplasticizer in cement paste, has also been found to be an effective dispersant of CNT [90]. Among the various cement admixtures such as alkylbenzene sulfonic acid (air entraining agent), styrene butadiene rubber copolymer latex, aliphatic propylene glycol ether including ethoxylated alkyl phenol, polycarboxylate, calcium naphthalene sulfonate, naphthalene sulphonic acid derivatives, and lignosulfonate, very stable dispersions have been obtained with the air entrainer, polycarboxylate, and lignosulfonate. However, the use of high concentrations of lignosulfonate required for effective CNT dispersion is not recommended to avoid delays in the setting time of the cementitious matrix [91]. Also, despite desired aqueous dispersion, the use of alkylbenzene sulfonic acid could not produce a homogeneous CNT dispersion in the hardened cement paste. On the contrary, the use of polycarboxylate resulted in a very good dispersion of MWCNT in water and also in hardened cement paste and, therefore, proved to be the preferred dispersant among the various admixtures used in cement.

Silica fume, an amorphous polymorph of silicon dioxide, is also used as a pozzolanic material in concrete production [92–94]. Silica fume consists of spherical particles with average diameter of 150 nm, and has been found to improve microfiber dispersion within cement [95, 96]. The influence of silica fume on carbon nanomaterial dispersion has also been studied [97]. It was observed that cementitious nanocomposites prepared through dry mixing of 2 wt.% CNF with cement and silica fume (10 wt.%) using a conventional three-speed mixer (followed by water addition) showed both CNFagglomerates as well as individually dispersed nanofibers. However, in absence of silica fume only CNF agglomerates were observed, indicating positive influence of silica fume [98]. The improved dispersion in the presence of silica fume was attributed to the smaller size (100 times smaller as compared to anhydrous cement particles) of silica fume

particles which could disrupt the van der Waals forces between individual CNFs, thereby mechanically separating some of them during the dry mixing process and reducing the CNF clumps. The most common approach to improving the dispersion of CNTs/CNFs in water or polymeric matrices is covalent functionalization. Frequently, carbon nanomaterials have been treated with strong acids such as nitric acid or a mixture of sulfuric and nitric acid (3 : 1) to oxidize the surface and create functional (e.g., carboxylic) groups. Covalent functionalization using acid mixture has been found to be successful in dispersion of CNTs within cementitious matrices [99]. Moreover, CNTs become tightly wrapped by the C-S-H phase of cement, due to covalent bonding between the COOH or C-OH groups of nanotubes and C-S-H. Similar observations have been made in the case of surface-functionalized CNFs using 70% nitric acid [100]. However, although surface-treated CNTs could be homogeneously dispersed within the cementitious matrix, the dispersed CNTs could not form a well-connected three-dimensional network (Figure 2.9) required for good conductivity, which is due to the reduced concentration of contact points and the coverage of nanomaterial surfaces by C-S-H [52].

Several researchers reported that carbon nanomaterials can significantly change the microstructure of cement, and this is one of the principal reasons for the benefits to mechanical properties of cementitious matrices.

Significant differences between the porosity of Portland cement and cement/CNT nanocomposites have been observed [107]. The total porosity and surface area decreased with CNT addition. This was attributed to the fact that CNTs filled in the pores, mainly the mesopores (size less than 50 nm), between the hydration products, thereby producing a denser microstructure than that of the unreinforced cement (Figure 2.10). Similar findings have also been made in the case of cement containing 0.5 wt.% surface-treated MWCNTs [53], which

29

resulted in 64% lower porosity and 82% lower pores with size more than 50 nm. On the contrary, cement composites containing micr-oscale fibers such as carbon showed much higher porosity than the Portland cement samples. Nano-indentation tests also showed lower probability of the porous phase presence in a cement nanocomposites containing 0.08 wt.% MWCNT when compared with plain Portland cement [81].



Figure 2.9 SEM images of cement nanocomposites with ((a), (b)) untreated CNTs and ((c), (d)) acid-treated CNTs [101].



Figure 2.10 SEM micrographs at different magnifications of 1 wt.% CNT/cement paste after 28 days of hydration [54].

Early investigations have indicated that CNTs have strong influence on the hydration process and hardness of cementitious composites [108]. In spite of inhomogeneous CNT dispersion in nanocomposites with cement/CNT ratio of 0.02 (by weight), Vickers hardness improved up to 600% in case of 0.4 and 0.5 water/cement ratios in early stages of hydration, although no improvement in hardness was observed after 14 days of hydration. These early results reflected the potential of CNT to improve the mechanical properties of cement. However, as in the case of polymer matrices, the reinforcing efficiency of CNT/CNF in cementitious matrices and the resulting mechanical properties of nanocomposites also depend on several critical factors. Dispersion of nanomaterials has been identified as one of the principal factors which influence mechanical properties. Therefore, parameters which control dispersion have strong influence on the mechanical properties. For example, the type and structure of surfactant were found to be very important with respect to mechanical properties. Among various surfactants such as SDBS, NaDC, TX10, AG, and CTAB, the highest flexural and compressive properties were achieved with NaDC, whereas the lowest variation as well as the second best flexural and compressive strengths were obtained in the case of 3:1 mixture of SDBS and TX10. The improvements in the case of NaDC were 35.45% and 29.5% as compared to plain cement paste. The highest improvement in the case of NaDC was due to good dispersion of MWCNTs as well as formation of a strong interface between the cement matrix and MWCNTs. Similarly, better mechanical properties in the case of SDBS and TX10 mixture resulted from the best dispersion ability of this combination, and also good bonding between MWCNTs and matrix. Microscopic investigations in the case of this surfactant combination suggested that MWCNTs were well distributed within the cement matrix as a net-like structure, and acted as bridges between the microcracks, resulting in superior mechanical performance [83]. Similarly, among the various cement admixtures, the improved dispersion of CNT in water as well as within cement was observed only with polycarboxylate; the cement paste containing 0.8% polycarboxylate and 0.5% CNT showed very good flow behavior even with a low water-cement ratio of 0.35, and provided a compressive strength 25% higher than the control cement [90]. The length and concentration of CNTs also influence their dispersion behavior and, therefore, are key factors controlling the mechanical properties of cementitious nanocomposites [81]. It has been noticed that short MWCNTs (10–30 µm) provided better dispersion and flexural properties even when used at higher concentrations (0.08 wt.%), whereas long MWCNTs (10–100  $\mu$ m) should be used at lower concentrations (0.048 wt.%) to maintain better dispersion and to achieve good flexural properties. It was also observed that short CNTs at higher concentrations were better in terms of mechanical properties due to their better dispersion, reduced CNT free volume of cement paste, and better filling of nano-sized voids [109]. However, reduction of CNF's aspect ratio due to either the debulking process or ultrasonication was found detrimental to mechanical properties, and it was observed

that a higher ultrasonication energy than optimum led to reduction in nanomaterials' aspect ratio, and deterioration of mechanical properties [110].

Homogeneous dispersion of CNTs/CNFs achieved through their growth onto cement particles was reported to provide 2 times higher compressive strength than the pristine cement composites after 28 days of hydration [104]. This dispersion process led to uniform distribution of CNTs and CNFs embedded into the hydration products of C-S-H phases and, therefore, bridged the adjacent cement particles, resulting in strong improvements in compressive strength. Although a homogeneous dispersion of carbon nanomaterials is highly necessary for enhancing

The mechanical performance of cementitious nanocomposites, it has been observed that even when nanomaterials are poorly dispersed, they can prevent the formation of shrinkage cracks and significantly improve the mechanical performance, especially when curing is performed in the absence of moisture for the first 24 hours [111].

The interface between nanomaterials and cementitious matrix controls the load transfer between them and, therefore, significantly influences the mechanical properties of nanocomposites. Formation of covalent bonds between COOH or C-OH groups of functionalized CNTs and the C-S-H phases of cement matrix has been observed through FTIR studies [99], and has also been supported by microscopic investigations which showed tight wrapping of functionalized CNTs by C-S-H phases. Cement nanocomposites containing surface-treated MWCNTs presented much better flexural and compressive properties when compared with plain cement paste. Flexural and compressive strengths improved up to 25% and 19%, respectively, using 0.5 wt.% functionalized CNT. It has been observed that ensuring a good dispersion through acrylic acid polymer wrapping does not ensure improved mechanical properties of nanocomposites, due to improper load transfer at the interface [86], whereas 0.045% of functionalized MWCNTs showed nearly 50% increase in compressive strength when dispersed using the same process, indicating strong influence of the interface. Improvement of mechanical properties using functionalized nanomaterials can be further enhanced through removal of carboxylated carbonaceous fragments (CCFs) from the nanomaterials surface [102]. It has been reported that the incorporation of functionalized CNTs (0.01 wt.%) containing CCFs resulted in only 13% improvement in compressive strength, whereas removal of CCFs using acetone resulted in significant improvements in compressive strength, up to 97%, using only 0.03 wt.% CNT. This was attributed to the fact that functionalized CNTs became less accessible for reaction with cement hydration products and their nucleation, due to presence of these CCFs. Similarly the presence of surfactant molecules on the nanomaterial surfaces was found detrimental to the mechanical properties of cementitious nanocomposites due to the blocking of direct contacts between surface functional groups and cement hydration products, and a reduction of 65% in compressive strength was observed using 4% Sodium dodecyl sulfate (SDS).

Use of surface-treated CNTs/CNFs improves the post-failure mechanical integrity of cement nanocomposites [100]. Cement samples containing 0.5 wt.% surface-treated CNFs were found to maintain better structural integrity than the control samples after compression testing. Better structural integrity in case of CNF/cement nanocomposites resulted due to the restriction of crack propagation by the entangled clumps of CNF inside cement cavities, leading to bridging of cracks, and also due to the presence of individually dispersed CNFs within the cement matrix. It was also observed that, after decalcification using ammonium nitrate solution for 95 days, the samples containing CNFs showed improved ductility. In spite of several benefits of using functionalized nanomaterials, the surface functionalization method should be used carefully in the case of cementitious matrices. There is a possibility that functionalized CNTs can absorb the

water present in the cement paste due to their hydrophilic nature, and may adversely affect the cement hydration process. It has been noticed that cement nanocomposites containing 0.5 wt.% carboxyl functionalized MWCNTs form lower amounts of tobermorite gel due to the improper hydration process, which significantly degraded the mechanical properties [112]. Besides surface functionalization, the interface in a carbon nanomaterial/cement nanocomposite also depends upon the surface features of nanomaterials. The CNF variety with rougher surfaces containing conically shaped graphitic planes was found to be very effective in enhancing mechanical properties as compared to the CNFs having smoother surfaces [110].

The improvement of mechanical properties achieved in the case of well-dispersed MWCNT/cement nanocomposites has been found to be much higher than that predicted using theoretical equations [81]. The decrease in cement porosity and the improvement of its microstructure are certainly among factors ignored by existing models which view nanomaterials purely as reinforcing systems. The increase in the amount of high-stiffness C-S-H phases in the presence of CNT, as revealed from the nano-indentation tests, is another reason for such strong improvements in mechanical properties. Improvement of microstructure is also the primary cause for enhancement of mechanical properties in case of non-autoclave foam concrete. It has been found that the use of CNTs (0.05% by mass) as the reinforcement of foam concrete stabilized its structure by decreasing the pore wall percolation and ensuring better pore size uniformity [113]. This resulted in a strong improvement in the compressive strength (70%) associated with a decrease in the average density of concrete from 330 kg/m3 to 309 kg/m3. Improvement of microstructure, and the resulting gains in mechanical properties with CNT addition has also been noticed in the case of fly ash cement [114–119]. Fly ash cement samples containing CNTs provided higher densities than control fly ash and PC samples, due to the filling of cement pores

by CNTs, which yielded a denser microstructure [120]. The compressive strength of fly ash cement composites containing 1 wt.% CNT reached that of PC at 28 days and 60 days, which is usually higher than the compressive strength of fly ash cement due to its slow hydration rate.

Hybrid cement nanocomposites are analogous to the multi-scale polymer nanocomposites containing reinforcements of different (e.g., nano and micro) scales. Hybrid cement nanocomposites containing both CNTs and nano-metakaolin (NMK) have been reported [121]. NMK is a silica-based material, which can react with Ca(OH)<sub>2</sub> to produce C-SH gel at room temperature. Incorporation of NMK into concrete has been found to significantly improve the early strength, increase the resistance to alkali-silica reaction and sulfate attack, and yield increased toughness and durability [122-125]. Additionally, homogeneous dispersion of exfoliated NMK was found to significantly improve the compressive strength of cement (18% using 6 wt.% NMK) due to the reduction of porosity and improvement of the solid volume and bond strength of cement through pozzolanic reactions between the silicon and alumina elements present in NMK and cement. Also, the presence of NMK could probably disrupt the attractive forces between CNTs during the dry-mixing process, causing their separation and individual dispersion. Additionally, the presence of NMK particles mixed with the dispersed CNTs could act as Si source for the formation of Ca-Si-rich phases. CNTs could further act as the nucleation sites for self-assembly of Ca-Si phases. Due to these reasons, addition of up to 0.02% CNT resulted in 11% higher compressive strength as compared to the mortar containing only NMK. Hybrid cement nanocomposites containing polyvinyl alcohol (PVA) micro-fibers and CNFs were also developed and reported to have higher Young's modulus, flexural strength, and toughness than plain cement, cement containing only PVA micro-fibers, or CNFs [82]. It was observed that cement containing CNFs provided much higher load-carrying capacity at the same CMOD (crack

mouth opening displacement) during the early stages of loading. Using only 0.048% CNFs, Young's modulus, flexural strength and toughness improved by up to 75%, 40% and 35%, respectively. On the contrary, use of PVA micro-fibers improved the Young's modulus and flexural strength only marginally, but the fracture toughness increased tremendously, retaining the load for ten times higher CMOD than plain cement. Therefore, in hybrid composites, the prepeak behavior was mainly controlled by CNFs, whereas the post-peak behavior was influenced mainly by PVA micro-fibers. Investigations of fractured surfaces suggested good bonding between cement and both CNFs and PVA microfibers, and bridging of micropores by PVA fibers and pores at nano-scale by CNFs. The hybrid cementitious composites showed up to 50% improvement in flexural strength, 84% improvement in Young's modulus, and 33 times (3,351%) improvement in fracture toughness over plain cement matrix. Similarly, hybrid cement nanocomposite bars containing 2.25% short carbon fibers and 0.5% MWCNT were found to have much higher tensile modulus (60%), load-carrying capacity (54%), and failure strain (44%) as compared to plain cement bars [126].

## 2.3 Ultra-High-Performance Concrete

Ultra-High Performance Fiber Reinforced Concrete (UHPC) is a superplasticised concrete with very low water/binder ratio that is reinforced with fibers, with an improved homogeneity resulting from removal of coarse aggregates and reduction of the fine aggregate size and content [1]. According to Richard and Cheyrezy [1], the ultimate compressive strength potential of UHPC is realized through thermal curing which activates pozzolanic reactions in the ternary binder of UHPC. A a large dosage of cementitious materials (cement, silica fume, and fly ash or slag) are typically used in UHPC. For instance, Rossi [2] presented an experimental study of the

mechanical properties of a UHPC mix with 1050 kg/m<sup>3</sup> cementitious materials content. Park [3] investigated the effects of hybrid fiber reinforcement systems on the tensile behavior of ultrahigh-performance concrete. The cementitions binder content in UHPC incorporates relatively high dosages of pozzolans (finer silica fume plus coarser fly ash or slag). Hassan [6] investigated the mechanical properties of UHPC with about 650 kg/m<sup>3</sup> cement, 420 kg/m<sup>3</sup> slag and 120 kg/m<sup>3</sup> silica fume. Tuan [7,8] demonstrated the possibility of using rice husk ash to replace silica fume in UHPC.

UHPC represents a breakthrough in concrete technology, providing steel-like compressive strengths of up to 250 N/mm<sup>2</sup> (or higher), and remarkable durability characteristics compared even with high-performance concrete. With proper use of steel fibers, it is now possible to design sustainable, lightweight reinforced and prestressed UHPC structures. Long-span girders, bridges, shells and high-rise buildings are some major applications of UHPC (Figure 2.11) [5]. UHPC's resistance to water, chloride diffusion, carbonation, chemical attack and abrasion is well-suited for structures exposed to harsh environments (e.g., marine, industrial effluents and sanitary sewer pipes), and public buildings with strict safety and maintenance requirements [6].



Figure 2.11 An example of UHPC bridge applications in the United States [7].

A key consideration in development of UHPC is achievement of high packing densities through proper size distribution of particulate constituents. Packing density can be evaluated at different scales. First, the particle size distribution affects the packing density of aggregates, which in turn determines the volume of voids to be filled with paste. With a higher packing density, the volume of paste required for filling the voids between aggregate particleswould be smaller, and the volume of excess paste (paste in addition to that needed for filling the voids between aggregate particles) available to form paste films on aggregate surfaces would be larger [55]. Within the powder-size particulate matter (dry cementitions binders and any micro-scale fillers), the void content tends to be quite large if only ordinary Portland cement is used [56].To overcome this problem, supplementary cementitious materials finer than OPC, such as condensed silica fume [57] and fly ash [58] can be added to fill the voids between cement particles in order to improve the packing density of cementitious materials (Figure 2.12).

Several theoretical packing models have been developed for simulating the packing of multiblended solid particles (two or more size classes of particles blended together) for the purpose of predicting and optimizing the packing densities of cementitions paste, mortar and concrete [59-64]. More recently, Wong and Kwan [65] and Kwan and Fung [66] compared their experimentally measured packing densities with the theoretically predicted values of existing packing models to assess the of existing models. Computer simulations have been developed to study the packing of particles [67-69]. For fine and coarse aggregates, there are codified test methods for measuring the dry packing density [70, 71]. Some models rely upon successive combination of constituent materials or size fractions rather than individual particles. For example, Lees (1970)[45] proceeds successively from coarsest to finest materials while Dewar (1983) proceeds in the reverse direction. Some authors, including Andersen and Johansen (1989)[53], Roy et al. (1993) [90], Goltermann et. Al. (1997) [46] and Palbol (1994)[65], utilize ternary diagrams or packing triangles. Sedran et al. (1994) [71] and de Larrard (1995) [92] use the viscosity theory developed by Mooney (1951) [68].



Figure 2.12 improved packing density resulting from the blending of particles of different size.

# 2.3 Pullout Behavior of Steel Fibers, and Reinforcing and Prestressing Steel

Fiber reinforced concrete offers improved mechanical characteristics compared to plain concrete. Notable gains in tensile strength have been realized when steel fibers arrest and bridge across cracks. The pullout behavior of fibers crossing cracks in cement is critical to the contributions of fibers to the ductility, toughness, and impact resistance of concrete. The mechanical properties of UHPC are significantly influenced by the introduction of fibers, and the bond characteristics at the fiber-matrix interface. Therefore, it is important to investigate the bond properties and pullout behavior of steel fibers in UHPC. Fibers tend to be randomly oriented in concrete. Therefore, they pull out of concrete at different angles with respect to the crack. Fibers pulling out at different inclination angles provide different contributions to the resistance against of crack propagation [72-78]. The effect of fiber inclination angle on its pullout behavior is dependent upon the fiber aspect ratio, shape (straight, hooked, corrugated, etc.), and the steel and concrete material properties. While most fiber pullout models consider fibers that are aligned with the direction of (tensile) pullout force [79-81], some have proposed models to predict the pullout behavior of inclined fibers [82-86]. These models tend to be complex, and involve significant empirical parameters [87-90]. They try to consider some complex phenomena involved in inclined fiber pullout, including fiber plastic bending and matrix spalling (Figure 2.13). The steel fiber pullout behavior in concrete is influenced by the cementitions binder microstructure at the fiber-matrix interface, the microracking and spalling of concrete at highly stressed locations in the vicinity of fibers, and the fiber-matrix frictional behavior. These key factors influencing the fiber pullout behavior could benefit from the introduction of nanomaterials.



Figure 2.13 Fiber bending across crack, and spalling of the cementitious matrix at the fiber exit point.

# **CHAPTER 3**

# DEVELOPMENT OF A FRAMEWORK FOR MIX DESIGN OF CONCRETE NANOCOMPOSITES BASED ON PACKING DENSITY PRINCIPLES

## **3.1 Introduction**

Nanomaterials provide a large specific surface area for interacting with cement hydrates. Their nano-scale cross-sectional dimensions (diameter/thickness) and micro-scale length/planar dimension, however, could compromise effective interactions with the porous structure of cementitious paste. The relatively high capillary porosity (typically more than 10 vol. %) of cementitious paste, a large fraction of which approach 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 effective interactions of graphite nanomaterials with and thus their beneficial effects on cementitious matrices. Figure 3.1 provides a view of the size distribution of different (void and solid) constituents of cementitious matrices. Only the (nanostructured) calcium silicate hydrate offers the potential for development of massive (potentially primary) bonds with properly modified graphite nanomaterials. Neither capillary (and larger) pores nor micro-scale crystals match this capability of calcium silicate hydrate. Figure 3.2a schematically depicts a graphite nanomaterial occurring largely outside calcium silicate hydrate (with effective binding qualities) within 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 cementitious matrix), but would not effectively contribute to the mechanical performance of the matrix. One can overcome this drawback by employing some commonly used practices in concrete (and high-performance concrete) mix design. The porosity and volume fraction of the micro-scale crystalline constituents of concrete can be reduced, and the capillary pore size distribution can be shifted towards nanometer scale for effective interactions with nanomaterials (Figure 3.2b) through: (i) maximizing the packing density [91] of the particulate matter in concrete while retaining the desired level of fresh mix workability; (ii) inducing pozzolanic reactions [92] which replace micro-scale crystalline products of cement hydration with calcium silicate hydrate of reduced density which effectively fills capillary pores and bonds to nanomaterials; and (iii) lowering the water/cementitious ratio through effective use of (normal or high-range) water reducers, which lower the size and content of capillary pores and also benefit the dispersion of nanomaterials. This section focuses on the key principle of maximizing the packing density of concrete using a (common) consolidation effort while retaining desired fresh mix workability. This process employs a (commonly available) fine pozzolan at adequate quantities to render pozzolanic effects. The use of water-reducers (and high-range water reducers in the case of higher-performance concrete materials), which is commonly practiced in concrete production, is an inherent aspect of developing concrete mix designs which enable maximum use of the distinctly high specific surface area and engineering properties of graphite nanomaterials. It should be noted that such refined mix designs enable development of concrete nanocomposites which realize balanced gains in diverse engineering properties through effective use of nanomaterials (schematically depicted in Figure 3.2b). Improvements in some material properties of concrete (e.g., moisture barrier qualities and conductivity) depend more upon the physical

presence of nanomaterials than their interactions with cement hydrates. Such properties can thus be improved effectively using graphite nanomaterials without refining the concrete mix design.



Figure 3.1 Dimensional ranges of voids and solids in hydrated cementitious paste [91].



(a) Conventional



(b) Refined

Figure 3.2 Schematic depiction of the conventional and refined microstructures of cementitious matrix incorporating a graphite nanomateiral (C = capillary pores; H = micro-scale crystalline products; A = calcium silicate hydrate)[93].

## **3.2 Packing Density: Basic Principles**

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

Particulate matter of uniform grain size cannot realize high packing densities. For example, spherical grains of similar size can reach packing densities of only 0.52 and 0.74 in cubic and tetrahedral packing structures of Figures 3.3a and 3.3b, respectively [91]. Packing density can be increased through the use of particles of different dimensions, with finer particles filling the space between coarser particles (Figure 3.4) [94]. 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 buildup in young concrete due to exothermic hydration reactions are also among the benefits of reducing the cementitious paste content 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 [96].



Figure 3.3 Cubic and tetrahederal packing structures of spherical particles of similar size [91].



Figure 3.4 Dense packing of particles of different dimensions [94].

Given a unit volume filled with particles, packing density (or packing degree) is defined as the volume of solids in this unit volume, and is equal to one minus the volume occupied by voids. Packing density gives an indication of how efficiently particles fill a certain volume. If a high volume of particles can be 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  $(\phi)$  can be expressed as follows:

$$\varphi = V_s / V_t = V_s / (V_s + V_e) = 1 - e$$
(3.1)

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 ( $V_e/V_t$ ).

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 the major factors affecting packing density. The significance of surface texture effects depend upon the particular system. Packing density also depends upon the compaction method and the dimension of the container. Packing density tends to be lower when particles are simply poured into the container, and increases when the poured sample is consolidated using methods such as tapping with a rod and vibration. Interestingly, as-poured crushed aggregates may have a lower (loose) packing density than similar round aggregates, but the vibrated packing density of the same crushed aggregates could be more than that of round ones. It has been suggested that loose packing density correlates better with the shape and texture of particles, and that risk of segregation is lower when particles are just poured. Compacted packing densities, on the other hand, exhibit less variability. Packing density can be evaluated in air (dry packing), or in water (or other liquids). For particles retained on No. 200 sieve (>75 µm in size, covering mostly aggregates but not cementitious materials), dry packing (in oven-dried or saturated surface dry

state) has been used successfully to predict the behavior of concrete. For finer particles (<75 µm in size), however, dry packing does not reflect the packing behavior in saturated condition (in fresh concrete mixtures) due to important inter-particle forces. Water demand tests have been proposed to measure the packing density of powders (cement, fly ash, and aggregate particles less than 75 µm in size). In fresh concrete mixtures, a higher packing density of aggregates reduces the theoretically required paste or water content for achieving a targeted level of workability. Among the major constituents of concrete, cementitious materials are more costly; cementitious paste is also responsible for the shrinkage, heat of hydration and some durability problems of concrete. Optimization of concrete mixtures thus seeks, within the constraints imposed by workability considerations, to minimize the content of cementitious materials. Therefore, an objective of concrete mix design is to combine available (fine and coarse) aggregates in a way that near-maximum packing density is achieved while meeting the workability requirements.

For cementitious materials and finer aggregates ( $<75 \mu m$  particle size), packing density in saturated condition correlates better with their packing behavior in concrete. The Vicat test (ASTM C187) is recommended for assessment of packing density in saturated condition. The resulting values of wet packing density provide a basis for comparing different combinations of cementitious materials and micro-scale aggregate particles as far as their effects on the cementitious paste and water demands are concerned. The wet packing density can be expressed as follows:

$$\phi = \frac{V_{solids}}{V_{total}} = \frac{1}{1 + \frac{W_w}{W_{mf}}} SG_{mf}$$
(3.2)

where,  $W_w$  = weight of water

W<sub>mf</sub> = weight of micro-scale particles (fines/powder)

 $SG_{mf}$  = Specific gravity of micro-scale particles.

For aggregates >200 µm in particle size, dry packing density correlates with packing behavior in fresh concrete. Method of compaction is a factor here. While loose (as-poured) dry packing density of aggregates have been considered, 'vibrated-plus-pressure' packing density and 'rodded' packing density (ASTM C29) have been considered for use in the 'compressible packing model' (CPM) [97]. Aggregate particles can be oven-dried or saturated surface dry, and dry packing density can be measured in a 0.1-ft<sup>3</sup> container for fine aggregates and the fraction of coarse aggregate that is <3/8 in (9.5 mm) in particle size, and in a 0.25-ft<sup>3</sup> container for coarser aggregate. The container should have an inside diameter that is at least five times the maximum aggregate size. If a weight W of aggregate with specific gravity SG fills a container of volume V<sub>c</sub>, packing density,  $\alpha$ , can be expressed as follows:

$$\alpha = \frac{V_s}{V_c} = \frac{W}{V_c SG}$$
(3.3)

The 'wall effect' correction can be made as follows:

$$\alpha' = \left[1 - (1 - k_w)V_p\right]\alpha\tag{3.4}$$

where,  $\alpha' = \text{packing density corrected with wall effect}$ 

 $\alpha$  = measured value of packing density

 $V_p$  = disturbed volume by the wall effect

 $k_w$  = constant depending on particle angularity (0.88 for round particles, and 0.73 for crushed particles)
$V_p$  is calculated under the assumption that, due to the wall loosening effect, packing density is affected within a distance of d/2 from the wall, where d = mean particle size. Hence,

$$Vp = \pi/4 \left[ D^2 H - (D - d)^2 (H - d/2) \right]$$
(3.5)

where:

D = Interior diameter of the container

H = Interior height of the container

Additionally, for the 'Compressible Packing Model' (CPM), virtual packing,  $\varphi$ , is calculated as:

$$\varphi = \alpha' (1 + 1/K) \tag{3.6}$$

where

K = index of compaction (= 9 for 'vibrated-plus-pressure' packing)

# **3.3 Packing Models**

Packing density models provide methodical means of developing particle blends with high packing densities. Such models would reduce the time devoted to trial-and-adjustment experimental work for tailoring mix designs with available combinations of materials. Three major packing models are introduced in this section: (i) Theory of Particle Mixtures (TPM); (ii) Compressible Packing Model (CPM); and (iii) Europack

## 3.3.1 Theory of Particle Mixtures (TPM)

This method [98] requires loose packing density, mean size (based on grading) and the specific gravity (density) of each particulate constituent. For cementitious materials (and other micro-scale fines), packing density is determined using the Vicat test. It has been suggested that the mean diameter of cementitious materials and other micro-scale fines could be estimated using the Blaine fineness test if the size distribution is not available. The TPM method works with

voids ratio (volumetric ratio of voids to solids), U, which can be related to packing density,  $\phi$ , as follows:

$$U = 1/\phi - 1$$
 (3.7)

The voids ratio of a blend of two particulate materials follows the voids ratio diagram shown in Figure 3.5. The coordinates of points A to F can be calculated using the equations presented below together with Tables 3.1 and 3.2 which present the spacing factor (m) and the empirical coefficients ( $k_{int} \& k_p$ ) used in the model.



Figure 3.5- Voids ratio diagram [98].

$$U_n = nU_1^{"}$$
(3.8)

$$n = \frac{U_{o}^{*}}{(1 + U_{1}^{*} + U_{o}^{*})}$$
(3.9)

$$U_{1}^{"} = \frac{(1+U_{1})U_{o}^{"}}{(1+U_{o}^{"}) - (1+Z)^{3}} - 1$$
(3.10)

$$n = \frac{U_{o}^{*}}{(1 + U_{1}^{*} + U_{o}^{*})}$$
(3.11)

$$Z = k_{int} + [(1 + U_o)^{1/3} - 1 - k_{int}]r^{kp}$$

$$U_o^* = (1 + U_o)(1 + mr)^3 - 1$$
(3.12)
(3.13)

Points in voids ratio diagram	Spacing factor , m
A (n=0)	0
В	0.3
С	0.75
D	3
E	7.5
F (n=1)	α

Table 3.1 Spacing factors (m) [98].

Table 3.2 Empirical coefficients (k<sub>int</sub> and k<sub>p</sub>) [98]

Point in voids ratio diagram	K <sub>int</sub>	K <sub>p</sub>
В	0.12	0.60
С	0.06	0.65
D	0.015	0.80
Е	0.0	0.90

# 3.3.2 Compressible Packing Model (CPM):

CPM is a mathematic model which recognizes that packing density is a function of the combined effects of the shape, texture and grading of particulate constituents (and their proportions), and the compaction method. A compaction method using vibration and pressure is suggested to improve the predictions of the model. The model can account for the presence of supplementary cementitous materials (mineral admixtures). CPM can be used to determine the water demand of

concrete (in terms of the packing structure, water/binder ratio, and targeted material properties) [99] . Some key outcomes of the model include packing density of aggregates and concrete, rheological characteristics of fresh concrete (yield stress and plastic viscosity), slump, air content, stability and placeability, heat of hydration, and hardened concrete compressive strength and shrinkage.

CPM allows for combined use of many cementitious materials and aggregate constituents. The packing density and mean diameter of each particulate constituent have to be determined. For cementitious materials and other micro-scale fines, packing density is determined based on measurement of water demand; the original work uses vibrated-plus-pressure packing density.

Inputs to the CPM model include the density, mean size, and virtual packing of each particulate constituent. Virtual packing is the maximum packing that could be obtained theoretically via particle by particle accommodation, and corresponds to a compaction factor, K, of infinity. In reality, it is not possible to attain such a high degree of packing; therefore, virtual packing is calculated by measuring the packing density,  $\varphi$ , and using Equation 3.14 with the compaction factor, K, corresponding to the compaction method used (presented in Table 3.3).

In order to determine the virtual packing density,  $\phi_v$ , first the actual packing is obtained experimentally; subsequently, depending on the compaction method, virtual packing is calculated using Equation 3.14, which is a particular case of Equation 3.15 for mono-sized particles.

$$\varphi_{v} = \varphi / (1/k + 1)$$
 (3.14)

$$K = \sum k_{i} = \sum_{i=1}^{n} \left[ (y_{i} / \varphi v_{i}) / (1 / \varphi - 1 / \gamma i) \right]$$
(3.15)

where,  $K = \text{compaction index which is a measure of the energy required to compact a mix, and ranges from 4 to 9 representing loose to hard compaction of pure aggregate [98] (Table 3.3 for typical values)$ 

n= number of fractions [100]

 $\varphi_{vi}$  = virtual packing of each fraction

 $y_i = volume of each fraction$ 

 $\gamma_i$  = virtual packing of the blend when class i is dominant

$$\gamma_{i} = \frac{\beta_{i}}{1 - \sum_{j=1}^{i-1} \left[ 1 - \beta_{i} + b_{ji} \beta_{i} (1 - 1/\beta_{j}) \right] y_{j} - \sum_{j=i+1}^{n} \left[ 1 - a_{ij} \beta_{i} / \beta_{j} \right] y_{j}}$$
(3.16)

where:

 $y_i$  = volume fraction of size class i related to the total solid volume (including volume of fiber with size  $d_p$ ) [100]

 $\beta_i$  = residual packing density of size class i

a<sub>ji</sub> and b<sub>ij</sub>, represent the loosening effect and the wall effect exerted on grains (Figure 3.6)

$$a_{ij} = \sqrt{1 - (1 - d_j / d_i)^{1.02}} \quad \text{when } d_j \le d_i$$
(3.17)

$$b_{ij} = 1 - (1 - d_i / d_j)^{1.50}$$
 when  $d_i \le d_j$  (3.18)

The wall and loosening effects occur when fines in the blend of particulate matter occur in the vicinity of coarse aggregates (or boundaries) [101]. Wall effect produces increased void contents near coarse particles or other boundaries, and loosening effect yields increased void contents when fine particles disrupt optimum packing of coarse particles.



Figure 3.6 Wall and loosening effects in a binary blend of particulate matter [102].

Table 3.3 Values of the compaction factor (index) for different compaction methods [98].

Compaction Method	К
Loose / Simple Pouring	4.1
Striking with Rod	4.5
Vibration	4.75
Vibration + Pressure	9.0
Wet Packing	6.5

For mixes with fiber, the best fit has been found with K=3.6 [103]

Figure 3.7 shows the relationship between compaction factor and packing density. A compaction method combining vibration and 10 MPa with >74  $\mu$ m (plus No. 200) particle size is found to yield a compaction factor of 9. A water demand test has been suggested for cementitious materials and other micro-scale fines [98].



Figure 3.7 Compaction index (K) versus packing density (φ) [98].

## 3.3.2 Europack

Europack is software which is used for determining the proportions of particulate matter (aggregates and cementitious materials). Europack requires the following input information: specific gravity (density), dry rodded packing density (ASTM C29), and characteristic diameter of each particular component. Characteristic diameter is defined as the diameter for which the cumulative probability of the Rosin-Raimmier distribution is 0.37 [97]. This corresponds approximately to the sieve size associated with 63% of the material passing. Europack determines the packing density of 'n' particulate constituents by combining two or three at a time. Once the proportions of aggregates and cementitious materials have been selected, the required amount of water can be determined using conventional concrete mix proportioning methods (e.g., ACI 211) [104]. Europack yields ternary and binary diagrams (Figure 3.8) which depict the packing density for different values of three or two particulate constituents.



Figure 3.8 A typical outcome of Europack [98].

# **3.4 Equivalent Diameter of Fibers**

Based on the assumption that replacing a non-spherical particle with a virtual spherical particle can produce a similar packing behavior, a model has been proposed for calculating the equivalent diameter for virtual spherical replacements of cylindrical particles:

$$d_{p} = \left(3.1787 - 3.6821 \times \frac{1}{\varphi} + 1.5040 \times \frac{1}{\varphi^{2}}\right) \times d_{v}$$
(3.19)

where,  $d_p$  is the equivalent packing diameter,  $d_v$  is the volume diameter (diameter of a sphere having the same volume as the particle), and  $\phi$  is the sphericity (ratio of the surface area of the sphere having the same volume as the particle, to the actual surface area of the particle). The values of  $d_v$  and  $\phi$  can be obtained as follows:

$$d_v = 1.145 \times \sqrt[3]{L_f/d_f} \times d_f \tag{3.20}$$

$$\varphi = 2.624 \times \frac{\left(\sqrt[3]{(L_f/d_f)}\right)^2}{1 + 2 \times (L_f/d_f)}$$
(3.21)

where:

d<sub>f</sub> is the fiber diameter (mm)

 $L_{f}$  is the fiber length (mm).

The compressible packing model (CPM) has been modified for calculating the packing density of multi-component aggregate/fiber blends where fibers are treated as described above. The model was extended by treating fibers as spherical particles with equivalent packing diameter  $d_p$ .

# **3.5** Applications of Compressible Packing Model (CPM) to Different Classes of Concrete.

The compressible packing model (CPM) was used for evaluation of the packing behavior of the following classes of concrete: (i) ultra-high-performance concrete UHPC), including one with nanofiber; (ii) high-strength concrete (HSC); (iii) normal-strength concrete (NSC); (iv) self-consolidating ultra-high-performance concrete SCC UHPC); and (v) self-consolidating normal-strength concrete (SCC NSC).

The mix designs, calculated packing densities and the relative contributions of each particulate (or fibrous) constituent of the various classes of concrete considered in packing analyses are summarized from Table 3.4 to 4.18 and Figures from 3.9 to 3.20. Figure 3.21 compares the packing density of normal strength concrete (NSC), high strength concrete (HSC) and ultra-high performance concrete (UHPC) with normal fresh mix workability (i.e., not self-consolidating). Packing density is observed to increase with increasing concrete strength, which is expected due

to the lower porosity of concrete materials with higher Packing density. A similar trend is observed with self-consolidating concrete materials (Figure 3.22). Relative contributions of different particulate constituents towards packing of normal strength, high strength and ultrahigh performance concrete materials are presented in Figure 3.23. These results indicate that concrete materials with increasing strength levels tend to receive greater contributions from finer particular materials towards achieving higher Packing levels. The contribution of micro-scale fibers towards packing density of ultra-high performance concrete is close to 10%. The nanofiber dosage we have identified (which is significantly less than that of micro-scale fibers) also makes a contribution of about 10% towards packing density of ultra-high performance concrete. In the case of self-consolidating concrete materials (Figure 3.24), finer particulate matter tends to contribute more towards Packing with increasing compressive strength (as was the case with non-self-consolidating concrete). In the single self-consolidating ultra-high performance concrete concrete considered here, the contribution of micro-scale fiber toward Packing is about half that of non-self-consolidating ultra-high performance concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Micro Sliced	75	0.82	0.59	0.20	0.12	
Cement	500	0.81	0.45	0.34	0.21	
Sand≤2mm	680	0.81	0.40	0.39	0.24	
Limestone	243	0.81	0.54	0.25	0.15	
Steelfiber (L/D=30/0.55)	5.75	0.79	0.70	0.09	0.06	0.79
(Crushed Limestone) < 10 mm)	850	0.87	0.44	0.35	0.22	
Water	127					
Superplasticiser/Cement	3.7%					

Table 3.4 Ultra-high-performance concrete [12].



Figure 3.9 Contributions of different constituent materials in Table 3.4 to the packing density Ultra-high-performance concrete.

Material type	wt (gram)	% Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Silica fume	300	0.69	0.38	0.40	0.16	
cement	900	0.65	0.35	0.43	0.18	
CNF	1.05	0.61	0.57	0.21	0.09	
Sand(0-0.18)	360	0.60	0.45	0.33	0.14	
Sand (0.18-0.5)	860	0.67	0.33	0.45	0.19	
Steel fiber 13mm/0.175	88.76	0.44	0.58	0.20	0.08	0.78
Gravel	500	0.80	0.40	0.38	0.16	
Water	240					
Superplasticizer	59.2					

Table 3.5 Ultra-high-performance concrete [105].



Figure 3.10 Contributions of different constituent materials in Table 3.5 to the packing density of ultra-high-performance concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Steelfibers12mm/0.2mm	156	0.97	0.67	0.11	0.09	
Fine sand (150 - 600 $\mu$ m )	1020	0.92	0.39	0.39	0.33	
Portland cement	712	0.68	0.45	0.33	0.28	0.79
Ground quartz	211	0.77	0.58	0.19	0.16	0. 78
Silica fume	231	0.75	0.62	0.16	0.14	
Superplasticizer	30.7					
Accelerator	30					
water	109					

Table 3.6 Ultra-high-performance concrete [94]



Figure 3.11 Contributions of different constituent materials in Table 3.6 to the packing density of ultra-high-performance concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% contribution	Total Packing density
Slica Fume	59.4	0.71	0.64	0.04	0.05	
Cement	448	0.69	0.47	0.21	0.25	
Fine Agg <4.75 mm)	497	0.72	0.45	0.23	0.27	0.68
Coarse Agg ( $\leq 19$ mm)	1160	0.74	0.32	0.36	0.43	0.08
Super plasticizer	12.4					
Water	217.4					

Table 3.7 High strength concrete



Figure 3.12 Contributions of different constituent materials in Table 3.7 to the packing density of high-strength concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Cement	500	0.74	0.52	0.15	0.26	
Silica Fume	40	0.77	0.60	0.06	0.06	
Fine Agg. <4.75 mm)	700	0.75	0.49	0.27	0.29	
Gravel (≤ 19mm)	1100	0.52	0.39	0.37	0.39	067
Super plasticizer (L/100 kg)	2.5					
Water	162					

Table 3.8 High strength concrete [106].



Figure 3.13 Contributions of different constituent materials in Table 3.8 to the packing density of high-strength concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Cement	586	0.78	0.64	0.13	0.27	
Sand <4.75 mm)	611	0.83	0.65	0.12	0.26	
Limestone Agg (≤ 19 mm)	1139	0.87	0.54	0.23	0.47	0.77
Super plasticizer (kg/cwt)	0.77					0.77
Water	146.5					
W/C	0.25					

Table 3.9 High strength concrete [107]



Figure 3.14 Contributions of different constituent materials in Table 3.9 to the packing density of high-strength concrete.

Material type	Wt. (gra m)	Packi ng densit y	Packing density w/o material type	% Rise	% Contributi on	Total packi ng densit y
Cement Type III	251	0.53	0.56	0.12	0.18	
NaturalConcreteRiverSand<4.75	768	0.79	0.47	0.21	0.31	
Crushed Limestone (≤ 19mm)	1112	0.84	0.42	0.26	0.39	0.68
Fly Ash Class C	84	0.71	0.60	0.08	0.12	
Super plasticizer	0.8					
Water	131					
Retarder	0.6					

Table 3.10 Normal strength concrete [108]<sup>I</sup>.



Figure 3.15 Contributions of different constituent materials in Table 3.10 to the packing density of normal-strength concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Cement Type III	335	0.75	0.65	0.04	0.11	
Natural Concrete River Sand <4.75 mm)	768	0.76	0.56	0.13	0.34	
Crushed Limestone (≤ 19mm)	1112	0.70	0.48	0.21	0.55	0.69
Super plasticizer	1.8					
Water	148					
Retarder	0.6					

Table 3.11 Normal strength concrete  $[108]^{II}$ 



Figure 3.16 Contributions of different constituent materials in Table 3.11 to the packing density of normal-strength concert.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Cement Type I	450	0.75	0.60	0.05	0.27	
Fine Agg <4.75 mm)	680	0.72	0.60	0.05	0.17	
Gravel (≤19mm)	1150	0.73	0.46	0.19	0.66	0.65
Super plasticizer (L/100 kg)	1.5					
Water	180					

Table 3.12 Normal strength concrete [106].



Figure 3.17 Contribution of different constituent materials in Table 3.12 to the packing density of normal-strength concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Cement	460	0.72	0.59	0.13	0.23	
Fine Agg <4.75 mm)	648	0.68	0.55	0.17	0.31	
Coarse Agg ( $\leq$ 19mm)	1180.4	0.78	0.46	0.26	0.45	0.72
Super plasticizer	2.3					
Water	193.3					

Table 3.13 Self-consolidating normal-strength concrete.



Figure 3.18 Contributions of different constituent materials in Table 3.13 to the packing density of self-consolidating normal-strength concrete

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
cement	499	0.60	0.53	0.13	0.23	
Fly ash	141	0.60	0.64	0.02	0.04	
Fine Agg <4.75 mm)	743	0.76	0.45	0.21	0.37	
Coarse Agg limestone (≤ 16mm)	759	0.83	0.45	0.21	0.37	0.66
Water	198					
Superplascticizer % powder content	0.76					

Table 3.14 Self-consolidating normal-strength concrete [109].



Figure 3.19 Contributions of different constituent materials in Table 3.14 to the packing density of self-consolidating normal-strength concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Cement	264	0.76	0.54	0.16	0.16	
Slice Fume	36	0.64	0.68	0.02	0.02	
Lime Powder	180	0.66	0.58	0.12	0.12	
Natural sand <4.75 mm)	917	0.75	0.35	0.35	0.35	
Coarse Agg. limestone (≤ 20mm)	764	088	0.34	0.36	0.36	0.70
Super plasticizer% (powder content)	2.2					
Water	192					

Table 3.15 Self-consolidating normal-strength concrete [110].



Figure 3.20 Contributions of different constituent materials in Table 3.15 to the packing density of self-consolidating normal-strength concrete.

Material type	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Silica fume	200	0.76	0.65	0.07	0.07	
Quartz powder (0- 10µm)	285	0.69	0.40	0.32	0.35	
Cement	665	0.70	0.52	0.20	0.22	0.72
Quartz (0.3-0.8mm)	1019	0.90	0.39	0.33	0.36	
Superplasticizer	23					
Water	178					

Table 3.16 UHPCSCC concrete mixes [111].



Figure 3.21 Contributions of different constituent materials in Table 3.16 to the packing density of self-consolidating ultra-high performance concrete.

Material type	Wt. (gram)	packing density	packing density w/o material type		% Contribution	Total packing density
silica fume	183	0.73	0.68	0.07	0.07	
quartz (0.3-0.8mm)	398	0.87	0.47	0.28	0.29	
quartz powder (0- 10µm)	261	0.69	0.56	0.19	0.19	
cement	609	0.74	0.57	0.18	0.18	0.75
crushed basalt (2- 5mm)	936	0.88	0.49	0.26	0.27	
superplasticizer	21.1					
water	163					

Table 3.17 Self-consolidating ultra-high-performance concrete [111]



Figure 3.22 Contributions of different constituent materials in Table 3.17 to the packing density of self-consolidating normal-strength concrete.

Type of particle	Wt. (gram)	Packing density	Packing density w/o material type	% Rise	% Contribution	Total packing density
Silica fume	270	0.70	0.51	0.21	0.19	
Cement	950	062	0.37	0.35	0.32	
Quartz powder (50µm)	350	0.69	0.52	0.20	0.18	
Quartz (0-0.5mm)	550	0.92	0.43	0.29	0.26	0.72
Steel Fiber (L/d= 8/0.15)	310	092	0.66	0.06	0.05	
Superplasticizer	55					
Water	235					

Table 3.18 Self-consolidating ultra-high-performance concrete [112].



Figure 3.23 Contributions of different constituent materials in Table 3.18 to the packing density of self-consolidating ultra-high performance concrete.



Figure 3.24 Packing densities of normal strength concrete (NSC), high strength concrete (HSC) and ultra-high-performance concrete (UHPC) materials with normal fresh mix workability (means & standard errors).



Figure 3.25 Packing densities of self-consolidating normal strength concrete (SCCNSC) and self-consolidating ultra-high performance concrete (SCC UHPC) (means & standard errors).



Figure 3.26 Relative contributions of different particulate constituents towards packing of selfconsolidating normal strength concrete (SCC NSC) and self-consolidation ultra-high performance concrete (SCC UHPC) (means & standard errors).



Figure 3.27 Relative contributions of different particulate constituents towards packing of selfconsolidating normal strength concrete (SCC NSC) and self-consolidation ultra-high performance concrete (SCC UHPC) (means & standard errors).



Figure 3.28 Relative contributions of different particulate constituents towards packing of selfconsolidating normal strength concrete (SCC NSC) and self-consolidation ultra-high performance concrete (SCC UHPC) (means & standard errors).

## **3.6 Development of UHPC Mix Design Procedures**

## 3.6.1 Packing Density of UHPC

The blend of all particulate matter (aggregates, cement, supplementary cementitious materials, powder, etc.) used in UHPC should provide a particle size distribution which favors achievement of high packing densities. The convenient approach to satisfying this requirement, which has so far governed the design of UHPC mixtures, involves (Figure 3.29) elimination of coarse aggregate, limiting the maximum size of fine aggregate to about 0.6 mm [113], replacement of a relatively large fraction of cement with substantially finer silica fume [114], and occasional use of powders (fillers) with fineness levels intermediate between those of cement and silica fume [113] or even finer than that of silica fume [115]. The conservatism which is prevalent in design of UHPC mixtures has led to a strong emphasis on the use of distinctly high-quality aggregates and fillers [113, 116]. These conservative measures, however, require use of materials which are unfamiliar to the concrete industry, and are not readily available in many locations. Few exploratory investigations, on the other hand, have indicated that UHPC can be produced with more conventional and readily available materials [117-119]. These investigations have demonstrated the viability of using commonly available fine and even coarse aggregates in UHPC as far as the blend of granular matter (including cementitious materials) is proportioned to yield desired particle size distributions. The potential for beneficial use of abundant supplementary cementitious materials (ground granulated blast furnace slag and coal fly ash) in conjunction with cement and silica fume [113, 120], and replacement of silica fume with rice husk ash [121, 122] in UHPC have also been demonstrated. One purpose of this section is to develop guidelines for proportioning locally available particulate (granular) matter (including cement, silica fume, other supplementary cementitious materials, aggregates, fibers, and

optionally commonly available powder) for achieving a dense particle packing without compromising the potential for achieving desired fresh mix characteristics.



Figure 3.29 Typical size distributions of the particulate matter used in UHPC [123].

Design of a dense granular structure constitutes the foundation for design of UHPC mixtures. The granular structure in UHPC should yield a desired balance of rheological attributes, packing density, and chemical reactivity of constituents. Packing density models provide methodical means of developing particle blends with high packing densities. Such models would reduce the time devoted to trial-and-adjustment experimental work for tailoring mix designs to suit available materials. A number of packing models are available, including those reviewed in previous sections. Compressible Packing Model (CPM) was used to develop the mix design procedures for UHPC. This model was presented in section 3.3(ii), with supplementary information provided in section 3.4.

## **3.6.2** Selection of Particulate Components

Crushed granites obtained from Michigan (MI) and New Mexico (NM) were used as coarse aggregates. MI and NM natural sands were used as fine aggregates. Ordinary Type I Portland cement (manufactured by Lafarge) was used in UHPC mixture. Silica fume was provided by Norchem, and ground granulated blast-furnace slag (GGBFS) was supplied by the Lafarge South Chicago plant (Grade 100 Newcem). Quartz powder with an average particle size of 3.9 µm was provided by AGSCO Corporation, Illinois. The particle size distributions of these particulate constituents are shown in Figure 3.30; these size distributions were assessed by sieve analysis, or provided by manufactures. The packing density of each particulate constituent was measured by weighing a one-liter container filled with the particles consolidated on a vibrating table over two minutes. The measured values of packing density are presented in Figure 3.31.



Figure 3.30 Particle size distributions of aggregates, cement, slag, silica fume, and quartz powder.



Figure 3.31 Measured packing densities of the various particulate constituents used in UHPC.

Prior to optimizing the UHPC mix proportions for maximizing the overall packing density, aggregates alone were proportioned to maximize their packing density and minimize void content. The reduced void content between aggregate particles benefits the fresh mix workability of UHPC at a constant binder-to-aggregate ratio. This is because the binder content required to fill the voids between aggregates is minimized, leaving more of the binder content available for coating and lubricating the aggregates (i.e., reducing the inter-particle friction) and thus improving fresh mix workability

Table 3.19 shows the initial UHPC mix designs, and their packing densities predicted using the packing density equations (Eqs. 3.16 through 3.18, and also Eqs. 3.19 and 3.20). Mix #1 has 55 vol. % crushed granite, and 45 vol. % natural sand; the binder comprises 70% cement, 10% silica

fume and 20% slag. The predicted packing density of Mix #1 is 0.723. In Mix #2, where the silica fume content of binder was increased to 20%, the slag content was decreased to 10%, and quartz powder was introduced as 20% of total binder composition, packing density increased to 0.787, which is at a satisfactory level for UHPC. Packing density decreased for Mix #3 where, when compared with Mix #2, the quartz content of binder was lowered to 10% and the slag content raised to 20%. In Mix #4 when compared with Mix #3, the crushed aggregate and natural sand decreased were by 30%, 10% respectively, silica sand was added to keep total aggregate constant, limestone powder was increased 8%, silica fume content was increase by 10%, the packing density increased to 0.788 Mix # 5 when compared with Mix# 4, incorporated by steel fiber 1.1 vol. %, introduction of steel increased the packing density by 3.2%. In Mix #6 when compared with Mix #4, nanofiber was added 0.04 vol. % and steel fiber removed; these measures increased the packing density to 4%. Mix #7 incorporated steel fiber and carbon nanofiber, which produced the highest packing density 0.825.

Mix #	1	2	3	4	5	6	7
Total aggregates	1383	1383	1383	1383	1383	1383	1383
Crushed granite (#7)	772.37	772.37	772.37	525.54	525.54	525.54	525.54
Natural sand	610.63	610.63	610.63	553.2	553.2	553.2	553.2
Silica sand	0	0	0	304.26	304.26	304.26	304.26
Binder	1037.25	1037.25	1037.25	1037.25	1037.25	1037.25	1037.25
Cement	726.075	518.625	518.625	518.625	518.625	518.625	518.625
Silica fume	103.725	207.45	207.45	228.195	228.195	228.195	228.195
Slag	207.45	103.725	207.45	103.725	103.725	103.725	103.725
Limestone powder	0	207.45	103.725	186.705	186.705	186.705	186.705
Steel fiber	0	0	0	0	94.212	0	94.212
Carbon nanofiber	0	0	0	0	0	0.69	0.69
Packing density	0.723	0.787	0.778	0.788	0.813	0.820	0.827

Table 3.19 Initial UHPC mix designs (kg/m3) and their predicted packing densities.

## 3.6.3 Contributions of Nanomaterial towards Total Packing Density

The test data presented in table 3.19 provided a basis to validate the correlation between the contributions of modified graphite nanomaterials to concrete material properties and the packing density of concrete. It was discovered that nanomaterials, at relatively low volume fraction, make meaningful contributions towards increasing the packing density of ultra-high-performance concrete, thereby benefiting the fresh mix workability and hardened material properties of UHPC. Analysis by the compaction packing model indicated that graphite nanomaterials, at only 0.04 vol. % account for about 9% of the packing density of ultra-high-performance concrete nanocomposites (Figure 3.32). This notable contribution at such low concentration is due to the fine geometry of nanomaterials, which extends the particle size distribution of the particulate matter into the nano-scale range.




#### 3.7 Approach to UHPC Mix Proportioning

The packing density model presented above provided a basis to develop an approach to mix proportioning of ultra-high-performance concrete (UHPC). A flowchart for the approach to UHPC mix design developed in the project is presented in Figure 3.33. This approach was followed in design of UHPC mixtures considered in the experimental work presented in the following chapters.



Figure 3.33 Flowchart outlining the approach to UHPC mix design.

#### **3.8 Discussion**

Fresh concrete is a dispersion of particulate matter with a broad size distribution in water. Addition of graphite nanomaterials extends this size range well into nano-scale dimensions. An important consideration in size gradation of the particulate (and fibrous) matter in ultra-high performance concrete is the need to maximize packing density with due consideration given to the type and extent of the consolidation effort. Theoretical models were employed to determine the packing densities of different categories of concrete materials considered in the experimental program (normal-strength, high-strength, and ultra-high-performance). Packing density was found to be lowest for normal-strength concrete, and highest for ultra-high-performance concrete. Addition of nanomaterials at low dosages was found to make improportionally high contributions to the packing density of concrete materials, which was due to their fine geometry. Experimental results generated in the project confirmed the correlation between the packing density of particulate matter and the contributions of nanomaterials to concrete material properties. This finding indicated that packing density can provide a viable basis for design of ultra-high-performance concrete nanocomposites.

Mix design procedures were developed by maximizing the packing density and ensuring smooth size distribution of the particulate matter in UHPC for achieving ultra-high strength levels and desired fresh mix workability. The packing density model provided the theoretical basis for proportioning the UHPC mixtures. Adequate binder content, use of supplementary cementitious materials of different reactivity and particle size distribution, and use of readily available mineral powders and chemical admixtures constitute other key aspects of UHPC mix design.

# **CHAPTER 4**

# MATERIAL SELECTION, OPTIMIZATION, AND CHARACTERIZATION OF ULTRA-HIGH-PERFORMANCE CONCRETE

# **4.1 Introduction**

Ultra-high-performance concrete (UHPC) achieves distinctly high mechanical, impermeability and durability characteristics by reducing the size and content of capillary pores, refining the microstructure of cement hydrates, and effective use of fiber reinforcement. The dense and fine microstructure of UHPC favors its potential to effectively disperse and interact with nanomaterials, which could complement the reinforcing action of fibers in UHPC. An optimization experimental program was implemented in order to identify the optimum combination of steel or polyvinyl alcohol (PVA) fiber and relatively low-cost carbon nanofiber in UHPC. The optimum volume fractions of steel or PVA fiber and carbon nanofiber were used and as micro- and nano-scale reinforcement identified for balanced improvement of flexural strength, ductility, energy sorption capacity, impact and abrasion resistance of UHPC were 1.1% and 0.04%, respectively. The optimum volume fractions for PVA fiber and carbon nanofiber were 0.37% and 0.047% respectively. Complementary/synergistic actions of nanofibers and steel or PVA fibers in UHPC were noticed, which were attributed to their reinforcing effects at different scales, and the potential benefits of nanofibers towards the interfacial bonding and pullout behavior of fibers in UHPC. Modification techniques which enhanced the hydrophilicity and bonding potential of nanofibers to cement hydrates were used to enhance their reinforcement efficiency in UHPC.

# **4.2 Selection of Materials**

The materials selected for use in ultra-high-performance concrete are described in the following:

# **4.2.1 Cement**

Type I Portland cement was used in all experiments. Table 4.1 present the composition of the type I Portland cement used in the project.

Oxide	Content, per cent
CaO	60-70
SiO <sub>2</sub>	17-25
AL <sub>2</sub> O <sub>3</sub>	3-8
Fe <sub>2</sub> O <sub>3</sub>	0.5-6.0
MgO	0.5-4.0
Alkalis (as Na <sub>2</sub> O)	0.3-1.2
SO <sub>3</sub>	2.0-3.5

Table 4.1 Composition of the Type I Portland cement.

## 4.2.2 Aggregates

Aggregates significantly impact the performance characteristics of UHPC. While the focus of the project is on the use of locally available materials for scalable and economical production of UHPC, aggregates should still be selected carefully for use in UHPC. Coarse aggregates of

different types, shapes, textures, strengths and mineralogy will make different contributions to the mechanical and physical attributes of UHPC [8, 124] An investigation by Wu et al. [125] indicated that the effect of coarse aggregate type on the strength of concrete tends to be more significant in higher-strength concrete.

Figure 4.1 shows an aggregate classification map for the United States, which provides general types, classified based on hardness that are abundantly available aggregate qualities expected in different geographic regions. Dense limestone, granite, and harder aggregates are recommended for use in UHPC. For selected rock types, attention should be paid to the physical and mechanical properties of rocks, which may vary depending on their origins. Direct measurement of the unconfined compressive strength of rocks may be considered simple, but it is expensive and time-consuming, and requires well-prepared rock samples which may not be available. Other indirect tests, such as Schmidt rebound number, point load index, Shore hardness, sound velocity and Los Angeles abrasion can be used [126-130]. In this research, the L.A. abrasion test was used as an indirect measure for the mechanical properties of the aggregates received from Michigan and other states.



Figure 4.1 The Classification map of the United States for aggregates [131].

Other important criteria for selection of coarse aggregates suiting UHPC are maximum size and particle size distribution. It is commonly accepted that aggregate size should be decreased as the targeted strength of concrete increases. Beyond 140 to 200 MPa (20 to 30 ksi), the aggregate size should not exceed 10 mm (3/8) in in structural concrete [132], although some experimental studies have suggested that UHPC with aggregates up to 19 mm (3/4 in) may produce compressive strengths as high as 180 MPa (26 ksi) [120, 133]. It should be noted that existing UHPC mixture do not generally use coarse aggregates. This research used locally available crushed granite and limestone from mid-Michigan and New Mexico (the vicinity of Holloman AFB) as coarse aggregate in UHPC.

Readily available natural sand from Michigan and New Mexico were used as fine aggregates in UHPC, and silica sand was used occasionally used to improve the packing density of the particulate matter. Fineness moduli ranging from 2.5 to 3.2 are recommended for the fine aggregates used in high-strength concrete in order to realize desired fresh mix workability [132].

## **4.2.2.1 Experimental Evaluation of Aggregates**

The following properties of the fine and coarse aggregates selected for use in UHPC were evaluated: bulk specific gravity, absorption capacity, L.A. abrasion, and soundness. The bulk specific gravity and absorption capacity of coarse aggregates were tested following ASTM C127 procedures. The ASTM C131 methods were used for conducting the L.A. abrasion tests on coarse aggregates. In the case of fine aggregates, abrasion resistance was assessed using the Micro-Deval abrasion test following ASTM D7428 procedures.

#### 4.2.2.1.1 Micro-Deval Abrasion Test Result for Fine Aggregates

The Micro-Deval test method has been found to provide a good measure for the amount of weak, soft materials such as shale in fine aggregate (sand). The gradation of natural sands to be used in this test is shown in Table 4.2.

Passing		Retained			
Sieve No.	Opening (mm)	Sieve No.	Opening (mm)	Mass (g) (%)	(%)
4	4.75	8	2.36	50	10
8	2.36	16	1.18	125	25
16	1.18	30	0.600	125	25
30	0.60	50	0.300	100	20
50	0.30	100	0.150	75	15
100	0.15	200	0.075	25	5
Total mass of sample			500		

Table 4.2 Fine aggregate gradation for Micro-Deval test.

After drying of sand specimens, 500 g of sand was soaked in water for 24 hours. The sample was then placed in a ball mill (Figure 4.2a) with 750 ml of water and 1250 g of  $9.5\pm0.5$  mm diameter steel balls (Figure 4.2b) to abrade the sand sample. The ball mill used for performance of the Micro-Deval test was rotated at 100 revolution per minute (rpm) for 15 minutes. The sample was then washed to remove <75 µm matter, oven dried, and weighed. The percent loss of the original mass of sand was calculated. Experimental results (Figure 4.3) indicated that the Michigan (MI) and New Mexico (NM) natural sands are comparable in terms of percent loss (12%), which is a good performance per Canadian specification which requires a maximum micro Deval loss of 20% for concrete sand [134].



Drum



Steel balls

Figure 4.2 The drum and steel balls used in Micro-Deval test.



Figure 4.3 Percent weight losses of fine aggregates

## 4.2.2.1.2 Los Angeles Abrasion Test Results for Coarse Aggregates

The L.A. abrasion test measures the weight loss of a coarse aggregate sample placed in a rotating drum (Figure 4.4a) with steel balls (Figure 4.4b). As the drum rotates, aggregates degrades by abrasion and impact with steel balls and other aggregate particles. Once the test is complete, the calculated mass of aggregate that has broken apart to smaller sizes is expressed as a percentage

of the total mass of aggregate. Therefore, lower values of L.A. abrasion loss indicate aggregates that are tougher and more resistant to abrasion.



Drum



(b) Steel balls

Figure 4.4 Los Angeles abrasion test equipment and steel balls.

The L.A. abrasion test results for Michigan and New Mexico coarse aggregates are presented in Figure 4.5. The results reported in the literature for different coarse aggregates are presented in Figure 4.6. A comparison of Figures 4.5 and 4.6 indicates that the L.A. abrasion loss for the limestone coarse aggregate (39%) is high when compared with the typical loss value of 30%, indicating that the limestone considered here is of low quality. Therefore, limestone was not used in production of UHPC. Both MI and NM granites offer desired L.A. abrasion losses.



Figure 4.5 Los Angeles abrasion losses of coarse aggregates.



Figure 4.6 Reported values of Los Angeles abrasion loss for different coarse aggregates [135].

4.2.2.1.3 Density, Water Absorption Capacity and L.A. abrasion Test Results

Table 4.3 presents the density, water absorption capacity and L.A. abrasion test results for the coarse and fine aggregates selected for use in ultra-high-performance concrete (UHPC). The abrasion test

Materials	Density g/cm3	Absorption %	L.A. abrasion %
Granite (MI)	2.67	1.10	21.0 (LA)
Granite (NM)	2.67	2.67	18.3 (LA)
Natural sand (MI)	2.59	1.38	12.1 (Micro-Devel)

Table 4.3 Physical and mechanical properties of local aggregates.

#### 4.2.3 Carbon Nanofiber (CNF)

The relatively low cost of CNF is an attractive feature in development of bulk composite materials for structural applications. High mechanical properties, low coefficient of thermal expansion, and high electrical conductivity are achieved in CNF reinforced composites [136]. Carbon nanofibers are assemblies of graphene cones; secondary bonding of these cones compromises the tensile properties of carbon nanofibers. The cost of preparing carbon nanofibers is less than that of carbon nanotubes due to the synthesis techniques used [137]. The carbon nanofibers (Figure 7) used in UHPC mixtures have diameters in the 60-150 nm range, and lengths ranging from 30 to 100  $\mu$ m, specific surface area of 50-60 m<sup>2</sup>/g, true density of ~1.95 g/cm3, and purity of >95%. These nanofibers were purchased from Pyrograf Products, Inc.



Figure 4.7 Transmission electron microscope images of carbon nanofibers.

# 4.2.4 Steel Fiber (SF)

The steel fiber was Dramix straight high- strength fiber copper coated with 13 mm (0.51 in) length and 0.2 mm (0.008 in) diameter (aspect ratio = 65),, with a tensile strength of between 690 and 1000 MPa (96,600 and 140,000 psi) and a modulus of elasticity of 210,000 MPa (30,457 ksi), according to the manufacturer was used in UHPC nanocomposites mixtures, (Figure 4.8a) .

# 4.2.5 Polyvinyl Alcohol Fiber (PVA)

The PVA (polyvinyl Alcohol) fiber used in UHPC (Figure 4.8b) was 13 mm (0.512 in) in length and 100  $\mu$ m (0.004 in) in diameter, specific gravity of 1.3 and tensile strength of 1200 MPa (174Ksi).



(a) Steel fibers



(b) PVA fibers

Figure 4.8 Fibers used in UHPC mixtures.

# **4.3 Experimental Optimization of Carbon Nanofiber Use in Ultra-High-Performance Concrete in Combination with Steel Fiber**

Developments in ultra-high-performance concrete (UHPC) have been enabled by the use of relatively large volume fractions of (steel) fibers which overcome the problems with the brittleness and (to some extent) the susceptibility to (restrained autogeneous) shrinkage cracking of rich (high-cementitious-content) ultra-high-performance concrete materials. The high compaction density and relatively fine capillary pore system of UHPC makes it a safe starting cementitious matrix for evaluation of the contributions of graphite nanomaterials to concrete material properties.

Efforts towards optimum use of carbon nanofiber in combination with steel fiber were planned in order to verify the following hypotheses: (i) micro- and nano-scale reinforcement systems in ultra-high-performance concrete make complementary contributions towards enhancement of material properties by rendering reinforcing effects at different scales; and (ii) there are synergistic actions of nano- and micro-scale reinforcement in ultra-high-performance concrete because nano-scale reinforcement improves the bonding and pullout behavior of micro-scale reinforcement.

The objective of optimization was to produce a desired balance of fresh mix workability (flow), flexural strength, maximum deformation and energy absorption capacity, abrasion resistance, and compressive strength. These properties were given equal weights in the optimization process. Based on past experience and cost considerations, upper limits of 4 vol.% and 0.24 vol.% were defined in the optimization experimental program for steel fiber and carbon nanofiber dosages, respectively. In later experimental studies, where PVA fiber was used, an upper limit of 2 vol.% was defined for the PVA fiber dosage. It should be noted that an

optimization experimental program generally considers few excursions beyond these upper limits in order to verify their viability.

Optimization experimental programs were implemented in conjunction with the work on surface modification of graphite nanomaterials for improving their compatibility with cementitious matrices. The optimization experimental program was thus conducted with unmodified carbon nanofibers; both modified and unmodified nanofibers were used when the optimum reinforcement system was evaluated.

It is worth mentioning that the use of carbon nanofibers (alone or in combination with steel fibers) impacts a broad range of concrete material properties. The work reported herein deals with a limited breadth of concrete material properties. The term "optimum" dosage of nanofibers would thus be valid for the particular grouping of material properties (and cementitious materials) considered here.

#### 4.3.1 Experimental Program

An optimization experimental program was conducted, with the dosages of carbon nanofiber and steel fiber considered as the variables to be optimized. Based on past experience, preliminary experimental results and cost considerations, upper limits of about 4% and 0.24% by volume of anhydrous cementitious materials were chosen for steel fiber and carbon nanofiber, respectively. It should be noted that an optimization experimental program typically incorporates few excursions beyond these assumed upper limits to test their viability.

The optimization experimental program developed based on response surface analysis principles is summarized in Table 4.4. The materials used in the experimental program and the ultra-high-performance concrete mix design are introduced in the following.

Run	Code	Code	Uncode vol. % of cementations (vol. % of concrete)	Uncode vol. % of cementations (vol. % of concrete)
	CNF-0X	SF	SF	CINF-0X
1	0	-1.414	2 (0.59)	0 (0)
2	1	-1	4 (1.18)	0 (0)
3	0	0	2 (0.59)	0.12 (0.04)
4	-1.414	0	0 (0)	0.12 (0.04)
5	1.414	0	4.8 (1.43)	0.12 (0.04)
6	0	0	2 (0.59)	0.12 (0.04)
7	0	0	2 (0.59)	0.12 (0.04)
8	1	1	4 (1.18)	0.24 (0.08)
9	-1	-1	0 (0)	0 (0)
10	0	0	2 (0.59)	0.12 (0.04)
11	0	0	2 (0.59)	0.12 (0.04)
12	1	1.414	2 (0.59)	0.289 (0.08)
13	-1	1	0 (0)	0.24 (0.08)
14	-1.414	0	1 (0.30)	0 (0)
15	0	0	1 (0.30)	0.12 (0.04)
16	0	1.414	2.414(0.71)	0.12 (0.04)
17	1.414	0	1(0.30)	0.289 (0.09)
18	1	1	2 (0.59)	0.24 (0.04)
19			3(0.89)	0 (0)

 Table 4.4 Volume fractions with respect to anhydrous cementitious materials (concrete) of steel

 fiber and carbon nanofiber used in the optimization experimental program.

The materials used for preparation of ultra-high -erformance concrete mixtures were: Type I Portland cement, undensified silica fume (with ~200 nm mean particle size, ~15 m<sup>2</sup>/g specific surface area, and >105% 7-day pozzolanic activity index), superplasticizer (ADVA® Cast 575,

polycarboxylate-based, conforming to ASTM C494 Type F, designed to impart high workability without segregation tendencies), silica sand (>99.5 wt.% SiO<sub>2</sub>, ball milled and sieved to two particle size categories: 0.1-0.18 mm and 0.18-0.5 mm), granite coarse aggregate (with 8 mm and 3.5 mm maximum and mean particle size, respectively), oxidized carbon nanofiber obtained from Applied Sciences, Inc. (brand name Pyrograf III ® Type PR24), and copper-coated steel fiber.

The ultra-high-perofrmance concrete mix design is presented in Table 4.5. The dosages of steel fiber and carbon nanofiber in this concrete matrix were altered following the optimization experimental program (see Table 4.3).

Mix Ingredient	Relative Weight
Cement Type I	0.75
Silica Fume	0.25
Sand (0 -0.18 mm)	0.3
Sand (0.18- 0.5 mm)	0.42
Gravel ( $\leq 8 \text{ mm}$ )	0.42
Superplasticizer	0.049 ml
water	0.2

Table 4.5 Ultra-high-performance concrete mix design.

#### 4.3.2 Carbon Nanofiber Surface Modification

Dispersion of CNFs in the mixing water of cementitious materials could benefit from modifications which render the CNF surfaces more hydrophilic. The surface modification techniques employed in this study emphasize introduction of hydrophilic groups on the edges of graphene sheets which form the peripheral surface of CNFs. These modifications render the CNF surfaces more hydrophilic, facilitating their dispersion in aqueous media.

Polyacrylic acid (PAA), a polyelectrolyte with high density of COOH groups, was considered for adsorption upon (wrapping of) CNFs in order to improve their dispersion in water and interaction with cement hydrates. For this purpose, CNFs were dispersed in water in the presence of PAA; different polymer-to-nanomaterial weight ratios were investigated, and 0.1:1.0 was found to be the most effective. PAA can, besides dispersing nanofibers in aqueous media by rendering CNF surfaces highly hydrophilic, also effectively interact with the cementitious matrix by forming different secondary and primary bonds with calcium silicate hydrate (C-S-H). PAA can be physisorbed upon (wrapped around) graphite nanomaterials. To accomplish this, nanomaterials were mixed with PAA and superplasticizer in the mixing water of concrete, and stirred overnight.. The resulting dispersion was sonicated for 30 hours, following the procedure described in the following section.

#### 4.3.3 Carbon Nanofiber Dispersion Method

The procedures used for dispersion of CNF in the mixing water of concrete involved: (i) adding the required amounts of oxidized nanofiber and PAA to water, and stirring for 12-15 hours; (ii) sonicateing (Figure 4.9) the mix by repeating a cycle comprising (a) 10 minutes of sonication at 40, 50, 65 and 75% of maximal power (400 watts) with 1-minute breaks in between, (b) pulsing (1 minutes on, 30 second off) for 10 min at 80% of maximal power, and (c) repeating the previous (pulsing) step after 2 minutes of rest.



Figure 4.9 Dispersion of nanomaterials in the mixing water incorporating the superplasticizer.

# 4.3.4 Concrete Preparation

Following dispersion of CNF in the mixing water of concrete, normal concrete mixing procedures (per ASTM D192 and C305) were followed for preparation of UHPC nanocomposite. This procedure involved: (i) mixing the dry ingredients (cement, silica fume, fine and coarse aggregates) for 5 minutes in a mixer (Hobart Model A200F) at Speed 1; (ii) adding water (with dispersed nanomaterials), and mixing for 1 minute at Speed 1, 2 minutes at Speed 2, and (while adding steel fibers) 2 minutes at Speed 3; and (iii) casting concrete into molds per ASTM C192, and consolidating the specimens using a vibration table (FMC Syntron Power Plus) at intensity 10. Specimens were moist-cured inside molds (ASTM C192) at room temperature for 24 hours after casting, and were then demolded and subjected to 48 hours of steam curing at 90°C Figure 4.10. The specimens were then conditioned at 50% relative humidity and ambient temperature for 7 days prior to testing.



Figure 4.10 Steam curing chamber

# 4.3.5 Test Methods

The workability of fresh concrete mixtures was assessed using static and dynamic flow table tests (ASTM C230). Hardened concrete materials were subjected to (i) three-point flexure tests (ASTM C78) on 150×50×12.5 mm prismatic specimens,( Figure 4.11a); (ii) impact tests (ASTM D7136) on 150 mm square plates specimens with thickness of 12 mm, (Figure 4.11b); (iii) abrasion tests (ASTM C944) on cylindrical specimens with 150 mm diameter and 12 mm length, (Figure 4.11c); and (iv) compression tests (ASTM C109) on 50 mm cubic samples, (Figure 4.11d). Three replicated specimens were subjected to each of these tests.



(a) Flexure



(b) Impact

Figure 4.11 Experimental setups.

# Figure 4.11 (cont'd)



(c) Abrasion



(d) Compression

#### **4.3.6 Experimental Results and Discussion**

The trends in fresh mix static and dynamic flow test results (representing fresh mix workability) at different steel fiber and (unmodified) carbon nanofiber volume fractions (with respect to anhydrous cementitious materials) are presented in Figures 4.12. Figure 4.13a and 4.13b shows some minor (anticipated) loss of flow with increasing volume fraction of steel fibers (for different nanofiber volume fractions). Figure 4.13c and 4.13d, however, shows a minor (unexpected) rise in flow (i.e., gain in fresh mix workability) with increasing nanofiber volume fraction (at different steel fiber contents). This is unexpected because the high specific surface area of nanofibers is expected to adsorb a fraction of the mixing water, thus lowering fresh mix workability. The gain in fresh mix workability could have resulted from the rise in the packing density of concrete in the presence of nanomaterials, which enables more effective use of water (with superplasticizer) towards lubricating the particulate matter. Rolling of nanofibers against particulate matter and the highly hydrophilic nature of the modified nanofiber surfaces could also benefit the fresh mix workability.



Figure 4.12 Flow table test for ultra-high performance concrete with and without different volume fractions of nano- and/ or micro-scale reinforcement systems: (a) Static flow, (b) Dynamic flow.



(b)



Figure 4.13 Effects of steel fiber and carbon nanofiber volume fraction (with respect to anhydrous cementitious materials) on fresh mix static and dynamic flow (regression lines and 95% confidence intervals).

Figure 4.13 (cont'd)



(d) Dynamic Flow

The measured values of flexural strength, maximum deflection and energy absorption capacity (obtained from flexure test results), impact resistance, abrasion weight loss and compressive strength are presented in Figure 4.14. It should be noted that the experimental results of Figure 4.14 were produced with unmodified carbon nanofiber. Response surface plots based on these test data, which show the trends in effects of steel fiber and carbon nanofiber volume fractions on different material properties are presented in Figure 4.15. Synergistic actions of steel fibers and CNFs towards improvement of the flexural strength, impact resistance and abrasion weight loss can be observed in the response surface plots presented in Figures 4.15a, 4.15d and 4.15e, respectively, where peaks (or valley in the case of abrasion weight loss) are reached with a hybrid reinforcement systems comprising a moderate volume fraction of steel fiber and a relatively low volume fraction of carbon nanofiber. Similar (but weaker) synergistic actions can be observed for the maximum deflection and compressive strength test data presented in Figures 4.15b and 4.15f, respectively.



Figure 4.14 Results of experiments on hardened ultra-high-performance concrete material properties (means & standard errors).



(b) Maximum deflection



(c) Energy absorption capacity



(d) Impact resistance



(e) Abrasion weight loss




(a) Flexural strength, MPa

Figure 4.15 Response surfaces developed based on the test data produced for ultra-highperformance concrete materials.

Figure 4.15 (cont'd)



(b) Maximum deflection, mm





(c) Energy absorption capacity, N.mm



(d) Impact resistance, mm/mm



Surface plot of ABRA vs. CNF, SF

(e) Abrasion weight loss, g



Surface plot of COMP vs. CNF, SF

(f) Compressive strength, MPa

Desirability (canonical) analysis of experimental results was conducted in order to determine the optimum combination of steel fiber and carbon nanofiber for achieving balanced gains in UHPC. All properties were given similar weight and importance factors in the optimization process. The optimization response surface analysis used the mean values of experimental results as input, and sought to identify the reinforcement condition which simultaneously maximizes flexural strength (21.7 MPa target value), maximum deflection (27.9 mm target value), energy absorption capacity (4800 N.mm target value), impact resistance (6.68 mm/mm target value) and compressive strength (170 MPa target value), and minimizes abrasion weight loss (0.085 g target value). Outcomes of this optimization process indicated that an optimum hybrid reinforcement system comprises CNF at 0.145 vol.% of anhydrous cementitious materials (0.04 vol.% of concrete) and steel fiber at 3.55 vol.% of anhydrous cementitious materials (1.1 vol.% of concrete). This optimum reinforcement system is projected to yield mean flexural strength, maximum deflection, energy absorption capacity, impact resistance, abrasion weight loss and compressive strength values of 19.6 MPa, 26.6 mm, 4900 N.mm, 6.68 mm/mm, 0.085 g and 143 MPa, respectively. The fact that the optimized system comprises both steel fiber and CNF points at their synergistic actions towards enhancement of the UHPC material properties considered here.

# 4.3.7 Characterization of Optimum UHPC Nanocomposite with Unmodified and Modified Carbon Nanofibers

UHPC materials were prepared with the optimum combination of steel fiber and CNF dosages identified above, and were characterized using the experimental methods introduced earlier. While the tests data presented above were produced using unmodified (oxidized) CNFs, optimum systems were produced with unmodified and also with PAA-modified (oxidized) CNFs, noting that PAA modification, introduced earlier, was found to benefit the efficiency of CNF performance in cementitious materials (by improving their dispersion and interfacial interactions). As described earlier, PAA was introduced together with CNFs (at PAA: nanofiber weight ratio of 0.1: 1) to the mixing water of concrete prior to reinforcing the nanofiber dispersion process. Table 3 compares the mean values of flexural strength, maximum deflection, energy absorption capacity, impact resistance, abrasion weight loss and compressive strength of UHPC materials with and without PAA modification of CNFs as well as the corresponding mean values of plain UHPC and with a UHPC relatively high steel fiber content (2 vol.% of anhydrous cementitious materials). The experimental results summarized in Table 4.6 indicate that: (i) the optimum reinforcement system comprising a moderate dosage of steel fiber and a relatively low volume fraction of CNFs produces major gains in diverse UHPC material properties; (ii) PAA modification of CNFs further improves the performance characteristics of UHPC with optimum reinforcement system; and (iii) use of steel fiber at a relatively high volume fraction cannot produce the balanced gains in diverse engineering properties of UHPC enabled by the use of a moderate steel fiber content together with a relatively low CNF content (noting that high steel fiber contents negatively impact the fresh mix workability and economics of UHPC). The optimum combination of steel fiber with PAA-modified CNF brings about 50%, 240%, 2700%, 236%, 1200% and 5% improvements in the flexural strength, maximum deflection, energy absorption capacity, impact resistance, abrasion resistance and compressive strength of (plain) UHPC, respectively. The corresponding improvements in material properties of UHPC with relatively high steel fiber volume fraction are 34%, 54%, -4%, 18%, 400% and 34%, respectively. These findings point at the high value rendered by modified CNF towards enhanced of (fiber reinforced) UHPC material properties.

UHPC Type	Flexural Strength MPa	Maximum Deflection mm	Energy Absorptio n Capacity N.mm	Impact Resistance mm/mm	Abrasion Weight Loss, gr	Compressive Strength MPa
Plain	13.4	1.15	140	1.75	1.5	151
High Steel Fiber Content	15.0	19.0	4106	4.99	0.584	119
Optimum, CNF	19.4	24.4	3669	5.4	.15	152
Optimum, PAA-CNF	20.1	29.2	3925	5.88	0.11	159

Table 4.6 Mean values of material properties for plain and optimally reinforced ultra-highperformance concrete (UHPC) materials, and UHPC with a relatively high steel fiber content.

The experimental results and analyses presented above point at synergistic and complementary effects of CNF and steel fiber in concrete. These effects could be attributed to: (i) reinforcing effects of CNF and steel fiber at different scales, with nanofiber primarily mitigating formation and propagation of microcracks, and steel fiber mainly hindering growth and opening of larger cracks; (ii) beneficial effects of CNFs on the pullout behavior of steel fibers from concrete; and (iii) nano-scale spacing of CNFs in concrete, which significantly benefits the barrier and durability characteristics as well as the abrasion resistance of concrete.

### 4.4 Experimental Optimization of Carbon Nanofiber Use in Ultra-High-

#### **Performance Concrete in Combination with PVA Fibers**

When compared with steel fibers, polymer fibers offer improved stability in adverse environments, lower diameters and higher aspect ratios which could benefit their reinforcement efficiency. Polymer fibers also offer the potential for improving the fire resistance of concrete structures (a sacrificial role associated with their relatively low melt/combustion temperatures). Polymer fibers, on the other hand, provide lower elastic moduli than steel, which reduces their reinforcement efficiency in concrete. Among the polymer fibers used in concrete (polypropylene, PVA, nylon), PVA fibers offer elastic moduli (~30 GPa) which are about an order of magnitude higher than those of polypropylene and nylon (but still well below that of steel, which is 200 GPa). Poly (vinyl alcohol), PVA, has a relatively simple chemical structure with a pendant hydroxyl group which benefits its interfacial interactions with cement hydrates.

Given the distinctions between steel and PVA fibers, an optimization experimental program was conducted in order to determine if the synergistic actions of carbon nanofibers and steel fibers could also occur between carbon nanofibers and PVA fibers.

#### 4.4.1 Experimental program

In order to find the optimum dosage of nano- and micro-scale reinforcement, an optimization program was designed based on the response surface analysis principles. Thirteen different combinations of CNF and PVA fiber volume fractions were considered in this test program. The maximum PVA fiber volume fraction beyond which fresh mix workability would be compromised was identified as 2.0% by volume of anhydrous cementitious materials. An upper limit of 0.24% by volume of anhydrous cementitious materials was chosen for carbon nanofiber. It should be noted that an optimization experimental program incorporates few excursions beyond these upper limits in order to test their viability. The optimization experimental program is presented in Table 4.7.

			Uncode	Uncode	
	Code	Code	vol. % of cementations	vol. % of cementations	
Run			(vol. % of concrete)	(vol. % of concrete)	
CNF		PVA	CNF	PVA	
1	0	0	0.12 (0.04)	1 (0.3)	
2	0	0	0.12 (0.04)	1 (0.3)	
3	0	1.41421	0.12 (0.04)	2.4 (0.7)	
4	-1	1	0 (0)	2 (0.6)	
5	1	-1	0.24 (0.08)	0 (0)	
6	0	0	0.12 (0.04)	1 (0.3)	
7	1	1	0.24 (0.08)	2 (0.6)	
8	0	-1	0.12 (0.04)	0	
9	0	0	0.12 (0.04)	1 (0.3)	
10	-1.4121	0	-0.04971	1 (0.3)	
11	-1	-1	0 (0)	0 (0)	
12	1.41421	0	0.29 (0.097)	1 (0.3)	
13	0	0	0.12 (0.04)	1 (0.3)	

Table 4.7 Volume percent with respects to anhydrous cementitious materials (concrete) of PVAfiber and carbon nanofiber used in the optimization experimental program.

#### **4.4.2 Experimental Results**

The fresh mix (static and dynamic) flow test results for concrete mixtures with CNF and/or PVA reinforcement systems are summarized in Figures 4.16. The trends depicted in Figure 4.17 a and 4.17 b indicate that PVA fibers have pronounced adverse effects on fresh mix workability. Fiber

interactions and adsorption of water on their hydrophilic surfaces are some key factors damaging fresh mix workability. The experimental results presented in Figure 4.17 c and 4.17 d indicate that fresh mix workability is not strongly influenced by the addition of CNF (at the volume fractions considered here).



Figure 4.16 Flow table test for ultra-high performance concrete with and without different volume fractions of nano- and/ or micro-scale reinforcement systems (a) Static flow, (b) Dynamic flow.



(b)



Figure 4.17 Effects of PVA fiber and carbon nanofiber volume fraction (with respect to anhydrous cementitious materials) on fresh mix static and dynamic flow (regression lines and 95% confidence intervals).



139

Typical flexural load-deflection curves for UHPC materials with carbon nanofiber and/or PVA fiber reinforcement are presented in Figure 4.18. The hybrid reinforcement system comprising PVA fiber and carbon nanofiber is observed to transform the brittle UHPC material into a relatively ductile material with improved flexural strength. The flexural strength, maximum deflection and energy absorption capacity as well as the impact resistance, abrasion weight loss and compressive strength test results are presented in Figure 4.19. Response surface plots based on these test data, which show the trends in effects of steel fiber and CNF volume fractions on different material properties are presented in Figure 4.20. Synergistic actions of carbon nanofiber and PVA fiber towards improvement of concrete material properties are observed in the case of impact resistance and maximum deflection test results.



Figure 4.18 Typical flexural load-deflection curves of ultra-high-performance concrete materials with carbon nanofiber and/or PVA fiber reinforcement.



Figure 4.19 Experimental values of hardened ultra-high-performance concrete material properties (means & standard errors).







(d) Impact resistance



(e) Abrasion weight loss



(f) Compressive strength

Surface plot of FLEX vs. CNF, PVA



(a) Flexural strength, MPa

Figure 4.20 Response surfaces developed based on the test data produced for ultra-high-performance concrete materials with PVA and/or carbon nanofiber reinforcement.



Surface plot of DEFL vs. CNF, PVA

(b) Maximum deflection, mm



Surface plot of ACE vs. CNF, PVA

(d) Energy Absorption Capacity, N.mm



Surface plot of IMPACT vs. CNF, PVA

(d) Impact resistance, mm/mm



Surface plot of ABRA vs. CNF, PVA

(e) Abrasion weight loss, gr



(f) Compressive strength, MPa

Desirability (canonical) analysis of experimental results helped determine the optimum combination of PVA fiber and CNF for achieving balanced gains in engineering properties of UHPC. All properties were given similar weights, and the objective of optimization (response surface analysis) was to identify the reinforcement condition which simultaneously maximizes flexural strength (14.3 MPa (2070 psi) target value), maximum deflection (11.0 mm (0.43 in) target value), energy absorption capacity (1400 N.mm (398 lb.in) target value), impact resistance (4.50 mm/mm (4.5 in/in) target value), compressive strength (152 MPa (22 Ksi) target value), static flow (180 mm (7.2 in) target value) and dynamic flow (250 mm (10 in) target value), and minimize abrasion weight loss (1.12 g (0.04 oz) target value). Outcomes of this optimization process indicated that the optimum hybrid reinforcement system comprises carbon nanofiber at 0.17 vol.% of anhydrous cementitious materials (0.047 vol.% of concrete) and PVA fiber at 1.2 vol.% of anhydrous cementitious materials (0.37 vol.% of concrete). This optimum reinforcement system is projected to yield mean flexural strength, maximum deflection, energy absorption capacity, impact resistance, abrasion weight loss, compressive strength, static flow and dynamic flow values of 14.3 MPa (2070 psi), 11.0 mm (0.43 in), 1445 N.mm (411 lb.in), 4.13 mm/mm (4.13 in/in), 1.12 g (0.04 oz) and 139 MPa (20.1 Ksi), 127 mm (5.1 in) and 178 mm (7.0 in), respectively, which represent 9.2%, 1000.0%, 700.0%, 158.2%, 33.9%, 7.5%, -57.5%, and 28.8% improvements, respectively, over the corresponding properties of plain UHPC. The fact that the optimized system comprises both PVA fiber and CNF points at their complementary/synergistic actions towards enhancement of the UHPC material properties.

## 4.5 Comparison of Optimum Reinforcement Systems Incorporating Steel Versus PVA Fiber

The optimization experimental programs based on response surface analysis principles were designed and implemented in order to identify desired combinations of CNF with steel fiber or PVA fiber reinforced UHPC materials. The optimization process involved response surface

analysis of the mean values of experimental results, and sought to identify the reinforcement condition which simultaneously maximizes flexural strength, maximum flexural deflection at failure, flexural energy absorption capacity, impact resistance and compressive strength, and minimizes abrasion weight loss. All these engineering properties were given similar weight and importance.

The desired volume fractions of carbon nanofiber and steel or PVA fiber in different concrete materials, identified through response surface analyses of the optimization test data, are presented in Table 4.8.

	CNF, vol.% of	PVA, vol.% of	SF, vol.% of anhydrous cementitious materials	
	anhydrous cementitious	anhydrous cementitious		
	materials (vol.% of	materials (vol.% of	(vol.% of concrete)	
	concrete	concrete		
CNF+SF	0.145 (0.04)	-	3.55 (1.10)	
CNF+PVA	0.170 (0.05)	1.20 (0.37)	-	

Table 4.8 Optimum nano- and micro-scale reinforcement systems in UHPC.

UHPC materials with these combinations of nano- and micro-scale reinforcement were prepared as described earlier, and subjected to flexure, impact, compression, and abrasion tests.

The measured values of material properties with optimum (nano- and micro-scale) reinforcement systems (and the corresponding % improvements (over plain concrete) are presented in Table 4.9. Prediction of response surface analysis are also presented for comparison.

	UHPC with CNF and SF		UHPC with CNF and PVA	
	Measured	Predicted	Measured	Predicted
Flexural strength (MPa)	20.0 (47%)	19.6	13.9 (4.44%)	14.4
Maximum deflection (mm)	29.2 (2439%)	26.6	10.5 (813%)	11.0
Energy sorption (N mm)	3925 (2703%)	4900	1422 (915%)	1445
Abrasion weight loss (g)	0.11(92%)	0.09	1.18 (21%)	1.12
Impact resistance(mm/mm)	5.88 (236%)	6.09	4.60 (196%)	4.49
Compressive strength (MPa)	159 (5.29%)	154	142 (-5.96%)	139

Table 4.9 Performance characteristics (and % gains over plain concrete) realized with optimum nano- and micro-scale reinforcement systems.

The above comparisons indicate that: (i) the optimum combination of CNF with steel fiber performs markedly better than the optimum combination of CNF with PVA fiber in UHPC (which can be attributed to the high elastic modulus of steel fibers, and the toughening effects associated with inelastic flexural deformations involved in pullout of inclined steel fibers from the cementitious matrix); (ii) the optimum combination of CNF and steel fiber has significantly more fiber volume fraction than the optimum combination of CNF and PVA fiber, which can be attributed to the smaller diameter of PVA fiber and their hydrophilic surfaces which magnify the adverse effects of fibers on fresh mix workability.

The desired complementary effects of micro-scale (steel or PVA) fibers and CNF in concrete can be explained, in part, by the contributions of CNFs to the interfacial stress transfer from fibers to the cementitious matrix.

The SEM images the fractured surface of concrete, presented in Figure 4.21, provide indication for strong bonding of concrete to steel (Figure 4.21 a) and PVA (Figure 4.21 b) fibers. The high-magnification SEM image of Figure 4.22a shows the presence of CNFs within the cementitious paste at the PVA fiber interface zone, where they are expected to render reinforcing effects.

The prevalence of CNF pullout was noted at fractured surfaces (Figure 4.22b); the nanofiber dispersion within cementitious paste was also found to be reasonably uniform.



(a)

Figure 4.21 SEM images of steel fiber (a) and PVA fiber (b) at the fractured surfaces of ultrahigh-performance (UHPC)[93].

Figure 4.21 (cont'd)



(b)



<sup>(</sup>a)

Figure 4.22 (a) High-magnification image of carbon nanofiber (CNF) at a fractured surface of ultra-high-performance concrete (UHPC) near a PVA fiber, (b) SEM image at a fractured surface of UHPC, depicting pullout of uniformly dispersed nanofibers [93].

#### Figure 4.22 (cont'd)



(b)

## 4.6Characterization of Optimized Ultra-High-Performance Concrete Nanocomposites

#### 4.6.1 Experimental Program.

The main thrust of this section is to gain insight into the contributions of optimum nanomaterials and fibers toward improvement of diverse engineering properties of ultra-high-performance concrete. The engineering properties evaluated in this chapter include; slump (ASTM C143) for measurement of fresh mix workability, J-ring (ASTM C1621) for evaluating the fresh mix flow and passing ability, flow table (ASTM C124), compressive strength (ASTM C109) using 76 mm (3 in) diameter by 152 mm (6 in) height cylinders; split cylinder tensile strength (ASTM C496)
using 76mm x 152mm (3 in x 6 in) cylindrical specimens, flexure (ASTM C1018) on 51x51x279 mm (2x2x11 in) prismatic specimens by four-point loading; impact (ASTM D7136) on 150 mm (6 in) on 20 mm (0.8 in) thick; sorption rate (ASTM C1585) on 100 mm (4 in) diameter by 50mm (2 in) high spacemen, direct tension [138] on prismatic specimens 5cmx3cm (2 in x 1.2 in) in cross-section with total length of 29 cm (11.4 in); drying shrinkage length change (ASTM C157) using 76mmx76mmx285mm (3 in. x 3 in. x 11 ¼ in) specimens; and thermal conductivity and specific heat tests on 50mmx50mmx25mm (2inx2inx1in) prismatic specimens.

Comparative evaluations were made between micro-scale versus hybrid reinforcement effects on ultra-high-performance concrete properties in order to further verify the hypothesis that complementary use of nano- and micro-scale reinforcement can provide balanced gains in diverse engineering properties at viable cost, which cannot be achieved when nano- or microscale reinforcement is used alone.

#### **4.6.2 Experimental Results**

#### 4.6.2.1 Slump and Slump Flow

Slump (ASTM C143) (Figure 4.23a) is a common measure of the workability of normal fresh concrete mixtures. In the case of more workable mixtures (approaching or reaching the self-consolidating state), slump flow test (ASTM C1611) (Figure 4.23b) is also used as a measure of fresh mix flowability. The highly workable nature of the UHPC mixtures developed in this project rationalize the use of both slump and slump flow tests for more thorough assessment of fresh mix workability. Acceptable levels of fresh mix workability depend upon the type of structure and the construction method. On large, heavily reinforced concrete structures, a slump of >200 mm (7.87 in) and slump flow of >500 mm (19.69 in) are considered to be acceptable.

For the selected UHPC mixture with different straight steel fiber (SF) and carbon nanofiber (CNF) volume fractions, the slump and slump flow test results are presented in Figures 4.24 and 4.25 respectively. Increasing the steel fiber volume fraction slightly lowered the fresh mix workability. The addition of carbon nanofiber on the other hand, produced a slight improvement in fresh mix workability, which could be attributed to their benefits to the packing density of the particulate matter due to the extension of the size distribution into the nano-scale (which lowers the water content lost to filling the space between particles).



(a)



(b)

Figure 4.23 (a) Slump and (b) slump flow tests.



Figure 4.24 Slump test results for UHPC with steel fiber and carbon nanofiber reinforcement.



Figure 4.25 Slump flow test results for UHPC with steel fiber and carbon nanofiber reinforcement.

# 4.6.2.2 Flexure

The flexure test setup (Figure 4.26) followed the ASTM C1609 procedures for fiber reinforced concrete. This test method enables precise measurement of flexural deformations as net values

exclusive of extraneous effects caused by seating or twisting of specimen on its supports, and any deformations of the support system. The precise measurement of deformations as well as loads enables monitoring of the load-deformation behavior for assessment of the flexural energy absorption capacity and ductility (maximum flexural deformation at failure) of UHPC with discrete reinforcement systems. This setup uses two displacement transducers to obtain the average midspan flexural deformation, and a load cell for measurement of the applied load. The flexure test specimens were 50 mm x50 mm x280 mm (2inx2inx11in) prisms, they were subjected to four-point loading.



Figure 4.26 Flexure test setup.

Plain UHPC failed in a brittle manner (Figure 4.27a), and provided a relatively low flexural strength. UHPCs with different discrete reinforcement systems all exhibited ductile failure modes with extended fiber pullout and desired toughness characteristics (Figure 4.27b). Typical flexural load-deflection curves for plain UHPC and those with different steel fiber and carbon nanofiber reinforcement systems are presented in Figure 4.28a. The flexural strength test data (mean values and standard errors) are summarized in Figure 4.28b. Steel fibers and especially the combination of steel fibers and graphite nanomaterials produced significant (up to 300%) gain in the flexural strength of plain UHPC (which was found to be statistically significant at 0.05 significance level). Any of the discrete fiber reinforcement conditions considered here more than doubled the flexural strength of plain UHPC. This results from the direct reinforcing action of fibers and also their contributions towards control of (restrained) shrinkage microcracking of UHPC. Among the discrete reinforcement conditions considered, only that comprising 2 vol.% of steel fiber produced gains in flexural strength which were statistically different (at 0.05 significance level) from those realized by other discrete reinforcement systems. The flexural strength of plain UHPC tripled with introduction of 2 vol. % steel fibers. Another observation in Figure 4.28b is that stoage at 50% relative humidity from 10 to 28 days produced a significant rise in flexural strength. The contributions of nanomaterials and also storage in ambient conditions to the flexural strength of UHPC may be attributed partly to the improvements in fiber-matrix bonding and pullout behavior in the presence of nanomaterials and with the curing, respectively. The desired moisture qualities of UHPC could allow for continued moist curing of the specimen interior even when exposed to an environment 50% relative humidly. The flexural energy absorption capacity (defined as the area under the load-deflection curve) test results for UHPC with different discrete reinforcement systems are summarized in Figure 4.28c. Discrete

reinforcement is observed to produce a significant rise (by one to two orders of magnitude) in the flexural energy absorption capacity (which reflects the toughness characteristics) of UHPC. Energy absorption capacity increased with increasing steel fiber content. Another observation is that the hybrid (multi-scale) reinforcement system comprising 1.1 vol.% steel fiber and a relatively low dosage (0.04 vol.% )of carbon nanofiber produced higher energy absorption capacity (when compound with 1.1 vol.% steel fiber used alone).

The plain and fiber reinforced UHPC materials developed in the project provide flexural strengths of 16.7 MPa (2.4 ksi) and 36-40 MPa (5.3-5.8 ksi), respectively. These flexural strengths should be compared against the ~4 MPa (~0.6 ksi) and 27-37 MPa (3.9-5.4 ksi) flexural strengths of normal-strength concrete and commercial UHPC (Ductal) [139], respectively. The plain and fiber reinforced UHPC materials developed in the project thus provide flexural strengths that are about 4 and 10 times respectively, the flexural strength of normal-strength concrete. The flexural strength of the fiber reinforced UHPC materials. The flexural strength of normal-strength of the fiber reinforced UHPC materials. The flexural strength of fiber reinforced UHPCs made with specialty raw materials. The flexural strength of fiber reinforced UHPC is much greater than the 8-12% of compressive strength which applies to plain concrete.



Bottom view

Figure 4.27 Failed plain and fiber reinforced UHPC specimens tested in flexure.

Figure 4.27 (cont'd)



Side view

(a) Plain UHPC



Bottom view

(b) Fiber reinforced UHPC



# Reinforcement Type

(a) Flexural load-deflection behavior

Figure 4.28 Flexure test results for selected UHPC materials with different discrete reinforcement conditions.

Figure 4.28 (cont'd)



(b) Flexural strength (means & standard error)



(C) Flexural energy absorption capacity (means & standard errors)

The flexure test results presented above indicate that small dosages of carbon nanofiber provide UHPC with balanced gains in the flexural strength and energy absorption capacity. Finally, it should be noted that longer-term storage at 50% relative humidity produced further gains in the flexural strength of UHPC beyond the early-age values.

Split tension tests (ASTM C496) were performed on 102x203 mm (4x8 in) cylindrical specimens. This test indirectly measures the tensile strength of concrete by compressing a cylinder through a line load applied along its length. This load configuration creates a lateral tensile stress in the cylinder across the vertical plane of loading. A relatively uniform tensile stress field is created over the middle 75 percent of the cylinder's diameter along the plane of loading, and the maximum tensile stress occurs at the center of the cylinder. The maximum tensile stress ( $f_{\theta}$ ) is calculated as:

 $f_{\theta}=2P/(\pi.l.d)$ 

where :

P is the load applied to the cylinder,

l and d are the length and diameter, respectively, of the cylindrical specimen.

Split tension test is normally conducted on standard concrete mixtures that do not contain fiber reinforcement. The cylinder will fail when its tensile strength is reached; therefore, the peak load carried by the cylinder can be used to determine the splitting tensile strength of concrete using the equation presented above. Fiber reinforced concrete, and in particular UHPC with fiber reinforcement, tend to behave differently, with the crack initiation signifying the beginning of a new phase in material behavior, but not failure of the material. With UHPC in particular, load will continue to increase after cracking, and the cracks that form initially are so small that identification without microscopic investigation may not be possible. Figure 4.29 shows a failed fiber reinforced UHPC split tension test specimen. In spite of the distinct split tension behavior of fiber reinforced concrete, the equation presented above was still used to obtain an approximate measure for the UHPC tensile strength based on the split tension test results. The results

presented in Figure 4.30 point at significant gains in split tensile strength of plain UHPC resulting from the use of different discrete reinforcement system considered in here. When compared with flexural strength (Figure 4.28b), the contributions of discrete reinforcement to split tensile strength is somewhat less dramatic; however, some discrete reinforcement systems still double the split tensile strength of plain UHPC. Split tension test result also point of the complementary effect of steel fiber and carbon nanofiber forward enhancing the UHPC performance.

The plain and UHPC nanocomposites developed in the project provided 10-day split tensile strengths of 8.69 MPa (1.26 ksi) and 13.9 MPa (2.02 ksi), respectively. These values should be compared against ~2.5 MPa (0.3 ksi) split tensile strength of normal-strength concrete [140].



Figure 4.29 A typical fiber reinforced UHPC specimen after failure in split tension test.



Figure 4.30 Split tensile strength test results (means & standard errors).

### 4.6.2.4 Direct Tension

Direct tension tests were performed following the procedures developed recently for use with fiber reinforced high-performance concrete [138]. The tension test setup is shown in Figure 4.31. The prismatic tension test specimens were 5cmx3cm (2 in x 1.2 in) in cross-sectional dimensions, with a total length of 29 cm (11.4 in). Each specimen was braced with four aluminum plates adhered at ends, and the gage length along which tensile deformation was measured was 6.6 cm (2.6 in). While plain UHPC specimens failed in a brittle manner at a low tensile strength, fiber and nanofiber reinforced UHPC specimens exhibited a ductile failure mode

with extended fiber pullout in the post-peak range of behavior beyond initial cracking (Figure 4.32). Observations of failed UHPC tension test specimens indicated that aggregates ruptured at tension cracks, which is unlike the prevalence of aggregate pullout at cracks in normal-strength concrete. This observation points at strong binding of aggregates to the UHPC binder. The prevalence of aggregate rupture at cracked surfaces was also apparent in plain UHPC specimens (Figure 4.33), which partly explains the highly brittle nature of plain UHPC.



Figure 4.31 Tension test setup.



Figure 4.32 Fiber reinforced UHPC specimen after failure in direct tension.



(a)

(b)

Figure 4.33 Cracked section of (a) plain UHPC, and (b) fiber reinforced UHPC, both exhibiting a prevalence of aggregate rupture.

Figure 4.34 provides a clear depiction of the crack bridging action of fibers, which benefits the post-cracking behavior of fiber reinforced UHPC.



Figure 4.34 Bridging of a crack by fibers in fiber reinforced UHPC.

The direct tension tests results produced for UHPC mixtures with different discrete reinforcement systems are presented in Figure 4.35. The direct tension test is rarely used with plain concrete because minor misalignments tend to significantly lower the measured values of tensile strength. This drawback also applies to fiber reinforced concrete, although to a lesser extent. An important observation here is that many of the discrete reinforcement systems considered in the project produce a strain-hardening behavior. This suggests that the post-cracking tensile resistance provided by the fibers bridging cracks exceeds the cracking resistance of fiber reinforcement system, could yield more pronounced multiple cracking in tension (which significantly benefits the toughness and energy absorption capacity of fiber reinforced UHPC). The post-peak tensile behavior and the ultimate strain capacity of the fiber reinforced UHPC uther considered in the project are desirable. Some direct tension test specimens with steel

fiber (with and without graphite nanomaterials), which exhibited multiple cracking, produced a particularly desired initial post-peak behavior.

Figure 4.35b compares the tensile strengths of plain UHPC and UHPC materials with different discret reinforcement systems. Tensile strength increased significantly with the addition of steel fibers. The use of a relatively low dosage of graphite nanomaterials (CNF) further improved the tensile strength of steel fiber reinforced UHPC, which points at the potentially improved fiber-matrix bonding and pullout behavior in presence of nanomaterials. The measured values of (direct) tensile strength in Figure 4.35b are lower than the corresponding flexural and split tensile strengths, which may be attributed to the uniform nature of tensile stresses across the volume of test specimen in direct tension testing. The accelerated (high-temperature) curing of adhesives used with end plates in tension test specimens could have lowered the tensile strength of UHPC by introducing (internally restrained shrinkage) microcracks. The UHPC with fiber reinforcement developed in the project produced tensile strengths of 9.6-11.3 MPa (1.39-1.64 ksi), which are comparable to those provided by existing UHPC materials made with specialty raw materials [138].



(a) Tensile stress-strain behavior

Figure 4.35 Direct tension test results for UHPC materials with different discrete reinforcement systems.



(b)Tensile strength test results (means and standard error)

## 4.6.2.5 Impact Resistance

The high strength and toughness of UHPC (with discrete fiber reinforcement) should translate into high impact resistance if blast-resistant reinforced concrete structures are to be built with UHPC. An assessment of the impact resistance of the selected UHPC mix was made through performance of low-velocity impact tests on UHPC specimens with different discrete reinforcement systems. Impact test procedures followed the drop-weight test method of ASTM D7136. The test setup shown in Figure 4.36a drops a weight of 7.78 kg (17.1 lb) onto a plate specimen fixed using steel plates (as clamps) on all edges. A spherically shaped tip (Figure 4.36b) transfers the impact energy to the center of the UHPC plate specimen. The UHPC impact test specimens used at this stage of the project were circular plates with 15 cm (6 in) diameter and 2 cm (0.79 in) thickness. The exposed surface of the specimen after clamping (fixing) within steel plates was a 10 cm (4 in) square area. Based on preliminary tests performed on plain and fiber reinforced UHPC specimens, respectively. The force time-history under impact tests on plain and fiber reinforced UHPC specimens, respectively. The force time-history under impact was acquired in each test at a rate of 15,000 per second.



Overall view



Impactor with spherical tip



The force time-history acquired in impact tests can be processed to yield the absorbed (and elastic) energy of impact. The kinetic energy,  $E_k(t)$ , of a mass, m, dropping at a velocity,  $v_0$ , can be expressed as [141]:

$$E_k(t) = \frac{mv_0^2}{2} - \frac{m[v_i(t)]^2}{2}$$

where,

ui (t) is the velocity at time t after impact, which can be expressed in terms of the experimental value of force.

F can be calculated using the equation  $v_i(t) = v_0 - \frac{1}{m} \int_0^t F dt$ .

The initial impact condition is schematically depicted in Figure 4.37a. An example impact force time-history graph is presented In Figure 4.37b for a typical low-velocity impact. Acceleration at  $t = t_i$  can be calculated using the Newton second law of motion  $(a_i=F_i/m)$ . The impact test yields the experimental value of  $F_i$  (versus time), drawn using the Daq Lab software during testing. Displacement of the impactor could be easily calculated as a derivative of velocity with respect to time. Hence the displacement time-history can be obtained using the experimental force time-history. The impact energy developed in the UHPC plate can then be obtained as the total of elastic energy ( $E_e$ ) and absorbed energy ( $E_a$ ) values (Figure 4.37c). The elastic energy region shown in Figure 4.37c represents the quantity of the rebound energy from the specimen. The area which remains under the force–displacement graph gives the work performed on the specimen (the energy absorbed in the specimen).





Figure 4.37 Processing of the impact test results [142].

Under impact loading, the plain UHPC specimen failed in a brittle manner via radial cracking (Figure 4.38a). With discrete fiber reinforcement, thorough penetration of the impactor tip was mitigated (Figure 4.38b). Fibers effectively bridged the cracks, and their pullout behavior effectively absorbed the impact energy, and prevented total penetration or shattering of the specimen.



(a) Plain UHPC





Bottom View

(b) Fiber reinforced UHPC



Figure 4.39 compares the impact load time-histories of the plain UHPC as well as UHPC materials with discrete reinforcement systems . Plain UHPC exhibited a typical bell-shaped curve, and failed in a highly brittle manner. UHPC materials with 1 vol. % steel fiber, 1.1 vol. % steel fiber plus 0.04 vol.%, carbon nanofiber or 1.5 vol. % steel fiber exhibited more than one major peak with continuously reduced peak loads. Past investigations have suggested that fiber pullout during the failure process produces the "shoulder peaks" observed here [143].

The time-histories of impact energy absorption derived from the measured load time-histories are presented in Figure 4.40 for UHPC with different discrete reinforcement systems. The total impact energy absorption test results are presented in Figure 4.41. The discrete reinforcement systems considered here increased the impact energy absorption capacity of plain UHPC. Different discrete reinforcement systems produced statistically similar impact energy absorption capacities, with higher impact energy absorption capacities realized with higher steel fiber volume fractions.



Figure 4.39 Impact load time-histories of UHPC with different discrete reinforcement systems.



Figure 4.40 Time-histories of the impact energy absorption of UHPC with different discrete reinforcement systems.



Figure 4.41 Total absorbed energy of UHPC with different discrete reinforcement systems..

#### 4.6.2.6 Length Change

The high binder content and the low water/cementitious ratio of UHPC can produce relatively large autogenous shrinkage. Internal and external restraint of shrinkage makes UHPC susceptible to microcracking and cracking. Discrete reinforcement can play an important role in hindering restrained shrinkage cracking of UHPC. The UHPC mix designs developed in the project intentionally incorporate larger (fine and coarse) aggregate contents in order to reduce the cementitious binder content and thus autogenous shrinkage of UHPC. The reduced binder content and the specific composition of binders in the UHPC mix designs developed in the project also lower the temperature rise during hydration, thus controlling development of thermal stresses and the potential for related cracking. An assessment was made of the autogenous shrinkage of the UHPC mix design developed in the project; effects of discrete reinforcement on shrinkage movements were also investigated.

Three 7.6cmx7.6cmx28.5cm (3 in. x 3 in. x 11  $\frac{1}{4}$  in) specimens from each UHPC mix were tested for length change following ASTM C157 procedures. At an age of 23  $\frac{1}{2}$  (+/-  $\frac{1}{2}$ ) hours, just prior to initiating thermal curing, each specimen was removed from its mold, and then placed in the comparator for initial reading of length (Figure 4.42). The length of the specimen was then measured again at 10 days of age, and the change in specimen length was calculated. The percent length change (relative to initial length) reflects the (predominantly) autogenous shrinkage strain of the specimen. Since autogenous shrinkage occurs during the hydration process, and since the bulk of UHPC hydration occurs during thermal curing, it is hypothesized that length change prior to and after thermal curing (and equilibration at 50% relative humidity) provides a reasonable measure of autogenous shrinkage.

Figure 4.43 shows the average (percent) length change values for the UHPC mix developed in the project with different discrete reinforcement conditions. Experimental results suggest that sharp (as much as an order of magnitude) drops in autogenous shrinkage can result from introduction of fibers. The smallest shrinkage was exhibited by UHPC reinforced with 1.1 vol.% steel fiber and 0.04 vol.% carbon nanofiber. Effects of discrete reinforcement on shrinkage movements of UHPC seem to be more pronounced than the corresponding effects in normal concrete. This finding partly explains why the UHPC mixtures developed in the project (with

discrete fiber reinforcement) were found to be far more resistant to restrained shrinkage cracking than the plain UHPC mixtures which have been tried for construction of larger structures. The benefits can be more pronounced with the addition of ~0.04 vol.% carbon nanofiber. The contributions of fibers (and nanofibers) towards control of shrinkage movements can be attributed to their restraining effects associated with their high specific surface area, strong interfacial bonding, and distribution across the UHPC volume.



Figure 4.42 UHPC specimen placed in comparator for measurement of length.



Figure 4.43 Length change (autogeneous shrinkage) test results for the UHPC mix with different discrete reinforcement conditions ( means and standard error).

#### 4.6.2.7 Moisture Sorption

The durability of concrete in aggressive environments depends largely upon its barrier qualities against penetration of moisture and aggressive ions [144, 145]. Among the primary transport mechanisms (capillary sorption, permeation and diffusion), sorption of moisture via capillary action is the one with the greatest impact on concrete durability [146, 147]. A large fraction of concrete in service is only partly saturated after equilibrating with the relative humidity of the environment. Upon exposure to moisture (potentially carrying aggressive ions), concrete can thus uptake the solution via capillary action. Moisture sorption tests were conducted in order to assess the sorption characteristics of the UHPC mix developed in the project with different discrete reinforcement conditions. ASTM C1585 procedures were adopted for assessment of the

sorption characteristics of UHPC. Cylindrical specimens with 100 mm (4 in) diameter and 50 mm (2 in) height (Figure 4.44) were used for this purpose. The sides and top surfaces of specimens were covered with impermeable adhesive sheets, and the bottom surface was immersed (1-3 mm depth) in water. Mass gains of specimens (due to capillary sorption of water) were measured at frequent time intervals (with the wet surfaces patted dry prior to weight measurement).

Moisture sorption test results for the UHPC mix with different discrete reinforcement conditions are presented in Figure 4.45. The total moisture sorption of plain UHPC is few times less than that of plain normal concrete, which reflects upon the lower capillary porosity and also the less interconnected nature of this pore system in UHPC. The total moisture sorption of UHPC is also observed to drop with fiber reinforcement. This drop (~30%) was found to be statistically significant (at 0.05 significance level); the differences in moisture sorption of UHPCs with different discrete reinforcement conditions were not statistically significant. The lowest moisture sorption was exhibited by the UHPC with 1.1 vol. % steel fiber and 0.04 vol.% carbon nanofiber, which verify the benefit of adding carbon nanofiber.



Figure 4.44 Moisture sorption test setup.



Figure 4.45 Total moisture sorption of UHPC with different discrete reinforcement conditions.

#### 4.6.2.8 Thermal Conductivity and Specific Heat

Field thermal curing of UHPC would be influenced by its thermal conductivity and specific heat, which determine the potential to retain the heat of hydration and to avoid development of temperature gradients (and thermal stresses) within large UHPC structures. Thermal conductivity, specific heat and other thermal tests were conducted on UHPC specimens with different discrete reinforcement conditions [148]. The thermal conductivity and specific heat tests were performed within the temperature range of 20-90°C (68 - 194 F).

Thermal conductivity is defined as the rate of heat flow to temperature gradient, and represents the uniform flow of heat through concrete of unit thickness over a unit area subjected to a unit temperature difference between the two opposite faces. Concrete contains moisture in different forms; the type and amount of moisture significantly influence thermal conductivity. Specific heat is the amount of heat per unit mass required to change the temperature of a material by one degree, and is generally expressed in terms of thermal (heat) capacity which is the product of specific heat and density. Specific heat is strongly influenced by moisture content, aggregate type, and density of concrete [149]. Specific heat involved in temperature change. Sensible heat ascribes to the heat involved in thermodynamic reaction during temperature change. Latent heat refers to the energy absorbed or released by the material during phase transition. Materials may absorb considerable amount of energy during physiochemical changes, and thus specific heat values are influenced by any potential phase transitions in materials.

Thermal conductivity and specific heat tests were performed on 50mmx50mmx25mm (2in x 2in x 1in) prismatic specimens. Thermal conductivity and specific heat values were measured using a commercially available equipment (Hot Disk TPS 2500S thermal constant analyzer) shown in Figure 4.46. This equipment is connected to a furnace, in which a specimen can be exposed to the targeted temperature. This state-of-the-art equipment utilizes a Transient Plane Source (TPS) technique to measure thermal properties of materials from room temperature to 100°C. A flat source sensor is placed between the two halves of the specimens, which acts like a heater (constant-effect generator) and a detector (resistance thermometer) at the same time. When a constant heat source is applied, the temperature in the sensor rises, and heat flow occurs in the

specimen. The test specimen must have a uniform temperature distribution throughout its volume at the time of measurement [148].



Figure 4.46 The hot disc test equipment used for measurement of the thermal conductivity and specific heat of UHPC.

The values measured at room temperature and 90°C ( $194^{\circ}F$ ) for thermal conductivity (k) and specific heat ( $c_p$ ) of UHPC with different discrete reinforcement conditions are presented in Figures 4.47 and 4.48, respectively. The following observations can be made based on the measured values of thermal conductivity and heat capacity (specific heat,  $c_p$ , is the ratio of heat capacity to density):

Room temperature thermal conductivity (k) of UHPCs with different discrete reinforcement conditions ranges from 2.43 to 3.35 W/m°C, and conductivity at 90°C (194°F) ranges from 1.70 to 2.60 W/m°C. As compared to normal-weight concrete (with  $k_{20}=0.35$  W/m°C), UHPC has significantly higher thermal conductivity at both ambient and 90°C (194°F); this can be

attributed to the higher density of UHPC. The addition of steel fiber increased the thermal conductivity of UHPC slightly (the rise was not statistically significant), and carbon nanofiber at a low volume fraction significantly increased the thermal conductivity of UHPC (the rise was found to be statistically significant). The contribution of carbon nanofibers to the thermal conductivity of UHPC can be explained by the high thermal conductivity of nanofibers and their percolation at relatively low volume fraction.

Room-temperature specific heat ( $c_p$ ) of UHPC is ~1350 J/kg°C, and specific heat at 90°C (194°F) ranges from 1508 to 2400 J/kg°C. As compared to normal-weight concrete (with  $c_{p20}=960$  J/kg°C), UHPC has higher specific heat. The measured density for UHPC is in the range of 2480-2530 kg/m<sup>3</sup>, which is higher than that of normal concrete. The incorporation of steel fiber and carbon nanofiber did not have statistically significant effects on the specific heat of UHPC.


Figure 4.47 Thermal conductivity test results UHPC (mean & standard error).



Figure 4.57 Specific heat test results UHPC (mean & standard error).

## **4.7 Discussion**

In development of ultra-high performance concrete (UHPC), one important consideration is the size gradation of the particulate (and fibrous) matter in concrete for maximizing their packing density, which is influenced by the type and extent of the consolidation effort. Carbon nanofiber offers distinct features for effective reinforcement of cementitious matrices in the pre- and post-crack ranges of behavior. In this investigation, a comprehensive optimization experimental work

was designed based on response surface analysis principles, and implemented for identifying optimum combinations of carbon nanofiber and steel fiber in ultra-high performance concrete. It was found that a hybrid discrete reinforcement system comprising unmodified carbon nanofiber at 0.145 vol.% of anhydrous cementitious materials (0.04 vol.% of concrete) and steel fiber at 3.55 vol.% of anhydrous cementitious materials (1.1 vol.% of concrete) provided balanced gains in engineering properties of ultra-high performance concrete. This optimum reinforcement system was used to evaluate the effects of nanofiber surface modification on UHPC material properties. The surface modification technique employed in the project emphasized introduction of hydrophilic groups on graphite nanomaterials in order to facilitate their dispersion in aqueous media. Polyacrylic acid (PAA) with high density of COOH groups, at 0.1 (PAA):1.0 (carbon nanofiber) weight ratio was added to the mixing water prior to dispersion of nanofibers in order to introduce hydrophilic groups on the surfaces of carbon nanofibers.

Outcomes of the optimization experimental program indicated that: (i) the optimum hybrid reinforcement system comprising a moderate dosage of steel fiber and a relatively low dosage of carbon nanofiber produced major gains in diverse material properties of ultra-high performance concrete; (ii) introduction of hydrophilic groups on the grapheme edges comprising the peripheral surfaces of carbon nanofibers improved the performance characteristics of ultra-high performance concrete with optimum reinforcement system; (iii) optimum hybrid (nano-and micro-scale) reinforcement surpassed high volume fraction of micro-scale (steel) fiber in terms of hardened material engineering properties and fresh mix workability. The optimum combination of steel fiber with PAA-modified carbon nanofiber produced 50%, 240%, 2700%, 236%, 1200% and 5% improvements in the flexural strength, maximum deflection, energy absorption capacity, impact resistance, abrasion resistance and compressive strength of (plain)

UHPC, respectively. The corresponding improvements over material properties of ultra-high performance concrete with a relatively high steel fiber volume fraction were 34%, 54%, -4%, 18%, 400% and 34%, respectively.

A hybrid (micro-/nano-scale) reinforcement system comprising carbon nanofiber (CNF) and Polyvinyl alcohol (PVA) micro fiber was optimized for balanced improvement of ultra-high performance concrete (UHPC) material properties. The oxidized carbon nanofiber used in this investigation approach is the desired geometric, mechanical, physical and stability characteristics of carbon nanotube (CNT) at substantially lower cost. When compared with micro-scale (PVA) fibers, CNF offers distinct features for effective control of micro crack inception and growth. Micro- and nano-scale reinforcement offer the potential for complementary/synergistic actions in high-performance cementitious matrices because they function at different scales, and also because nanofibers can enhance the bonding and pullout behavior of micro-scale fibers. Surface treatment methods were developed to enhance the dispersion and interfacial interaction of CNF in cementitious materials. An optimization experimental program was designed and implemented in order to identify the optimum dosage of PVA and modified CNF in ultra-high-performance concrete (UHPC). The material properties included fresh mix workability, flexural strength, energy absorption capacity and maximum deflection, impact and abrasion resistance, and compressive strength. Experimental results confirmed the synergistic/complementary actions of nano- and micro-scale reinforcement in UHPC. The optimum reinforcement system, which comprised PVA fiber and CNF at 0.37 and 0.047 vol. % of concrete, respectively, improved the flexural strength, maximum deflection, energy absorption capacity, impact resistance, abrasion weight loss, and compressive strength of plain UHPC by 9.2%,1000.0%, 700.0%, 158.2%, 33.9% and 7.5%, respectively. At the volume fractions considered here, modified CNF did not

significantly alter the workabilities of fresh UHPC mixtures; PVA fiber, on the other hand, compromised the UHPC fresh mix workability.

Optimum combinations of CNF with steel fiber performed better than the optimum CNF/PVA systems. This could be attributed to the high elastic modulus of steel fibers, and the toughening effects associated with inelastic flexural phenomena involved in pullout of inclined fibers from the cementitious matrix. In UHPC, the optimum combination of CNF and steel fiber comprised a significantly higher fiber volume fraction than the optimum combination of CNF and PVA fiber, which could be attributed to the smaller diameter and hydrophobic surfaces of PVA fibers which magnify their adverse effects on fresh mix workability. This may be explained by the more pronounced losses of workability with introduction of PVA fibers when compared with steel fibers.

The experimental data generated on various aspects of UHPC performance indicated that combination of 1 vol.% straight steel fiber and 0.04 vol.% carbon nanofiber provides the UHPC mixture developed in the project with a desired balance of fresh mix workability, flexural and tensile strengths, energy absorption capacity (toughness), impact resistant, dimensional stability, moisture sorption resistance, and heat resistance.

#### **CHAPTER 5**

# THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF SINGLE FIBER PULLOUT BEHAVIOR IN ULTRA-HIGH-PERFORMANCE CONCRETE NANOCOMPESTES

### **5.1 Introduction**

Addition of steel fibers to concrete leads to reduced brittleness and control of crack width. Such beneficial effects arise from the crack bridging action of fibers which induce bond-slip mechanisms that effectively dissipate energy. Interfacial bonding and fiber pullout behavior are major factors influencing the performance characteristics of UHPC composites and nanocomposites. A key hypothesis of this project concerns the benefits of nanomaterials towards the interfacial bonding and pullout behavior of fibers. Single fiber pullout tests were conducted in UHPC materials prepared with and without nanomaterials in order to verify this hypothesis. Fiber pullout tests have been used to characterize and optimize the bond strength and pullout behavior of fibers in concrete. Most investigations have focused on the behavior of fibers aligned with the loading direction (Figure 5.1). Such aligned fibers, however, experience pullout mechanisms which are not representative of those existing in actual conditions where randomly oriented fibers pullout of concrete.



Figure 5.1 Schematics of single fiber bond and pullout test with fiber aligned with the loading direction . (a) pre-critical load; (b) partial debonding (c) full debonding and pullout [150].

The pullout behavior of steel fibers embedded in UHPC (with and without nanomaterials) at different inclinations with respect to the loading direction (Figure 5.2) was investigated. The single fiber pullout test results were used together with theoretical models in order to evaluate the effects of nanomaterials on the bonding and pullout behavior of fibers in UHPC. Besides fiber debonding and frictional pullout along the interface, other phenomena were considered, including fiber bending, matrix spalling, and local frictional effects. The contributions of these micromechanisms depend upon the fiber inclination angle, the presence of nanomaterials,

concrete bonding, and other material properties which need to be taken into account for modeling purposes.



Figure 5.2 Micromechanisms involved in pullout of an inclined fiber from concrete [24, 151].

A theoretical model was developed, and used together with single fiber pullout test results in order to investigate the effects of nanomaterials on the fiber pullout behavior. The results allow for evaluation of the synergistic actions of fibers and nanomaterials towards enhancement of the ultra-high-performance concrete toughness characteristics.

#### 5.2 Theoretical Modeling of Single Fiber Pullout Behavior

#### 5.2.1 Overview of theoretical pullout models

A micromechanical model was developed for pullout behavior of a single fiber from concrete, Naaman and Nammur [88] proposed an analytical model of the bond behavior using the relationship between pullout behavior and the shear stress–slip curve at the interface; Also, the model was further improved by considering empirical values of the post-debonding frictional stresses in lieu of constant friction values [88].

The pullout behavior of steel fiber in an ultra-high strength cementitious matrix model that modeling of the pullout behavior of steel fibers from ultra-high performance concrete (UHPC) has followed the approach proposed by Naaman [87], which considers the effects of fiber inclination angle revers the loading direction. A more comprehensive theoretical model was developed in this research for pullout behavior a sigle fiber with different inclination angles. The model was used to explain the synergistic actions of fibers and nanomaterials towards enhancement of the ultra-high performance concrete toughness characterstics.

Naaman and Nammur proposed a model for steel fiber pullout behavior, which derivation has been the details of which as presented in detals in Naaman [88]. Figure 5.3 presented a basic bond (shear) stress-slip relationship at the interface of fiber and concrete matrix. The bond shear stress–slip curve is linear elastic up to the point where the bond strength  $\tau_{max}$  is reached. Beyond this point frictional pullout occurs at a typically assumed constant frictional shear stress of  $\tau_{f}$ , which falls below  $\tau_{max}$  [88]. Figure 5. 4 illustrate the free-body, diagram of steel fiber considered by Naaman and Nammur. This model is applicable only to aligned fibers. The model developed subsequently for fiber pullout from ultra-high strength cementitious matrix has been modified to take into account the effect of fiber inclination angle.



Figure 5.3 Bond shear stress versus slip relationship [88].



Figure 5.4 Free-body diagram of steel fiber during pullout [88].

The ultra-high strength cementitious matrix model subdivides the pullout behavior into two parts. The first part covers the ascending segment of the pullout deflection behavior, which consists of the perfectly bonded state, and partially debonded state. The second part covers the descending behavior which relates to the fully debonded state [87].

The pullout behavior of an inclined fiber in the ascending part can be expressed by the equations presented below. Equations (5.1) and (5.2) are for the perfectly bonded state and Equations (5.3) and (5.4) represent the behavior in the partially debonded state. Apparent shear strengths are adopted here to reflect the effects of fiber inclination angle, such as the snubbing and matrix spalling effects, on load - slip behaviors.

$$P_{\text{crit}}(\theta) = \frac{\pi d_f \tau_{\max(\text{app})(\theta)}}{\lambda} \left[ \frac{1 - e^{-2\lambda l}}{\left(1 - \frac{1}{Q}\right)\left(1 + e^{-2\lambda l}\right) + \left(\frac{1}{Q}\right)2e^{-\lambda l}} \right]$$
5.1

$$\binom{P}{\Delta}(\theta) = \frac{1}{1+\gamma\left(\frac{2\theta}{\pi}\right)^n} \frac{\lambda A_m E_m}{Q-2} \frac{1+e^{-\lambda l}}{1-e^{-\lambda l}}$$
 5.2

$$P(\theta) = \pi d_f \tau_{f(app)}(\theta) u + \frac{\pi d_f \tau_{max(app)}(\theta) u}{\lambda} x \frac{1 - e^{-2\lambda(l-u)}}{\left(\frac{2}{Q}\right)\left(e^{-\lambda(l-u)}\right) + \left(1 - \frac{1}{Q}\right)\left\{1 + e^{-2\lambda(l-u)}\right\}}$$
 5.3

$$\Delta(\theta) = \left[1 + \gamma \left(\frac{2\theta}{\pi}\right)^{n}\right] \frac{1}{A_{m} E_{m}} \left\{P(\theta)(Q-1)u - \frac{\pi d_{f} \tau_{f(app)}(\theta)u^{2}}{2} (Q-2) + \left(P(\theta) - \pi d_{f} \tau_{f(app)}(\theta)u\right) \left(\frac{1 - e^{-\lambda(l-u)}}{1 + e^{-\lambda(l-u)}}\right) \frac{Q-2}{\lambda} - \pi d_{f} \tau_{f(app)}(\theta)ul\right]$$
5.4

The pullout behavior of inclined fiber in the descending part, which is governed by frictional slip after the peak load are modeled using the following equations.

$$P(\theta) = = \pi d_{fd} \tau_f (\Delta) \chi$$
 5.5

$$\tau_{fd} (\Delta) = \tau_{f(app)}(\theta) \exp\{-\eta (\Delta - \Delta_{o})^{\alpha}\} x \frac{\{1 - \exp\left[\frac{-4v_{f}\mu\chi}{E_{f}d_{f}(\frac{1+v_{m}}{E_{m}} + \frac{1-v_{f}}{E_{f}}\right]\}}{\{1 - \exp\left[\frac{-4v_{f}\mu l}{E_{f}d_{f}(\frac{1+v_{m}}{E_{m}} + \frac{1-v_{f}}{E_{f}}\right]\}}$$
5.6

where:-

 $P_{crit}(\theta)$  is the critical load  $P_{crit}$  for the load when the shear stress acts on a fiber inclined by angle  $\theta$  at x = 1.

d<sub>f</sub> is the fiber diameter.

u is length of the debonded zone.

 $\tau_{\max(app)}(\theta)$  is the maximum apparent bond strength for the fiber inclined by angle  $\theta$ .

$$\lambda \text{ is } \sqrt{KQ} \;\; , \; K = \!\!\frac{\pi \; d_{f\,k}}{A_m \; E_m} \;\; \text{ where } k \; \text{is bond modulus, } Q = 1 + \frac{A_m \; E_m}{A_f \; E_f}$$

 $\Delta$  is the end slip of fiber at full debonding.

 $\Delta_o$  is the end slip of fiber at the end of full debonding.

 $\boldsymbol{A}_m$  ,  $\boldsymbol{E}_m$  are area and elastic modulus of the matrix.

 $A_{f}$ ,  $E_{f}$  are area and the elastic modulus of fiber.

 $\gamma$  is a constant number equal 100 for the ultra-high performance matrix.

 $\tau_{f(app)}(\theta)$  is the apparent bond strength on a fiber inclined by angle  $\theta$ .

v<sub>f</sub> is Poisson's ratio of fiber.

 $\mu$  is the friction coefficient at the fiber–matrix interface.

 $\eta$  is a coefficient representing the exponential shape of the descending branch of the bond shear stress versus slip curve.

 $\alpha$  is a constant determining the initial slope of the frictional slip behavior.

 $\chi$  is the embedded length of the fiber with  $\chi = \frac{1}{1 - \Delta_0} (1 - \Delta)$ .

# 5.2.2 The model Developed for Inclined Fiber Pullout from Ultra-High-Performance Concrete

The pullout model presented in previous section for ultra-high-strength cementitious matrix. The model assumed a friction coefficient ( $\mu$ ) of 0.3 based on Pallett, Peter work [152], which has been obtained for two surfaces (concrete and steel) in temporary contact, without considering the strength of concrete or the type of steel (e.g., fiber, bar). This approach may not be able to distinguish between pullout behavior of fibers from ultra-high-strength concrete with and without nanomaterials. The model developed have intends to consider these distinctions using experimental works., the experimental setup considered, here is shown in Figure 5.5, where a segment of fiber is embedded in UHPC with the other segment occurring outside concrete (used for grapping to apply tensile forces during pullout tests.



Figure 5.5 Schematic description of the micromechanical model.

The contribution of fiber friction to pullout load ( $F_{fri}$ ) is calculated using a Coulomb model given by Eq. (5.7). In this equation,  $\mu$  and  $F_{norm}$  correspond respectively to the friction coefficient and the normal load. This normal load is assumed to be composed of the reaction load  $E_y$  and of a contribution of moment M. (Figure 5.6). The assumed support condition of points A and C (Figure 5.6) allow for decomposition of the reaction moment into two equivalent reaction loads  $A_y$  and  $C_y$  as shown in Figure 5.6. Eqs. (5.8) and (5.9) are analytical expressions of these loads, where L<sub>0</sub> is the embedded fiber length.



Figure 5.6 Modeling of the embedded segment 2 of fiber.

$F_{fri} = \mu F_{norm}$	5.7
$A_{y} = \frac{M}{L_{o}}$	5.8
$C_y = - \frac{M}{L_o}$	5.9

These loads are added to  $E_y$  to obtain the full normal load  $F_{norm}$ :

$$F_{norm} = E_y + A_y + C_y$$
 5.10

Figure 5.7 shown the reaction loads  $E_y$  and M generated by P at the fixed end (E). Analytical expressions of these reaction loads are given by Eqs. (5.11) and (5.12).



Figure 5.7 Modeling of segment: deformation of the tow-beams system and reaction loads generated by the application of P.

The initial fiber geometry described in Figure 5.7 shows that the fiber at its exit point from the matrix (E) is not aligned with the pullout axis. The fiber segment (A–B) of length  $L_1$  corresponds to the free initial fiber length outside the matrix. The fiber segment (E–A) of length  $L_2$  appears after fiber extraction and/or matrix spalling. The inclination angle of the embedded fiber length is  $\theta$  with respect to the pullout axis.

$$E_{y} = -P \sin(\theta) - B_{y} \cos(\theta)$$
 5.11

 $\mathbf{M} = \mathbf{P} \left( \mathbf{L}_2 \sin \left( \theta \right) \right) + \mathbf{B}_{\mathbf{v}} \left( \mathbf{L}_1 + \mathbf{L}_2 \cos \left( \theta \right) \right)$ 

#### **5.3 Experimental Results and Discussion**

Single-fiber (inclined) pullout tests were conducted inorder to investigate the influence of nanomaterials on the pullout behavior of fibers with different orientations. Straight steel fibers were tested at four different of orientation angles  $(0^{\circ}, 30^{\circ}, 45^{\circ}, 60^{\circ})$ . Among the large number of different fiber pullout test setups that can be found in the literature, one was selected to closely simulate the actual condition of a randomly oriented fiber bridging a crack. This selection required material in which the fiber is embedded should be subjected to a tensile stress when a tensile force is applied to the fiber. The selected test setup is shown in Figure 5.8, with the surrounding concrete subjected to bending tensile stresses. Furthermore, the test setup must allow for application of an inclined pullout force to fiber. Since the free end of fiber is clamped by the testing machine, it has to be both vertically aligned and straight to start the test. As a consequence, the fiber has to be bent prior to the testing. Figure 5.8 shows the single fiber pullout test fixture, which allows for holding the specimen in place without applying additional lateral pressure on the fiber. Fiber slip was measured using a linear variable differential transformer (LVDT). Each fiber pullout test result is described by a pullout load versus slip relationship, as schematically depicted in Figure 5.9.

The steel fiber used in pullout test had a diameter of 0.2 mm (0.008 in) and a constant embedded length 6.5 mm (0.25 in). The ultra-high-performance concrete material used in pullout tests was introduced in chapter 4.



Figure 5.8 Single fiber pullout test setup.



Figure 5.9 Typical fiber pullout load–slip curve.

Experimental pullout load-slip relationships for straight steel fibers with different inclination angles are presented in Figures 5.10 to 5.13. Three replicated test was performed for each condition. Since there are no background test data on pull-out behavior of fibers from ultra-high-performance concrete nanocomposites, the variations in test results are unknown, and the three replications used here was a first attempt to gain insight into the fiber pullout behavior in UHPC nanocomposites. The peak load and the load-slip behavior were enhanced significantly with increasing inclination angle up to 45°, and then deteriorated with further increase of inclination angle to 60°. Beyond the peak load, friction is considered to play a major role in fiber pullout behavior. The contribution of friction to pullout load and, in case of inclined fiber, that of fiber sequential plastic deformation (in bending) and straightening provide for retention of the peak load as fiber slips before the drop of fiber load with increasing slip.







Figure 5.11 Pullout load-slip behaviors of fibers with inclination angle of 30° from plain UHPC.



Figure 5.12 Pullout load-slip behaviors of fibers with inclination angle of 45° from plain UHPC.



Figure 5.13 Pullout load-slip behaviors of fibers with inclination angle of  $60^{\circ}$  from plain UHPC.



Figure 5.14 Average pullout load-slip behavior of fibers with different inclination angles from plain UHPC.

All straight fibers pulled out of concrete without the occurrence of fiber rupture. The sequential plastic deformation of inclined fibers (via bending- straightening action) is more pronounced for higher fiber inclination angles. For inclined fibers, spalling of the matrix (i.e. local matrix damage due to the bending of the fiber at its exit point) was observed. An increase of fiber inclination angle increased the peak pullout load and the total pullout energy up to on optimum inclination angle at  $45^{\circ}$ . Beyond this optimum inclination angle, the pullout behavior degraded with increasing inclination angle to  $60^{\circ}$ . In addition, the initial ascending slope of the load–slip curve increased with increasing inclination angle up to  $45^{\circ}$ , and then decreased. The ascending

behavior starts with a perfectly bonded condition partially, and then debonded occurs. The descending behavior corresponds to a fully debonded state.

Figures 5.15 to 5.18 present pullout load-slip test of fiber with different inclination angles for ultra-high-performance concrete reinforced with 0.04 vol. % carbon nanofiber. Figures 5.19 and 5.20 present the average pullout load-slip and bond stress-slip test results, respectively, for ultra-high-performance concrete reinforced with 0.04 vol. % carbon nanofiber. The trends in the fiber inclination effects on pullout- slip behavior are similar to those observed with plain ultra-high-performance concrete. It is worth mentioning that the individual fiber pullout tests performed at 0° inclination angle showed greater variation than those performed at 30, 45 and 60° inclination angles. This could reflect the fact that fiber pullout behavior at 0° inclination angle relies largely on the fiber-matrix interfacial behavior, while those at other inclination angles rely on both matrix properties and fiber-matrix interfacial behavior. The interfacial characteristics could be more variable than the matrix properties.



Figure 5.15 Pullout load-slip behavior of steel fiber with inclination angle of 0° from UHPC reinforced with 0.04 vol. % carbon nanofiber.



Figure 5.16 Pullout load-slip behavior of steel fiber with inclination angle of 30° from UHPC reinforced with 0.04 vol.% carbon nanofiber.



Figure 5.17 Pullout load-slip behavior of steel fiber with inclination angle of 45° from UHPC reinforced with 0.04 vol.% carbon nanofiber.



Figure 5.18 Pullout load-slip behavior of steel fiber with inclination angle of 60° from UHPC reinforced with 0.04 vol.% carbon nanofiber.



Figure 5.19 Average pullout load-slip behavior of steel fiber with different inclination angles from UHPC reinforced with 0.04 vol.% carbon nanofiber.

Figure 5.20 compares the pullout load-slip behavior of steel fibers from plain versus carbon nanofiber reinforced ultra-high-performance concrete for fibers of different inclination angles. The addition of nanofibers to ultra-high-performance concrete is observed to significantly improve the peak pullout load, and the overall ductility of fiber pullout behaviors. The fiber pullout load-slip behavior tends to be a more tortuous in the presence of carbon nanofiber. the contribution of nanomaterials to the fiber pullout strength are similar at different inclination angles. The corresponding contributions to the ductility of steel fiber pullout seem to be more significant at inclination angles of  $30^{\circ}$  to  $45^{\circ}$  when compared with  $0^{\circ}$  and  $60^{\circ}$ .



(a)

Figure 5.20 Pullout behavior of steel fiber from plain UHPC versus UHPC reinforced with carbon nanofiber for different fiber inclination angles.

Figure 5.20 (cont'd)



(b)

Figure 5.20 (cont'd)



(c)

Figure 5.20 (cont'd)



(d)

An important hypothesis of the project is that nanomaterials enhance the concrete material properties through multi-faceted interactions with the concrete structure and failure mechanisms. Nanomaterials render these effects partly due to their distinct geometric attributes. There seem to be positive interaction between steel fiber and nanomaterials, which lead to their synergistic action towords improving the concrete material properties. Nanomaterials seem to enhance the

reinforcing efficiency of fibers by improving their interfacial bonding and pullout behavior for fibers of different inclinations angles (Figures 5.22 and 5.23). This finding supports the hypothesis that there are synergistic actions of nano-and micro-scale reinforcement in ultra-high-performance concrete. The contribution of nanomaterials to the interfacial bonding of steel fibers in concrete could be attributed to the increased density of matrix <u>which be enabling</u> to the bond strength of fibers and their interfacial friction during pullout and also control of microcracking in the interfacial region and at the fiber exit point.

The pullout behavior of steel fibers embedded in ultra-high performance concrete without or with carbon nanofiber was analyzed using the results of pullout tests together with the pullout model presented in Eqs. 5.1 Through 5.12. Table 5.1 presents the model parameters which were derived using the fiber pullout test results.

	Plain UHPC			UHPC- CNF				
	0	30	45	60	0	30	45	60
$\tau_{max(app)}$ (N/mm <sup>2</sup> )	5.12	13.3	17.3	7.56	8.43	16.8	21.9	10.45
$k \ (N/\ mm^3)$	4.89	16.0	24.8	6.54	9.53	20.5	29.9	13.4
η	0.696	0.725	0.557	0.643	0.525	0.858	0.639	0.837
μ	0.260	0.256	0.250	0.261	0.554	0.567	0.577	0.562
β	1	2.80	6.80	5.40	1	2.71	6.61	5.73

Table 5.1 The model parameters for ultra-high performance concrete

The empirically derived parameters of the fiber pullout model presented in Table 5.1 indicate that:

- Shear Strength ( $\tau_{max}$ ) at peak load increased with increasing fiber inclination angle up to  $45^{\circ}$ , and then decreased. The shear strength values were higher for ultra-high performance concrete reinforced with carbon nanofiber. The rise in bond shear strength with introduction of nanofibers partly explains the synergistic action of fibers and nanofibers in ultra-high performance concrete. This benefit of nanofibers can be attributed to the improved packing density, the local reinforcing effect, and possibly the reduced bleeding and improved microstructure of cement hydrates in the presence of nanofibers.
- The bond modulus k at peak load increased with increasing fiber inclination angle up to 45°, and then decreased. The k values were higher for ultra-high performance concrete reinforced with carbon nanofiber.
- The values of Q and λ depend upon concrete (reinforced with carbon nanofiber) and steel fiber properties. η is a coefficient representing the exponential shape of the descending branch of the bond shear stress versus slip curve which reflects the debonded interfacial shear behavior. η increased with the addition of carbon nanofiber to ultra-high performance concrete.
- The coefficient of friction µ between the fiber and ultra-high performance concrete increased from 0.260 to 0.570 with introduction of carbon nanofiber. The contribution of nanofibers to the ultra-high performance concrete packing density and local damage resistance can be used to explain this experimental observation.
- The slip coefficient (β) represents the Δ<sub>peak</sub>(θ)/ Δ<sub>peak</sub>(0) ratio where Δ<sub>peak</sub>(θ) denotes the slip corresponding to the peak load for fiber inclination angle θ, and Δ<sub>peak</sub>(0) is the slip corresponding to the peak load for the aligned fiber. The slip coefficient (β) did not vary

significantly for ultra-high performance concrete materials without and with nanofiber. The following relationships apply to the three fiber inclination angles considered:-

$\Delta_{\text{peak}(30)} = 3.0  \Delta_{\text{peak}(0)}$	5.13
$\Delta_{\text{peak}(45)} 7.0 \Delta_{\text{peak}(0)}$	5.14
$\Delta_{\text{peak}(60)} = 5.5  \Delta_{\text{peak}(0)}$	5.15

In the case of UHPC with nanomaterials,  $A_{com}$  and  $E_{com}$  (cross sectional area and the elastic modulus of concrete nanocomposites) should be used in theoretical calculations.

Figures 5.21 and 5.24 represent comparisons between experimental results and theoretical prediction of the characteristic features of fiber bond-slip relationship. These comparisons, which are made for ultra-high performance concrete with and without carbon nanofiber reinforcement, indicate that the peak fiber pullout load increase by an average of 46% with introduction of nanofibers. The critical peak pullout load increases by an average of 26%, the debonding pullout load by 33%, and the displacement at peak pullout load by 36% with introduction of carbon nanofibers. There are generally good agreements between the experimental and theoretical fiber pullout behavior at different inclination angles, noting that the model incorporates a number of empirical coefficients derives using the experimental results.



Figure 5.21 Theoretical vs. experimental values of average critical pullout load for ultra-highperformance concrete with and without carbon nanofiber.


Figure 5.22 Theoretical vs. experimental values of average peak pullout load for ultra-highperformance concrete with and without carbon nanofiber.



Figure 5.23 Theoretical vs. experimental values of average debonding pullout load for ultra-highperformance concrete with and without carbon nanofiber.



Figure 5.24 Theoretical vs. experimental values of average displacement at peak pullout load for ultra-high-performance concrete with and without carbon nanofiber.

Scanning electron microscope (SEM) images of a pulled-out of fiber as well as the hole left after fiber pullout in plain ultra-high performance concrete are presented in Figures 5.25 through 5.27, and for ultra-high-performance concrete reinforced with carbon nanofiber in Figure 5.28 through 5.30. Interfacial failure seems to be prevalent in ultra-high-performance concrete without carbon nanofiber, while a thin layer of cementitious material largely covers the steel fiber surface in ultra-high-performance concrete with nanofiber. This observation points at the strong interfacial bonding of ultra-high performance concrete to steel fiber. The hole left after fiber pullout also seemed smoother without nanofiber, and exhibited rough interior surfaces and edges in UHPC with carbon nanofiber.

Pullout of inclined fibers causes spalling of the cementitious matrix at fiber exit points, with the size of spalled part decreases during pullout (Figure 5.31). The geometry of the spalled part depends upon the fiber inclination angle (Figure 5.32). Carbon nanofibers could be detected on the fractured surfaces of the spalled parts for cementitious materials with carbon nanofiber (Figure 5.33). This observation provides further support for the imminent presence of nanofibers in the critically stressed regions in the vicinity of nanofibers. This phenomenon partly explains the synergistic reinforcing actions of fibers and nanomaterials in UHPC.



Figure 5.25 SEM image of pulled-out steel fiber in ultra-high-performance concrete without carbon nanofiber.



Figure 5.26 High-magnification SEM image of pulled-out steel fiber in ultra-high-performance concrete without carbon nanofiber.



Figure 5.27 SEM image of the hole left after pullout of steel fiber in UHPC without carbon nanofiber.



Figure 5.28 SEM image of pulled-out steel fiber in ultra-high-performance concrete with carbon nanofiber.



Figure 5.29 High-magnification SEM image of pulled-out steel fiber in ultra-high-performance concrete with carbon nanofiber.



Figure 5.30 SEM image of the hole left after pullout of steel fiber in ultra-high-performance concrete with carbon nanofiber.



Figure 5.31 Spalled parts of UHPC at fiber exit point.



(a)



(b)

Figure 5.32 Spalled parts of UHPC at exit points of fibers with inclination angles of (a)  $30^{\circ}$ , (b)  $45^{\circ}$ , (c)  $60^{\circ}$ .

Figure 5.32 (cont'd)



(c)



(a)



(b)

Figure 5.33 (a) SEM images at different magnifications of carbon nanofibers on fractured surfaces of UHPC with carbon nanofiber.

#### **CHAPTER 6**

# CONTRIBUTIONS OF NANOMATERIALS TO THE PULLOUT BEHAVIOR OF DEFORMED BARS AND STRANDS FROM ULTRA-HIGH PERFORMANCE CONCRETE NANOCOMPESTES

### **6.1 Introduction**

The bond between the reinforcement and matrix in a reinforced brittle matrix is an important factor affecting the mechanical behavior of composite. Pullout tests were conducted in this project in order to study the bond behavior of reinforcing or prestressing steel in ultra-high performance concrete. Bonding of reinforcing/prestressing steel in concrete is mainly mechanical in nature, resulting from interlocking of bar surface deformations (or strand surface features) in concrete (Figure 6.1a). As bond stress increases, the surface deformations (ribs) will first cause local stress rise and inclined cracking (Figure 6.1 b). After formation of inclined cracks, tensile stress of the steel bar/strand is transmitted to concrete via the contact force applied on the surface of ribs. The radial component of this contact force is called the splitting pressure, and it may result in split cracking of concrete (Figure 6.2) provided that it becomes large enough. However, if the confinement of concrete prevents split cracking, the dominant failure mode will be by shear pullout (Figure 6.3).

This chapter presents the results of an experimental investigation of the effects of carbon nanofiber on the bond behavior of reinforcing and prestressing steel in ultra-high-performance concrete. This investigation involved pull-out tests on 12.7 mm (0.5 in) diameter deformed reinforcing bars or prestressing strands in ultra-high-performance concrete.



<sup>(</sup>b)

Figure 6.1 (a) Pull-out force applied to an embedded bar; (b) Inclined cracking of concrete caused by slippage of deformed reinforcing bar.



Figure 6.2 Split cracking of ultra-high-performance concrete caused by slippage of deformed reinforcing bar.



(a) Deformed steel bar

Figure 6.3 Sheared segment of ultra-high-performance concrete in pullout tests performed on deformed bars and prestressing strands.

Figure 6.3 (cont'd)



(b) Prestressing strand

## 6.2 Analysis of The Deformed Bar and Strand Pullout Behavior

An empirical approach to analysis of deformed bar pullout behavior [93] was employed in order to analyze the pullout test data generated in the project. From Bond stress-slip curves for deformed steel bars embedded in ultra-high-performance concrete with micro-scale (steel fiber) and hybrid (mico- and nano-scale) discrete reinforcement systems, the average bond stress  $\tau$ during loading (Figure 6.4) was calculated using Eq. 6.1.



Displacement (mm)

6.1

Figure 6.4 Typical pullout load-displacement curve.

$$\tau = \frac{P}{\pi \, d_h \, l_h}$$

where:

- P : pullout load
- $d_b$ : diameter of the bar or strand
- $l_b$  : embedment length of the bar or strand

Hence, the maximum bond strength  $\tau_{max}$  can be calculated as follow:

$$\tau_{max} = \frac{P_{max}}{\pi \, d_b \, l_b}$$

where :

*P<sub>max</sub>*:peak pullout load

Concrete strength is generally considered to be a key factor determining the bond strength. It is generally assumed that the local bond strength  $\tau_{max}$  is correlated with the square root of the concrete compressive strength  $f_{c}$ ; the local bond strength is thus generally expressed as a normalized bond strength ( $\tau^*$ ).

$$\tau_{max}^* = \frac{\tau_{max}}{\sqrt{f_c}}$$
 6.3

The CEB-FIP Model Code (MC90) proposes the following empirical expression for deformed steel bars in unconfined concrete (with good bond condition):

$$\tau^*_{max} = 2.0$$
 6.4

In the case of ultra-high-performance concrete, a higher normalized bond strength has been proposed in the literature [153] [154]:

$$t_{max}^* = 5.0$$
 6.5

The main thrust of the bond investigations conducted in this research was to assess the effect of graphite nanomaterials on the bond strength of deformed steel bars and prestressing strands in ultra-high-performance concrete and high-strength concrete.

### **6.3 Experimental Program and Test Results**

#### 6.3.1 Deformed Bars

Pullout tests were carried out in accordance with the procedures used in the literature [154]. Two types of #4 (12.7 mm, 0.5 in.) diameter deformed bars (uncoated and epoxy coated) were used. A

150 mm diameter and 150 mm high cylinder enclosed each bar. The cylinder was made using the UHPC mix design #7 in Table 3.6, with a single deformed bar embedded vertically along its central axis (Figure 6.5). Based on past experience [154], the steel reinforcement may yield when the embedded length exceeds 2 times the bar diameter ( $lb = 2d_b$ ) in ultra-high performance concrete. The bonded length of deformed bar in cylindrical specimen was thus 2 times the bar diameter ( $lb=2d_b$ ), instead of 5d<sub>b</sub> (RILEM recommendation). The non-bonded regions of the bar were sheathed with PVC pipes. A pullout load was applied using a servovalve-controlled hydraulic test system with a maximum load capacity 500 KN at a displacement rate of 0.5 mm/min. Two LVDTs were used to measure bond slip between the bar and concrete at the loaded and free ends of the bar. The experimental setup is shown in Figure 6.6.



Figure 6.5 Pullout test specimen.



Figure 6.6 Pullout test setup.

The pullout test specimens were prepared in a vertical position in laboratory using plastic molds. During casting and subsequent consolidation of concrete via vibration, the concentrically placed steel bars were held in position using a steel fixture (Figure 6.7a). The uncoated and epoxy-coated steel bars evaluated in this investigation are shown in Figure 6.7b. In order to prevent excess water evaporation from fresh concrete, the test specimens were covered with a plastic sheet soon after casting and consolidation. The specimens were demolded 24 hours after casting, and then steam cured at  $90^{\circ}$ C over 48 hours.



Figure 6.7 (a) Pullout test specimen, and (b) uncoated (left) and epoxy-coated (right) steel reinforcing bars.

The individual pullout load-deformation test results for uncoated deformed bars embedded in UHPC with different reinforcement conditions are presented in Figures 6.8 through 6.11. Comparisons are made between mean pullout load-deflection curves of uncoated deformed bars in UHPC with different discrete reinforcement systems in Figure 5.12. Steel fibers when used alone at a relatively high volume fraction, and especially carbon nanofiber at a relatively low volume fraction (used without or with steel fiber) benefit the peak pullout load and the post-peak ductility of the uncoated deformed bar in UHPC. The individual test results for epoxy-coated deformed bars in UHPC with different discrete reinforcement systems are shown in Figures 5.13 through 5.16. The mean values of pullout load-deflection curves for epoxy-coated bars are compared in Figure 5.17 for UHPC materials with different discrete reinforcement systems. The trends are similar to those observed with uncoated steel bars. Steel fiber at relatively high volume

fractions, and especially carbon nanofiber at a relatively low volume fraction (used alone or with stele fiber) benefit the peak pull-out load and post-peak ductility of the epoxy-coated bar pullout behavior in UHPC.



Figure 6.8 Individual pullout load-slip test results for uncoated deformed steel bar in plain UHPC.



Figure 6.9 Individual pullout load–slip test results for uncoated deformed steel bar in UHPC with 1 vol.% steel fiber.



Figure 6.10 Individual pullout load–slip test results for uncoated deformed steel bar in UHPC with 0.04 vol.% carbon nanofiber.



Figure 6.11 Individual pullout load–slip test resulst for uncoated deformed steel bar in UHPC with 0.04 vol.% carbon nanofiber and 1 vol.% steel fiber.



Figure 6.12 Mean pullout load–slip test result for uncoated deformed steel bar in UHPC with different discrete reinforcement systems.



Figure 6.13 Individual pullout load-slip test results for epoxy-coated deformed steel bar in plain UHPC.



Figure 6.14 Pullout load–slip test results for epoxy-coated deformed steel bar in UHPC with 1 vol.% steel fiber.



Figure 6.15 Individual pullout load–slip test results for epoxy-coated deformed steel bar in UHPC with with 0.04 vol.% carbon nanofiber.



Figure 6.16 Pullout load–slip test results for epoxy-coated deformed steel bar in UHPC with 0.04 vol.% carbon nanofiber and 1 vol.% steel fiber.



Figure 6.17 Mean pullout load–slip test results for epoxy-coated deformed steel bar in UHPC with different discrete reinforcement systems.

The pullout test results for deformed steel bars embedded in ultra-high-performance concrete materials with different discrete reinforcement systems were analyzed using the approach presented in Eqs. 6.1 through 6.5. The results are presented in Tables 6.1 and 6.2. Epoxy-coating of deformed steel bars did not significantly lower their bond strength to ultra-high-performance concrete, which could be due the specific failure modes considered in the bond tests conducted in this investigation. The failure mode in the bond tests involved shearing of concrete (with no split cracking). The confinement provided by the volume of concrete surrounding the embedded bar in these tests, and the short bond length made measured value of bond strength more dependent on concrete material properties than the steel surface conditions.

For both uncoated and epoxy-coated deformed bars, the highest bond strength was obtained with hybrid (steel fiber and carbon nanofiber) reinforcement system, followed very closely by the case with carbon nanofiber reinforcement. The bonded segments of deformed bars in pullout tests are shown in Figures 6.18a and 6.18b for uncoated and epoxy-coated bars without and with carbon nanofiber. Figure 6.18b indicates that introductions of carbon nanofiber increased the amount of concrete retained on deformed bar between deformations. This could have resulted from the improved adhesion of the high-density binder incorporating nanofibers, and effective control of the cementitious binder microcracks by nanofibers at the steel interface. This observation concurs with the gain in bond strength with introduction of carbon nanofiber. The introduction of carbon nanofiber seems to enhance the bond strength of ultra-high performance concrete in the vicinity of deformed bars where local stress rise occurs in concrete. The gains in the packing density and bond strength of ultra-high-performance concrete with introduction of nanofibers can explain the observations made in Figure 6.18. In Tables 6.1 and 6.2, normalized bond shear strengths,  $\tau^*_{mas}$ , increase with introduction of nanofibers. This observation indicates that the contributions of nanofibers to bond strength surpasses those to the compressive strength of UHPC.

Reinforcement Type	f <sub>c</sub> '	P <sub>max</sub> (KN)	τ <sub>max</sub> (MPa)	$\tau^*_{max}$
Plain	164	65.3	64.5	5.03
CNF	179	74.3	73.3	5.48
SF 1%	178	69.6	68.7	5.15
0.04% CNF+1% SF	179	75.1	74.1	5.54

Table 6.1 Summary of pullout test result for uncoated #4 steel bars.

Reinforcement Type	f <sub>c</sub> ' (MPa)	P <sub>max</sub> (KN)	$\tau_{max}$ (MPa)	$\tau^*_{max}$
Plain	164.00	63.19	62.39	4.87
CNF	179.00	73.89	72.95	5.45
SF 1%	178.00	68.80	67.92	5.09
0.04% CNF+ 1% SF	179.00	74.67	73.72	5.51

Table 6.2 Summary of pullout test result for epoxy-coated #4 steel bars.



(a)

Figure 6.18 Shearing failure modes of UHPC in deformed steel bars (uncoated and epoxy-coated) embedded in ultra-high-performance concrete without (a) and with (b) carbon nanofiber.



(b)

### **6.3.2 Prestressing Strand**

Bonding of prestressing strands to concrete is a critical factor governing the structure performance of pre-tensioned concrete structures. The effects of graphite nanomaterials on the bond and pullout behavior of prestressing strands embedded in ultra-high-performance concrete and high-strength concrete were investigated in this research.

#### 6.3.2.1 Strand Embedded in Ultra-High-Performance Concrete

Pullout tests were carried out in accordance with the procedures introduced in Section 6.3.1. seven-wire strands with 12.7 mm (0.5 in.) diameter (Figure 6.19) were used in this investigation.
The preparation and curing conditions as well as the specimen size and test method were similar to those described in Section 6.3.1. Two types of nanomaterials were considered: graphite nanoplatelet (NP) and carbon nanofiber (CNF). The graphite nanoplatelets (NP) used in this research had 6 nm average thickness and 25  $\mu$ m average planar dimension, with a typical specific surface area of 120-150 m<sup>2</sup>/g (manufactured by XG Sciences). The nanoplatelet (NP) dosage in ultra-high performance concrete was 0.21 vol.%, selected based on previous research [155]. Pullout tests were performed quasi-statically using a servovalve- controlled hydraulic test system with a maximum load capacity 500 KN at a displacement rate of 0.5 mm/min. Two LVDTs were used to measure the bond slip between the strand and concrete at loaded and free ends of the strand. A load cell was used to measure the value of pullout load. The experimental setup is shown in Figure 6.20.



Figure 6.19 Seven-wire strand with 12.7 mm (0.5 in.) diameter.



Figure 6.20 Strand pullout test setup

Pullout load – slip behaviors of UHPC with none, steel fiber, graphite nanoplatelet, carbon nanofiber presented in Figures 6.21 through 6.24 respectively . Mean bond stress-slip curves for strands embedded in ultra-high-performance concrete with different discrete reinforcement systems (none, steel fiber, graphite nanoplatelet, carbon nanofiber) are shown in Figure 6.25. Graphite nanomaterials at relatively low volume fractions (0.04% for carbon nanofiber, and 0.21% for graphite nanoplate) are observed to be more effective than steel fiber a relatively high volume fractions (1.1%) in improving the bond strength and the bond stress-slip behavior of prestressing strands in UHPC. The gains in bond strength and bond stress-slip behavior of nanomaterials to tensile, flexural and other mechanical characteristics of ultra-high-performance concrete. The contributions of nanomaterials to the bond stress-slip behavior of prestressing strands in UHPC also exceed the corresponding contributions to the bond stress-slip behavior of prestressing strands in UHPC.



 $Figure \ 6.21 \ Pullout \ load-slip \ behaviors \ of \ UHPC \ without \ reinforcement.$ 



Figure 6.22 Pullout load – slip behaviors of UHPC with 0.21% graphite nanoplate



Figure 6.23 Pullout load – slip behaviors of UHPC with 0.04% carbon nanofiber.



Figure 6.24 Pullout load – slip behaviors of UHPC with 1.1% steel fiber.



Figure 6.25 Pullout load – slip behaviors of UHPC with different discrete reinforment conditions.

Table 6.3 summarizes the bond strength test results, and presents the calculated values of peak bond stress  $\tau_{max}$  and the normalized peak bond strength  $\tau^*_{max} = \tau_{max} / \sqrt{f_c'}$ . Introduction of relatively low dosages of nanomaterials is observed produce the gratest contributions to the absolute and normalized values of bond strength. The rise in normalized bond strength with introduction of nanomaterials implies that the benefits of nanomaterials to the bond strength of UHPC to prestressing strands far exceed the corresponding benefits to the compressive strength of UHPC.

Reinforcement Type	fc'(MPa)	P <sub>max</sub> (KN)	$\tau_{max}$ (MPa)	τ* <sub>max</sub>
Plain	164	16.8	16.6	1.30
0.04% CNF	179	28.9	29.2	2.18
1% SF	177	25.2	24.9	1.87
0.21% NP	157	27.9	27.5	2.19

Table 6.3 Summary of strand pullout test result.

The pullout (bonded) segments of prestrssing strands were subjected to optic microscopic investigations using Olympus SC100 (Figure 6.26). In the case of UHPC with nanomaterials (Figure 6.27a), most grooves formed between wires on the strand surface were filled with the cementitions nanocomposite after pullout. The SEM image of Figure 6.27a represents the conditions of pull-out strand surface areas observed in the presence of nanomterials. The higher density and somewhat improved flowability of binders incorporating nanomaterials as well their effective microcrack control capabilities in the highly stressed regions at the strand interface can be used to explain this observation. In the case of plain UHPC (Figure 6.27b), only some of the grooves were filled with the cementitions matrix after pullout. This observation points at the complexity of bond failure in prestrssing strands, and provides some insight into the mechanisms through which nanomaterials benefit bonding of UHPC to prestressing strands.



Figure 6.26 Optic microscopy Olympus SC 100.



(a)

Figure 6.27 Optic microscope images of the bonded segment of prestressing strand after pullout from UHPC with (a) and without (b) carbon nanofiber.

Figure 6.27 (cont'd)





## 6.3.2.2 Strand Embedded in High-Strength Concrete

High-strength concrete (HSC) is increasingly used in bridges and parking structure, where both strength and durability are important considerations. Actually, most pretensioned concrete structures are constructed with high-strength concrete. Therefore, the effects of nanomaterials on the pullout behavior of presstrsing strands embedded in high-strength concrete were investigated. The mix design for HSC is presented in Table 6.4. The nanoplatelets used here were oxidized, and incorporated high moisture contents which prevented secondary bonding of the nanoplatelet surfaces. Simplified procedures could thus be used for dispersion of graphite nanoplatelet, involving addition of the required amount of nanoplatelets to the mixing water, and stirring for 12-15 hours. The HSC bond test specimens were kept inside molds at room temperature for 20

hours after casting, and were then demolded and immersed in lime-saturated water for seven days prior to testing (ASTM C192).

Mix Component	Weight proportion	
Cement Type I	1	
Silica Fume	0.10	
Natural Sand (0 - 2.00 mm)	2.64	
Crushed Granite ( $\leq 9.5 \text{ mm}$ )	2.64	
Water	0.41	
Superplasticizer	0.017	

Table 6.4 High strength concrete mix design.

Figures 6.28, and 6.29 are shown the load pullot -slip curves for behavior of prestressing strand in high-strength concrete without and with graphite nanoplatelet reinforcement respectively ,and the mean pullout load-slip curves for prestressing strands embedded in high-strength concrete with and without nanoplatelets are shown in Figure 6.30. Nanoplatelets are observed to benefit the bond strength and pullout behavior of prestressing strands in high-strength concrete. As expected, nanoplatelets tend to be more effective in enhancing the bond behavior of ultra-high-performance concrete than high-strength concrete. This finding supports a primary hyposis of this research, indicating that the high packing density, fine microstructure and high cementitious binder content of UHPC make it particularly compatible with nano-scale reinforcement.



Figure 6.28 Pullout load-slip behavior of prestressing strand in high-strength concrete without reinforcement.



Figure 6.29 Pullout load-slip behavior of prestressing strand in high-strength concrete with graphite nanoplatelet reinforcement.



Figure 6.30 Average Pullout load-slip behavior of prestressing strand in high-strength concrete without and with graphite nanoplatelet reinforcement.

Table 6.5 present the values of bond strength ( $\tau_{max}$ ) and normalized bond strength ( $\tau^*_{max} = \tau_{max} / \sqrt{f_c^T}$ ) for prestressing strands in high-strength concrete without and with nanoplate reinforcement. The contributions of nanoplate towards the bond strength of high-strength concrete to prestressing are significant, and exceed the corresponding contributions of nanoplatelets to high-strength concrete mechanical properties. The normalized bond strength increased by 70% with introduction of a relatively low dosage of graphite nanoplatelets.

Table 6.5 Summary of pullout test result for high strength concrete without and with graphite nanoplatelet (NP) reinforcement.

Reinforcement Type	fc'(MPa)	P <sub>max</sub> (KN)	$\tau_{max}$ (MPa)	$\tau^*_{max}$
Plain	57	10.7	9.06	1.20
NP	53	15.1	14.94	2.05

The significant contributions of graphite nanomaterials at relatively low dosages, when compared with steel fibers at relatively high dosages, to the bond behavior of strands can be attributed to the imminent presence of closely spaced nanomaterials in the highly stressed regions occurring in the vicinity of strands. The x-ray (and SEM) images (Figure 6.31), produced for a pullout test specimens made with steel fiber reinforced ultra-high-performance concrete, provides support for the hypothesis that the 'wall' effect in the vicinity of steel fibers. Therefore, the reinforcement efficiency of steel fibers tends to be compromised\_in close proximity to steel reinforcement which would be highly stressed during pullout. While x-ray images could not capture nanomaterials, the SEM image presented in Figure 6.31 supports the strong presence of closely spaced nanomaterials in close proximity to the steel reinforcement. Therefore, the 'wall' effect observed with steel fibers does not seem to be an issue with nanomaterials. Since these observation related to the distinct advantages of nanomaterials over steel fibers in terms of spacing and number per unit area of carbon nanofibers, a theoretical treatment of these issues is presented in the following.



Figure 6.31 X-ray and SEM images for steel fiber reinforced UHPC incorporating a steel bar.

### 6.4 Theoretical Treatment of the nanomaterial Spacing and Concentration

Close spacing is a key geometric feature of nanomaterials in concrete, which influences a host of material properties (ranging from moisture sorption resistance to control of microcrack formation and propagation). The close spacing of nanomaterials in the vicinity of deformed bar and strand surfaces could explain the effectiveness of nanomaterials in enhancing the bond and pullout behavior of bars and strands. The reduced moisture movement (bleeding) in the presence of

closely spaced nanomaterials could also reduce accumulation of moisture below deformed bars and strands, thereby improving bond behavior. Finally, the benefits of the high specific surface area of nanomaterials with active surfaces to the microstructure of cementitious materials could also benefit the bond attributes of concrete.

The average spacing (*S*) between inclusions (nanomaterials or fibers) of diameter *d* at volume fraction  $V_f$  can be expressed as follows:

$$S = \frac{K \cdot d}{V_f^{0.5}}$$
 6.6

where, K is a constant ~1.0 (ranging from 0.8 to 1.38 depending on the nanomaterial orientation and the assumptions made in calculations). The calculated values of average spacing are presented in Figure 6.32 as a functional of volume fraction for carbon nanofiber, graphite nanoplate, and let steel fiber used in the project. The average spacing between steel fiber is observed to be one thousand times that between carbon nanofiber.



Figure 6.30 Calculated values of average spacing versus volume fraction for carbon nanofiber, graphite nanoplatelet, and steel fiber.

Figure 6.33 compares the calculated number per unit cross-sectional area of carbon nanofiber, graphite nanoplate, and steel fibers as a function of volume fraction. The number per unit area of carbon nanofiber is observed to be about six orders of magnitude greater than that of steel fiber, which highlights a distinguishing feature of nanomaerials versus conventional fibers as discrete reinforcement systems. This close spacing of nanomaterials makes them effective against microcrack formation and propagation in the highly stressed regions near the bar and strand surfaces.



Figure 6.31 Calculated values of the number per unit cross-sectional area versus volume Fraction for carbon nanofiber, graphite nanoplatelet, and let steel fiber.

#### **6.5 Discussion**

The effects of nanomaterials on the bond behaviors of deformed steel bars and prestressing strand in ultra-high performance concrete was investigated in this chapter. The highest bond strength for uncoated and epoxy-coated deformed steel bars was obtained with the ultra-high performance concrete reinforced with carbon nanofiber. Carbon nanofiber, when used alone or with steel fiber, produced important gains in the bond strength and pullout behavior of (uncoated and epoxy-coated) deformated bars in ultra-high-performance concrete. Steel fibers may have positive effects on some mechanical properties of ultra-high performance concrete due to their ability to control crack growth and improve the microstructure of concrete. In areas intimately surrounding the steel bar surface, where microcrack control is critical for improvement of bond strength, however, steel fibers may not be as effective because of the 'wall' effect, which refers to the disturbance of fiber distribution and orientation in areas approach the reinforcing steel surfaces. Microstructural investigations indicated that the 'wall' effect does not apply to nanomaterials. Hence, nanomaterials are more effective than steel fibers in enhancing bonding of concrete to steel reinforcement. This was further confirmed by normalizing the bond strength to (uncoated) deformed steel bars by dividing bond strength to the split tensile strength of UHPC. The results presented in Table 6.6 indicate that the resulting normalized bond strength increases with introduction of carbon nanofiber, and actually decreases with introduction of steel fiber. Hence, steel fiber is more effective in enhancing the bulk material properties than the bond strength of UHPC to deformed bars. Similar but more pronounced trends applied to the bond strength of UHPC to prestressing strands (Table 6.7). The surface morphology, deformation mechanisms and stress systems generated during pullout of prestressing strands are more complex than deformed steel bars. These distinct features of prestressing strands could explain

the particularly high contributions of nanomaterials to the bond strength and pullout behavior of prestressing strands (when compared with deformed bars) in UHPC. Finally, the experimental observation that nanoplatelets make more significant contributions to the bond strength of UHPC, versus high-strength concrete, provides support for the distinct features of UHPC which makes it particularly compatible with nano-scale reinforcement.

Reinforcement Type	Normalized bond strength
Plain	7.73
0.04% CNF	8.37
1% SF	4.99

Table 6.6 Bond strengths of uncoated #4 deformed bars normalized with respects to the UHPC split tensile strength.

Table 6.7 Bond strengths of prestressing strand normalized with respects total UHPC split tensile strength.

Reinforcement Type	Normalized bond strength
Plain	2.06
0.04% CNF	3.40
1% SF	1.83
0.21 % NP	3.11

### **CHAPTER 7**

# CONCLUSIONS, AND RECOMMENDATIONS FOR FUTURE RESEARCH

## 7.1 Conclusions

The following key conclusions could be derived from the project outcomes.

- 1. Fibers of micro-scale diameter and nanomaterials offer complementary and synergistic actions in ultra-high-performance concrete (UHPC). The optimum reinforcement system for UHPC comprises both fibers and nanomaterials, with the nanomaterial dosage about an order of magnitude smaller than the fiber dosage. This project emphasized applications of lower-cost graphite nanomaterials (primarily carbon nanofiber and, in some cases, graphite nanoplatelets). The fibers used in the project were either PVA or steel fibers; higher-modulus steel fibers were found to be more effective than PVA fibers in UHPC.
- 2. Ultra-high-performance concrete relies upon a high packing density of the particulate matter to realize a distinct balance of engineering properties. The particulate matter in UHPC ranges in size from few hundred nanometers to few (and up to several) millimeters. Nanomaterials at relatively low volume fractions make measurable contributions to the packing density of UHPC. This is accomplished by extending the size of particulate matter down to few nanometers range. Nanomaterials fill the voids between

larger particles, freeing water to lubricate particles and enhance fresh mix workability. Theoretical calculations supported by experimental results support valuable contributions of nanomaterials towards raising the packing density of UHPC. Mix design procedures centered around maximizing the packing density were developed for UHPC incorporating nanomaterials.

- 3. The synergistic actions of fibers and nanomaterials in UHPC were attributed to the beneficial contributions of nanomaterials towards bonding and pullout behavior of fibers. An integrated theoretical-experimental investigation was undertaken to verify this effect of nanomaterials. Steel fibers of different inclinations were pulled out of UHPC materials with and without graphite nanomaterials. Nanomaterials at relatively low volume fractions were found to make significant contributions to the pullout behavior of steel fibers embedded in UHPC. Theoretical evaluation of the pullout test data indicated that nanomaterials raise the bond strength and the friction coefficient at the fiber-UHPC interfaces. These experimental findings were attributed to: (a) the local reinforcing action of closely spaced nanomaterials in the highly stressed regions located in the vicinity of fibers; (b) the rise in packing density of the UHPC matrix which benefits fiber-matrix interactions; and (c) improvement of the fiber-matrix interfacial microstructure by mechanisms such as reduced bleeding and nucleation of cement hydrates on the high surface area of nanomaterials. Microstructural observations provided partial support for these mechanisms through which nanomaterials enhance fiber bonding and pullout behavior in UHPC.
- 4. Nanomaterials were found to make significant contributions to the pullout behavior of deformed steel bars and prestressing strands embedded in UHPC (and high-strength

concrete). These benefits of nanomaterials at relatively small volume fractions distinguished them from those offered by steel fibers at relatively high volume fractions. The significant contributions of nanomaterials to the bond strength and pullout behavior of steel deformed bars and prestressing strands, which exceeded the corresponding contributions of nanomaterials to the mechanical properties of UHPC, could be attributed to: (a) the imminent presence of closely spaced nanomaterials in the highly stressed regions occurring in the vicinity of steel bars and strands (considering that the distribution and orientation of steel fibers tends to be disturbed by the 'wall' effect in the vicinity of bars and strands); (b) the rise in packing density of UHPC in the presence of nanomaterials; and (c) the improved microstructure of cementitous matrix in the interfacial regions caused by the nucleating action of the high specific surface area of nanomaterials, and their benefits towards reducing the bleeding of cementitious matrix.

5. The dispersion and reinforcing actions of nanomaterials in UHPC benefited from introduction of functional groups on nanomaterial surfaces which benefited their hydrophilic attributes and the potential for bonding to cement hydrates. Carbon nanofibers, when compared with carbon nanotubes, provide a high density of active sites for surface functionalization.

### 7.2 Recommendations for Future Research

Research in the following areas is warranted based on the outcomes of this project.

1. The contributions of nanomaterials towards bonding and pullout behavior of prestressing strands (and to some extent deformed steel bars) in ultra-high-performance and highstrength concrete materials are of practical value. Further research is needed to better define the mechanisms through which nanomaterials benefit the bond and pullout behavior of prestressing strands (and deformed bars), and to devised refined structural design techniques which reflect these contributions of nanomaterials. Theoretical models need to be developed for the bond strength and pullout behavior of deformed bars and prestressing strands in the presence of nanomaterials in UHPC.

- 2. More extensive microstructural investigations are required in order to better understand the mechanisms through which nanomaterials benefit the bond strength and pullout behavior of fibers in ultra-high-performance concrete. The theoretical models developed in the project for fiber bonding and pullout behavior need to be further refined, and used towards better defining the mechanisms through which nanomaterials benefit fiber bonding and pullout behavior.
- 3. The systematic approach to UHPC mix design based on the packing density principles need to be refined, and applied towards improved design of ultra-high-performance as well as high-strength and normal-strength concrete materials. These mix design principles need to be used towards efficient use of nanomaterials in different categories of concrete materials.
- 4. The work conducted in this project on ultra-high-performance concrete needs to be extended to cover beneficual use of nanomaterials in high-strength and normal-strength concrete. Microstructural and theoretical investigations need to be conducted in order to explain the differences in nanomateril contributions to the engineering properties and failure mechanisms of normal-strength, high-strength and ultra-high-performance concrete materials.
- 5. Comparative investigations need to be conducted on broader categories of nanomaterials in order to assess their effects on the microstructure, failure mechanisms and engineering

properties of different categories of concrete materials. Various surface modification techniques need to be developed and evaluated for promising nanomaterials with the objective of facilitating their dispersion and enhancing their reinforcement efficiency in different categories of concrete materials.

6. Structural design methods need to be developed for reinforced and prestressed concrete nanocomposites, and the impacts of nanomaterials on the structural efficiency, initial and life-cycle economy and sustainability of concrete structures need to be assessed. The results should be used for identifying and prioritizing the commercially viable applications of nanomaterials in concrete-based infrastructure systems.

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