Investigating High Energy Mixing in Cement-based Materials

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One of the current challenges to nano-engineering cementitious composite materials is obtaining properly dispersed nano-sized particles in the cementitious composite matrix. Properly dispersed nanoparticles can lead to an improved particle packing density, a key parameter to improving the mechanical, chemical, and sustainable properties of the cementitious composite. Broadening the particle size distributions of cementitious materials, such as ultra-high performance concrete (UHPC), to include additional nano-sized particles is a challenge that requires a better understanding of how they self-assemble in the cementitious matrix. Thus, the purpose of this research is to investigate the role mixing plays in multi-scale, multi-phase self-assembling cement-based material systems. This is achieved through three objectives. The first objective is to investigate resonant acoustic mixing, a mixing method not common to the concrete industry, and its ability to act as a high-intensive mixer. The second objective is to consider how using resonant acoustic mixing affects the assemblage of UHPC with carbon nanofiber inclusions and cement paste with carbon nanoplatelet inclusions. The third objective is to understand the origins of high-shear mixing and how it influences the development of cement hydration. To achieve these three objectives a systematic analysis is carried out that includes quantifying the mixing energy demand; analyzing surface characteristics through scanning electron microscopy, inverse gas chromatography, dynamic light scattering, and mercury intrusion porosity; and applying rheological theory to connect macroscopic properties to the fundamental properties of the materials. The results show that mixing is a very important parameter to multi-scale, multi-phase self-assembling cement-based materials and should be considered more in concrete research.
Investigating High Energy Mixing in Cement-based Materials

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A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
at the
University of Connecticut

2018
APPROVAL PAGE

Doctor of Philosophy Dissertation

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Acknowledgments

I would like to thank my major advisor Dr. Kay Wille for introducing me to the world of UHPC and concrete. Thank you for challenging me and allowing me to explore my own path and topics that I am most interested in.

My deepest gratitude to my co-major advisor Dr. Nicolas Roussel for taking a chance on me and inviting me to join your research group. I am forever grateful for your guidance, attention, patience, feedback, and support you have given me. Your enthusiasm for research is inspirational. I will always remember the opportunities brought to me by you. I cannot thank you enough.

To my advisor Dr. Hela Bessaies-Bay, I cannot thank you enough for your kindness, constant attentiveness, intelligent and thoughtful feedback, passion, and enthusiasm, especially about cats and life. You have been the best mentor and I very much appreciate all you have given me.

I would like to thank my committee member Dr. Michael Accorsi for his commitment to providing me the funding I needed throughout my Ph.D. My two main fellowships that have sustained my entire research were from the Department of Homeland Security and the Department of Education.

I would also like to thank the French Embassy of the United States for providing the Chateaubriand fellowship that opened my pathway to France.

I would like to express gratitude to the American Concrete Institute and the Northeast Transportation Training and Certification Program for their graduate scholarships that helped me cover conference costs.

Thank you to Dr. Michael Papantonakis and Dr. Andrew McGill from the Naval Research Laboratory for their guidance and mentoring. It was a pleasure learning from you.

Thank you to the many other professors who have influenced my growth as an academic and a professional at UConn, especially Dr. Mei Wei, Dr. Radenka Maric, Dr. Aida Ghiaei, Dr. Norman Garrick, Dr. Arash Zhagi, Dr. Ramesh Malla, Dr. Radenka Maric, and Dr. Bryan Huey.

Thank you to the many friends I made at UConn along the way – Masoud, Ned, Manish, Rui, Mandy, Mostafa, Alicia, Kevin, Lilly, Patrick, and the whole structures graduate group in CEE.

Thank you to the many friends I made at IFSTTAR along the way – Iris, Rim, Nadia, Jennifer, Blandine, Patrick, Emmanuel, Oumayma, Badreddine, Janine, Fariza, Wenqiang, Yazmin, Florian, and Robert.

Thank you to my best friends – Rhoda and Erin. Your encouragement and advices helped me succeed.

Finally, my sincerest gratitude to my family, especially my sister Frieda and my mom, who have always provided me with emotional and encouraging support to continue to pursue my academic goals, and to the memory of my step-mother Diane, who encouraged me to start this journey.

And to my wife, Audrey, thank you for joining me on this doctoral roller coaster ride and giving all your love and support so that we can finish it together.
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Glossary

UHPC  ultra-high performance concrete
CNF   carbon nanofiber
GNP   graphene nanoplatelet
RAM   Resodyn Acoustic Mixing®
RM    Resodyn Mixing
HM    Hobart Mixing
RT    room temperature
IT    ice temperature
NCNF (N) no carbon nanofibers
RCNF (R) rinsed untreated CNF
WCNF (W) polyvinyl phenol polymer wrapped CNF dried powder form
SCNF (S) polyvinyl phenol polymer wrapped CNF in a dispersed in water solution form
NSC   normal strength concrete
HSC   high strength concrete
NG    no graphite
PG    powdered graphite
HG    heptane-graphite emulsion
C-S-H calcium-silicate-hydrate
CH    calcium hydroxide
Chapter 1. Introduction

1.1. General
Over the last century developments in cement-based construction materials such as pumpable concrete, ultra-high performance concrete, sprayable concrete, and supplementary cementitious materials infused concretes have been achievable because of advancements in chemical and inorganic admixtures and not from changes to the chemistry of Ordinary Portland Cement (OPC) [1-3]. These advances in concrete have made it the most abundant, locally sourced, and consumed material by humans outside of water. As the demand for infrastructure rises, concrete is the only viable material to sustain this demand [4]. While OPC production accounts for 5-8% global carbon dioxide emissions, the next century’s developments in concrete-based construction materials, will need to dissect the elements of OPC and reassemble them in new manners.

Biernacki et al. [5] in their extensive review on this challenge have put forth seven scientific pathways critical to the development of new cementing agents and construction solutions. The work in this dissertation addresses three of these scientific pathways which are: finding the next generation of instruments and expanding the capabilities of current instruments towards construction materials, creating smart construction materials with nanoparticle inclusions, and advancing additive manufacturing in concrete materials. The lane chosen within each of these three pathways will be met in several ways.

One of the most critical aspects to assembling multi-phase and multi-scale materials is the assembling method itself. For this dissertation the assembling method means the mixing process itself that includes the type of mixing device and the mixing energy this device brings to the system. Current mixing technologies for the concrete industry have not changed much in the last
century relying heavily on planetary type mixers with shearing tools that provide low mixing energies to the system. [6,7]. High-intensive mixers that provide high energy input to the system and have power consumption instrumental capabilities have advanced the field of high performance concretes and concretes with supplementary cementitious materials [8,9], yet they still rely on tool agitation as a means for mixing. These types of mixing instruments may not be able to handle the mixing energy demands of the next generation of cementing agents and construction solutions. Exploring mixing technologies used in other fields [10] and building upon these ideas to create new mixing technologies with smart or intelligent functionalities [11-13] built-in is one possible avenue to take. This is especially important for creating smart construction materials with carbon nanoparticle inclusions [14-16].

Identifying surface characteristics that will result in a favorable assemblage of several multi-scale and multi-phase particles is also another important parameter to consider. Current techniques in cement-based materials rely on characterization techniques such as wetting contact angle, laser diffraction, and gas adsorption techniques like BET [17]. Expanding the capabilities of these techniques and finding new techniques will improve the understanding of powder agglomeration, dispersibility, packing and, hence, the rheology of the fresh state of the materials which is a critical factor in the fluidity of cementitious materials.

Additive manufacturing, also known as three-dimensional printing, of cement-based materials has gained strong momentum in recent years [18]. Yet, the strong rheological requirements can add to higher costs for this construction technique due to the complexity of chemical admixtures needed to obtain the correct structural build-up [19-21]. High shear mixing can open the door for low cost cement acceleration that can be added to the design of printing heads allowing for a faster liquid-to-solid transition of the printable material [22].
1.2. Research Objectives

The overall goal of this research dissertation is to develop and implement interdisciplinary and collaborative solutions to the engineering challenges presented in the previous section. To this end, the objectives of this dissertation are to investigate the following:

1) ResonantAcoustic® Mixing (RAM) Technology. This type of mixing device relies on an acoustic pressure wave to mix materials together and comes with built-in sensors to monitor the evolution of mixing.

2) The feasibility of using RAM mixing to disperse carbon nanoparticles in cementitious materials. The types of carbon nanoparticles chosen are graphite nanoplatelets (GNP) and carbon nanofibers (CNF), with and without polyvinyl phenol polymer-wrapping. These two carbon nano-size materials were chosen due to their cost and abundant availability.

3) Surface energy analysis via inverse gas chromatography (IGC) for CNF-UHPC composites and powders.

4) The physical origins of the effects mixing cement paste brings. The heart of the project is to learn many material characterization skills and apply them to different questions relating to cementitious materials. Rheology, electron microscopy, dynamic light scattering particle analysis, mercury intrusion porosimetry, laser diffraction, and calorimetry are the characterization techniques.

5) The role nano-size particles play within cementitious materials.

1.3. Organization of Dissertation

This dissertation is organized in eight chapters. Chapter 1 contains the background, objectives, and scope of this work. Chapter 2 provides a general literature review that includes reviews on mixing technology, carbon nanoparticle inclusions, nanosilica, rheology of concrete, ultra-high
performance concrete, and material characterization techniques. Chapter 3 presents the materials and mixing methods, while Chapter 4 presents the experimental methods. Chapters 5 – 7 focus on resonant acoustic mixing and UHPC with carbon nano inclusions. Chapter 8 – 9 takes a closer look at the origins behind the effects of high shear mixing and the consequences on cement paste. Finally, Chapter 10 offers conclusions and thoughts on future works.

Chapter 2. Review of Literature

2.1. Mixing Technology
Intensive high-shear mixers have become the industry standard in producing well-mixed UHPC. It has been shown that they are reliable and efficient mixers that reduce mixing times, improve mixing energy distributions, and possess built-in power consumption monitoring [6,8,9,23,24]. As the interest grows to produce UHPC as a multi-functional material, such as with the incorporation of carbon nanotubes [25] or other types of nano-size particles [26-28], or in a more economical manner, such as with the utilization of local materials, higher cement replacement, or poorer quality materials [29,30], the mixing procedure becomes the essence of producing high quality UHPC. This will require more research into not only the effects of the mixing procedure, but also the type of mixer used. This part of the review highlights some findings on current mixing technologies.

The cement and concrete industry mainly rely on impeller agitation mixers where the main mixing mechanisms are shear and convection [31] via a blade or paddle tool. More in-depth reviews of these types of concrete mixing technologies are found in [6,32]. However, a recent study by Remus et al [33] used ultrasound-assisted mixing to assess spread and compressive
strength properties. They found that the compressive strength increased, while the spread decreased depending on the strength of the ultrasound mixing.

The powder industry employs multiple mixing technologies such as tumbler mixers, gravity silo mixers, micro-streaming, pneumatic blenders, and agitation mixers [10]. Among these types of mixers, reciprocating movement agitation and acoustic bubble micro-streaming mixers could possibly work with cementitious materials as vibration helps reduce the volume of voids and improve the packing density in a mixture [34]. Reciprocating agitator mixers work by moving the mixing medium back and forth usually by a vibrating plate to obtain a uniform mixing distribution (Figure 1a). The power consumed by the mixing is dependent on the frequency, amplitude, and diameter of the plate [35]. Bubble acoustic streaming mixers exploit the acoustic resonance frequency of air bubbles to create micro-mixing convection streaming zones around the mixing media particles [36] (Figure 1b)

**Figure 1** Two examples of mixing technologies used in other industries: a) reciprocating agitation mixer in which the vibrating plate is moved by a mechanical crank according to [35], and b) acoustic bubble microstreaming in which an air bubble resonates when subjected to a sound field of a matching resonate frequency according to [36].
[35], and b) acoustic bubble microstreaming in which an air bubble resonates when subjected to a sound field of a matching resonate frequency according to [36].

The resonant acoustic mixer (RAM) used in the experimental program uses a mixing principle like these two mixing principles. The mixing system consists of a three-mass system, spring assembly, and loaded mixing vessel. A motor that subjects the mixing media to a reciprocating agitation movement controls the spring assembly. The system attains resonance when the stored forces in the spring and the inertia forces from the mass equal each other. The resonance of the mechanical system translates to the mixing media as a longitudinal acoustic pressure wave with a short amplitude and high frequency. The amplitude is approximately 1.27 cm (0.5 in) or less for an acceleration of 100G, where G is the acceleration of gravity (9.81 m/s) [37]. The exact frequency is affected by the vessel mass, fill level, compressibility of the material, coupling of the material to the vessel walls, material density, vessel geometry, internal vessel pressure, and mixing regime. RAM adjusts its resonance frequency to account for changes in these factors. For this work, the standard deviation from the nominal 60 Hz resonance was approximately 2 Hz. Figure 2 illustrates the RAM system.
Figure 2 (a) The acoustic laboratory size mixer LabRAM and (b) the schematic of its mixing technology [38].

2.2. Mixing Energy Demand
The practice of monitoring the mixing evolution of a concrete’s microstructure through the power curve, or the cohesion curve, has become the most developed monitoring technique in the last decade [6,8,11,39]. As power is linearly related to acceleration, the acceleration curves were used to monitor the UHPC microstructure development for this study. Moreover, the stages of mixing were based on [40,41] after liquid loading, where the acceleration curve is divided into five stages of mixing that are each defined by force dissipation mechanisms (Figure 3). The fluctuation of the acceleration curve is defined as the difference between three consecutive measurements.

In the first stage, immediately after the liquid is introduced into the mix, the acceleration sharply increases as the microstructure is in a dry granular state dominated by frictional forces. After about 10s – 15s of mixing there is a slight change in curvature of the acceleration curve, corresponding to a decrease in the fluctuation curve; this is the start of the second stage. During this stage the microstructure develops into a wet granular structure that is dominated by frictional and cohesive forces as now the water is slowly saturating the granules and forming bridges with surrounding granular structures. The leveling of the acceleration curve corresponds to the saturating of the granules and the slight dip before the maximum peak acceleration, $a_{peak}$, corresponds to the saturation of the liquid bridges between granules. This peak is defined as the maximum cohesion point and the end of the second stage. For the third stage the acceleration curve decreases, and the microstructure resembles a hard paste dominated by cohesive forces.

The fourth stage is defined by the second transition point, the fluidity point. Here the acceleration curve starts to increase again with a fluctuating response. The microstructure is now
a soft granular fluid suspension dominated by cohesive and viscous forces. The fluctuations are due to granules slowly breaking up and dispersing into the suspension. The fifth and final stage is defined when the acceleration and fluctuation curves level off. The microstructure has become a fluid suspension dominated by viscous forces.

![Acceleration and Fluctuation Curves](image)

**Figure 3.** A mixing acceleration measurement profile with its fluctuations between 3 different measurements. Each mixing stage and transition point is identified and associated with its respective dissipation origin forces.

### 2.2. Carbon nanoparticle inclusions

#### 2.2.1. Carbon nanofibers

The material science field is increasingly developing new types of carbon nanocomposites that exploit carbon’s unique electrical and mechanical properties more efficiently [42]. While the majority of research concerning 1D carbon nano-reinforcement in cementitious materials has
focused on carbon nanotubes, several studies have been conducted on carbon nanofibers (CNF) in cement paste and ultra-high performance concrete [43-49]. Compared to carbon nanotubes (CNTs), CNFs are one order of magnitude lower in cost and 2 – 3 orders of magnitude higher in available volume, making CNFs an attractive 1D nano-reinforcement for mass produced cementitious materials. However, much like CNTs, a common challenge researchers face is how to adequately disperse CNFs into cement without sacrificing the advantageous properties of the carbon material. The literature has shown that using a polycarboxylate based superplasticizer with light ultrasonication can effectively disperse CNFs in water better than if they were added directly to cement [45,48-50]. Sanchez et al. [46] proposed that the CNF/cement interfacial bond could be improved upon by adding silica fume, whose average particle size is in between that of CNF and cement. Furthermore, they suggested that using organic solvents and surfactants could potentially interfere with the hydration mechanisms of cement. Recent research by Barbhuiya and Chow [51] found that cement composites with CNFs showed higher amounts of HD-C-S-H.

Carbon nanotubes consist of concentric graphene cylinders and are nanoscale in length, whereas carbon nanofibers are conical structures with graphitic shells that are at an angle to the axis of fibers and are microscale in length[52]. The difference in crystallinity and length scale that CNFs have compared to CNTs lead to lower mechanical properties, but higher production amounts and lower costs [53]. These differences could be advantageous in construction applications that call for increased durability [14,16] and impact resistance [44] for cement-based materials.

Incorporating carbon nanofibers into cementitious materials requires thoughtful dispersion processes and dispersion quantifying methods [50,54]. The dispersion processes of Abu Al-Rub et al. [43,47-49] and Tyson et al. [55] included ultrasonication of either untreated and acid-treated CNFs with water and superplasticizer before adding the sonicated solution to cement powder through a
high-speed kitchen blender. Metaxa et al. [45], Sbia et al. [44], Meng and Khayat [56], and Wang et al [57] used ultrasonication as well, but used a three speed planetary mixer to mix the CNF solution into the cementitious powders. To the author’s knowledge, the study by Alrekabi et al [58] is the only group to have used a high-intensive mixer in combination with ultrasonication of a CNF solution.

Ultrasonication is by no means the only dispersion process seen in the literature. Nasibulin et al. [46,47] grew CNFs directly on cement grains. However, with only a 2% increase in mechanical strength, they postulated that the CNFs interfered with the cement hydration. Sanchez et al. [46] postulated that surface treating CNFs and/or dispersing them in organic solvents and surfactants could potentially interfere with the hydration mechanisms of cement and thus suggested dry mixing CNFs with cement, using a three-speed planetary mixer, and adding silica fume, whose average particle size is in between that of CNF and cement, to improve the CNF/cement interfacial bond. However, results indicated that sonication still led to better dispersion and further studies [14,16,59] used light bath sonication to disperse CNFs in a solution before adding them to the cementitious powders.

The most common dispersion qualifying method is through scanning electron microscopy (SEM) micrograph images. The literature [45,48,59,60] has shown, through SEM images of fractured surfaces, that clusters of CNFs form inside the cementitious matrix no matter the dispersion process. The work by Tyson [61] was the first (to the author’s knowledge) to theoretically quantify dispersion of CNFs in an ideal material with spherical packing. The author did this with image analysis and determining the mean free path spacing between CNFs. Stephens et al. [15] is the first group to develop an in-situ method to quantify the dispersion of CNFs in a cement-based matrix. This quantification method was able to clearly demonstrate that the state of
the CNF solution was not indicative of the final dispersion state in the hydrated cement paste. The authors concluded that the key factor for optimizing flexural properties was through the homogeneous dispersion of CNF agglomerates within the cement matrix. Further work by this group [14,16] has shown that with a homogeneous dispersion of CNF agglomerates, improvements to the chemo-mechanical properties can be obtained.

While these studies are a good start, more research is still needed. The material science group at NRL has developed a non-destructive surface modification method that disperses CNFs in water by wrapping polyvinyl phenol polymer around each fiber. This idea of wrapping CNFs with a polymer treatment could have a place in cementitious materials.

2.2.2. Graphene nanoplatelets

The promise of graphene for material applications comes from its highly advanced electrical, thermal, and mechanical properties. Thermal conductivities as high as \( \sim 5,000 \text{ W/mK} \), Young’s modulus values of up to \( \sim 1.0 \text{ TPa} \), and breaking strengths of \( \sim 40 \text{ N/m} \) have been reported [62]. Currently, the most commonly used graphene involves the oxidation of graphene to graphene oxide (GO). Graphene oxide is a 2D sheet of carbon with a mixture of oxygen, carboxyl, hydroxyl and epoxy functionalities that give it enough electrostatic repulsion to counter the van der Waals attractive forces between sheets as well as a hydrophilic nature allowing it to disperse in water [63]. It is the oxygen functionalities that have attracted initial investigations of GO in cement paste [64-66]. Lv et al. found that incorporating GO into cement paste changed the morphology of the cement hydration products into a more polygonal shape indicating that the oxygen sites of GO are interacting with cement particles and their hydration products. Gong et al. [67] found that indeed enhanced production of hydrates, improvements to tensile and compressive strength, as well as a reduction in porosity occurred. This demonstrates that graphene oxide reinforcement has potential.
However, given the need for cementitious materials to have large industrial scale applications, the use of graphene-oxide is limited due to the difficulty and cost of its production. The formation of graphene oxide is either done with chemical modification that can significantly damage the pristine graphene sheet and hinder its advantageous properties or chemical vapor deposition that requires high production costs [68]. It would be tremendously advantageous to use pristine graphene to lower the cost and boost film conductivity.

Pristine (untreated and unmodified) graphite nanoplatelets (GNP) are 2D natural flake graphite materials with ABA or ABCA stacking and having a thickness and/or lateral dimension less than 100 nm [42]. Milling ultra-thin graphite flakes is a cost-effective method compared to producing pure multi-layer graphene sheets. Recently, Woltonist et al. [68,69] have developed a one-step technique to produce laterally macroscopic, transparent, and conductive films from GNPs. This is accomplished by modest sonication of natural flake graphite in a water/heptane mixture to form continuous films at the interface between two immiscible liquids. It is estimated a savings of 95% is achieved with this emulsion method over graphene oxide production; a promising feature for large scale concrete applications. Chapter 6 presents a study on this.

2.2.3. Carbon nanoparticle comparisons
Determining the type carbon nanoparticle inclusion to include in a cement-based construction material is dependent on a variety of factors, especially cost. From Table 1, it is apparent that carbon nanotubes are the highest in production costs, while graphite flakes are the lowest on average. The properties also have different ranges in their dimensions. Overall, the dispersion procedure taken will influence the final enhancement, if at all, to the concrete material.

Table 1 Comparison of properties for carbon nanoparticles.

<table>
<thead>
<tr>
<th>Material Name</th>
<th>Specific Gravity (g·cm⁻³)</th>
<th>Length (μm)</th>
<th>Diameter (nm)</th>
<th>Elastic Modulus (GPa)</th>
<th>Tensile Strength (GPa)</th>
<th>Thermal Conductivity (W·m⁻¹K⁻¹)</th>
<th>Electrical Resistivity (S·m⁻¹)</th>
<th>Avg Price ($/lb)</th>
</tr>
</thead>
</table>
2.3. Nanosilica inclusions

The most commonly studied nano-sized particle used in cement and concrete is nanosilica [73]. It has shown to improve concrete macroscopic properties, such as compressive strength and durability [74]. To exploit all the beneficial properties of nanosilica, further research needs to be done on its dispersion and stability in a cementitious hydrating environment. Therefore, more ways to control process methods and particle properties should be investigated. The following paragraphs will highlight some of these concepts.

2.3.1. Silica Process Methods and Silica Particle Properties

When considering the different process methods for nanosilica, it is important to consider silica fume. While silica fume is considered a micro-sized particle, nano-sized particles (smaller than 100 nm) do exist in the particle size distribution. The process route of silica fume, a by-product of the silicon and ferro-silicon alloy industries, starts with reducing quartz at high temperatures (2000 °C) in an electric arc furnace. The quartz oxidizes and condenses into small amorphous silica spheres [75]. Another high heat process method is that of fumed silica or pyrogenic silica. Pyrogenic silica is produced from the flame hydrolysis of silicon tetrachloride (SiCl₄) at around 1800 °C [76]. This process produces an amorphous powder in the submicron particle range.

Additionally, there are process methods that do not require such high heat. One such process is the precipitation method first developed by Iler [77]. In this method a sodium silicate precursor is acidified at temperatures between 50 °C to 100 °C resulting in nanosilica precipitating out. This method has also been used with rice husk ash as a precursor [78]. Another process method is the
sol-gel process, also known as colloidal nanosilica. At room temperature the pH of an organosilicon solvent (e.g. tetraethyl orthosilicate-TEOS) is adjusted to the gelling point of silica. The gel is then filtered and either dried or dispersed in solution [79]. A special method developed by Stöber falls under this process method [80]. Finally, alternative process biological methods of nanosilica do exist such as the olivine and sulfuric method [81].

The reactive sites on a silica particle surface are silanol groups (Si–O–H). Three types of silanol groups can exist on the surface- isolated (Si–OH), germinal (Si–OH$_2$), and etherial (Si–O–Si) [82]. The frequency and density of these groups depend on the synthesis method. Pyrogenic silicas and silica fume have less silanol groups than colloidal silica and precipitated silica due to condensation that occurs during synthesis [83]. Silanol groups form hydrogen bonds with ions and other polar molecules very easily. Therefore, nanosilica can be well dispersed in water with a basic pH value of 7-9 [77,84-87]. This is due to hydrogen bonding between the deprotonated surface silanol groups and the water molecules, leading to a formation of a water layer around the particle.

However, as the pH value rises above 10 dissolution of silica leads to ion-exchange mechanisms displacing the protons of the silanol groups [77,84,88]. This prevents water from forming a hydrogen bond with the silanol group impeding the particle dispersion. In high pH silica bonding can occur, if one silica particle contains a dissociated silanol and another silica particle contains an associated group. They link together through an acid-base interaction. Beyond pH of 12 it is postulated that silanol groups will fully disassociate, leading to destabilization and aggregation of silica particles [85,88]. Thus, in a cementitious pore environment well-dispersed nanosilica hydrosols will most likely experience a degree of re-agglomeration. This degree is still unkown and may depend on the initial hydrosol stabilizer, the specific surface area, surface reactivity,
primary particles size, and porosity of the nanosilica particle. Further investigations will need be undertaken to examine this degree of re-agglomeration and how detrimental the it is.

2.3.2. Silica Particle in Hydrating Cementitious Matrix

The process method chosen will greatly influence the particle dispersity. Dispersity is a function of particle shape, size, size distribution, morphology, surface-to-volume ratio, porosity, and chemical characteristics [89]. To understand the dispersity of silica in a cementitious matrix these property parameters need to be taken into consideration. In a recent study Quercia et al. [79] compared how different process methods change the morphological and textural characteristics of different amorphous nanosilicas. Particle parameters such as specific surface area (SSA), particle size, pore size distribution, porosity, and shape were compared to see how slump-flow properties of normal concrete mortar were affected. Their study demonstrated that SSA, porosity, and average primary particle size are the parameters with the largest influence on slump. In a related study, Quercia et al. [90] studied the water demand of these different nanosilicas. They noticed that the pH of the pore fluid differed depending on the process route of the silica used. Additionally, they found that colloidal silica had less relative pozzolanic index compared to other production methods. They postulated that surface area determines the agglomeration state which in turn determines the relative pozzolanic reactivity. While these studies show that textural and morphological parameters have a large influence on the water demand and on the agglomeration state of the silica particles in normal concrete environments, considerations of the chemical reactivity of the silica surface, the superplasticizer-silica particle interactions, and lower water-to-cement (w/c) ratios were not investigated.

Recently, Oertel et al. [76,83,91] attempt to address some of these issues. In their investigations they compared conventional silica fume, pyrogenic silica, and Stöber synthesized nanosilica particles comparing the specific surface area, silanol group densities, and solubility in alkaline
suspensions. Oertel proposed two reaction paths for silica: (i) pozzolanic reaction or (ii) nucleation seeding effect. Interestingly though, the authors found that the Stöber particles did not appear to follow either path. Instead they found that silicate ions, formed from the dissolution of silica, interacted with alkali ions (Na$^+$ and K$^+$) that were immediately released upon hydration of cement clinker. These alkali cations react with silicate ions and form alkali silicate oligomers. Additionally, Ca$^{2+}$ ions that are released from the dissolution of cement clinker interact with silicate ions to form calcium silicate oligomers and in some cases calcium alkali silicate oligomers. This oligomerization may lead to a calcium rich silicate gel layer that surrounds the silica particles. This gel layer may prevent the silica particles from acting as nucleation seeding sites for calcium-silicate-hydrate (C-S-H) or taking part in a pozzolanic reaction with calcium hydroxide (CH).

Furthermore, the UHPC mix with Stöber particles did not show increased early day strength or accelerated heat curves like the pyrogenic silica and silica fume UHPC mixes. However, the Stöber particle mixes did show that the 28 day compressive strength was comparable and even a little higher than the other forms of silica. While, the authors’ findings show that surface reactivity of silica is an important parameter to consider in understanding dispersion mechanisms, their investigations focused on particle sizes larger than 100 nm. Additionally, consideration of the superplasticizer-silica interactions was not addressed.

Nanosilica not only has potential to interact with the cement hydration products, but also to interact with high range water reducing polymers in the matrix. It has been shown that current commercially available superplasticizer polymers exhibit incompatibilities with nanosilica [92]. Glotzbach et al. [93] used AFM to study silica-silica particle interactions in a closed fluid cell. The fluid cell was injected with a fluid environment similar to the pore environment of a cement paste. Four different plasticizer polymers were injected at separate times into the fluid cell to observe the
interaction forces between silica particles in the presence of plasticizer. In this study a commercially available PCE with a high molecular weight, and three custom-made polymers were used. Shear and force measurements showed that the commercial polymer was most incompatible with silica particles. Its large backbone and long side chains might lead to particle bridging. The smaller polymers with shorter side chains and different functionalities were more compatible. The study by Glotzbach demonstrated that better dispersing polymers are needed for nanosilica. One possible route is functionalization of nanosilica surface with organic molecules similar to current dispersing polymers used for cement and silica fume. Shin et al. [94] functionalized nanosilica particles with poly(ethylene glycol) methacrylate (PEGMA) by treating Stöber silica particles with triethoxyvinylsilane (VTES) before grafting PEGMA via UV-photopolymerization on them. While, the research intentions were not for cement this could be a possible route to take in finding more compatible dispersing polymers for nanosilica.

The literature review presented in this section resulted in a proceedings paper for the NICOM V Conference [95] and thus there was no experimental component to this topic.

2.4. Rheology of concrete
Concrete is often called ‘liquid stone’ for its ability to go from a liquid state to a solid state in a matter of hours [96]. From a physical point of view, concrete is a suspensions of various grain sizes in a continuous fluid phase, where the continuous fluid phase is the cement paste [97]. For cement pastes, water is the fluid phase and cement powder is the suspended phase. When discussing the mixing of concrete, it is necessary to understand the underlying fluid dynamics behind this multi-phase, multi-scale colloidal dispersion. While this is an active field of research, when discussing the rheology of concrete, it is better to start with the basics.
2.4.1. Newtonian Fluids

A Newtonian fluid is a fluid that follows the constitutive law:

\[ \tau = \mu_0 \dot{\gamma} \]  

(1)

where \( \tau \) is the shear stress, \( \mu_0 \) is the material’s viscosity, and \( \dot{\gamma} \) is the shear rate. (See Figure 4 for the definition of shear rate.)

Figure 4 Shear profile of a liquid with height H moving at a velocity V between two parallel planes. The shear rate is defined as the ratio between the height and velocity.

Some examples of Newtonian liquids are water and oils. No matter how the Newtonian liquid is stressed, it will always remain a liquid and return to its original state; i.e. it cannot deform. Its stress curve is curve 1 in Figure 5.

2.4.2. Non-Newtonian Fluids

Liquids that can store energy and deform are called yield stress liquids [98]. There are two classes of these types. The first type acts as a solid at rest, but with an applied stress acts as a liquid. Examples of these are cements, mayonnaise, and ketchup. The second type acts as a liquid at rest but acts as a solid when stress is applied. An example of this is when egg whites are beaten into stiff peaks. The stress that defines these transitions is called the yield stress. It is the stress needed to overcome the initial state (liquid or solid) to transition the material to the next state (solid or liquid). The shear stress defined in Equation (1) can be written as [99]:

\[ \tau = \eta(\dot{\gamma})\dot{\gamma} \]  

(2)
where $\eta(\dot{\gamma})$ is the apparent viscosity of the material and is dependent on the shear rate. Thus, finding the apparent viscosity is the challenge in describing the constitutive laws governing non-Newtonian liquids.

The simplest example of a non-Newtonian fluid is one that is at rest but once given the right amount of stress starts to flow and behave like a Newtonian liquid (See curve 2 in Figure 5). This type of fluid was first suggested by Bingham and Green in 1919[100] and henceforth has been referred to as the Bingham model. The equation for the Bingham model is:

$$\tau = \tau_0 + \mu \dot{\gamma} \quad (3)$$

where $\tau_0$ is the yield stress and $\eta(\dot{\gamma}) = \mu$ is the viscosity.

For other types of non-Newtonian fluids, the modeling is more complex. In 1926 the research of Herschel and Bulkley [101] suggested a simple power law to explain the behavior of a fluid that upon flowing increases according to a power law. They used the following constitutive power law:

$$\tau = \tau_0 + k \dot{\gamma}^n \quad (4)$$

where $k$ is a constant denoted often as the consistency factor and $n$ is a constant that determines how the fluid behaves under high shear rates. If it increases in stress $n > 1$ and is called shear thickening and if it decreases in stress $n < 1$ and is called shear thinning behavior. Equation (4) is referred to as the Herschel-Bulkley equation.
Non-Colloidal Suspensions

A suspension is a fluid with another phase dispersed inside of it. Suppose a fluid is Newtonian and the dispersed phase is not governed by colloidal attractive forces that originate from Van der Waals forces [102], then Einsten in 1956 [103] proposed the suspension has viscosity defined as:

\[ \mu = \mu_0 (1 + 2.5\phi) \]  

where \( \mu_0 \) is the interstitial fluid viscosity and \( \phi \) is the solid volume fraction defined as the total volume of the solids divided by the total volume in the system. This expression has been well-verified since then for values less than 2% for \( \phi \).

For suspensions that are more crowded, the non-colloidal particles start to interact and the Einstein relation becomes invalid. Many models have been proposed to predict the viscosity for a dense system. The most well-known is the Kreiger-Dougherty [104,105] expression for the viscosity:
\[ \mu = \mu_0 \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5\phi_m} \] (6)

\(\phi_m\) is the maximum solid volume fraction. This expression has been found to work for maximum solid volume fractions between 0.57 – 0.605 depending on the orientation of the suspended particles[106,107].

Of course, not all suspension fluids are Newtonian and not all suspended particles are monospheres nicely spaced apart. Finding a constitutive law that governs multi-phase non-Newtonian suspension is an ongoing research field in rheophysics. However, experimental evidence has shown [107-110] that using the maximum packing fraction of dry particles can be used in place of the maximum solid volume fraction.

2.4.4. Particle Packing Density
Finding the optimal particle packing density of powders is a subject found in many fields such as the powder industry and the pharmacy industry. However, it is a very complex problem as factors such as particle shape, particle size, particle size distribution, mixing vessel size, and the mixing rate all play very important parts. Thus, a good way to start modeling particle packing is to look at monospheres dispersed in a known size container. This is a well-known mathematics problem that has been looked at many times [111,112] and it is generally accepted the highest packing fraction is 0.74. However, at this point the particles cannot move, which is not the best choice for materials that want to act as a fluid. The term random loose packing is often used to refer to the maximum packing fraction that still allows for fluidity.

For materials, like concrete that are not made up of identical particles, finding the maximum particle packing density is a challenge. The simplest model is multiple sized two-dimensional spheres. This type of problem is referred to as the Apollonian packing of circles problem, first
notably discussed in 1943 by Kasner and Supnick [113]. This system is a continuous series of circles that are imbedded in the gaps between packed larger circles that are imbedded in the gaps between even larger packed circles, and so forth (see Figure 6). The maximum packing fraction is given as:

$$\phi_m = \left(1 - \frac{d_{min}}{d_{max}}\right)^{d-d_f}$$

(7)

where $d_{min}$ and $d_{max}$ are the minimum and maximum diameters, respectively, and $d_f$ is the fractal dimension. For Figure 6 the fractal dimension is three.

**Figure 6** Apollonian packing of circles.

2.4.5. *Relating to Concrete*

The theory presented in the first four sub-sections of this section on rheology of concrete relate to concrete in the following manner.

Concrete was first modeled as a Bingham fluid by Tattersall [114]. The large aggregates act as a single dispersant into a semi-Newtonian fluid that is the cement paste. The word semi-Newtonian
is operative because there is only a certain time frame where this applies before structuration of the material starts to happen. However, fresh concrete within the first 30 min or more can be considered this. However, cement paste is not a Bingham fluid, and acts more like a Herschel-Bulkley fluid or even another model developed by Casson [115].

Self-compacting concretes and other superplasticized concretes, also fail to adhere to the Bingham model. Feys et al. [116] found that the Bingham model gave negative values for the yield stress. They proposed instead that the steady state flow behavior be modeled by a two parameter Bingham model given as:

\[ \tau = \tau_0 + \mu_a \dot{\gamma} + c \dot{\gamma}^2 \]  

(8)

Another issue with relating the rheological properties of concrete to its particle packing density is that the Apollonian circle model is not valid for concrete as it restricts movement among the particles. Concrete needs to be fluid for it to be workable. De Larrard and Sedran [117] proposed instead the Linear Packing Density Model (LPDM) for grain mixtures. This model expanded upon the Furnas model [118]. The Furnas model showed that for a two-sized particle system, the packing density is a function of the fraction of fine particles to coarse particles. The maximum packing density increases for an increasing fraction up until about \( \frac{1}{4} \), then decreases again. In the model of De Larrard and Sedran [119] two geometric interactions between particles – the wall effect and the loosening effect (see Figure 7) are included in the model. Furthermore, they propose that for \( n \)-classes of particles, that the total packing density is a superposition of each class packing density.
The model by De Larrard and Sedran was a scientific approach that was able to demonstrate that concretes with high packing fractions could be made.

2.5. Ultra-High Performance Concrete

Research in cement hydration, pozzolanic reactivity, particle packing density, and cement-polymer interactions led to the development of ultra-high performance concrete (UHPC) [148]. UHPC is generally defined as a concrete composite with a compressive strength exceeding 150 MPa (22 ksi), a low water-to-binder ratio (w/b ≈ 0.2) and a high volume (30-50%) of filler and reactive micro-sized particles, such as cement, fly ash, quartz powder and silica fume [78].

The work not only by De Larrard and Sedran [117] but also Richard and Cheyrezy [120], who designated this type of concrete as reactive powder concrete, is what really start the push for UHPC. In their studies they found that optimizing an UHPC mix design requires a very high particle packing density [121], a low water-to-binder ratio [122], and a minimum amount of air voids to minimize the porosity as much as possible [123]. A cement with a C2S + C3S content greater than 65%, a C3A content of less than 8%, a C4AF content at a minimum, and an average particle size of less than 10 microns has been found to be optimal for UHPC [123,124]. The
addition of secondary cementitious materials (SCMs) such as silica fume with a low carbon content is preferred to achieve a desired workability, which Wille et al. [29] defined as a UHPC that has a slump of at least 280 mm. Reduction of the grain size, a sand-to-cement ratio of 1-1.4, and a delayed addition of 2/3 of the HRWR all are components to an excellent material design for UHPC[30,125,126].

The consequences of an excellent material design for UHPC results in flexural strengths that range from 25 – 40 MPA and compressive strengths that are greater than 150 MPA[126]. The porosity also aids in improved durability properties as well [56,127].

2.6. Microstructural characterization techniques
Effective microstructural characterization of cementitious materials is the focus of this review section. Many different characterization techniques exist with each having their own challenges in getting meaningful results for cementitious materials as cement is a reactive and time-dependent material. The biggest challenge is sample preparation [17]. Results will be poor if the sample is not prepared correctly. The next big challenge is to know which test to use for the microstructural property of interest that can give the most quantitative and useful results given the time and expense of the research project. For example, to analyze the heat flow of hydrating cement paste isothermal conduction calorimetry is preferred over semiadiabatic calorimetry [128]. Porosity can be measured through several methods such as dynamic vapor sorption, mercury intrusion porosimetry, scanning electron microscopy, or nuclear magnetic resonance [129]. Such differences will be further reviewed in this section.

2.6.1. Electron Microscopy
Electronic Microscopy is good for the assessment of a composite matrix[17]. A general schematic is shown in Figure 8. An electron beam is shot from a laser to collide with a sample [130]. The
resolution depth depends on the machine, but typically is around 1 – 5 microns. Close to the surface the electron beam makes inelastic collisions with electrons in the specimen. These are called secondary electrons. They are good for a qualitative assessment of the morphology of a fracture surface as the brightness correlates to the angle they exit the surface. Their resolution is around 0.5 – 5 nm, depending on the machine.

The incident electrons that make elastic collisions with electrons in the material are called back-scattered electrons. These electrons carry the same energy as the incident electrons and are directly related to the atomic number of the interacting element. They are very sensitive to the angle of incidence, and thus, why the specimen needs to be as planar as possible when using this function. This function allows for the quantitative assessment of the porosity or interfacial interaction zones of the matrix. The resolution is usually around 50 – 500 nm.

For the incident electrons that have enough energy to continue into the surface of the material, they can knock out inner shell electrons of an element. This results in an x-ray being emitted that is a characteristic of the energy of the element. Quantitative assessment of the chemical composition of the composite matrix is possible from the analysis of these energy dispersive x-rays when properly configured for cement-based materials.
2.6.2. Dynamic Light Scattering

Figure 9 demonstrates the principal behind Dynamic light scattering (DLS). An incident laser beam of monochromatic light is directed at a given volume of particles suspended in a liquid beam [131]. The molecules in the volume of the sample that is illuminated by this planar electromagnetic wave experience an electromagnetic force by this wave. The molecular charges accelerate and emit photons from a given position. A detector is set up such that it captures all light waves scattered at a certain angle (Figure 9a). Because of the Brownian motion of these molecules, that is the random movement due to the thermal energy in the medium, the detected scattered light intensity fluctuates with time. Brown motion describes particle collision forces due to random thermal energy in the medium. The faster a particle moves, the smaller in size it is, and the scattered intensity fluctuates more (Figure 9b). From statistical physics a time-dependent correlation function can be computed to express the dynamical properties of the molecules in the solution (Figure 9c). By using the speed of the particles, and the Stokes-Einstein relationship [132], a distribution of the diameter sizes of the particle can be determined (Figure 9d).
Figure 9  Dynamic Light Scattering schematic. An APD detector captures the scattering intensity and sends it to a digital signal processor that then translates this to a size distribution.

The particle diameter size range for the Malvern Zetasizer ZS is between 0.6 nm to 6 μm. It operates with a red laser with a wavelength of 633 nm. Back scattering detection at an angle of 173° is used to reduce the effect of multiple scattering which can arise from dust contamination or from a high concentration of particles. This angle is close to 180° where the effect of multiple scattering is at its minimum.

2.6.3. Isothermal Calorimetry

Hydration is an exothermic process that lasts a long time [133]. Figure 10 is an example of the heat signature of cement. The first stage is the dissolution phase. In this phase the aluminate phases dissolve in the water. This period last about 20-30 min. The second phase is the induction period. Nucleation of hydrates does occur at this stage, but not at a high rate [134]. This stage makes up the bulk of the setting time and lasts up to 6 hours normally. The third stage is the acceleration phase. The steepness of the slope relates to the rate of nucleation and growth of the CSH. This phase usually lasts around 12 hours but varies on the kinetics. The fourth stage is the deceleration
phase. This stage lasts for days and months. The fifth and final stage is the diffusion phase. This lasts for the remainder of cement’s life. Diffusion of ions through the cement porous medium is the governing factor at this stage [135]. Hydration heat flow is one material characterization technique fresh concrete and cement. This heat flow signature is used to thermodynamically model the material’s structural buildup.

![Diagram of heat flow/thermal power over time]

**Figure 10** General schematic of heat flow of cement hydration.

2.6.4. Adsorption Isotherms

Adsorption isotherms describe how much of a material is adsorbed onto another material. In the case of cement materials, the general interest is how much polymer admixture is adsorbed onto the surface of a cement grain and how much stays in the interstitial fluid. This adsorption amount is really a consumed amount, as polymer admixtures favor interactions with hydration products [136].

To experimentally determine the adsorbed amount of polymer on a cement surface, the most common method used is a Langmuir adsorption model [137]. This model assumes that the adsorbate behaves like an ideal gas in isothermal conditions [138]. The adsorption isotherm is a function of pressure and time. As the amount of adsorbate increases with increasing pressure, it covers the absorbent. At a certain pressure, however, the adsorbate achieves full monolayer
coverage, and thus it reaches a plateau with an increase in pressure [139]. Any further increase with pressure would mean a multi-layer adsorption.

When used in the field of cement materials, often it is more useful to relate the pressure to the amount of polymer left in the solution versus the adsorbed/consumed polymer. Figure 11 shows a schematic of the Langmuir model used in this research. $\Gamma$ represents the adsorbed amount of polymer per mass of cement, and $C_e$ represents the concentration of polymer remaining in the pore fluid [140].

![Figure 11](image)

**Figure 11** Adsorption Isotherm of polymers on cement.

### 2.6.5. Mercury Intrusion Porosimetry

Mercury Intrusion Porosimetry (MIP) was first used for concrete rocks by L. Edel’man in 1961 [141]. Since then, MIP has become the most commonly used method to determine the pore size distribution for cement pastes [142]. The principle behind MIP is to subject non-wetting mercury to high and low pressures to force it to intrude pores of a given sample. The high and low pressures determine the pore size that is intruded. The intruded volume is recorded at incremental pressure steps and then converted to pore volume ($P$) versus pore size ($d$) using the Washburn equation [143] given as:
where $\theta$ is the contact angle the mercury makes with the pore entry and $\gamma_{Hg}$ is the surface tension of mercury. The pore volume and pore size can then be plotted as the cumulative pore volume or as the derivative pore volume as a function of pore radius. The cumulative pore volume plot is good for interpreting the capillary porosity of the cement sample, while the derivative pore volume is for the pore connectivity.

Recently there has been some discussion on the validity of MIP [144]. Mercury intrudes only the connected porosity that can be reached by the mercury at given pressures. This means that for one, the mercury can only intrude pore sizes related to the pressure. For another, the mercury is measuring the pore entry size distributions rather than pore size distributions (Figure 12). This effect is commonly referred to as the “ink-bottle” effect. Nevertheless, if samples are treated properly, as in the solvent exchange method to arrest hydration of the cement [144], then results of mercury intrusion porosimetry can provide an accurate picture of the capillary porosity of the specimen.
Figure 12  MIP is challenged when it come to distinguishing different pore volumes from the same pore entry size.

2.6.6. Inverse Gas Chromatography

Inverse Gas Chromatography (IGC) is a physicochemical characterization technique. It is opposite to Gas Chromatography (GC) by means of what is analyzed. GC passes several different probe molecules through a sample and the molecules that pass through are separated and analyzed. IGC does not separate mixtures of substances into their components, but measures the value of one in the presence of another, e.g., the rate of a chemical reaction in the presence of a diffusion phenomenon [145] (see Figure 13). IGC can be used to characterize many surface thermodynamic properties such as heat of sorption, surface free energy, dispersive surface energy, non-dispersive energy, permeability, diffusion, and surface heterogeneity. Just as with GC the type of probe molecules used will determine the property of interest. Probe molecules are selected based on the contribution to the surface energy they bring. Non-polar linear alkanes help characterize the dispersive contribution of the surface energy through van der Waals interactions. Acid/base groups and aromatic molecular probes characterize the specific surface energy through the Lewis-acid base interactions [146].
Chapter 3. Materials and Mixing Methods

Mixing is the focus of this dissertation. Thus, the purpose of this chapter is to give details of the mixing method used in this study along with the materials and compositions.

3.1. Properties of Materials

3.1.1. Ultra-High Performance Concrete Materials

Type I white cement conforming to ASTM C150 [147] was used in all UHPC and high strength cement paste mixtures (Chapters 5 – 7). A commercially available high-range water reducer conforming to ASTM C494 [148] Type A & F polycarboxylate (PCE) superplasticizer (SP), with specific gravity of 1.06 and solid content of 29%, was used at 1% by weight of cement (bwoc). White silica fume (SF) and quartz powder (QP) were used as secondary cementitious and filler materials, respectively. Three different sizes of aggregates were used in two UHPC mixes. UHPC 1 consisted of fine grade quartz sand (QS1) with a medium particle size of $d_{50} \sim 0.18$ mm and a maximum size of $d_{\text{max}} \sim 0.30$ mm. UHPC 2 consisted of fine grade quartz sand (QS2) with a medium particle size of $d_{50} \sim 0.10$ mm and a maximum size of $d_{\text{max}} \sim 0.21$ mm and a coarse grade quartz sand (QS3) with a medium particle size of $d_{50} \sim 0.42$ mm and a maximum size of $d_{\text{max}} \sim 0.60$ mm. Table 2 provides the mineral and physical composition of the materials used in this study.
3.1.2. Cement Paste Materials

The cement used for the cement paste rheological experiments in Chapter 8-9 was CEM I 52.5R, equivalent to ASTM Type I, Ordinary Portland cement of specific gravity 3.15. Its chemical and mineralogical compositions obtained through inductively coupled plasma-optical emission spectroscopy (ICP-OES) and differential thermal and thermogravimetric analysis (DTA-TG), as well as its Bogue composition, are given in Table 3. The free lime was determined by extraction with hot ethylene glycol [149]. The mineralogical composition and cement powder size are given in Table 4.

### Table 2 Physical and mineralogical properties of UHPC constituents.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Nomenclature</th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃S + C₂S</th>
<th>C₃A</th>
<th>C₄AF</th>
<th>SiO₂</th>
<th>Specific Surface Area/ Mean Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>White Cement Type I</td>
<td>C</td>
<td>74%</td>
<td>13%</td>
<td>87%</td>
<td>5%</td>
<td>1%</td>
<td></td>
<td>395 m²/kg</td>
</tr>
<tr>
<td>White Silica Fume</td>
<td>SF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;96%</td>
<td>d₅₀ ~0.15μm</td>
</tr>
<tr>
<td>White Quartz Powder</td>
<td>QP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;99%</td>
<td>d₅₀ ~1.7μm</td>
</tr>
<tr>
<td>Quartz Sand, fine</td>
<td>QS1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d₅₀ ~0.18 mm</td>
</tr>
<tr>
<td>Quartz Sand, extra fine</td>
<td>QS2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d₅₀ ~0.10 mm</td>
</tr>
<tr>
<td>Quartz Sand, coarse</td>
<td>QS3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d₅₀ ~0.42 mm</td>
</tr>
</tbody>
</table>

### Table 3 Chemical and Bogue composition of Portland cement given in percentage %.

| C₃S  | C₂S  | C₃A | C₄AF | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | Na₂O | K₂O | SO₃ | Cl  | CaO free | Loss on Ignition |
|------|------|-----|------|------|-------|-------|------|------|------|-----|-----|-----|------|-----------------|------------------|
| 65.47| 5.31 | 2.56| 12.70| 19.08| 3.63  | 4.18  | 61.9 | 0.72 | 0.27 | 2.73| 2.44| 0.07| 0.78 | 2.25            |

### Table 4 Mineralogical composition and size of the cement powder used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃A</th>
<th>C₄AF</th>
<th>SiO₂</th>
<th>Dᵥ10</th>
<th>Dᵥ50</th>
<th>Dᵥ90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>64%</td>
<td>14%</td>
<td>2.5%</td>
<td>14%</td>
<td>21%</td>
<td>1.49μm</td>
<td>8.11μm</td>
<td>28.75μm</td>
</tr>
</tbody>
</table>
The quartz powder is a commercial product (C400) provided by Sibelco. Particle size distribution was measured by laser diffraction using a Malvern Mastersizer 3000 instrument (Malvern Instruments Ltd., Malvern, UK) and results are reported in Figure 14. The cement and quartz maximum packing fractions measured according to the water demand protocol [150], were 57% and 52%, respectively. In this study, a commercial polycarboxylate ether-type (PCE) provided by Sika was used in liquid form.

![Particle size distribution of the cement and quartz powders used in this study.](image)

**Figure 14** Particle size distribution of the cement and quartz powders used in this study.

### 3.1.3. Carbon Nanoparticle Materials

For the work in **Chapter 6**, Nano-24 grade graphite from Ashbury Carbons was chosen for its average flake size of 1 µm. The surface area was 350 m²/g and lamella thickness index (LTI) was 7-8. The graphite to cement ratio was set to 0.005% bwoc. To prepare the graphite heptane emulsion the procedure was as follows: 1.4 mg of bulk pristine graphite for every ml of water was first put into a 20 mL glass scintillation vial. Then, n-heptane (Fisher Scientific, HPLC grade) was added at amounts of 7:4 water:heptane by volume, and then tip sonicated (Cole-Parmer 750 W Ultrasonic processor) for 15 min at 40% power to exfoliate the graphite and disperse it into the heptane. After the sonication, water was added, and the system was bath sonicated again briefly to help move the graphite nanoplatelets to the interface. Several emulsions were made with HRWR incorporated, but it was found the stability of the emulsion did not change.
Three treatments of CNFs (Pyrograph Products, Inc.) were considered for Chapter 7, and included pristine CNFs, that have been rinsed and dried for any impurities from the manufacturer (RCNF), polyvinyl phenol wrapped CNFs that were dried (WCNF), and polyvinyl phenol wrapped CNFs that were kept in a solution (SNCF). CNFs were added at a ratio of 0.1% by cement mass. Table 5 provides the properties of the carbon nanoparticle inclusions in this work.

Table 5 Carbon nanoinclusions physical properties.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Specific gravity (g·cm⁻³)</th>
<th>Length (µm)</th>
<th>LTI/Diameter (nm)</th>
<th>SSA (m²·g⁻¹)</th>
<th>Elastic modulus (GPa)</th>
<th>Tensile strength (GPa)</th>
<th>Carbon Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNP</td>
<td>1</td>
<td>7-8</td>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>CNF</td>
<td>2.0</td>
<td>30-100</td>
<td>60-150</td>
<td>45</td>
<td>600</td>
<td>7</td>
<td>95</td>
</tr>
</tbody>
</table>

3.2. Mixture Compositions

The mixing proportions for the UHPC and HSC mixtures used in Chapters 5 - 7 were based off the recommendations provided in [123]. The silica fume and silica powder proportions remained the same at 25 mass% of the cement. They did not replace part of the cement but were added to enhance the solid volume fraction of the UHPC. The water-to-cement (w/c) ratio was varied between 0.25 and 0.21 to change the solid volume fraction. While this can affect the hydration mechanisms of the cement, only the U21 series was utilized for the comparative study with the paddle mixer to avoid this problem. The compositions for the UHPC in Chapter 5 are presented in Table 6, the NSC and HSC pastes in Chapter 6 are presented in Table 7, and the UHPC composition for the CNF-UHPC composites in Chapter 7 is shown in Table 8. The mixture composition for the cement or quartz powder systems is given in Chapter 8-9.

Table 6 UHPC 1 mixture proportions by weight of cement.

<table>
<thead>
<tr>
<th>UHPC Mix Series</th>
<th>Mixer Type</th>
<th>C</th>
<th>SF</th>
<th>QP</th>
<th>QS1</th>
<th>Water</th>
<th>HRWR (% of solid)</th>
</tr>
</thead>
</table>

36
Table 7 NSC and HSC Mix Proportions by weight of cement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cement</th>
<th>Water</th>
<th>HRWR</th>
<th>Graphite</th>
<th>Heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSC_NG</td>
<td>1</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NSC_PG</td>
<td>1</td>
<td>0.30</td>
<td>0.002</td>
<td>0.0005</td>
<td>-</td>
</tr>
<tr>
<td>HSC_NG</td>
<td>1</td>
<td>0.25</td>
<td>0.002</td>
<td>0.0005</td>
<td>0.0428</td>
</tr>
<tr>
<td>HSC_PG</td>
<td>1</td>
<td>0.25</td>
<td>0.002</td>
<td>0.0005</td>
<td>-</td>
</tr>
<tr>
<td>HSC_HG</td>
<td>1</td>
<td>0.25</td>
<td>0.002</td>
<td>0.0005</td>
<td>0.0428</td>
</tr>
</tbody>
</table>

Table 8 CNF-UHPC Composition Mix by weight of cement.

<table>
<thead>
<tr>
<th>C</th>
<th>SF</th>
<th>QP</th>
<th>CNF</th>
<th>QS2</th>
<th>QS3</th>
<th>HRWR</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHPC</td>
<td>1</td>
<td>0.25</td>
<td>0.25</td>
<td>0.001</td>
<td>0.304</td>
<td>0.709</td>
<td>0.01^a</td>
</tr>
</tbody>
</table>

\^a solid content

3.3. Resonant Acoustic Mixing Methods

3.3.1. Resonant Acoustic Mixing (RAM) Overview

A lab scale version of RAM called the LabRAM (R or RM) was used as the mixing source for this research. The LabRAM, capable of accelerating the designated media up to 100 G, was controlled through provided OEM software called RAMWare. The frequency input parameter was set to auto to ensure the mechanical system stayed in resonance, the vital principle behind RAM. By keeping the mechanical system in resonance, the force, and hence the acceleration, can be controlled by adjusting the intensity of the amplitude of the wave (given as ‘% mixing intensity’).

For the fundamental spring-mass-damper system (Figure 2b) [151], the equation of motion is given in Equation (10):

\[
m \frac{d^2}{dt^2} x(t) + c \frac{d}{dt} x(t) + k x(t) = F_0 \sin(\omega_f t)
\]

where the left-hand side represents the system forces in terms of inertia forces, with \( m \) the mass of the vessel, the mixing forces, with \( c \) defined as the damping coefficient, and the stored forces,
where \( k \) is the spring constant; and the right-hand side is the input force, \( F_0 \), and \( \omega_f \) is the resonance frequency. **Equation (10)** represents a forced, damped mechanical vibration system. At resonance, the inertia forces cancel the stored forces resulting in a first order differential equation equal to

\[
c \frac{d}{dt} x(t) = F_0 \sin(\omega_f t)
\]  

Solving **Equation (11)** for the displacement and subsequently the acceleration results in the following

\[
x(t) = A \cos(\omega_f t)
\]  

\[
\ddot{x}(t) = -\omega_f^2 A \cos(\omega_f t)
\]  

where \( A \) represents the peak amplitude to the driving force with respect to the starting center point. It is directly related to the driving force, but inversely related to the damping coefficient. **Equation (13)** demonstrates that the acceleration is linearly related to the amplitude. Thus, if the mechanical system is in resonance the ‘% mixing intensity’ directly relates to the acceleration of the material. This means, for example, an input of 70% mixing intensity results in an acceleration of 70G.

The power at peak acceleration was developed by [152] and is given as

\[
P_{mix} = \phi_{peak} F_{rms} \left( \frac{\Delta P}{100} \right) a_{peak} \cdot \frac{G}{2\pi f}
\]  

where \( t_{mix} \) is the total mixing time and \( P_{mix} \) is the total power that goes into the mixture, \( \phi_{peak} \) is the correction factor from peak to root-mean-square (rms), \( F_{rms} \) is the machine force constant, \( \Delta P \) is the difference in power intensity from loaded to unloaded mass, \( a_{peak} \) is the peak acceleration, \( f \) is the resonant frequency, and \( G \) is the gravitational constant. The correction
factor and machine force are machine variables and are set to a value of 0.707 and 70 N ± 4N, respectively. Hence, using Equation (14) the total specific mixing energy can be calculated as

\[ E_{mix} = \frac{P_{mix} \cdot t_{mix}}{mass} \]  

(15)

3.3.2. RAM Method at Room Temperature

RAM samples were prepared using the input routine given in Figure 15a using the following 4-step mixing protocol:

1. Mix the dry materials all together at an intensity of 95% for 120s. [123] notes that by mixing all the dry constituents first the chance that agglomerates of very fine particles will form is reduced. Though, contrary to [123], the authors found that the order of placement in the mixing vessel did not make much of a difference; however, to ensure good compaction of the less dense materials (e.g. silica fume), aggregates were added last;

2. After dry mixing, the routine was paused and a well was formed in the dry mix. The water was combined with the HRWR before being poured inside the well. The well was subsequently covered up before returning the vessel to the LabRAM;

3. The mixture mixed for 50 – 215s after water contact before pausing for 30s – 90s to allow the heat to dissipate and to scrape an excess material off the sides of the vessel;

4. Finally, the mixture was subjected to an additional 60s – 210s of mixing. The response to the intensity routine (e.g. the acceleration) was then recorded (Figure 15b).
Figure 15 An example of the a) input intensity routine and b) the acceleration response measurement. The maximum acceleration is taken as $a_{\text{peak}}$.

Figure 16 shows a visual of the mixing steps.

Mix powders first. Add liquid in a well. Stop to scrape sides. Mix until fluid state. Mixed UHPC.

Figure 16 Mixing protocol for UHPC mixes given in Table 6.

3.3.3. RAM Method at Ice Temperature

Noting that temperatures after mixing in the LabRAM could reach 40°C, an ice bath method to dissipate the heat of mixing was employed. Samples were mixed using a small glass 8 oz vessel inserted into a 16 oz vessel filled with ice. The constituents were sealed in the first jar with paraffin film wrapped around the vessel to ensure no liquid could get into the vessel. The temperature of the ice bath ranged from 4°C to 10°C. As the mixing vessel was very small the powders were mixed in two steps before being combined. First, the cement and quartz powder were mixed
together. Then the quartz sand and silica fume were mixed together. The mixing reduced the volume of the powders enough to combine both and then mixing more. The powders were then added to the liquid. Figure 17 gives a visual summary of the mixing protocol.

![Figure 17 Mixing protocol for UHPC mix designated as NCNF given in Table 8.](image)

**Figure 17** Mixing protocol for UHPC mix designated as NCNF given in Table 8.

3.3.3. **RAM Method for graphite nanoplatelets (GNPs)**

Five series of samples were prepared as given in Table 7 – normal strength paste (w/c 0.30) with and without pristine powdered graphite and high strength cement paste (w/c 0.25, 0.2% HRWR) with or without either pristine powdered graphite or heptane-graphite emulsion. Mixing was performed using either a three-speed Hobart laboratory bench mixer with a standard designated paddle or the LabRAM mixing device.

For the HSC_NG samples, the HRWR was added to the water first, then it was added on top of the cement powder and mixed between 3 – 5 minutes. For the HSC_PG samples, results showed that there was no difference whether the powder was mixed first with the cement powder or with the water and HRWR. The HSC_HG samples, trial results found that first mixing the heptane-graphite emulsion with the cement, then adding the remaining water and HRWR produced the best results. Figure 18 shows on the left-side the process for the H/NSC-PG samples, and on the right-
side the H/NSC-HG samples. For the emulsion samples, a layer of heptane would form at the top and needed to be siphoned off before pouring into the molds.

**Figure 18** Mixing protocols for GNP-cement paste samples given in Table 7.

3.3.4. **RAM Method for carbon nanofiber (CNFs)**

Samples were mixed under ice temperature conditions ranging from 4°C to 10°C. The following 5-step mixing protocol was followed:

1. Mix the cement, silica fume, and quartz powders together at an intensity of 95% for 60s.
2. Mix the CNF, water, and HRWR for 60s at 50% intensity in a separate vessel.
3. Add little by little the powders to the liquid constituents and mix for 3 min at 95%.
4. Pause the routine. Add the sands and mix for 2 min at 95% intensity.
5. Pause the routine to scrape the sides. Mix for 60s -180s more at 95% intensity.

The acceleration response was monitored during the mixing process and saved for analysis. **Figure 19** shows the intensity routine and the mixing protocol.
Mix powders first. Add dry to liquid. Wrap in parafilm. Place in ice bath. Mixed CNF-UHPC.

Figure 19 Mixing Protocol for CNF-UHPC mixes given in Table 8.

3.4. Hobart Mixing Method

Samples were also prepared using a three-speed Hobart laboratory paddle bench mixer (H or HM) with a standard designated paddle (Figure 20).

Figure 20 (a) The Hobart 3-speed 12-L capacity paddle mixer and (b) its associated paddle.
The mixing protocol followed the recommended protocol given in [123]. It consisted of the following 4 steps:

1. The silica fume and sand are mixed together for 3 min at speed 1 (107 rpm);
2. The quartz powder and cement are added for another 3 min of mixing at speed 1;
3. The water is combined with all the HRWR and poured into the powders for 2 min;
4. The speed is increased to level 2 (198 rpm) for another 11 – 15 min.

Total time of mixing from dry to wet was between 19 – 25 min. For this study, the fill level of the mixing container was around 1.5 L – 2.0 L or about 17% fill level.

Hobart mixing with powered GNPs was also performed with a similar protocol.

3.5 Mixing Method for Cement Paste

A delayed mixing protocol was chosen to reduce the likelihood that the aluminates would co-precipitate with the studied admixtures [153]. While complete prevention of co-precipitation is never the case in fresh cement paste, this protocol exhibited decreased variations of the system with time [154]. Cement pastes were prepared using a Turbo test Rayneri VMI mixer with four mixing speeds chosen—840 rpm, 1400 rpm, 2100rpm, and 2800 rpm (see Figure 21). The diameters of the mixing blade and beaker were 3 cm and 8 cm, respectively.
The mixing protocol was a three stage process (see Figure 22). In the first stage, 200 g of cement was added to 90% of the water and then mixed for 90s. In the second stage, the cement paste was left to rest for 20 min. In the third stage the paste was continuously mixed for 120s, where at the 60s mark the remaining water and the PCE (varying between 0.0% - 1.2% solid content by weight of cement) was added to the mixing paste. The amount of water in the PCE solution was considered in the w/c calculation.
After the last stage of mixing, the paste was left to rest for another 15 min for the polymer to reach adsorption equilibrium in the system. Then the paste was centrifuged at 1000 times the gravitational acceleration (g = 9.81 m/s²) for 5 min. Finally, the liquid phase was extracted and filtered with a polyvinylidene fluoride (PVDF) 0.45 μm membrane (Millipore) (see Figure 23). The preparation protocol was the same for the quartz powder system.

Figure 23 After mixing, the paste was centrifuged at 1000g for 5 min, the pore solution was collected, and filtered with a PVDF 0.45μm filter before analysis.

Chapter 4. Experimental Methods

Several experimental methods were used during this dissertation. This chapter summarizes the various methods that were used.

4.1. Methods for measuring Fresh State Properties of UHPC
The following methods were used in Chapters 5 – 7 to measure the workability and rheological properties of the UHPC and H/NSC samples.
4.1.1. Workability

The allowable mass limit for the LabRAM is 500g and the volumetric limit of the mixing vessel used is 500mL. Due to the low bulk density of the non-compacted dry powders filling the mixing vessel to its maximum capacity of 500mL, about half this volume of fresh cementitious material can be produced. This amount of material is not enough to fill the standard cone (1.376mL) described in ASTM C230 [19]. Hence, a modified cone (Mini) was manufactured with dimensions half of the standard cone (Standard), and thus a volume ratio of 1:8, to test the spread flow properties (Figure 24a). The volume to fill the mini cone is 172mL.

Figure 24 (a) Spread Flow measurements were taken using a mini cone with half the dimensions of the cone designated in ASTM C230, and (b) measured using a tape measure.

All UHPC mixes were tested using both cones. The corresponding spread diameter ratios between the two cones were then recorded using standard measuring tape of an accuracy of a millimeter and averaged over 4 measurements (Figure 24b). Spreads were taken 20 minutes after water contact with the cement. Comparisons of the spread flow values of the standard cone to the mini cone showed a nearly constant spread ratio of 2.5 (Figure 25) with an R square value of 0.984.
Figure 25 Correlation between the ASTM standard and the modified mini cone.

4.1.2. Steady State Rheology

Steady-state flow rheological measurements were obtained using a Malvern Kinexus Pro+ Rheometer (Figure 26a) with a cup and serrated bob geometry (Figure 26b). Rheological tests were conducted between 15-20 minutes after water contact with the cement to ensure the material was in the dormant period [155]. The steady-state protocol utilized a hysteresis loop sequence as used in previous studies for normal concrete [156,157]. The protocol was as follows (Figure 26c):

1. Pre-shear at a constant shear rate of 10 s\(^{-1}\) for 30 s,
2. Rest for 30 s,
3. Increasing linear shear ramp from 0.9 s\(^{-1}\) to 10 s\(^{-1}\) for 90 s,
4. Decreasing linear shear ramp from 10 s\(^{-1}\) to 0.9 s\(^{-1}\) for 90 s.
(a) Malvern Kinexus Pro+. (b) Cup and bob geometry. (c) Steady-State rheological sequence.

**Figure 26** Flow rheology testing a) equipment, b) geometry, and c) protocol used in this study.

The area within the hysteresis loop was computed to relate to the structuration of the material [158] as shown in **Figure 27**.

![Typical thixotropic hysteresis loop in this study. The grey area is related to the energy needed to breakdown the material’s structure.](image)

**Figure 27** Typical thixotropic hysteresis loop in this study. The grey area is related to the energy needed to breakdown the material’s structure.

As with most concretes that contain high ratios of polymer, a standard Bingham flow model (**Figure 28a**) results in negative yield stress values due to the non-linear behavior of the material [116]. Therefore, a modified Bingham model (**Figure 28b**), given in (16), was applied to the rheological data.
\[ \tau = \tau_0 + \mu \dot{\gamma} + c \dot{\gamma}^2 \]  

This model is preferred over the Herschel-Bulkley model (Figure 28c) because its parameters can be related to the physical properties of yield stress and plastic viscosity. In Equation (16) the yield stress, defined as the stoppage of flow or when the shear stress in the material is no longer plastic, is given by \( \tau_0 \), the plastic viscosity, defined as the resistance to flow, is given by \( \mu \), and the second order term, \( c \) (Pa-s\(^2\)), relates to the shearing behavior of the material. If shear stress decreases with an increase in strain (\( \frac{c}{\mu} < 0 \)) the material is said to be shear thinning. Conversely, if shear stress increases with an increase in strain (\( \frac{c}{\mu} > 0 \)) the material is designated as shear thickening. If the shear stress is linear with strain (\( \frac{c}{\mu} = 0 \)), then it is Newtonian.

Figure 28 Different rheological behaviors and the models applicable to UHPC [116]. For this study the best fitting model was the Modified Bingham model.

4.2. Methods for measuring Fresh State Properties of Cement Paste

Dynamic rheological experiments were conducted using a Bohlin C-VOR shear rheometer equipped with a Vane geometry. The Vane tool diameter, outer cup diameter and depth were 25 mm, 50 mm and 60 mm, respectively (see Figure 29a).
After the mixing process the paste was loaded into the geometry and pre-sheared at 150 $s^{-1}$ for 150s before the start of the time sweep dynamic test (see Figure 29b). In order to measure the evolution of the kinetics of the rigid interactions network, an oscillating strain of amplitude lower than the rigid critical strain [159] was applied. This ensures that the system is purely elastic, and the measured stress is in phase with the applied oscillating strain [160]. Thus, the oscillating strain of amplitude was set to 0.03% at a frequency of 1 Hz. To capture the elastic storage modulus fully the time of the test was set to 2 h.

4.3. Methods for measuring Mechanical Properties of UHPC

4.3.1. Compression Strength

ASTM C109- Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens) [161] was followed for compression testing. Specimens were cast in 50-mm (2 in.) cubic brass molds and vibrated for approximately 30s. The specimens were covered and placed in a controlled curing room for 24h at 20°C before being demolded and placed in a lime-saturated water bath at 20°C. Before testing, the load surfaces were ground to
ensure the specimens were loaded uniformly leading to results with high consistency. The compressive strength was taken as maximum force divided by the average area of the load face surfaces.

4.3.2. Peak Flexural Strength
A non-standard three-point bending test was used to obtain the maximum flexural strength. Beams with average dimensions of 15 cm × 2.5 cm × 2.5 cm (6 in × 1 in × 1 in) were cast in a high-density polypropylene (HDPE) beam mold. The specimens were covered and placed in a controlled curing room for 24h at 20°C before being demolded and placed in a lime-saturated water bath at 20°C. Averages were taken for 3 specimens per mix with the standard deviation taken per sample.

For specimens in Chapters 6-7, 28 day equivalent strength values were obtained by rapidly aging the specimens via a heat steam curing method for 48h at 95°C (68°F).

4.4. Scanning Electron Microscopy
Scanning Electron Microscopy (SEM) was performed with three different SEM machines located at three different facilities. Thus, the sample preparation and methods for each machine differed slightly from each other. The following is a generalized summary of the methods.

SE-SEM sample preparation consisted of first hammering or gently breaking specimens into small pieces about 1 mm in diameter. The specimens were treated with isopropyl alcohol to stop the hydration mechanism and then left to dry in an air tight container to prevent carbonation. Specimens were coated with gold at UConn or carbon at NRL to improve the conductive face of the specimen. Several pieces were then chosen at random to be prepared for secondary-electron scanning electron microscopy (Zeiss Leo 1455 SE-SEM). As the SEM machine was in a clean room facility at NRL, no pictures could be taken for the preparation of the sample. The SEM picture provided from UConn was performed by Doug Hendricks, a fellow lab member of ACMC.
4.4.2. Back Scattering Electron Scanning Electron Microscopy (BSE-SEM)

The sample preparation for BSE-SEM was more laborious. First the specimen needed to be broken and placed in a small plastic container, approximately 1.5 cm in diameter. Then in a cup enough resin to cover the specimen was made at a ratio of 25:3 g of EpoFix Resin to EpoFix Hardener (Figure 30a). The resin was introduced into the container under a vacuum to ensure the minimum amount of air bubbles got stuck with the resin (Figure 30b). Once the resin completely covered the specimen, the specimen was put aside, and the resin was allowed to harden over a period of 24 hours (Figure 30c). A Struers Accutom-50 diamond saw was used to cut the specimen such that it had a planar surface (Figure 30d-e). A Struers grinding polishing machine was then used to polish the specimen through a series of decreasing grain size (Figure 30f-h). After polishing the specimen was set aside for another 24 hours to allow enough time for the polishing alcohol residue to evaporate (Figure 30i). The specimen was then coated with a carbon coater (Leica) to create a conductive surface on the plane (Figure 30c).
Figure 30  Sample Preparation for back scattering electron scanning electron microscopy.

4.5. Mercury Intrusion Porosimetry
Mercury intrusion porosimetry (MIP) was used to characterize the pore structure of the CNF-UHPC composites. This technique is based on the intrusion of a non-wetting fluid (mercury) into the connected pore structure under increasing pressure. The Washburn equation is used to relate the pressure to the entry pore size. Samples were crushed to obtain a mass of 1g. The dried samples were placed in the dilatometer and the air was removed. The measurement was in two steps for two different populations of the pores. In the first step a pressure of 100kPa was applied to intrude the larger pores. In the second step, the pressure was increased up to 400 MPa which allowed the mercury to intrude pore entries down to 2 nm.

4.6. Inverse Gas Chromatography
A Hewlett-Packard gas chromatograph fitted by Surface Measurement Systems (SMS) with a flame ionization detector (FID) was used for the Inverse Gas Chromatography (IGC) measurements. Glass columns of 30 cm in length and 4 cm in diameter were packed with a tap-and-fill method with specimens that were grounded up by hand and then sieved through a #200 or #140 sieve. Each column was packed with 100 mg – 150 mg of material. Before the columns were subjected to each of the gas probes, they were conditioned for 60 minutes at 60°C. All runs
were at 60°C with an injection flow rate of 10 sccm. The probes listed in Table 9 were selected based off the limited literature on IGC and cement [146,162-164]. The dead-time was determined by methane injection. A Flame Ionization Detector (FID) was used to determine retention times.

### Table 9 Selected probes used in this study.

<table>
<thead>
<tr>
<th>Probe Molecule</th>
<th>Type</th>
<th>Probe Molecule</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>aromatic</td>
<td>Methane</td>
<td>n-alkane</td>
</tr>
<tr>
<td>Chloroform</td>
<td>aromatic</td>
<td>Octane</td>
<td>n-alkane</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>polar</td>
<td>Nonane</td>
<td>n-alkane</td>
</tr>
<tr>
<td>Methanol</td>
<td>polar</td>
<td>Decane</td>
<td>n-alkane</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>polar</td>
<td>Undecane</td>
<td>n-alkane</td>
</tr>
</tbody>
</table>

#### 4.7. Dynamic Light Scattering

The concentration of particles remaining in the filtered interstitial pore fluid after mixing and filtering was determined by Dynamic Light Scattering (DLS). Measurements were performed using a Zetasizer nano S from Malvern Instruments, operating at an incident light wavelength of 633 nm, scattered light detection angle of 173°, and constant temperature of 25 °C. The value of the scattered intensity was computed from the average of five independent measurements. DLS is generally used to measure the size distribution by intensity of particles or polymer coils in a liquid medium. In this work, the measured scattered intensity was further used to study the nanoparticles in cement pore solution and estimate their concentration.

Plotted in Figure 31a, the size distribution by intensity of cement pore solutions solution at different relative concentrations obtained through calcium hydroxide dilution. The calcium hydroxide solution (i.e. lime) was prepared by adding to distilled water 0.85g/L of Ca(OH)₂. The presence of nanoparticles with a size around 130nm can be seen. Figure 31b shows that the light intensity scattered by these nanoparticles, which corresponds to the peak area from 30 nm to 1000 nm, can be moreover correlated to their concentration in the cement pore solution. In the following
work, the concentration of nanoparticles in the pore solution will be estimated by measuring the scattered intensity (i.e. peak area).

**Figure 31** (a) The size distribution by intensity of cement pore solutions at different relative concentrations (i.e. the ratio between concentration of the solution after dilution with calcium hydroxide solution and the concentration of the initial solution) and (b) the corresponding peak area as a function of the relative concentration. The pore solution is obtained from a cement paste prepared at W/C=0.3, containing 0.4% PCE and mixed at the speed of 840 rpm.

**4.8. Adsorption Isothermals**

Total Organic Carbon (TOC) analysis was used to measure the adsorption of the PCE on the surfaces of the cement or quartz powders. The TOC analyzer in this study was manufactured by Shimadzu. The adsorption levels of different dosages of PCE on the mineral phases of the powder were found by taking the difference between the total organic carbon content of a reference PCE solution and the amount of PCE extracted from the pore solution of a cement or quartz powder paste. The amount of organic carbon content in the powders from the production process cannot
be neglected as it strongly affects the measurements if left aside. The subsequent measurements were taken from pastes with incremental increases in PCE dosage. The adsorption isotherms were then computed to determine the saturation levels of the PCE on the surfaces of the cement or quartz powders.

4.9. Isothermal Calorimetry

The thermal power and heat of hydration of the cement pastes were monitored for the first 48 hours using a TAM Air microcalorimeter (Thermometrics) at a constant temperature of 20 °C. Samples were mixed according to the mixing procedure and then 5g of paste was placed inside the calorimeter cell. All samples were balanced with a reference cell having the same heat capacity.

Chapter 5. Evaluation of Resonance Acoustic Mixing Technology using Ultra High Performance Concrete

5.1. Introduction

The focus of this research is to mix UHPC by employing a novel type of mixing technology that combines the principles of reciprocating movement agitation and acoustic streaming micromixing zones called ResonantAcoustic® Mixing (RAM) technology. RAM is an innovative type of mixing technology that works on vertical reciprocating movement of springs to apply a short amplitude and high frequency (~60Hz) acoustic pressure wave that induces mixing [165]. Micromixing zones and bulk movements of the material are created without the contact of any mixing elements [166]. As an in-container reciprocating movement agitator, RAM has already shown potential in the pharmaceutical [167] and food [37] industries, and thus, could have potential in the cement and concrete industry as well.
In this study, the authors monitored the mixing efficiency of RAM for producing high quality UHPC through acceleration consumption curves, specific mixing energy, and spread flow properties. Then, a designated UPHC mix was selected to assess its fresh state properties and mechanical properties compared to a table top paddle mixer. The aim of this paper is twofold – 1) to test the suitability of RAM for mixing UHPC, and 2) to investigate how RAM mixing compares to a commonly used mixer in the cement and concrete industry.

5.2. RAM Monitoring Methods
As with any intensive shear mixer, the time, the power, the water-to-cement ratio, and the fill level all have an influence on the acceleration curve and change the location of the cohesion and fluidity points [39]. Hence, a series of tests (Table 10) were performed to monitor how the acceleration and fluctuation curves change as these four parameters change for RAM mixing.

These tests were then analyzed to find the most optimized routine for each specific UHPC tested in this study using specific mixing energy and spread flow workability tests. An average of 3 measurements per sample test were taken. The standard deviation was taken to be twice the median of the measurements.

Table 10 Mixing Parameters of RAM monitored.

<table>
<thead>
<tr>
<th>Series</th>
<th>Intensity (%)</th>
<th>Fill Level (%/g)</th>
<th>Water-to-Cement</th>
<th>Mix Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
<td>40, 50, 60, 70, 80</td>
<td>44/221</td>
<td>0.25</td>
<td>300</td>
</tr>
<tr>
<td>Fill Level</td>
<td>50</td>
<td>50/250, 70/350, 100/500</td>
<td>0.23</td>
<td>300</td>
</tr>
<tr>
<td>W/C</td>
<td>50, 70</td>
<td>50/250, 100/500</td>
<td>0.21, 0.23, 0.25</td>
<td>300</td>
</tr>
<tr>
<td>Time</td>
<td>70</td>
<td>100/500</td>
<td>0.25</td>
<td>150, 270, 300</td>
</tr>
</tbody>
</table>
5.3. Results

5.3.1. Monitoring RAM through acceleration curves

Acceleration and fluctuation curves defined two types of granular growing behavior for wet powder agglomeration, that is, Stepwise Growing Behavior (SGB) and Continuous Grown Behavior (CGB) [168]. From these results it can be observed the lower % mixing intensity levels are of an SGB nature, while the curve for 80% mixing intensity is more of a CGB form. The difference between the two is whether the material acts as individual agglomerates or as one large agglomerate. In a vertical oscillating system, at maximum amplitude the particle can experience free fall if there are no other forces acting on it. It is assumed that this is the case for RAM. Thus, the maximum amplitude, $A$, velocity, $v$, and height, $h$, a particle can achieve through free fall is given as

$$A = \frac{\ddot{x}}{\omega_f^2} \quad (17)$$

$$v = A \cdot \omega_f \quad (18)$$

$$h = \frac{v^2}{2G} \quad (19)$$

where $\ddot{x}$ is the maximum acceleration, $\omega_f$ is the resonance frequency, and $G$ the gravitational constant. Increasing the intensity increases the acceleration and thus the free fall height the material experiences with the vertical oscillatory movement. According to Equation (13) when the RAM mixer is in resonance the peak acceleration increases linearly with intensity. Hence, for a mixing intensity of 40%, the material experiences 40G of acceleration. For a resonance frequency of 60 Hz, this equates to an amplitude of 2.76 mm, a velocity of 1.0 m/s and free fall height of 55 mm. For an intensity of 80%, the amplitude and velocity are twice this, but the free fall height is 4 times greater.
It can also be seen from the fluctuation curves that the start of the largest fluctuation peak correlates to the cohesion point of the mix and the end correlates to the fluidity point (Figure 32). This type of behavior has been seen in other studies as well for power fluctuation curves [39,41]. Furthermore, when the fluctuation curve becomes constant or very close to zero, this is denoted as the time to reach a state of full dispersion. The time to reach this point decreases with an increase in mixing intensity. Past research has denoted a similar point called the stabilization time [6,8] which can be related to the optimal mixing time. Finally, it can also be observed that the acceleration curve, once it reaches this point becomes the same value as the mixing intensity, e.g. 80G at 80% mixing intensity, and therefore, indicating the RAM is at complete resonance once it reaches full dispersion.

Figure 33 shows the acceleration and fluctuation curves for the Fill Level Series. Fill level herein is defined as a percentage of mass, with 100% or 500g being the maximum fill level. Results show that at a 50% (250g) fill level, the peak acceleration is 5-10% higher in intensity than the mixing intensity level, while the 70% (350g) fill level is 5% lower. For 100% (500g) fill level, the peak acceleration is reduced by approximately 10-15%. As the amplitude is inversely related to the damping coefficient by the relationship $F_0/c$ (see Eq.(11), then likewise the acceleration is too. At resonance, the system is critically damped, and c is equal to $2\sqrt{km}$ [169]. Hence, if there is a 50% increase in mass, there must be about 14.1% reduction in acceleration, which is what is presented Figure 33c for the average acceleration curve. Furthermore, as the fill level increases the time it takes to reach the cohesion and fluidity points also increases. The reduction in acceleration means a reduction in mixing force intensity, and hence, a difference in cohesion behavior of the mixture is observed.
As the apparent volume of the mixing level is initially full at the start of mixing, there is less space to fully reach the maximum free fall height adding to the reduction in impact force the material feels from the vessel’s boundaries. Nonetheless, like the Intensity Series results, the width of the largest fluctuation peak, or the largest two consecutive peaks, corresponds to the stage of mixing between the cohesion and fluidity points, and the point where the fluctuation curve reaches a constant state denotes the final state of the mixture. From Figure 33b and Figure 33c it appears more time was needed for higher fill levels to reach this point.
In Figure 34 the results for the W/C Series are presented. Figure 34a-c show results for a fill level of 50% and mixing intensity of 50%, while Figure 34d-f show results for a fill level of 100% and mixing intensity of 70%. Several observations can be made. First, the length of the cohesion stage increases with decreasing w/c ratios. This is expected as it has been seen in past research [6,8,39] with decreasing water to powder ratios. Second, for the 50% fill level results, the peak acceleration increases as the w/c ratio decreases going from the expected 50% mixing intensity for w/c 0.25 (Figure 34a), to an increase of 5% to 10% for w/c 0.23 (Figure 34b) and 0.21 (Figure 34c), respectively. This type of behavior is not intuitive as the opposite is expected. Yet, recalling Figure 32c for 80% mixing intensity, where the length of the cohesion stage increased with an increase in intensity being attributed to the switch between SGB to CGB, then it is suggested that when the w/c ratio decreases the material accelerates not as individual agglomerates, but as one large agglomerate. Thus, the RAM machine needs to increase the
acceleration to break the cohesive bonds between the material and the vessel walls before further liquid distribution can take place. Conversely, for the 100% fill level, the peak acceleration decreases with decreasing w/c ratios. It is 20% less than the % mixing intensity for the higher w/c ratios of 0.25 and 0.23 and close to 30% less than the mixing intensity for the lowest w/c ratio. Lastly, the length of the cohesion stage for the highest w/c ratio (Figure 34d) remains the same (compared to Figure 34a), but for lower w/c ratios the length decreases, indicating the increase in fill level is helping the cohesion of the material along.

**W/C Series**

![Graphs showing acceleration and fluctuation over time for different W/C ratios and fill levels.](image-url)
Figure 34  Average acceleration and fluctuation measurements for the W/C Series. LHS: the fill level and intensity level are each 50%. The mix series are a) U25, b) U23 and c) U21.

RHS: the fill level is 100% and the intensity level is 70%. The mix series are d) U25, e) U23 and f) U21.

5.3.2. Monitoring RAM through specific mixing energy and spread flow

Shown in Figure 35 are the specific mixing energies and spread flows for the specified test series given in Table 10 Mixing Parameters of RAM monitored. The specific mixing energy (SME) of a mix is a property that is used to compare laboratory mixes to field mixes for oil well cement slurries [170,171]. It is dependent on the time of mixing and the total mass of the system (see Eq. (17)).

In Figure 35a the spread-flow shows a decreasing trend as the % mixing intensity increases from 50% to 80%, while the SME shows an inverse trend. For the Intensity series, the time of mixing was the same for each intensity, however, the acceleration curves in Figure 32 demonstrate that the optimal mixing time varied for each intensity level. For example, for 80% mixing intensity the optimal mixing time was on average 200s. Using this in Eq. (17)) results in an optimal SME closer to 85 kJ/kg, which is the SME value for 70% mixing intensity. Nonetheless, even this value
is not the most optimum SME value, which for this mix series is around 45 kJ/kg for 50% mixing intensity.

For the Fill Level mix series, the spread flow values are larger at 50% fill level, but level out by 70% fill level (Figure 35b). With an increase in fill level, the SME decreases and thus a longer time of mixing and/or a higher peak acceleration is needed to obtain the same SME for a lesser fill level. Even still, the spread flow values do not appear to be affected from the drop in SME.

In Figure 35c and Figure 35d the change in w/c ratio and its effects on the spread flow and SME values are depicted. The increase in spread flow values is expected when the w/c ratio is increased. However, an increase in spread flow does not always correlate to an increase in SME values as these values change according to mass, mixing time, and % mixing intensity levels. For example, the spread values increase for the U25 mixture when both the fill level and % mixing intensity increase (Figure 35d), while the converse is true for the U21 mixture (Figure 35c). The spread flow values also increase when the mixing time increases (Figure 35e), though it can also decrease if the mixing time is too long (Figure 35a).
5.3.3. Comparison of Fresh State Properties of RAM to a Table Top Paddle Mixer

To assess how RAM mixing affects the fresh state and hardened state properties of a given UHPC mixture, a comparative study to a table top paddle mixer was undertaken. All results for the RAM were for a mixing intensity of 70% and a fill level of 100% (500g), as the best spread values for all the UHPC mixtures (see Figure 35) were found at this setting. shows the results of the rheological tests. The area enclosed is the hysteresis area which represents the energy needed to break down a material’s structure as well as the amount of structuration that builds up after

Figure 35 The spread flow values compared to the specific mixing energy: a) Intensity Series, b) Fill Level Series, c) W/C Series where the fill level and intensity level are each 50%, d) W/C Series where the fill level and intensity level are 100% and 70%, respectively, and e) Time Series for U25 where the fill level and intensity level are 100% and 70%, respectively.
shearing stops [116,158]. The largest differences can be found for the U25 mixture series and the smallest for the U23 series.

Figure 36 Average shear flow curves for a) U25, b) U23, and c) U21, where R means RAM mixer and H means Hobart mixer.

Shown in Figure 37 and summarized in Table 11 are the fresh state properties from these flow curves and the spread flow cone tests between the two mixers. In Figure 37a the spread flow values show an increase in spread value for the U21-H and U25-H series (Table 6), but not much difference between the two mixers for the U23 series. Figure 37b shows the yield stress values between the two mixers with the U21-R series showing a much higher yield stress than the U21-H series. Such a difference should be reflected in the spread value, however, as the spread flow depends on a variety of other factors than the material itself such as the surface tension of the
spread cone, the spread surface, and the thickness of the spread compared to the diameter, the spread value can only be taken as an approximation of the yield stress. The modified Bingham model estimates closer to the true value of the yield stress \([116,172]\).

In Figure 37c, the viscosity values for the U23 series are the same, while for the U25 series the RAM mixer has a higher viscosity. The hysteresis loop areas are presented in Figure 37d. Overall, the RAM mixer shows higher shear thickening behavior (Figure 36) than the Hobart mixer. This explains why the yield stress is higher and the spread values are lower for the RAM mixer.

### Table 11 Summary of fresh state rheological properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hysteresis Loop Area (J·m(^{-3})·s(^{-1}))</th>
<th>(\tau_0) (Pa)</th>
<th>(\mu) (Pa·s)</th>
<th>(c) (Pa·s(^2))</th>
<th>Spread (mm)</th>
<th>Spread(_{eqv}) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U25 – R</td>
<td>15.81</td>
<td>1.95</td>
<td>3.93</td>
<td>0.15</td>
<td>136.9</td>
<td>334.4</td>
</tr>
<tr>
<td>U25 – H</td>
<td>6.70</td>
<td>1.49</td>
<td>2.28</td>
<td>0.03</td>
<td>141.3</td>
<td>345.4</td>
</tr>
<tr>
<td>U23 – R</td>
<td>25.60</td>
<td>3.82</td>
<td>6.40</td>
<td>0.23</td>
<td>132.6</td>
<td>323.7</td>
</tr>
<tr>
<td>U23 – H</td>
<td>28.57</td>
<td>4.55</td>
<td>6.17</td>
<td>0.12</td>
<td>129.4</td>
<td>315.7</td>
</tr>
<tr>
<td>U21 – R</td>
<td>83.08</td>
<td>9.70</td>
<td>15.43</td>
<td>0.68</td>
<td>106.6</td>
<td>258.8</td>
</tr>
<tr>
<td>U21 – H</td>
<td>69.34</td>
<td>6.50</td>
<td>18.35</td>
<td>0.42</td>
<td>111.3</td>
<td>270.4</td>
</tr>
</tbody>
</table>
Figure 37 Flow properties. a) spread-flow, b) modified Bingham yield stress, c) modified Bingham viscosity, and d) hysteresis area.

5.3.4. Comparison of Mechanical Properties of RAM to a Table Top Paddle Mixer

Since the U21 series showed more differences in the fresh state properties between the RAM mixer and the Hobart mixer, this series was chosen to conduct mechanical tests for the hardened state properties comparison. Compression results are shown in Figure 38a and flexural results in Figure 38b. The first observation that can be made is that there is a considerable increase in mechanical strength comparing the results using the RAM mixer to the Hobart mixer. The most notable increase is in the early age properties at 3 days (7 days for flexure) where there is a strength improvement of around 30% while the later age strengths show between 16% to 20% improvements in strength.
The improvement in mechanical strength properties can be attributed to a variety of factors such as reduction in the air content, better dispersion or packing of the particles, or an increase in microstructural development with being affected by the energy imparted to the mixing container. The air content affects the compressive strength as follows [123]

\[
f'_c = -216 \times (w/c) \times \text{air}^{1/3} + 230; \quad f'_c \text{[prism]} \text{ is in MPa}
\]  

(20)

Thus, for example, an air content of 10% reduces the compressive strength by approximately 21 MPa. The difference between the \( f'_{c-28d} \) of the U21-H and U21-R mixes is about 28 MPa. This would mean the air content of the U21-H would have to be on the order of 25%. According to [123] the air content of the U21-H mix is between 1 and 5%. Thus, it is inferred that the improvement to the mechanical properties is a result due to better packing of the matrix and/or change of microstructure, such as seen with a high intensive mixer. Therefore, it is of value to verify, at least qualitatively, that the RAM mixer acts like a high intensive mixer.

**Figure 38** U21 mix average a) compressive strengths for 3d, 7d, 28d, and 56d, and b) flexure strengths for 7d and 28d. HR
5.3.5. Verification if RAM is an intensive mixer

To be a high intensive mixer usually means the mixer imparts a high shearing action to the system. As the RAM does not work on a shearing principle, but instead of a resonant acoustic vibrational principle, it is not apparent whether it can be considered a high intensive shear mixer. All the properties presented in the previous sections illuminate high intensive mixing properties. The acceleration curves and the specific mixing energy show values often seen in high intensive shear mixers. In fact, the American Petroleum Institute (API) SME standard for a standard paddle mixer is on the order of 5.5 kJ/kg [170]. The RAM mixer shows SME values one to two orders higher than these energy values. The increase in rheological properties, decrease in workability, and increase in mechanical properties all show behavior of a high intensive shear mixer for UHPC.

Thus, to further explore the hypothesis that RAM mixing is high intensive mixing, the acceleration curve profile, converted to normalized power using Eq. ((14), of the RAM mixer is compared to the power curve profile of a 6L Eirich (Hardheim, Germany) high intensive shear mixer (Figure 39 and Table 12). The fill levels are kept between 80 – 90% and the temperature was also monitored.

The first remark that can be made is that the normalized power curves share the same profile. While the peak energy is different (418 kJ for Eirich and 17 kJ for RAM) the specific mixing energy is close to similar. Where the two mixers deviate is the spread values. The Eirich has a higher spread value than the RAM, signifying that the workability is better. This can partially be attributed to the difference of 4°C final temperature between the two mixes. Other factors that can affect the workability are the air content and the consistency of the mix. Further study is needed of the RAM to quantitatively verify that it is an intensive mixer, but qualitative evidence demonstrates that is has the potential to be one.
Figure 39 Normalized Power Consumption curve comparison of High Intensive Shear Mixer to RAM mixer.

### 5.3.6. Comparison of the Microstructure of RAM to a Table Top Paddle Mixer

The effects of RAM on the microstructure of the designated UHPC mix in Table 8 (without CNFs) through back-scattering electron scanning microscopy (BSE-SEM), inverse gas chromatography (IGC), and mercury intrusion porosimetry (MIP) are studied in this section. Comparisons are made between RAM mixed at room temperature (RM-RT) and RAM mixed under an icy bath temperature (RM-IT).

IGC results for the table top mixer and the RAM are given in Figure 40. The RAM samples overall have a lower affinity to the aromatic and polar probes than the paddle mixed samples. The dispersive energy is also lower for the RAM samples than the paddle mixed ones. These results imply that the work of adhesion and dispersion is different for the two mixes. Consequently, the higher affinity to these probes opens the possibility that the paddle mixed samples are more prone

<table>
<thead>
<tr>
<th></th>
<th>Eirich</th>
<th>RAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Container Fill Level</td>
<td>80%</td>
<td>90%</td>
</tr>
<tr>
<td>Energy (kJ)</td>
<td>418</td>
<td>17</td>
</tr>
<tr>
<td>Energy/mass (kJ/kg)</td>
<td>34.9</td>
<td>34.0</td>
</tr>
<tr>
<td>Spread (mm)</td>
<td>113</td>
<td>104</td>
</tr>
<tr>
<td>Max Temp (°C)</td>
<td>35.0</td>
<td>39.1</td>
</tr>
</tbody>
</table>
to corrosive or chloride agents adhering to the surface of the concrete, which can affect the durability properties of the concrete.

**Figure 40** Surface characteristics of UHPC mixed with a paddle mixer (H) and with the RAM at room temperature (R-RT) and icy temperature (R-IT).

The results for the MIP are shown in **Figure 41**. The area underneath the curve relates to the volume of pore entries in the specimen. From the data, it appears that the RAM mixed at ice temperature has the largest area, then the RAM mixed at room temperature, and then the paddle mixed samples. This implies that the RAM mixed specimens contain higher volumes of smaller pore sizes than the paddle mixed specimens.
**Figure 41** MIP results for UHPC mixed with a paddle mixer (H) and with the RAM at room temperature (R-RT) and icy temperature (R-IT).

Indeed, just from a visual inspection between the RAM-RT and the HM samples in **Figure 42** the HM samples have large air bubbles, while the RAM-RT has very little pores visible.

![Figure 42](image)

a) Hobart  
b) Resodyn LabRAM

**Figure 42** Visual inspection of hardened state.

The results for this section are presented in **Figure 43**. The inner C-S-H product is lighter around the HM samples (top of **Figure 43**) than the RAM at room temperature (middle) and at icy temperature (bottom). C-S-H with darker colors have been shown to be denser and with different mechanical properties than their lighter counterparts [17].
Inner C-S-H region
Figure 43 Inner C-S-H region is lighter around the Hobart (top) mixed samples than the RAM (RT middle, IT bottom) mixed samples.

The interfacial transition zone (ITZ) is almost non-existent in the UHPC mixes. What is more interesting is that the RAM mixes show more abrasion on the aggregates as shown in Figure 44.
Figure 44  Abrasion of the aggregate is lighter around the Hobart (top) mixed samples than the RAM (RT middle, IT bottom) mixed samples.

5.4. Discussion

The previous sections established that the RAM mixer is qualitatively a high intensive mixer. While the principle of RAM is not shear mixing, results from intensive shear mixing can still be applied to better understand and discuss the nature of the microstructural development of the UHPC in this study.

RAM works on the principle of transferring the potential energy of its springs to the kinetic energy of the particle collisions inside the vessel. There is no shearing tool interaction with the material and hence it can be said that RAM energy distribution is uniform. It is known that high mixing intensity accelerates the hydration kinetics and changes the physical and chemical nature
of cement paste [173-175]. These phenomena originate from the high shear forces increasing the surface diffusion and decreasing the thickness of the diffuse double layer around the cement particles, and thus increasing the interparticle attractive forces [175]. The results are an increase in rheological properties, a decrease in workability, and increase in thixotropy, and sometimes an increase in mechanical strength. Thus, while RAM does not incorporate shear mixing by impeller action into the mixing material, it does introduce a velocity profile of micro-mixing and bulk-mixing zones. Initially, this profile is from frictional forces between particles, but as the system evolves into a paste and then a suspension, the velocity profile becomes a moving fluid, moving at an acceleration up to 100 times gravitational acceleration. From the RAM microstructural results presented here an increase in hydrate kinetics and a change in physical and chemical microstructure occurs. Thus, the evidence suggests that the RAM mixer is a high energy mixer compared to a standard table top paddle mixer.

5.5. Conclusions
The works presented in this research chapter offer a qualitative study of acoustic resonance mixing. The LabRAM by Resodyn Acoustic Technology® is a mixer that relies on reciprocal agitation movement rather than mechanical impeller or paddle agitation. In this study this mixer was used to mix ultra-high performance concrete. The following conclusions can be drawn:

1. RAM mixing does not have a tool that directly interacts with the mixing medium. This makes it an attractive mixing device as it reduces the cost of wear and tear of the mixing device. Furthermore, the non-direct mixing action could be beneficial in cases where the interaction of the mixing tool and the mixing medium is an important parameter to consider, such as the case with fiber containing materials where the fibers can be bent from the mixing tool.
2. RAM mixing is meant to operate at the system’s resonance frequency. Thus, the main parameters that affect the final mixing outcome are the amplitude of the resonance acoustic pressure wave, the time of mixing, and the fill level of the vessel. More work will be needed to quantify the direct relationship of these parameters to the properties of the UHPC mix.

3. Compared to a table top paddle mixer, RAM mixed at room temperature showed reduced flow and workability properties, but RAM mixed at ice temperatures showed an increase in fluidity and workability.

4. A 30% increase in 3-day and 20% increase in 28-day mechanical properties were observed in UHPC specimens mixed with RAM. The improved mechanical properties support the understanding that there is more uniform mixing energy transmitted to the system during mixing which enhances cement hydration and reduces air voids.

5. RAM can be considered qualitatively a high intensive mixer, yet further studies are needed to fully understand the mixing process of acoustic resonance mixing and its effects on cement and UHPC properties.

6. Finally, this investigation demonstrates that this innovative mixing technology could have a place in concrete mixing technology.

Chapter 6. Characterization of high-strength cement paste with pristine graphite and heptane-graphite emulsion

6.1. Introduction
Incorporation of nano-carbon particles such as carbon nanotubes and carbon nanofibers in cement paste, mortars, and concretes like UHPC are already showing it is possible to improve mechanical and transport properties on the microstructural level [43,45]. Both steel and carbon fibers represent
one-dimensional (1D) reinforcement [27]. Recently, work has been published on how two-dimensional (2D) reinforcement, in the form of graphene oxide, improves or changes the properties of ordinary Portland cement (OPC) paste [64,67,176,177]. The study presented in this chapter is a preliminary investigation on incorporating this unique graphene-heptane emulsion into high strength cement paste. Comparisons with powder pristine graphene and with normal strength cement paste are made. Two mixing methods are utilized, and an assessment of flexural and compressive strengths are conducted to see if any change of mechanical properties arise.

6.2. Background

The formation of water-in-oil emulsions by graphite takes advantage of the surfactant character of graphene sheets recently described by [68,69]. Graphite is found to spontaneously spread at high energy interfaces, exfoliating into graphene sheets that sit at the water-oil interface and lower the free energy of the system. This provides for the extensive exfoliation of graphite without the input of large amounts of mechanical energy or the use of aggressive oxidation methods (as in the formation of graphene oxide, or GO), both of which damage the graphene sheets and add to the cost of the material.

The thermodynamics of the graphene spreading have been investigated by computational methods, and the results show a steep increase in the energy of the system as the graphene sheets are moved from the oil-water interface. The kinetics of the system, however, are less well understood. Smaller graphene sheets sizes form emulsions much faster than do larger sheets. For this reason, graphite of a flake size centered at approximately 1 µm is used and from experience, it forms very stable emulsions.
6.3. Mechanical Testing

The Resodyn samples were aged naturally. Samples were tested at 3d, 7d, and 28d equivalent for the Hobart samples and 28 days for the Resodyn mixtures. Three-point bending testing was performed on specimens to obtain the maximum flexural strength at 3d, 7d and 28d equivalent for the Hobart mixtures and just 7 days for the Resodyn samples. The beams for the Hobart specimens were with average dimensions of 16 in. × 1 in. × 1 in. (40.6 cm × 2.5 cm × 2.5 cm) while the Resody samples had dimensions of 16 in. × 1 in. × 0.3 in. (40.6 cm × 2.5 cm × 0.8 cm) were cast in a high-density polypropylene (HDPE) beam mold. The beams were then cut into three sections and each section was tested at least once to obtain an average flexural strength. Table 13 shows the difference in mechanical testing for the two different mixing methods. The amount of material and the time for testing was the reason for the difference between the two mixing methods.

<table>
<thead>
<tr>
<th>Mixing Type</th>
<th>Compression</th>
<th>Flexure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dimensions (mm)</td>
<td>Days tested</td>
</tr>
<tr>
<td>H</td>
<td>50 × 50 × 50</td>
<td>3, 7, 28*</td>
</tr>
<tr>
<td>R</td>
<td>50 × 50 × 50</td>
<td>28*</td>
</tr>
</tbody>
</table>

6.4. Results

Compression results are shown in Figure 45. Due to the limited amount of graphite materials the heptane-graphite emulsion series was not tested and only the 28 days strengths were tested for the PG series. At best 28d graphene and graphite emulsion specimens show marginal gains for the Hobart mixed samples, but not so for the Resody mixed samples. The lack of improvement in strength could be not only due to improper dispersion of the graphite, but changes to porosity and/or rate of hydration, changes in hydration products, and mixing technique.
Figure 45 Compressive strengths for the (left) Resodyne mixed samples and (right) Hobart mixed samples.

Results for the flexural strength are shown in Figure 46. Due to the limited amount of heptane-graphite emulsion, 3 and 28 day strengths were not tested for this series for the Resodyne mixed samples. The 7 day RAM samples had a 72% improvement in flexural strength for the HSC_PG series, while the HSC_HG showed no improvement. For the HM samples, there was a decrease in strength overall for the HSC_PG series and the HSC_HG series.

Figure 46 Flexural strength assessment samples for the (left) Resodyne mixed samples and (right) Hobart mixed samples.
6.5. Discussion
Any lack of improvement is due to improper dispersion of the graphite, or to the impact graphite has on porosity, rate of hydration, morphology of hydration products, or to the mixing technique. The flexural strength of the 7d graphite specimens mixed with the Resodyn LabRAM, could indicate that the mixing energy is an important factor. There is on average a 72% improvement when powdered pristine graphite is added to high strength cement paste. This result could not be replicated with the Hobart Mixer. In fact, results showed a decrease in strength on par with HSC. This decrease could be attributed to the fact that pristine graphite does not contain the compatible oxygen sites that graphene oxide has. It has been shown that compatibility from graphene oxide with cement arises from its oxygen sites [178] which creates a stronger bond with the developing hydration products. Perhaps the lack of oxygen sites in pristine graphite make it less likely to bond with the matrix and cause other interactions. It is hypothesized that when the heptane-graphite emulsion is introduced to the cement matrix its hydrophobic nature allows the heptane to travel through the pore structure to the top of the paste, where it evaporates at room temperature, inserting the graphite in the hydrating matrix. While mechanical results can only give an indirect assessment of this hypothesis, the heptane-graphite emulsion has no effect or even a detrimental effect on these properties, indicating that perhaps it is not a suitable dispersing agent for cement. More in-depth analysis of the microstructure is needed to fully conclude this.

6.6. Conclusions
In this study pristine graphite and a heptane-graphite emulsion were introduced into high strength cement paste and normal strength cement paste. A focus on mixing technique and mechanical strength (flexural and compressive) were used as indirect assessment tools to determine whether a pristine, non-oxide form of graphite, either in powder form or in an emulsion with heptane, changed the properties of high strength cement paste. Of the two types of mixing devices used, a
standard Hobart paddle mixer or ResonantAcoustic® Mixing, the ResonantAcoustic® mixer showed an average of 72% increase in flexural 7 day strength with pristine powdered graphite high strength cement. Results with the heptane-graphite emulsion showed no improvement or even a decrease in both compressive and flexural strength. Further investigations will need to be conducted to analyze the microstructure such as changes in porosity or hydration products, as well as understand how the mixing energy imparted into the mix affects the properties. While preliminary results indicate that heptane is probably not the most compatible dispersant in cement, finding a more suitable emulsion could still be of interest.

Chapter 7. Characterization of Ultra-High Performance Concrete with Polymer Wrapped Carbon Nanofibers

7.1. Introduction
The objective of this study is to investigate the influence of high mixing energy on the dispersion of carbon nanofiber in ultra-high performance concrete (CNF-UHPC). The investigative methods include rheology, electron microscopy, surface energetics, and mechanical testing. Three treatments of CNFs are considered and include pristine CNFs, that have been rinsed and dried for any impurities from the manufacturer, polyvinyl phenol wrapped CNFs that have been dried, and polyvinyl phenol wrapped CNFs that have been kept in a solution.

7.2. Results
7.2.1. Monitoring the Mixing Energy Input
Acceleration curves were collected for each CNF-UHPC composite mix to study the cohesion points for each of the mixes. From the literature [6,9,40] the cohesion point represents the transition
between a powder granule state to a fluid paste state. It occurs at the peak power of the mixing device. **Figure 47** shows the acceleration curve for the NCNF-UHPC mix starting from the point of liquid loading until the end of mixing. The dark black curve represents the average of three mixes. The peak acceleration, designated as the cohesion point, occurs around 90 s, while the end of mixing was around 360 s. The end of mixing was determined when the standard deviation between the acceleration curves converges to zero.

![Model of Acceleration](image.png)

**Figure 47** The acceleration curve for the NCNF-UHPC control mix. The maximum cohesion point occurs around 90s, while the optimal mixing time is at 360s.

**Figure 48** shows the averaged acceleration curve for the WCNF-UHPC mixes. The cohesion point and end of mixing time have increased approximately 30s and 60s, respectively, compared to the control mix. The graphs for the RCNF-UHPC and SCNF-UHPC mixes were very similar.
The acceleration curve for the RCNF-UHPC control mix. The maximum cohesion point occurs around 120s, while the optimal mixing time is at 420s.

Table 14 summarizes the peak accelerations and the mixing times for all four mixes. From this summary, the acceleration peaks are around the same values, but the cohesion and end of mixing times differ. The RCNF-UHPC mixture has the longest times, followed by the WCNF-UHPC mixture, and then the SCNF-UHPC mixture.

Table 14 A summary of the mixing times and peak accelerations for the control and CNF-UHPC mixes.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Avg. peak acceleration (G)</th>
<th>Avg. time to reach peak (s)</th>
<th>Avg. mixing time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCNF</td>
<td>56</td>
<td>90</td>
<td>360</td>
</tr>
<tr>
<td>RCNF</td>
<td>60</td>
<td>125</td>
<td>480</td>
</tr>
<tr>
<td>WCNF</td>
<td>57</td>
<td>120</td>
<td>420</td>
</tr>
<tr>
<td>SCNF</td>
<td>60</td>
<td>100</td>
<td>380</td>
</tr>
</tbody>
</table>

Using Equations (14) and (15), the peak mixing specific energies were calculated for each of the mixtures. Figure 49 shows the results. There was a 47% increase in the mixing demand for the rinsed CNF series, a 38% increase for the wrapped CNF series in powder form, and a 17% increase for the solution form.
Figure 49 Peak mixing energy densities of the CNF-UHPC composites.

7.2.2. Workability

Spread flows were averaged for 3 specimens with 350g of material in the vessel. CNF clusters were visible in the CNF-UHPC mixes as shown in Figure 50.

Figure 50 Visibility of CNF clusters. From left to right – control, RCNF, WCNF, SCNF.

Figure 51 summarizes the spread results for each of the specimens. The wrapped CNF powdered samples showed a 3.5% decrease in spread compared to the control, while the solution samples showed a 2.5% decrease in spread. The rinsed CNF powdered samples were 1.3% less than the spread of the control.
**Figure 51** Spread flow results for the CNF-UHPC composites.

7.2.3. Steady-State Flow Rheological Tests

**Figure 52** shows the steady state flow rheological results for the CNF mixtures.

**Figure 52** Steady state rheological results.
The yield stress and viscosity were calculated using Equation (16). The hysteresis area was computed by taking the area underneath the ramp up curve and the ramp down curve. The hysteresis area relates to the shear stress or energy needed to break down and build up the structure of the material. Figure 53 shows the rheological results for each mixture.

Figure 53 The yield stress, viscosity, and hysteresis area for the CNF-UHPC mixtures.

The rinsed CNF series showed the highest rheological values, around 15%, and largest spread in data. The polymer wrapped CNF series both powder form and solution form were only slightly higher than the control mixture. The hysteresis loop area showed that the rinsed CNFs required the most energy to break down the material’s structure.

7.2.4. Mechanical Testing Results

Early age mechanical testing was done at 7 days for the mixtures. Figure 54 shows the results of the mechanical tests. The CNF-UHPC samples overall had an increase in both compression and flexure strength. The rinsed CNF series showed an increase of 10%, while the polymer wrapped CNF series showed an increase of 12% and 6% for powdered and solution form, respectively. The rinsed CNF series showed the highest increase in flexure strength, with a 23% increase. The
polymer wrapped CNF series showed mixed results. The powdered form showed an 8% increase, but the solution form showed a 15% decrease in strength.

Figure 54 The mechanical test results at 7 days for compression (left) and flexure (right).

7.2.5. Inverse Gas Chromatography Results

While gas chromatography is an analytical technique used to determine chemical information of materials, inverse gas chromatography (IGC) is a physical technique that is used to determine surface energetic properties of a material [179]. IGC involves the sorption of a vapor (probe molecule) with known physico-chemical properties onto an adsorbent stationary phase (e.g. cement paste powder) with unknown physico-chemical properties. The more interaction the vapor phase has with the adsorbent phase, the more energetic the surface is and the longer the interaction or retention times are. IGC data was analyzed with provided software that returned a surface energy parameter which then was divided into a dispersive and a specific component. The dispersive surface energy can be directly calculated from the retention times of a series of injected $n$-alkanes [180]. Table 15 displays the retention times for the injected $n$-alkanes probes for the powders and crushed UHPC samples. From the table silica powder and quartz powder showed higher retention
times than cement powder whereas the CNF-UHPC composites had longer net retention times than the control UHPC mix.

**Table 15** Net retention times take at the peak maximum.

<table>
<thead>
<tr>
<th>Material</th>
<th>methane</th>
<th>octane</th>
<th>nonane</th>
<th>decane</th>
<th>undecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>cement</td>
<td>0.47</td>
<td>0.58</td>
<td>0.74</td>
<td>1.14</td>
<td>2.6</td>
</tr>
<tr>
<td>silica fume</td>
<td>0.52</td>
<td>0.73</td>
<td>0.96</td>
<td>1.7</td>
<td>3.3</td>
</tr>
<tr>
<td>quartz powder</td>
<td>0.62</td>
<td>0.8</td>
<td>1</td>
<td>1.5</td>
<td>3.1</td>
</tr>
<tr>
<td>NCNF</td>
<td>0.47</td>
<td>0.58</td>
<td>0.73</td>
<td>1.14</td>
<td>2.3</td>
</tr>
<tr>
<td>RCNF</td>
<td>0.53</td>
<td>0.63</td>
<td>0.81</td>
<td>1.3</td>
<td>2.75</td>
</tr>
<tr>
<td>WCNF</td>
<td>0.53</td>
<td>0.66</td>
<td>0.86</td>
<td>1.49</td>
<td>3.3</td>
</tr>
<tr>
<td>SCNF</td>
<td>0.49</td>
<td>0.6</td>
<td>0.79</td>
<td>1.3</td>
<td>2.67</td>
</tr>
</tbody>
</table>

The specific contribution of the surface energy was obtained indirectly via the specific free energy and different acid-base theories, obtained by injecting a range of polar probe molecules [181]. **Figure 55** displays the specific and dispersive energies for the different aromatic and polar probes for the powders. From these graphs, silica powder and quartz powder are more sensitive than cement to the polar probe molecules whereas only quartz powder is more sensitive than cement for the aromatic probes. Cement appears to have a higher dispersive energy than the other powders.
Figure 55 The specific surface energy and dispersive energy for the cement (C), silica fume (SF), and quartz powders (QP).

Figure 56 displays the specific surface and dispersive energies for the CNF-UHPC composites. The CNF-UHPC composites with the CNFs in powdered form showed a higher dispersive energy than the control mix, whereas the mixture with a CNF solution showed the same as the control.
**Figure 56** The specific surface energy and dispersive energy for the control UHPC (N), rinsed CNF-UHPC (R), and polymer wrapped CNF-UHPC in powder form (W) and in solution form (S).

### 7.2.6. Mercury Intrusion Porosity Results

**Figure 57** shows the MIP analysis results. The data shown represents the total connected pores volume of the specimen that was intruded by mercury. The pore volume for the CNF-UHPC composite is slightly smaller, having a peak around 10 nm, while the control UHPC mixture has a peak closer to 50 nm. This shows that the CNF-UHPC composite contains a higher amount of smaller sized pores.

![Pore size distribution curves from MIP of UHPC with no CNFs (NCNF) and rinsed CNF-UHPC.](image)

**Figure 57** Pore size distribution curves from MIP of UHPC with no CNFs (NCNF) and rinsed CNF-UHPC.

### 7.3. Discussion

#### 7.3.1. The effects of polymer wrapped CNFs

From the results presented in this study, polyvinyl phenol wrapped CNF-UPHC composites exhibit slightly different results depending on whether they were introduced into the UHPC matrix as a
powder or as a dispersed solution. The powdered form shows higher mixing energy demand, rheological properties, and dispersive energies, while the solution form is more comparable to the control UHPC matrix. However, the mechanical properties are higher for the powdered form than the solution form. The difference in the surface characteristics could be a reason for this. Perhaps the orientation of the WCNFs in solution form interact more with the hydration mechanisms of the cement. Or perhaps drying the solution to obtain the powdered form destroys the polyvinyl phenol itself changing the surface properties of the CNFs. Nevertheless, the CNF-UHPC composites from untreated CNFs showed the highest mechanical properties and mixing demand.

7.3.2. High intensive mixing on CNF-UHPC composites

From the literature, the most common practice of mixing carbon nanofibers into cement paste or UHPC is through a rotary three-speed mixer [15,50,51,55-57,127,182,183] that has at most a capacity of 285 rpm. To the knowledge of the author, there have only been three studies that used a different mixing approach. Tyson used a high-speed kitchen blender [61] is his work, while Jiang et al. [184] used a stirrer that ranged from 500 – 200 rpm. Alrekabi et al. [58] used an intensive shear mixer. Furthermore, of all these studies on CNFs in cement or UHPC Jiang et al. [184] is the only that considered different mixing speeds on the rheological properties. Recent work by Sanchez et al. investigated the re-agglomeration of CNFs in cement paste and the effects that these CNF clusters have on the physico-chemical properties of cement paste. However, while they did not consider the mixing procedure for dispersing a CNF solution into the cement paste, they did conclude that the better dispersed the CNF clusters are in the paste the more likely the desired improvements for durability and strength are observed. Thus, it is reasonable to consider the mixing energy demand of CNFs in cementitious materials. The results presented in Figure 49 show that there is nearly a 50% increase in the mixing demand for CNF-UHPC mixtures to obtain
within 3% of the spread values. As the fluid state of the CNF-UHPC ages, the yield stress and viscosity increase requiring more energy to break them down upon re-mixing, as shown in Figure 53. This suggests that to maintain the desired rheological properties of a UHPC mixture the mixing demand needs to be included in future studies as CNFs require a higher mixing demand.

7.3.3. CNF clustering
The literature has shown that CNFs tend to agglomerate in a cement matrix [50,54,185] and transport freely in the absence of a pozzolanic material such as silica fume [186]. As the UHPC has high amounts of secondary cementitious materials added, it is expected that the CNFs will cluster, but the clusters will be trapped by the UHPC matrix and exhibit large separation distances as the amount of CNF inclusions is limited to 0.1% by cement mass. Figure 58 shows a micrograph of a smaller microcrack being bridged by CNFs and a larger microcrack showing a fractured CNF. This behavior is what led to an overall improvement to the CNF-UHPC composite mechanical properties.
Figure 58 Carbon nanofibers 1) bridging a micro-crack and eventually 2) fracturing.

Figure 59 shows evidence of CNF clustering in the composite material. A close-up of the cluster (Figure 60) shows the range in size of the CNFs, but more importantly the cluster of CNFs are only slightly entangled. This loose arrangement of CNFs gives evidence that the CNFs physically push aside the cementitious materials creating more micropores within the clusters and mesopores in the surrounding area. This has been seen in the literature already with work from Sanchez [14] and Meng [127].
Figure 59  CNF clusters are found several microns apart.
Surface energy characteristics and porosity results add support to this evidence that CNF clusters push the cementitious materials away to create a filtered pore space in the UHPC matrix. Additionally, Figure 60 shows that the CNF clusters are separated at large distances as was expected.

7.4. Conclusions
In this study rinsed untreated CNFs as well as polyvinyl phenol polymer wrapped CNFs were introduced into an ultra-high performance concrete by high intensive acoustic resonance mixing. The microstructural characterization techniques employed were inverse gas chromatography (IGC) and secondary-electron scanning electron microscopy. Additionally, mini-cone flow tests
and steady state flow rheological investigations on the fresh properties of the UHPC and UHPC-CNF mixes were performed in compliment to three-point bending tests and compression tests.

The following are the conclusions:

1. Polyvinyl phenol wrapped CNF-UHPC composites did not perform in terms of mechanical strength better than untreated CNF-UHPC composites.

2. Mixing CNFs into UHPC requires a higher mixing demand, nearly 50% more energy for this study. Future research is needed to understand the mixing demands for different cement-based materials.

3. CNF-UHPC composites did show an overall improvement in mechanical properties at 7 days even with CNF clusters present.

Chapter 8. Enhancing Printable Concrete Thixotropy by High Shear Mixing

8.1. Introduction
With the advent of concrete digital fabrication paving new ways of construction [18], controlling cement paste thixotropy is crucial to ensuring the desired final state of the material is achieved. Each digitally fabricated concrete layer must evolve from a fluid suspension during mixing and pumping to a cohesive material after deposition that maintains a strong interface with, and mechanical resistance to, the next deposited layer [160]. Consequently, thixotropy is very important for concrete digital fabrication as it enhances the structuration of cement paste.

From a practical view, thixotropy is mainly affected by CSH nucleation [160]. Thus, a very thixotropic concrete can be created by increasing the rate of nucleation of hydration products in the mixture. One way to increase this rate is by increasing the energy input of mixing [175]. Henceforth, in this work the is focus on how mixing could enhance thixotropy.
8.2. Results

8.2.1. Rheological Measurements

Plotted in Figure 61 the elastic storage modulus versus time for cement paste mixed at 840 rpm, 1480 rpm, and 2800 rpm. Results show that the storage elastic modulus as a function of time increases at a higher rate for the cement paste mixed at 2800 rpm versus 840 rpm. In Figure 62 the ratio of the elastic storage modulus of the two speeds is presented. It is linear, and the higher speed is approximately four times higher after 2 hours.

**Figure 61** Effect of mixing intensity on the elastic storage modulus of cement paste samples prepared with w/c ratio of 0.30 and 0.4% of PCE bwoc.
Figure 62 The ratio between the elastic storage modulus of the 2800 rpm versus 840rpm.

8.2.2. Isothermal Calorimetry

The heat evolution during the hydration of cement paste mixed at four different mixing speeds is presented in Figure 63. It is seen that the paste mixed at 2800 rpm reaches its maximum peak almost 4 hours before the paste mixed at 840 rpm. The maximum peak of this higher mixed paste reaches almost 1 mW·g⁻¹ higher in heat flow than the lower mixed paste. In general, the results show that increasing the mixing speed shifts the heat flow curve left, increases the slope and the maximum peak of the heat flow, but does not affect the overall shape of the curve.
Figure 63 The heat flow of cement paste (w/c 0.3, PCE dosage 0.4%) mixed at different speeds.

Plotted in Figure 64a the rate of the heat flow during the acceleration period and in Figure 64b the time of the maximum peak of heat flow during the acceleration period as a function of mixing speed. There appears to be an almost linear relation for both figures with higher mixing showing higher heat flow rates and shorter times to reach the maximum peak.
**Figure 64** a) The slope of the heat flow curve during the acceleration period and b) the time to reach the maximum peak as a function of mixing speed.

**8.2.3. Dynamic Light Scattering Measurements**

Shown in **Figure 65** the results of the DLS measurements. The higher mixing enhances the concentration of nanoparticles in a linear fashion. The DCR for the highest speed is half an order higher than the lowest speed.

![Graph showing peak scattering intensity vs. shearing speed](image)

**Figure 65** Cement powder in water (W/C 0.50) with 0.8% PCE dosage (by weight of cement) and increasing mixing speed.

**8.3. Discussion**

The main thing shown is that higher mixing enhances the thixotropy, the kinetics of hydration, and the concentration of nanoparticles in the suspending fluid of cement paste. These phenomena have been observed before. Han and Ferron [174] found that the mixing rate enhanced both the elastic storage modulus and the rate of heat evolution. Juillard et al. [175] were able to demonstrate that
two kinetics of cement hydration were affected by the mixing rate – the induction period and the acceleration period. An increase in the mixing rate led to a shortening of the induction period by decreasing the diffuse electrical double layer, which in turn increased the dissolution rate, and hence, the transportation rate of the ions that detached from the cement surface into the bulk pore fluid. The increase in the height of the main heat evolution peak was due to the mechanical action of the mixing, resulting in an increase in the detachment of C-S-H from the surface and their density.

Caruso et al. [187] highlighted the formation of nanoparticles in cement pore solution containing superplasticizers. They asserted that these nano-size particles are either nano-C-S-H, nano-etrtringite, nano-AFm, or interamolecular complexes of polymer and cations. However, they could not draw any further conclusions on whether one type of nanoparticle was more present than another and did not consider the consequences of the variations in mixing speed on the generation of these nanoparticles.

Consequently, it is suggested that an appropriate combination of mixing energy and superplasticizer dosage promotes hydration by scratching hydrates from the surface of cement particles, stabilizing them in the suspending fluid and hence generating additional nucleation surfaces.

The physical origins of thixotropy originate mainly from the rigid interactions network of C-S-H nucleation [160]. Thus, with higher mixing power the number of C-S-H bonds created by hydration increases and hence why thixotropy is enhanced and the setting time decreases.

8.4. Conclusion

This study aimed to understand how mixing can enhance the thixotropy of a cement paste. The results show that the storage elastic modulus as a function of time increases at a higher rate for the cement paste mixed at higher versus lower mixing intensity (i.e. approximately four times higher
after 2 hours). Using calorimetry analysis, it was found that higher mixing decreases the setting time and enhances the peak of the heat flow. By analyzing the nanoparticles present in the suspending fluid of the cement paste we show, in accordance with literature, that an appropriate combination of mixing energy and super-plasticizer dosage promotes hydration by scratching hydrates from the surface of cement particles, stabilizing them in the suspending fluid, and hence, generating additional nucleation surfaces.

These results open the door for low cost cement acceleration through just the mixing as well as the design of printing heads including high-shear micro mixers allowing for a faster liquid-to-solid transition of the printable material.

Chapter 9. Influence of mixing on the generation of nanoparticles in cement systems

9.1. Introduction

Mixing has a significant impact on the processing and ultimate behavior of cementitious materials. A substantial amount of work has been done on this topic and the literature reports that changes in the mixing rate during the concrete production process affect rheology [7,158,173,175,188,189], hydration kinetics [174,175,190-192], microstructure homogeneity [158,173,175,189] and early age mechanical strength [7,193,194]. Recent research has brought more understanding to the physical mechanisms causing these consequences for cement pastes. Juilland et al. [175] demonstrated that two kinetics of cement hydration were affected by the mixing rate – the induction period and the acceleration period. An increase in the mixing rate leads to a shortening of the induction period by decreasing the diffuse electrical double layer, which in turn increases the dissolution rate, and hence, the transportation rate of the ions that detach
from the cement surface into the bulk pore fluid. The increase in the height of the main heat evolution peak is due to the mechanical action of the mixing, resulting in an increase in the detachment of C-S-H from the surface and their density. Similarly for cement paste with filler mineral powder, Berodier and Scrivener [190] demonstrated that the observed increase in the hydration rate was more from the shearing conditions rather than the extra surface area provided for C-S-H formation. Moreover, research by Han and Ferron [173,174,195] and Juillard [196] established evidence that the consequences of mixing were amplified in the presence of superplasticizers. However, the origin of these changes is still not fully understood. Recent work by Caruso et al. [187] highlighted the formation of nanoparticles in cement pore solution containing superplasticizers. They asserted that these nano-size particles are either nano-C-S-H, nano-ettringite, nano-AFm, or intramolecular complexes of polymer and cations. However, they could not draw any further conclusions on whether one type of nanoparticle was more present than another and did not consider the consequences of the variations in mixing speed on the generation of these nanoparticles.

Thus, this study aims to understand better the mixing speed influence on the generation of nanoparticles in cement. Using dynamic light scattering the presence of these particles in the interstitial pore fluid of cement and quartz are probed. Then it is examined how the flocculated state of the system, ongoing hydration, and the mixing speed affects the concentration of the nanoparticles.

9.2. Non-reactive model suspension: The quartz powder system

9.2.1. Effect of the particle interactions

In this section the effect of particle interactions on the concentration of nanoparticles in the pore solution of a non-reactive model suspension is studied. Quartz particles have been used in literature
as a model suspension of cement particles for rheological measurements [197]. The interactions between quartz particles have been controlled by modifying the pH and ionic composition of the pore solution and by adding superplasticizers. It is known from literature that quartz particles completely disperse in water and do not flocculate [20]. In calcium hydroxide solution, Van der waals attractive forces between particles are at the origin of the flocculation of the suspension [198]. The magnitude of these forces can be decreased by the addition of PCE, which adsorb at the surface of quartz particles and increase the average interparticle distance. Unlike cement particles, the reactivity of quartz particles of the same size distribution is negligible in calcium hydroxide solution [199]. Plotted in Figure 66 the scattered intensity of the pore solution of quartz powder dispersed in de-ionized water versus calcium hydroxide (lime) solution. The intensity values of the quartz-water system are found to be two orders higher in magnitude than the quartz-lime system.

![Figure 66](image)

**Figure 66** Quartz powder dispersed in water versus a lime solution of a liquid/quartz ratio of 0.4 without PCE mixed at 2800 rpm.

In Figure 67 the scattered intensity is plotted as a function of PCE dosage in a quartz-lime system mixed at 840 rpm and 2800 rpm. As evident from the data, the intensity increases with
increasing PCE dosage until a plateau is reached for both mixing speeds. At this point the system tends towards the intensity value of the quartz-water system. Moreover, note that at high PCE dosages, around 0.8%, an increase in PCE dosage does not affect the scattered intensity of the pore solution. This critical concentration corresponds to the PCE dosage needed to attain quartz surface saturation from the TOC adsorption measurements.

**Figure 67** Quartz powder in a lime solution of a lime/quartz ratio of 0.4 and increasing PCE dosage mixed at low and high speeds. The horizontal dashed line corresponds to the scattering intensity of the quartz powder in water, while the vertical dashed line corresponds to the saturation level of the PCE.

The results for the quartz powder system support the conclusion that for a flocculated system, such as the quartz-lime system, nanoparticles agglomerate onto larger particles and do not remain in the pore solution. As soon as the system is deflocculated, either with no interactions, as in the quartz-water system, or by modifying the particle interactions by progressively covering the
surface with PCE, the same concentration of nanoparticles expected for a simple system is retrieved.

9.2.2. Effect of the mixing speed

Studied in this section the effect of mixing speed on the generation of nanoparticles in the pore solution of deflocculated quartz particles. Figure 68 depicts the scattered intensity for the quartz-lime system as a function of mixing speed at high PCE dosage. Observe that the scattered intensity is constant with increasing mixing speed, and moreover, reaches the value of the quartz-water system as previously showed. This result suggests that increasing the mixing speed in a deflocculated system does not change the concentration of particles. Now, moving on to a more complex system in which chemical reactions do occur, such as a cement-water system.

**Figure 68** Quartz powder in a lime solution with a lime/quartz ratio of 0.4 and PCE dosage of 1% (by weight of quartz powder) and increasing mixing speed. The dashed line corresponds to the scattering intensity of the quartz powder in water.
9.3. The cement system

9.3.1. Effect of cement reactivity and particle interactions

The reactivity and interaction of cement and water renders it difficult to obtain a chemically inert and deflocculated system, such as the quartz-water system. Thus to obtain such a nonreactive system, a cement-alcohol system is the preferred system, with isopropyl alcohol (IPA) as the most ideal solvent [200,201]. Hence, the cement reactivity and particle interactions were controlled by dispersing the cement in IPA.

In Figure 69 is a plot of the scattered intensity of cement mixed with IPA versus de-ionized water. The results show that the cement-IPA system is on order 5 times greater than the cement-water system. From what was learned from the quartz powder system, analyzing these results brings the conclusion that this is the number of nanoparticles expected in the deflocculated cement system. However, in the flocculated cement-water system, due to the attractive van der Waal forces [202], these nanoparticles flocculate and are no longer observed.

![Figure 69](image.png)

**Figure 69** Cement powder dispersed in water versus isopropyl alcohol, with a liquid/cement ratio of 0.4, mixed at the 2800 rpm.
Compare this system to a cement-water system, where PCE was used to increase the average interparticle distance and therefore decrease the magnitude of the attractive van der Waals forces [203-205]. Plotted in Figure 70 is the scattered intensity of the cement-water system versus PCE dosage. Much like the quartz-lime system, it is observed that the intensity increases with increasing PCE, demonstrating that as the system becomes deflocculated more particles are observed. However, contrary to the quartz-lime system where once the system was deflocculated the observable amount of small particles was the same as in the quartz-water system, in the deflocculated cement-water system it was noticed that the observable amount of small particles is not the same as in the cement-IPA system. In fact, the concentration is amazingly much higher. This suggests that the concentrations of particles seen in this system are not only coming from the anhydrous cement powder. Moreover, note that at high PCE dosages, around 0.8%, an increase in the PCE dosage does not affect the scattering intensity of the pore solution. It can be seen that this critical concentration corresponds to the PCE dosage needed to attain surface saturation. This result suggests that the concentration of nanoparticles in the solution is correlated to the concentration of PCE adsorbed at the surface of the cement; specifically, that the nanoparticles are displaced from the surface of the cement particles.
Figure 70  Cement powder in water with W/C of 0.4 and increasing PCE dosage mixed at low and high speeds. The horizontal dashed line corresponds to the scattering intensity of cement dispersed in IPA and the vertical dashed line corresponds to the PCE saturation level on the cement surface.

9.3.2. Effect of the shearing condition

Shearing was modified either by increasing the mixing speed or by increasing the solid volume fraction in the cement suspension by adding quartz powder to cement. It was not desirable to vary it through the water to cement ratio because this can change the reactivity of cement particles and affect the concentration of reactive particles in the suspension. Figure 71a, contrary to the quartz powder system, shows that increasing the mixing speed in a deflocculated cement-water system changes the concentration of particles. There appears to be a linear increase in scattering intensity as the mixing speed increases. Figure 71b demonstrates that increasing the solid volume fraction in the suspension through quartz powder addition also leads to an increase of the concentration of nanoparticles.
Results on both the mixing speed and solid volume fraction suggest that the shearing conditions during mixing significantly influence the concentration of nanoparticles in the cement pore solution. Accordingly, it follows to investigate further the shear rate induced between the particles during the mixing procedure.

Instead of computing the local shear rate $\dot{\gamma}_{\text{loc}}$ from the macroscopic shear rate $\dot{\gamma}$ by assuming that the particles are homogeneously distributed spheres and using a geometric relation, we assess the local shear rate by using the mechanical relationship between the macroscopic viscosity and the local viscosity. The energy density (or shear stress) is equal to:

$$\tau = \mu \dot{\gamma} = \mu_0 (1 - \phi) \dot{\gamma}_{\text{loc}}$$

(21)

where $\mu$ is the viscosity of the suspension, $\mu_0$ is the viscosity of the interstitial fluid and $\phi$ is the solid volume fraction. Then using the simplest relation from literature for the viscosity of the suspension as a function of concentration and particle packing [104]:

**Figure 71** Scattered intensity of the pore solution of cement paste in water (W/C 0.40) with 0.8% PCE dosage (bwoc) as a function of (a) increasing mixing speed and (b) increasing concentration of quartz powder added, which is mixed at 1400 rpm.
\[ \mu = \mu_0 \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \]  

with \( \phi_m \) the maximum packing fraction of the solid particles. This gives:

\[ \dot{\gamma}_{loc} = \frac{1}{1 - \phi} \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \dot{\gamma} \]  

Computed is the maximum packing fraction of the studied suspensions as a function of the relative proportion of quartz using the Compressive Packing Model (CPM) of De Larrard [150]. The main input needed is the particle size distribution of cement and quartz and their measured maximum packing fractions. Results show that when the quartz concentration varies between 2.5% and 10%, the virtual packing fraction remains almost unchanged and is around 62%. Therefore, this value to compute the local shear rate is used. Figure 72 shows the scattered intensity by the pore solution after mixing as a function of the computed local shear rate. Observe that the amount of small particles increases in the same fashion whether it is due to a change in the mixing rate or the volume fraction. By changing the shear rate produced in the gap between particles through the increase of the solid volume fraction or the mixing speed, the results provide a master curve that suggests a mechanistic link between the concentration of nanoparticles in the pore solution and the shearing conditions.
In fact, if the elastic modulus from the rheological results in Figure 61 is taken at the 10 minute mark, then a quantitative relation between the amount of nanoparticles in the system and the rheological properties of the system can be made, as shown in Figure 73. This relation between the elastic modulus and the relative concentration of nanoparticles and the relation of the amount of nanoparticles to the local shear inside the system, as given in Figure 72, gives a method to extrapolate a quantitative relation for the level of shear energy needed for the application desired for the final product.

**Figure 72** The scattering intensity as a function of local shear rate.
Figure 73 A quantitative relation between the concentration of nanoparticles in the system and the elastic modulus of the system.

9.3.3. The nature of these nanoparticles in cement paste

Our measurements in isopropanol suggest that part of the detected nanoparticles in the cement pore solution come from the anhydrous cement powder (see Figure 69). However, while these nanoparticles are detected in isopropanol, we expect them to rapidly dissolve when dispersed in water. By analyzing the composition of the pore solution containing nanoparticles, Caruso et al. [187] found a high content of magnesium, aluminum and iron, which are minority elements in anhydrous cement and thus discarded the hypothesis of ultrafine anhydrous cement particles. Moreover, they examined three hypotheses concerning the nature of these nanoparticles; namely the first hypothesis proposes the nanoparticles are nano-hydrates (i.e. nano-C-S-H, nano-Afm, nano-ettringite) stabilized by PCE [206-208], while the two remaining hypotheses propose two types of complexes between the PCE and the polyvalent cations [209-214].

For the latter two hypotheses, it would be expected to see a continuous increase in the concentration of nanoparticles when the PCE dosage increases. However, the results show that
above a critical concentration, corresponding to the PCE adsorption plateau at the surface of cement particles, the concentration of nanoparticles remains almost unchanged (see Figure 70). This result weakens the two last hypotheses and suggests that the concentration of nanoparticles in the solution is correlated to the concentration of PCE adsorbed at the surface of the cement; specifically, that the nanoparticles are displaced from the surface of the cement particles and stabilized in the pore solution. Furthermore, the master curve, which clearly shows that the nanoparticle concentration increases as the shear rate in the gap between the particles increases, supports the first hypothesis. This result suggests that the mixing process promotes the concentration of nanoparticles in the pore solution by scratching hydrates from the surface of cement particles. This hypothesis of mechanical detachment of hydrates is consistent with the work of Juillard et al. [175], who explained that the origin of the height increase of the main heat evolution peak as a function of mixing was due to an increase in the detachment of C-S-H from the surface and the formation of extra nucleation sites away from the surfaces. By means of SEM observation of the microstructure, they also showed an enhanced growth of C-S-H between the cement grains when the mixing speed increased. Similarly for cement paste with filler mineral powder, Berodier and Scrivener [190] demonstrated that the observed increase in the hydration rate was more from the shearing conditions rather than the provided extra surface area for C-S-H formation. Thomas and co-workers [10] showed the same consequences on hydration kinetics when pure C-S-H is added to a pure tricalcium silicate. Sowoidnich et al. [215] examined the aqueous phase of C3S with superplasticizers after 10 min and found nano-size C-S-H polymer clusters. When they examined C3S without polymers, they found no such clusters.

Moreover, Han et al. [6,8,13] and Juillard et al. [14] established evidence that the consequences of mixing on hydration kinetics were amplified in the presence of superplasticizers. The results
presented in this study showing an increase in the concentration of nanoparticles when the superplasticizer dosage increases could explain this trend. In fact, adsorbed PCE keeps dislodged nanoparticles [206-208] dispersed by hindering their agglomeration. It was shown in literature that the efficiency of C-S-H seeds depends on their dispersion and PCE is needed to stabilize them [215-218].

From the above frame of understanding, it is suggested that most of the nanoparticles that are being detected in the pore solution of a cement system with PCE are nano-hydrates. According to literature, these nano-hydrates could be nano-C-S-H. An interesting implication of this is that if it can be assumed that nano-C-S-H is the dominating detected nanoparticles, then a way of seeding the system without relying on synthesized nano-C-S-H particles is possible. This opens up a path to low cost cement acceleration through just the mixing and packing fraction.

9.4. Conclusion
This study aimed to better understand the mixing speed influence on the generation of nanoparticles in cement. By means of dynamic light scattering, the concentration of these particles in the interstitial pore fluid of both quartz and cement pastes was studied. For both quartz and cement systems, it was observed that for a flocculated system nanoparticles agglomerate onto larger particles and do not remain in the pore solution. As soon as the system is deflocculated their concentration in the pore solution increases. While the concentration of nanoparticles in quartz pore solution was independent on the mixing speed, it was noted that it increases in cement pore solution when the shearing conditions are increased. By changing the shear rate produced in the gap between cement particles through the increase of the solid volume fraction or the mixing speed, the results provide a master curve that suggests a mechanistic link between the concentration of nanoparticles in the pore solution and the shearing conditions. It is suggested, in accordance with
the literature, that the mixing process promotes hydration by scratching hydrates from the surface of cement particles.

Chapter 10. Conclusions and Future Work

10.1. Summary and Conclusions
The overall goal of this research dissertation was to develop and implement interdisciplinary and collaborative solutions to the engineering challenges that we face today. The objective of this dissertation was to investigate how high energy mixing affects cement-based materials. Providing high energy mixing was done in two ways. First, a different way of providing high energy mixing by means of ResonantAcoustic® Mixing (RAM) Technology. This type of mixing device relies on an acoustic pressure wave to mix materials together and comes with built-in sensors to monitor the evolution of mixing. Second, a high speed impeller blender was used to study the origins behind high energy mixing.

The investigation into RAM technology was divided into 4 steps. The first was to investigate the mixer itself and see how various parameter such as mass and mixing intensity affect the flow and workability properties of a UHPC mix. The second was to conduct a comparative study between RAM and a bench top paddle mixer. Third, a study on graphite nanoplatelets in normal/high strength cement paste was carried out. Finally, carbon nanofiber-UHPC composites were studied using RAM. Spread, steady-state rheology, compression and flexural strengths, mixing energy demand, porosity, surface adhesion energy, and electron microscopy were all the various experimental methods used in these studies.

The investigation into the origins behind high energy mixing on cement paste was divided into two steps. The first was to analyze an ideal non-reactive system by means of quartz powder. The
second half was to apply the simple concepts learned from this system to the cement system. Dynamic light scattering was the main technique used for this study. Though adsorption isotherms, time sweep dynamic rheological tests, and calorimetry were also used to elucidate the physical origins behind mixing.

From these studies on high shear mixing, the following conclusion were made:

1. RAM mixing does not have a tool that directly interacts with the mixing medium. This makes it an attractive mixing device as it reduces the cost of wear and tear of the mixing device. Furthermore, the non-direct mixing action could be beneficial in cases where the interaction of the mixing tool and the mixing medium is an important parameter to consider, such as the case with fiber containing materials where the fibers can be bent from the mixing tool. Or the mixing device needs to be integrated into a pump or 3D printer. RAM could have a place in concrete mixing technology.

2. Compared to a table top paddle mixer, RAM mixed at room temperature showed reduced flow and workability properties, but RAM mixed at ice temperatures showed an increase in fluidity and workability. A 30% increase in 3-day and 20% increase in 28-day mechanical properties were observed in UHPC specimens mixed with RAM. The improved mechanical properties support the understanding that there is more uniform mixing energy transmitted to the system during mixing which enhances cement hydration and reduces air voids.

3. RAM showed an average of 72% increase in flexural 7 day strength with pristine powdered graphite high strength cement. Results with the heptane-graphite emulsion showed no improvement or even a decrease in both compressive and flexural strength.
4. Polyvinyl phenol wrapped CNF-UHPC composites did not perform in terms of mechanical strength better than untreated CNF-UHPC composites. Though in general all CNF-UHPC composites did show an overall improvement in mechanical properties at 7 days even with CNF clusters present.

5. Mixing CNFs into UHPC requires a higher mixing demand, nearly 50% more energy.

6. By changing the shear rate produced in the gap between cement particles through the increase of the solid volume fraction or the mixing speed, the results provide a master curve that suggests a mechanistic link between the concentration of nanoparticles in the pore solution and the shearing conditions. It is suggested, in accordance with the literature, that the mixing process promotes hydration by scratching hydrates from the surface of cement particles.

7. These results open the door for low cost cement acceleration through just the mixing.

10.2. Future Work
While this dissertation answered some questions about high energy mixing, there is still many more to be answered. Future work that could address some of these questions would be to investigate the following:

1. RAM mixing is meant to operate at the system’s resonance frequency. Thus, the main parameters that affect the final mixing outcome are the amplitude of the resonance acoustic pressure wave, the time of mixing, and the fill level of the vessel. More work will be needed to quantify the direct relationship of these parameters to the properties of the UHPC mix. Perhaps some mechanistic link between the UHPC composition and the acceleration curves.
2. RAM can be considered qualitatively a high intensive mixer, yet further studies are needed to fully understand the mixing process of acoustic resonance mixing and its effects on cement and UHPC properties.

3. Further investigations will need to be conducted to more suitable substances other than heptane for a graphite emulsion intended for cement.


5. The mixing demands for different cement-based materials with CNFs and other carbon inclusions, nanosilica inclusions, and so forth.

6. Durability properties and how they are affected by different mixing methods.
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