May 2015

The Design of High Performance and Ultra-High Performance Fiber Reinforced Cementitious Composites with Nano Materials

Scott W. Muzenski

University of Wisconsin-Milwaukee

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THE DESIGN OF HIGH PERFORMANCE AND ULTRA-HIGH PERFORMANCE FIBER REINFORCED CEMENTITIOUS COMPOSITES WITH NANO MATERIALS

by

Scott Muzenski

A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Engineering at The University of Wisconsin-Milwaukee

May 2015
ABSTRACT
THE DESIGN OF HIGH PERFORMANCE AND ULTRA-HIGH PERFORMANCE FIBER REINFORCED CEMENTITIOUS COMPOSITES WITH NANO MATERIALS

by
Scott Muzenski

The University of Wisconsin-Milwaukee, 2015
Under the Supervision of Professor Konstantin Sobolev

The use of high performance and ultra-high performance cementitious composites (HPC/UHPC) in critical elements of infrastructure can be a sustainable alternative to conventional concrete. These materials provide superior durability, reducing the need for maintenance and early replacement. The use of special cements and nano-materials improve the strength and durability of HPC/UHPC composites by providing a denser microstructure. The addition of high performance fibers enhances the ductility and restricts the crack size, reducing water penetration in cracked material. In HPC, the addition of superhydrophobic admixtures further reduces water permeability and thus provides superior durability and freeze-thaw resistance by producing a preferred engineered air void structure. This air void structure can also be tailored to act as artificial flaws to promote multi-cracking and strain hardening behavior without significant reductions in compressive strength. In UHPC, a dense cementitious matrix can be achieved through the use of Al₂O₃ nano-fibers and oil well cement resulting in superior flexural and tensile properties and compressive strength exceeding 150 MPa. This was achieved by the low water to cementitious materials ratio required for oil well cement along with the seeding effect and
reinforcing of calcium silicate hydrate from the nano-fibers. Furthermore, the use of polyethylene fibers results in strain hardening and multi-cracking behavior in HPC/UHPC. This research aimed to optimize high performance or ultra-high performance cementitious composites with superhydrophobic admixtures and nano-materials based on multi-scale design of the material with three levels: cement paste, mortar, and fiber reinforced composite.

To analyze the high performance and ultra-high performance cementitious composites, the following investigations were performed:

- Testing the compressive strength and hydration of mortars to determine the optimal cement type, dosage of nano-material, and supplementary cementitious material;
- Analysis of cement pastes through microstructure characterization and hydration to define the mechanisms leading to improved behavior;
- Air void analysis of HPC to determine the best superhydrophobic admixture;
- Testing of compressive strength and flexural behavior for comparison of fiber types in UHPC;
- Mechanical and durability testing of UHPC with superhydrophobic air void systems.
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<tr>
<td>AASHTO</td>
<td>American Association of State Highway and Transportation Officials</td>
</tr>
<tr>
<td>ACI</td>
<td>American Concrete Institute</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>C$_2$S</td>
<td>Dicalcium Silicate</td>
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<td>C$_3$A</td>
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<tr>
<td>SCM</td>
<td>Supplementary Cementitious Composite</td>
</tr>
<tr>
<td>SECC</td>
<td>Superhydrophobic Engineered Cementitious Composite</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SF</td>
<td>Silica Fume</td>
</tr>
<tr>
<td>SP</td>
<td>Superplasticizer</td>
</tr>
<tr>
<td>TBP</td>
<td>Tributyl Phosphate</td>
</tr>
<tr>
<td>TG-DTA</td>
<td>Thermogravimetric-Differential Thermal Analysis</td>
</tr>
<tr>
<td>UHPC</td>
<td>Ultra-High Performance Concrete</td>
</tr>
<tr>
<td>VMA</td>
<td>Viscosity Modifying Admixture</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>-------------</td>
<td>--------------------------------------------------</td>
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<tr>
<td>W/C</td>
<td>Water to Cement Ratio</td>
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<tr>
<td>W/CM</td>
<td>Water to Cementitious Material Ratio</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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<tr>
<td>σ-CMOD</td>
<td>Stress vs. Crack Mouth Opening Displacement</td>
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ACKNOWLEDGMENTS

I would like to thank Professor Konstantin Sobolev for his support throughout this research. This work would not have be possible without his insight and contributions. His guidance and support throughout my graduate studies has been immense. I would also like to thank Dr. Ismael Flores for his endless hours helping me with mixes and providing terrific insight and thoughts for approaches to take within this research. Additionally, I would like to extend a great appreciation for Dr. Habib Tabatabai, Dr. Rani El-Hajjar, and Dr. Ilya Avdeev for being part of my dissertation defense jury.

I would also like to give a special thanks to all the undergraduate and graduate students at UW-Milwaukee who helped with testing of samples for this research. These students include: Rani Pradoto, Reza Moini, Emil Bautista, Marina Kozhukova, Sunil Rao, Justin Flickinger, Brandon Bosch, Clayton Cloutier, Joshua Hoheneder, Brent Kriha, Morteza (Babak) Janbaz, Rahul Ramachandran, Rahim Reshadi, Nate Havener, Katie LeDoux, Andrew Sinko, Alper Kolcu, Chris Ball, Seth Walsdorf, Craig Vindedahl, Jason Atchison, Kristian Nygaard, Mark Moyle, Gaven Kobes, Tyler Beinlich, and Jesus Castro Cortes.

Additionally, I would like to thank the pavements team at FHWA-TFHRC for their support with the Dwight D. Eisenhower Research Fellowship, including Dr. Jack Youtcheff, Ahmad Ardani, Dr. Jussara Tanesi, Dr. Jose Munoz, Rick Meininger, Dr. Mengesha Beyene, Dr. Igor De la Vargo, Dr. Haejin Kim, Anant Shastry, John Leavitt, and Senaka Samaranayake.
1. INTRODUCTION

The strength and durability of highway bridges are two key components in maintaining a high level of freight transportation capacity on the nation’s highways [1-3]. The average service life of concrete infrastructure in Wisconsin is 40-50 years, with up to 10% of bridge decks reinforced by uncoated rebar that need replacement after 30 years [1, 4]. Highways, bridges, and other critical transportation infrastructure components are deteriorating due to loading and deformation, aging, de-icing, and other detrimental factors in addition to rebar corrosion [1-3]. The average age of bridges throughout the United States in 42 years [5] indicating that many are reaching the end of their lifetime and will require replacement in the near future. It is estimated that over two hundred million trips are taken every day over bridges that are deemed to be structural deficient [5]. Additionally, the need to accommodate larger amounts of traffic is leading to the construction of newer bridges. The need for construction of newer bridges and repair or replacement of existing bridges reduces the traffic flow. Commuters and freight travel across these bridges daily, and if they are delayed, the economic costs are significant.

Indirect costs of highway bridge construction, in the form of environmental damage, are also being realized in relation to the production and recycling of basic concrete materials. Furthermore, the requirement for sustainable construction material is becoming more evident than ever before. With high focus on reducing greenhouse gases, the reduction of portland cement production for infrastructure purposes would reduce CO₂ emissions as this manufacturing process is one of the largest contributors. This can be accomplished by extending the lifetime of cement-based infrastructure elements. Additionally, the utilization of large amounts of supplementary cementitious materials or
by-products can even further reduce the demand for portland cement. High performance or ultra-high performance concrete may often require higher amounts of portland cement; however, the extended lifetime of structures with these materials will reduce the requirement for an additional portland cement production over the course of the service life of the structure. Additionally, the use of high performance and ultra-high performance concrete in structural members can lead to smaller structural sections saving on material volume.

Conventional portland cement-based concrete is brittle and inevitably develops cracks, often due to drying shrinkage during curing, which are further extended after loading and weathering. Previous research provided strong scientific background on a new generation of high performance fiber-reinforced superhydrophobic engineered cementitious composites (SECC) with enhanced durability and large ductility. These provide a sustainable material with an extended service life, which is required for critical parts of concrete infrastructure, especially the components of highway bridges. The SECC is a new advanced concrete material with polyvinyl alcohol (PVA) fibers and hydrophobic compounds that is under development at the University of Wisconsin-Milwaukee [6, 7]. This research work demonstrated that SECC is an advanced substitute to conventional concrete that can provide the strength and durability demanded in key regions of highway bridges.

The superhydrophobic hybridization approach [8-10] is a highly effective method for controlling the durability of concrete with mineral additives and by-products used as cement replacement. Due to this improved durability, the concept provides a shift in cement and concrete engineering that can serve as a backbone for the sustainable
development of concrete pavement and bridge infrastructure. Indeed, the developed SECC meets the highest sustainability benchmarks and can be used as the next technological platform for sustainable concrete structures with high performance and longer service life.

The time is right for a new paradigm to address the urgent need for highly durable and sustainable materials to meet the challenges to accommodate the future freight transportation. The developed SECC concrete is a new advanced material required for critical parts of highway bridges and other concrete infrastructure components; which can potentially transform the ways in which engineers build and repair highway infrastructure. High performance concrete such as SECC is a great alternative to conventional concrete to be used in critical areas of infrastructure because of its high durability.

The use of nano-materials in cementitious materials has also been improving the effectiveness of structures and critical infrastructure elements. Here, these small, usually 1 to 100 nm in diameter, particles enable nano- and micro-structural changes within the concrete that can demonstrate substantial benefits when used in small quantities. Nano-technology in concrete has emerged within the last couple of decades and has benefitted the industry by improving mechanical performance of concrete and composites, creating self-healing concrete, creating electrically conductive and self-healing concrete, acting as a viscosity modifier, providing the degradation of pollutants by the use of photocatalytic concrete, as well as many other applications [11]. Nano-modification of cementitious materials can also help to develop a new generation of ultra-high performance concrete (UHPC). Ultra-high performance concrete is a relatively new form of concrete with exceptional durability, compressive strengths of at least 150 MPa, improved ductility, and sustained tensile strength of at least 5 MPa. This material has been used in bridges
throughout the world to reduce the structural section size. The material is also reinforced with small, 3-dimensionally dispersed fibers that reduce the crack size. The addition of these fibers also helps to reduce the amount of shear reinforcement required for the structural members. Furthermore, the material is often used as precast elements, which can accelerate the construction process and since the material gains strength at a faster rate, lesser storage space and time is required for UHPC to cure. Field-cast UHPC also demonstrates improved properties and is capable of gaining the required strengths to continue construction or reopen traffic faster than conventional concrete.

The incorporation of superhydrophobic admixtures and additional nano-materials into “classical” UHPC formulations may prove to be very beneficial. Typically, as the strength of cementitious matrix becomes higher, the ductility of the fiber reinforced composite is reduced. To account for this, the strength of the cementitious matrix is often reduced when improved ductility of fiber reinforced composites is required. This reduction in strength can lead to compromised durability properties. In UHPC, the pore structure is often discontinuous which leads to lesser water ingress, therefore, the benefits of reduced absorption with superhydrophobic admixtures in UHPC may not be obvious; however, such admixtures can produce well dispersed “engineered” air voids that act as artificial flaws to promote multi-cracking and strain hardening behavior without loss of strength [12]. Furthermore, the addition of nano-materials such as nano-SiO$_2$ and Al$_2$O$_3$ nano-fibers may improve the structure of the cement paste and thus even further improve the mechanical properties of the composite. By combining all of these materials and concepts and using the resulting material in critical elements of infrastructure, a more efficient and long lasting highway system will be realized based on the reported research.
This requirement for more durable and sustainable concrete infrastructure leads to the need for new cement-based materials. In this case, ultra-high performance concrete may be the answer. In this research, ultra-high performance concrete can be created by using small quantities of nano-fibers in lieu of high quantities of silica fume to achieve the same high compressive strength. It is hypothesized that these nano-fibers can act as nucleation sites for the formation of hydration products, as well as acting as reinforcement for calcium silicate hydrates, restraining the formation of micro-cracks and thus improving strength. In ultra-high performance concrete, the use of entrained air may not be necessary for superior durability, but it is hypothesized that the use of these superhydrophobic admixtures can improve the flexural and tensile behavior of the composite by acting as artificial flaws to promote multi-cracking and strain hardening behavior.
2. BACKGROUND

2.1 FIBER REINFORCED CONCRETE

Concrete, the main cement-based material, is usually strong under compression loads, but weak in tension. Due to this reason, structural concrete utilizes reinforcement, which is often steel, to respond to loads imposed upon structural elements. The addition of structural reinforcement in concrete provides many benefits. The longitudinal reinforcement is often the main tensile load carrier for structural members under flexure. Transverse reinforcement improves the shear capacity of concrete members while at the same time adding confinement to concrete, thus improving concrete’s response to compressive loading. Although reinforcing bars are commonly considered to be the best solution for longitudinal reinforcement in structural concrete, the addition of 3-dimensional, randomly oriented fibers can provide many benefits, e.g., eliminate the need for transverse reinforcement and provide improved tensile properties. The use of fibers as reinforcement is technology that has been around for thousands of years. The Egyptians used horse hairs to reinforce mud bricks resulting in a less brittle material. More recently, fibers such as steel or glass have been used in cementitious materials. It has been found that the use of fiber reinforcement in structural members can greatly reduce the need for transverse reinforcement, especially in structures exposed to cyclic loading as the energy dissipation of structural members with fiber reinforcement is significantly higher [13, 14]. This, in turn, results in reduced labor costs associated with the installation of shear or transverse reinforcement [15]. Despite this, most applications of fiber reinforcement in cementitious composites have been for non-structural applications such as concrete art or reduction in shrinkage cracking. With recent advances in the use of fiber reinforced
concrete (FRC), structural applications are becoming more widespread. Fiber reinforced cementitious composites have been used as link slabs on bridge decks [16] and in prefabricated modular housing [17] as well as others. However, the use of fiber reinforced concrete has not yet been incorporated into ACI Building (ACI 318) or similar codes.

In many cases the bond between fibers and the cementitious matrix is critical in obtaining a desirable performance. If the bond is strong, the failure mechanism is governed by fiber rupture. If the bond is weak, the fiber pull out of the cementitious matrix will govern the failure. The first case may lead to stronger composites while the second may lead to the design of more ductile composites. In the case of a balanced combination, a strong and ductile cementitious composite may be engineered.

The addition of fibers can often reduce the workability of cementitious materials because the shapes of the fibers typically affect the flow properties in the same way as more angular aggregates reduce workability [18]. The workability of fiber reinforced composites is often dependent on the aspect ratio of the fiber, the fiber geometry, and volume fraction [19]. The workability of a fiber reinforced composite must be high enough so that the material can be placed and finished without excess effort.

When a crack forms in a cementitious composite that uses higher aspect ratio fibers, more fibers will bridge the crack and, therefore, provide a better post first crack response. However, these higher aspect ratio fibers will sometimes tend to ball together and become less effective.

Many different types of fibers have been used as reinforcement in cementitious composites. The most common type is steel fibers. Other types include glass, synthetic and natural fiber materials. All of these types can range in size and shape. When
considering steel fibers, their shapes include straight, crimped end wire, hooked end, spiral or twisted, as well as others. Crimped end and hooked end steel fiber can be used to generate a better bond to the cementitious composites. Here, the ends are deformed so that the fibers can achieve a better development much in the same way as structural steel reinforcement in concrete. The deformed ends may also help to maintain higher aspect ratios while reducing the potential for balling of the fibers. Steel fibers typically have no chemical bond with cementitious materials, therefore another method to increase the bond is related to roughening of the surface. Steel is also prone to corrosion. Therefore, it must be protected from corrosion, especially in more porous cementitious composites. Many types of steel fiber reinforcement include treated steel or stainless steel fibers. However, some grades of stainless steel may have different mechanical responses when exposed to harsh environments [20]. The use of steel reinforcement typically has little effect on the compressive strength of concrete and, in some cases, reduces the compressive strength because of the lower workability, entrapped air, and compact defects. However, there have been some cases where up to 15% increase in compressive strength was reported for composites with up to 1.5% (by volume) of fibers [21-23]. The maximum tensile load, on the other hand, may be increased by as much as 30 to 40% with the same volume of fibers [23]. In terms of flexure, the maximum strength may be improved up to 50 to 70% and up to 150% if the fibers are aligned [21, 24]. Other aspects such as impact loading, fatigue behavior, skid resistance, and shrinkage may be improved with the use of steel fibers. The use of steel fiber reinforcement has been used for applications such as shotcrete [25], airport pavement applications [26], roller compacted concrete [27], and many other applications.
Glass fiber reinforced concrete is another popular type of reinforcement for cementitious composites. Early research on glass fibers demonstrated that the high alkalinity of the cementitious matrix can reduce the strength of the fibers overtime and so such fibers may not be suitable for cementitious composites [28]. The development of alkali resistant glass fibers improved long-term integrity. Additionally, researchers have tried to alter the cementitious matrix in order to provide an effective glass fiber reinforced cementitious composite. The use of high alumina cement was proposed; however, increased porosity and decrease in strength was observed with this approach [29]. The most common use for glass fiber reinforced cementitious composites has been for exterior building facades. Other applications such as surface bonding, anchor connections, and floating docks were reported.

Another type of inorganic fiber is based on basalt. These are formed from basalt rocks through a melting process. The tensile strengths of these fibers can be higher than some glass fibers and can provide greater failure strain than some carbon fibers [30]. However, these fibers can be more brittle than others.

Synthetic fiber is another popular material used in cementitious composites. Some types of synthetic fibers include acrylic, carbon, polyester, polyethylene, polypropylene, and nylon. The diameter and length of these fibers vary as well. Acrylic fibers have been used as a replacement for asbestos fibers. Carbon fibers have been used due to their high tensile strength. These are added to form random distribution and orientation throughout a cementitious matrix. The use of carbon fibers has been shown to improve the impact loading and fracture toughness. Nylon fibers have also been used for impact or blast resistance [31]. Other benefits of nylon fibers include the improvement in toughness,
ductility and control of cracking when used at volumes between 0.5% and 3% [32, 33]. The post first crack behavior of nylon fiber reinforced cementitious composites is also desirable as the composite is capable of taking increased loads and have strain hardening behavior [32, 34]. Polyester fibers have typically been used in concrete to control the plastic shrinkage cracking and are typically added at relatively low (approximately 0.1% by volume) quantities. Polypropylene fibers have also been shown to improve the impact loading. These fibers are typically not capable to provide strain hardening behavior. Although the post first crack load carrying ability can be improved with higher quantities of fibers [35]. Increased post first crack strengths can be seen when these fibers are used collated fibrillated fibers [36]. Polyethylene fibers have demonstrated exceptional multi-cracking behavior and excellent load transferring ability after crack formation resulting in a strain hardening behavior. These post first crack loads continue to increase until the fibers begin to rupture [37].

Natural fibers have been used in cementitious composites, but are not as common as others. These types of fibers include coconut, sisal, sugar cane bagasse, bamboo, jute, flax, and other types of vegetable fibers. These fibers can add some mechanical improvements to the composites, although the long term response is affected by the low alkali resistance of the fibers.

2.1.1 Strain-Hardening Fiber Reinforced Cementitious Materials

A new type of fiber reinforced concrete with strain-hardening properties referred to by some as engineered cementitious composites (ECC) or polyvinyl alcohol ECC (PVA-ECC) has emerged. This material is known for its ability to withstand higher stresses after initial cracking. Most conventional fiber reinforced concretes, however, are capable of
withstanding stresses after cracking, but at lower values than first crack stresses (*Figure 1*).

*Figure 1: Strain hardening behavior of plain mortar, FRC, and PVA-ECC [38]*

The use of engineered cementitious composites has been studied extensively by researchers led by Prof. Victor Li at the University of Michigan. This material utilizes short (12 mm long) randomly oriented polyvinyl alcohol (PVA) fibers used at low volumes (approx. 2%) and exhibits resilient ductile performance under tension similar to steel [39]. The material also does not include coarse aggregates and contains a high quantity of cementitious materials.

This material has been developed based on micromechanical models. These PVA fibers are hydrophilic by nature and, therefore, have an extremely high bond with cementitious matrices. This produces a challenge for the design of the composite material as fibers tend to rupture instead of pulling out resulting in lower ductility [40]. To account for this strong bond, the fibers are often coated with an oiling agent to reduce the bond and thus result in a controlled pullout of the fibers instead of fiber rupture [41]. The principle
theories behind the mechanics based models state that the maximum tensile cracking strength must not exceed the maximum fiber bridging strength [42]. This means that in order to satisfy the models, the strength of the cementitious matrix must be restricted. However, with reduced strength of the cementitious matrix (e.g., by increase in water to cementitious material ratio (W/CM), use of high volumes of supplementary cementitious materials), the durability performance of the material could be also compromised.

The main property of fiber reinforced cementitious materials is the ability for fibers to bridge a crack. This can be monitored through the stress transmitted across a crack as it opens vs. deflection [43, 44]. When a crack is formed in a cementitious composite, the fibers bridging these gaps transfer the loads across the crack and distribute the stresses to other locations so that multiple cracks are formed. With more cracks formed, the material can exhibit a better tensile or flexural behavior. The maximum fiber bridging strength ($\sigma_{cu}$) and critical crack opening before the rupture ($\delta_p$) can be attributed to the fiber bridging capabilities and can be demonstrated by the complimentary energy (Figure 2). Improved complementary energy results in a better strain hardening properties. The weaker fiber-matrix bond lowers the maximum fiber bridging strength because of fiber pullout. However, when the bond is too strong, the fibers are not allowed to stretch and thus fiber rupture occurs resulting in a smaller critical opening ($\delta_p$). A compromise between these two processes must be made in order to achieve the highest complementary energy.
Figure 2: Stress ($\sigma_B$)-deflection ($\delta$) curve and the concept of complementary energy ($C$) 
[45]

Steady-state crack analysis can be used to analyze the complementary energy of the stress-deflection curves [46]. When the complementary energy is small, the crack will behave like a Griffith crack (Figure 3a), meaning the crack width will continue to grow. As the crack width grows, its width ($\delta_m$) will exceed the critical opening ($\delta_p$), resulting in fiber rupture, hindering the load carrying capacity and promoting strain-softening behavior. When the complementary energy is high, the crack will act as a steady state flat crack (Figure 3b) meaning that the crack width ($\delta_{ss}$) will not increase (crack width is smaller than $\delta_p$). This will maintain the load carrying capacity and stresses will be transferred back to the cementitious matrix. When a second crack forms and opens because of these stresses, the same steady-state crack must occur and the process must repeat for other stress levels and new cracks. This process can continue until a Griffith crack is formed. With larger volumes of steady-state cracks occurring, a material of higher ductility is obtained (engineered).
Figure 3: Griffith crack model for fiber reinforced composites with low complementary energy (a) and steady state flat crack model (b) for fiber reinforced composites with high complementary energy [45]

A set of equations were developed in order to model the pullout behavior of fibers in cementitious composites [47]. The process of fiber bridging occurs in 3 different stages (Figure 4). First the fibers resist the increasing load up to the peak fiber load ($P_a$) where the only deflections that occur are due to the sliding of the fibers and the elastic deformation of the free ends of the fiber. In this region, the fiber itself is transferring the load, whereas in later regions, the load is only resisted by frictional forces. Next, there is a drop from the peak load ($P_a$) to $P_b$. The larger this drop, the more significant the loss in bond strength between the fiber and the matrix.
Figure 4: Profile of a single fiber pullout curve [47]

The initial drop between $P_a$ and $P_b$ can be calculated by the chemical debonding energy value $G_d$. This is calculated by Eq. 1, where $E_f$ is the fiber axial Young’s modulus and $d_f$ is the fiber diameter [48]. If the drop is large, the debonding at the interface will be governed by fracture criteria rather than strength criterion [49, 50].

$$G_d = \frac{2(P_a - P_b)^2}{\pi^2 E_f d_f^3}$$  \hspace{1cm} (Eq. 1)

At $P_b$ the initial frictional bond strength ($\tau_0$) can be calculated based on the embedment length ($l_e$) and the fiber diameter ($d_f$) using Eq.2 and later used to determine if the fiber will experience slip-softening or slip-hardening.

$$\tau_0 = \frac{P_b}{\pi d_f l_e}$$  \hspace{1cm} (Eq. 2)

The final stage consists of whole fiber slippage where the frictional force is the only resistance. The fiber will experience the slip-softening if the coefficient $\beta$ is less than 0, experience constant friction if $\beta$ is equal to 0, and experience slip-hardening if $\beta$ is greater
than 0. Slip-hardening results in higher load resisting capacity. To determine which case will prevail, $\beta$ can be calculated from Eq. 3 from the initial slope of the curve at $P_b$.

$$\beta = \left(\frac{d_f}{l_f}\right) \left[\left(\frac{1}{\tau_0 \pi d_f}\right) \frac{\Delta P}{\Delta S'}\right]_{S' \to 0} + 1 \quad \text{(Eq. 3)}$$

The mechanics of crack propagation prior to fiber bridging is also a crucial property when designing a high strength fiber reinforced composite. Flaws are always present in cementitious composites and when loaded, stress concentrations tend to form around these flaws. These stress concentrations tend to form micro-cracks and upon further loading, these micro cracks turn into macro cracks where fibers or reinforcement are required to restrain the crack propagation. The area in front of the progressing crack, the frontal process zone (FPZ), must have a sufficient toughness in order to slow the progression of the crack. If this zone is strong enough, the crack growth will be restrained and stresses can transfer to other areas of the composite where additional cracks can form to result in multi-cracking and strain hardening behavior. This can be accomplished by restraining the micro-cracks in the FPZ from extending to the full crack, ultimately increasing the crack size.

To test fracture toughness of the FPZ in a fiber reinforced composite, tensile stress vs. crack mouth opening displacement ($\sigma$-CMOD) tests can be performed. These results can give a good indication of how the material will perform when actual cracks occur. The $\sigma$-CMOD curve can be divided into fiber zones to analyze the behavior of the FPZ [51] (Figure 5).
Nelson and Li (2002) discussed a set of equations to define these zones [51]. The first zone establishes the linear region where micro-cracks have yet to form. In this zone, the stress intensity factor ($K_L$) is less than the composite’s fracture toughness ($K_{IC}^C$) and the applied stress ($\sigma$) is less than the stress required to form the micro-cracks ($\sigma_A$). The composite fracture toughness can be calculated by Eq. 4 where $F(a/W)$ is the specimen shape factor [52].

$$K_{IC}^C = F\left(\frac{a}{W}\right)\sigma_A \sqrt{\pi a}$$  \hspace{1cm} (Eq. 4)

The second zone is the nonlinear deformation of the composite where micro-cracks begin to form. In this region the stress intensity factor is greater than $K_{IC}^C$ but less than composite fracture toughness which takes into account the energy absorbed by micro-cracks prior to localized crack formation ($K_{IC}^C$). The minimum and maximum applied stresses in this zone are defined as $\sigma_A$ and $\sigma_B$, respectively. At $\sigma_B$ a localized failure crack occurs.

The third zone is when this localized failure crack grows. The applied load continues to increase in this region, indicating that the additional stresses must be applied in order to increase the crack size. Here, the stress intensity factor is less than the materials resistance to crack formation ($K_{IC}^C-K_b$) where $K_b$ is the negative stress intensity factor due
to fiber bridging [53]. Propagation of this crack will remain stable if the rate of change in load stress intensity factor is less than the rate of change in material resistance defined by Eq. 5.

$$\frac{\partial K_L}{\partial a} < \frac{\partial}{\partial a}(K_{IC}^* - K_b) \quad \text{(Eq. 5)}$$

The fourth zone is when the crack propagation becomes unstable and the localized failure crack grows. At this time the applied load begins to decrease and $K_L$ equals $K_{IC}^* - K_b$; $K_b$ would be greater if referring to crack length.

The final zone (Zone V) is where the entire tensile load is carried by the fibers and the fiber bridging properties are defined as mentioned earlier. Nelson and Li (2002) found through experimental fracture mechanics testing and acoustic emissions testing, that PVA fibers, when compared to other fiber types, were able to provide a higher composite fracture toughness [51].

2.1.2 Superhydrophobic Fiber Reinforced Cementitious Materials

Recent developments have led to the creation of superhydrophobic fiber reinforced cementitious materials or superhydrophobic engineered cementitious composites (SECC). This material combines the concepts of fiber reinforced concrete with superhydrophobic hybridization. Superhydrophobic hybridization is based on the addition of hydrophobic, overhydrophobic, or superhydrophobic admixtures to cementitious materials. This engages interdisciplinary work combining biomimetics (lotus effect), chemistry (use of siloxane polymers), and nanotechnology (nano-SiO$_2$ particles) to improve concrete durability [8-11]. The idea behind this approach is combining ductile fiber reinforced cementitious composites with advanced air-forming admixtures to provide excellent freeze-thaw resistance. Due to the ultra-dense cementitious matrix, controlled crack
opening, and superhydrophobic modification, the resulting material is a highly durable cementitious composite.

Hydrophobic, overhydrophobic, and superhydrophobic surfaces occur when water droplets are placed on the surface and generate high contact angles where little to no water gets absorbed by the substrate. The opposite would be cement-based material’s hydrophilic surfaces resulting in low contact angles and high absorption by the substrate (Figure 6). High contact angles can be created by a combination of low surface energy coatings with water droplets and a multi-scale (or hierarchical) roughness [54]. These nature inspired surfaces resemble the lotus leaf. The leaf itself is coated in a hydrophobic wax layer providing a contact angle of about 103° [55]. At first glance the lotus leaf appears to have a smooth surface, but at the micro-scale there are several bumps or asperities. In addition to these micro-bumps, there are nano-bumps to produce the hierarchical surface roughness [56, 57].

![Figure 6: Contact angles of hydrophilic, hydrophobic, overhydrophobic, and superhydrophobic surfaces](image)

There are several possibilities of how to incorporate this concept into cementitious materials. First, a surface layer hydrophobic or superhydrophobic coating could be applied. This would utilize similar application concepts as concrete surface sealers that are commercially available. The problem with this concept is that if a crack is formed within the concrete, the sealing agent will open along with the crack, allowing water to penetrate
the material. This would only allow for short term benefits as cementitious materials will inevitably crack due to loading, expansion/contraction due to temperature variants, as well as many other phenomena. A second approach would be to create a 3-dimensional superhydrophobization within the material which would have water repellant properties even when the cementitious material cracks (Figure 7).

![Figure 7: Typical concrete sealers (left) and 3-D hydrophobization (right)](image)

The creation of a 3-dimensional hydrophobic and superhydrophobic (HSH) material can be achieved by using small quantities of polyethyl hydrosiloxane (PEHSO) or polymethyl hydrosiloxane (PMHS) agents combined with polyvinyl alcohol surfactant (PVAS) to create an emulsion. These hydrogen containing admixtures (used at a dose of 0.01 - 0.1% by weight of cementitious material), when added during the mixing process with cementitious materials, release hydrogen to produce small (10 – 100 µm) air voids [7]. The walls of these voids are then coated with the HSH layer rendering hydrophobic properties (the same concept of waxy surface of the lotus leaf). Additionally, if micro or sub-micro sized particles are added to the emulsion, they coat the surface of the voids, resulting in the surface roughness required to improve the hydrophobicity (reaching the overhydrophobic state). Finally, if micro, sub-micro, and nano-sized particles are added to the emulsion, the hierarchal surface roughness required for superhydrophobicity is achieved. The air voids created from the superhydrophobic admixtures provide a
controlled air void structure with little to no loss in compressive strength, precise air void spacing factors, and controlled size distribution (Figure 8). These air void properties can then be precisely controlled unlike many conventional air entraining admixtures where a loss of intended air during mixing, transport, or pumping is inevitable.

Figure 8: How the superhydrophobization of concrete works [Adapted from [7]]

The addition of entrained air to cementitious composites is critical to resist against freezing and thawing cycles. Freeze-thaw damage in concrete can be a serious issue drastically reducing the service life. The main affect occurs when water within the pore space of concrete freezes and expands. If there is no adequate room for this expansion, internal pressure occurs resulting in expansion and cracking of the concrete ultimately reducing the lifetime of the structures. For these reasons, entrained air is added to cementitious materials so that there is room water to expand upon freezing. It was proposed that if approximately at least 92% of the capillary voids in concrete are saturated, freeze-thaw damage will occur [59]. This can then be correlated to key parameters of concrete
mixes. It is known that in concrete with higher water to cement ratios (W/C), critical saturation occurs much easier thus affecting the freeze-thaw resistance. It was also determined that the samples with a lower W/C have lower permeability and, therefore, have a better resistance to freezing and thawing.

The mechanism behind the air entrainment requirement is based on the assumption that water within cementitious materials is intended to reach chemical and thermal equilibrium. Water flows between the air voids through capillary pores which can be represented as small hollow tubes. While occupying these voids, water is forced to escape to the zones with the lowest pressure, which is provided by larger air voids. Also, upon freezing, water flows under thermal gradients. This again draws water to the larger entrained air voids as freezing temperatures affect larger pore space zones prior to smaller ones. However, problems occur when the cement paste cannot accommodate the pressure from freezing and water is pushed through capillaries away from reservoirs and trapped. Once this occurs water freezes within the capillaries and causes internal pressures and damage. The best approach proposed for cementitious materials to resist freezing and thawing cycles is to create an air void system with desirable pore structure. The first step would involve the formation of a system with reduced porosity and fewer entrapped air voids which can be accomplished by using a material with a lower W/C. The entrapped air voids are typically non-spherical (which is not ideal for freezing and thawing) and large in size (which may drastically reduce the compressive strength). The next step is to create a system of small, well-dispersed air entrained voids. The smaller size voids can help to maintain higher compressive strength and good dispersion of these voids would result in a shorter distance for water to travel to the void from the capillaries to find escape during
freezing. Other types of pores present within cementitious materials; however, are not as easily controllable, are gel pores and cracks which may be due to loading, freezing and thawing, or shrinkage. The sizes of different pores within cementitious materials are reported in Table 1.

Table 1: Classification and Characteristics of Voids in Portland Cement Concrete Materials [60, 61]

<table>
<thead>
<tr>
<th>Type of voids</th>
<th>Size range</th>
<th>Shape</th>
<th>Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel pores</td>
<td>1-5 nm</td>
<td>Irregular</td>
<td>-</td>
</tr>
<tr>
<td>Capillary Voids</td>
<td>10-1000 nm</td>
<td>Irregular</td>
<td>Spaces left by mixed water</td>
</tr>
<tr>
<td>Entrained Air Voids</td>
<td>100 µm-1 mm</td>
<td>Spherical</td>
<td>Air Entraining Admixtures</td>
</tr>
<tr>
<td>Entrapped voids</td>
<td>1-10 mm</td>
<td>Spherical</td>
<td>Mixing of concrete</td>
</tr>
<tr>
<td>Micro- Cracks</td>
<td>0.01-0.2 mm</td>
<td>Irregular</td>
<td>-</td>
</tr>
<tr>
<td>Cracks</td>
<td>0.5-2 mm</td>
<td>Irregular</td>
<td>-</td>
</tr>
</tbody>
</table>

The air bubbles created with the help of air entraining admixtures must have certain properties to adequately resist the freezing and thawing cycles. The bubbles created must form a network of small, well distributed voids [59]. The requirement for a specific volume of air within cementitious materials is not enough to create a durable material. A concrete sample may have the prescribed volume of air; however, this volume may only be made up of a few large voids meaning that capillary water will have to travel further to reach the void and so travel distance would be longer than the maximum length limited by the tensile stress of the cement paste as defined by the following equation.

\[
l = \Delta h \frac{k A}{\eta Q}
\]

(Eq. 6)

Where \(\Delta h\) is the pressure gradient, \(\eta\) is the fluid viscosity, \(k\) is the permeability, \(Q\) is the flow rate, \(A\) is the flow area, and \(l\) is the length of the flow rate. If \(\Delta h\) is set to the
maximum tensile stress of the cement paste, the distance moisture would have to travel before causing damage can be calculated [59].

The distribution of air voids in hardened concrete is defined by the spacing factor, which is the measure of the average distance water would have to travel to reach the closest air bubble. This analysis can be performed in accordance with ASTM C 457 (Standard Test Method for Microscopic Determination of Parameters of the Air-Void System in Hardened Concrete). This theoretical distance has been reported by several researchers such as Pigeon and established that for a durable concrete, the spacing factor should be between 200 to 250 µm [62]. After this point, the freeze-thaw response of the material can be compromised.

There is some indication that in high performance cementitious materials with low water to binder ratios, the required spacing factor is not necessary [63]. There is also evidence that no entrained air voids are necessary for high-strength/high-performance cement-based materials. When tested under ASTM C 666 (Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing) high performance cementitious materials are considered to be durable. This standard procedure states that concrete needs to maintain a durability factor (measure of the ratio of relative dynamic modulus of elasticity during freeze-thaw exposure to that prior to exposure) of 60% through 300 cycles to be considered a durable material. There is no doubt that many high performance cementitious materials can meet this requirement; however this requirement can be relatively light and may not adequately represent the response of materials subjected to severe freeze-thaw cycling. In some regions, there could be 300 freeze-thaw cycles in as little to a few years, thereby reflecting a short service life had the concrete been designed
to only survive 300 cycles. Additionally, it may be difficult to relate freeze-thaw tests performed in laboratory settings to freeze-thaw cycles seen in the field. This is especially true as the procedures for ASTM C 666 may be easily misinterpreted. This procedure states that at the end of the thawing cycle the interior temperature of the specimens must be $4 \pm 3^\circ C$ and at the end of the freezing cycle the interior temperature of the specimens must be $-18 \pm 2^\circ C$. The cycling time must be between 2 to 5 hours with not less than 25% of the time used for thawing considering ASTM C 666 Procedure A and not less than 20% of the time use for thawing considering Procedure B. Of this, the time the specimens must remain close to the extreme temperatures ($<-16^\circ C$ and $>3^\circ C$) should be at least half the time used for freezing or thawing. Discrepancies often occur with temperature distributions within the chamber and specimens. Additionally, the time required for samples to be held at the maximum temperature can be short, leaving much doubt as whether or not the samples are completely thawing and experiencing a full freeze-thaw cycle. These could be various reasons leading to incorrect conclusions and misconceptions that some cement-based materials are more durable than they actually are.

It may be evident that for higher strength composites, the requirement for air content and spacing factor may differ. In fact, Pigeon (1996) suggested that when the water/binder ratio is lower than 0.25, air entrainment is not needed for good frost resistance [64]. Others are convinced that some amount of air entrainment is required for all concrete, regardless of water/binder ratio to not necessarily improve the freeze-thaw resistance, but to improve the workability placing, and finishing [63]. Lessard et al. (1994) performed a field test on two high performance concrete mixtures [65]. The only difference between these was that one contained air entrainment, producing 6.8% of air (including entrapped
and entrained air) and a spacing factor of 120 µm while the other consisted of no additional air entrainment and had 1.8% of entrapped air with a spacing factor of 520 µm. Despite of using a low water/binder ratio, the samples with no air entrainment did not survive 300 cycles of ASTM C666 freeze-thaw testing while the samples with air entrainment passed the test. In addition to this, field crews found that the placement and finishing of non-air entrained concrete to be much more difficult than that of the air entrained concrete [65]. There is still debate over whether or not air entrainment is required for high performance concrete with low water/binder ratios. Different cementitious materials, aggregates, admixtures, etc. are present in concrete; therefore the requirement for air entrainment should be investigated for different composites.

The use of air entrainment has helped to improve the flexural behavior in SECC. The small, well-distributed air voids throughout the cementitious matrix act as artificial flaws and promote multi-cracking and strain hardening behavior. It has been found that the addition of hydrophobic emulsions improves the flexural behavior of ECC. Likewise, the addition of over-hydrophobic emulsions provided even better flexural response. In a study performed by Muzenski et al. (2014) [12], the flexural behavior of ECC with no air entrainment was compared against samples with hydrophobic or over-hydrophobic emulsions. The hydrophobic emulsion consisted of PMHS with the addition of polyvinyl alcohol surfactant while the over-hydrophobic emulsion additionally incorporated metakaolin sub-micro particles to improve the surface roughness of the void. These were applied as single (0.250 kg of PMHS to 1 m³ of SECC) and double (0.500 kg of PMHS to 1 m³ of SECC) doses. It was also assumed that the over-hydrophobic emulsions (H_MK) could provide a more stable emulsion, resulting in a better air void structure, and thus
providing a better flexural response. This was evident from the droplet size \( H_{MK} \) which is smaller than that of hydrophobic emulsions (H) and thus resulting in smaller air voids throughout the matrix (Figure 9).

![Cumulative Distribution, %](image)

**Figure 9: Droplet size distribution of PMHS admixtures [12]**

Indeed, the contact angle created by applying a single or double layer of coatings on mortar tiles indicates that the emulsions are hydrophobic or over-hydrophobic (Figure 10). Although these contact angles were tested by applying coatings to flat mortar tiles, they may not necessarily represent the contact angles of water droplets on the walls of air voids. However, it may be assumed that the contact angles within the air voids can provide similar or comparable results.

![Single Coating vs Double Coating](image)

**Figure 10: The effect of PMHS admixtures on the contact angle of mortar tiles [12]**
The smaller droplet size of over-hydrophobic emulsions provides a better flexural behavior (Figure 11). Here, FRC with H_MK demonstrate a better flexural response vs. reference samples (R) and hydrophobic samples (H). FRC with a double dose of emulsion (H-MK2 and H2) tend to display a drop in mechanical properties (including lower compressive strength (Figure 12)) which is an indication that a higher dosage may generate excessive hydrogen and thus an excess of voids within the matrix. Additionally, the smaller droplets of the over-hydrophobic emulsions result in a better compressive strength with minimal reductions when comparing with reference samples, as the voids within the matrix are smaller and better distributed. This is typically the reason why many air entraining admixtures result in significant reduction in compressive strength as the voids are larger, often non-spherical, and not well dispersed. Despite these encouraging results, there is a significant decrease in strength of composites at an early age with the addition of emulsions; however, the strength values are comparable at later ages.

![Flexural Behavior Graph](image)

*Figure 11: The 28-day flexural behavior of ECC/SECC [12]*
As it is proved with the experimental results and based on fracture mechanics principles, the inclusion of air voids (or artificial flaws) initiates cracking and promotes multi-cracking and, as a result, strain hardening behavior in FRC. However, additional analytical modeling or finite element modeling of the material must be performed in order to refine the parameters such as spacing of voids and size of voids in order to achieve the best strain hardening response. Fiber bridging characteristics and fracture mechanics models can be used in these models to determine the best spacing of the voids. At this point, the air void properties can be changed by tailoring the superhydrophobic admixtures for droplet size and dosage for spacing.

The ECC/FRC with superhydrophobic emulsions also demonstrated improved durability properties. The main concept behind the incorporation of superhydrophobic air voids was that the walls of these voids would be water repellant and thus can reduce the water absorption in the material. This can clearly be demonstrated by the immersion

*Figure 12: Compressive strength of ECC/SECC [12]*
absorption tests conducted in accordance with ASTM C642 (Figure 13). In this experiment, four sets of samples were used, two with a water to cementitious material ratio (W/CM) of 0.3 and a sand to cementitious material ratio (S/CM) of 0.5 (E30 or REF30) and two with W/CM of 0.45 and a S/CM of 1.0 (E45 or REF45). For each W/CM, there was a set of samples with superhydrophobic emulsions (E30 or E45). The superhydrophobic emulsions in this study consisted of PMHS (and PVA) as a main ingredients. Next, metakaolin submicron sized particles and nano-SiO$_2$ particles were added to build the hierarchical structure required for superhydrophobicity. The results below demonstrate that when the emulsions are added (and so there is an additional entrained air and ultimately more porous space within the system), the water absorption is reduced. These results demonstrate that as samples become fully saturated, water can occupy only a fraction of the void space, thus should this approach minimize the damage due to the freezing and thawing.

![Figure 13: Water absorption after immersion of ECC/SECC [66]](image)

Not only is the water absorption of the samples with superhydrophobic emulsions reduced, but the rate of water absorption is lower (Figure 14). The increase in water absorption depth calculated by ASTM C1585 is much slower for samples with
superhydrophobic emulsions. Comparing these results with the above absorption immersion results, it can be concluded that there is more absorption in the reference samples (REF), and the time to reach the same level of absorption is much longer for emulsion samples (E). The same set of samples was used for this test as for the immersion absorption tests.

![Graph showing the rate of absorption of ECC/SECC](image)

*Figure 14: Rate of absorption of ECC/SECC [66]*

Rapid chloride permeability tests were also performed on ECC with superhydrophobic emulsions in accordance with ASTM C1202 at the age of 28 days. These specimens with superhydrophobic emulsions demonstrated improved behavior (*Figure 15*). Additionally, the use of materials designed with lower W/CM provided superior results. This indicates that in order to achieve low permeability the W/CM ratio must be lower. Additionally, the superhydrophobic walls of the air voids are reducing the permeability despite having an additional void space.
Freeze-thaw tests were performed based on an accelerated method with temperatures oscillating between -50°C and 20°C in both tap water and salt water (5% NaCl solution). This accelerated method was reported to accelerate the freeze-thaw damage by a factor of 5 [8]. Samples were tested every 50 or 100 cycles for relative dynamic modulus of elasticity and durability factor. The tap water and 5% NaCl solution were changed every time the samples were tested. The durability factor was calculated based on standard calculations of relative dynamic modulus of elasticity as described by ASTM C215.

Results from freeze-thaw testing demonstrate that the samples with a lower W/CM were able to survive 700 accelerated freeze-thaw cycles by maintaining a durability factor greater than 100 (Figure 16). This was not the case for samples with a higher W/CM, which began to drastically reduce stiffness or became untestable due to excessive surface wear between 300 to 450 accelerated cycles. Still these samples were able to maintain the minimum required durability factor of 60 through a minimum of 300 cycles to be considered durable materials (it may be assumed that these samples would have lasted even
longer had conventional freeze-thaw testing at -18°C been used). Moreover, these samples had a severe surface wear, especially when tested in 5% NaCl solution. Samples with a lower W/CM did not display much variation in durability factor when comparing the effect of superhydrophobic admixtures. However, it can be envisioned that if tested longer; the samples with superhydrophobic admixtures would provide a better performance. Based on the absorption, rate of absorption, and permeability data, the hydrophobicity of the air voids, reduces the amount of water that infiltrates the cementitious matrix. Therefore, the deteriorated samples with a higher W/CM and superhydrophobic admixtures (E45 Salt) displayed better performance compared to the reference (REF45 Salt). Similarly, the samples with a low W/CM and superhydrophobic admixtures can provide a better freeze-thaw resistance upon extensive exposure/testing.
Figure 16: Durability factor of ECC/SECC tested for freeze-thaw in tap water (top) and 5% NaCl solution (bottom) [67]

The SECC was implemented in a small field application as a repair slab on an existing driveway at the University of Wisconsin-Milwaukee [6]. The existing driveway had been severely deteriorated over the years due to poor subgrade conditions and corrosion of a steel pipe system used for hot water transport through the concrete. The driveway was also located in an area that experiences a significant number of heavily loaded trucks for a college campus and is exposed to severe freezing and thawing and
chloride exposures. These harsh conditions proved to be an ideal location to test the durability of the material. A 1.37 m (54 in.) wide by 4.27 m (14 ft.) long by 17.78 cm (7 in.) deep portion of the driveway was chosen for the slab design. The slab had eight (5.08 cm (2 in.) wide by 7.62 cm (3 in.) deep) hollow core sections with a 5.08 cm (2 in.) clear spacing. The top of the hollow core sections were 4.45 cm (1 ¾ in.) below the surface of the slab, allowing for a 1.90 cm (¾ in.) layer of electrically conductive carbon nano-fiber PVA-FRC material and a 2.54 cm (1 in.) layer of SECC cover. A drawing of the SECC slab section is reported in *Figure 17* below.

![Cross-section of SECC slab](image)

*Figure 17: Cross-section of SECC slab*

The layer of electrically conductive material was 1.90 cm (¾ in) deep and covered the full width and length of the slab. In this layer, 100 electrodes were spaced 15.24 cm (6 in) apart across the width of the slab and 20.32 cm (8 in) apart across the length. A PVA fiber mesh was placed on the bottom of this layer for mounting the electrodes and for additional reinforcement. This layer of electrically conductive material was used to detect the ingress of chlorides, crack formation, moisture exposure, and loading [68].

Similar FRC mixture proportions were used for this slab as discussed above and consisted of ground granulated blast furnace slag, silica fume, and metakaolin as
supplementary cementitious composites. The aggregates used were typical fine aggregate found in highway construction. Superhydrophobic admixtures and PVA fibers were used as components. The slab is expected to be monitored for its effectiveness in such a harsh environment and is expected to provide a superior performance compared to the adjacent conventional concrete or repair materials.

2.2 ULTRA-HIGH PERFORMANCE CONCRETE

Ultra-high performance concrete (UHPC) is a relatively new type of concrete with high strength and high durability. UHPC often includes a fiber reinforcement and thus provides a superior flexural and tensile performance when compared against conventional concrete or high performance concrete (HPC). UHPC is often defined to have the compressive strength of at least 150 MPa and includes high binder content with tailored aggregate quantities, sizes, and types [69]. Other definitions include a sustained minimum post-cracking tensile strength of at least 5 MPa [70]. The ability to achieve such high compressive and tensile strengths can be attributed to the discontinuous porous structure of the extremely dense cementitious matrix [70].

2.2.1 Binder Properties of UHPC

The binder properties of any cementitious material are often considered as one of the most important features contributing to its performance. These properties are of even greater importance when UHPC is considered. The water to binder ratio is one of the key parameters and a lower water to binder ratio is required for higher strength. In UHPC, the water to binder ratio can be as low as 0.15 [71-73], however UHPC properties were achieved with water to binder ratios of 0.25 or less [74-76].
The type of binder and type of additional supplementary cementitious materials are also of key importance when designing a UHPC. Silica fume was the key material to create UHPC with superior strength [71, 74]. As silica fume is an ultra-fine supplementary cementitious material with smaller average particle diameter and larger specific surface area than other cementitious materials (Figure 18), it is able to occupy the void space (interfacial transition zone) between the aggregates and paste. This, in turn, results in a better bond between the paste and the aggregate, which is often a limiting factor in the material’s strength. In UHPC, silica fume is often used at a content of 10-30% by mass of cement [77, 78], but is often considered at an optimal dosage of 25% [74, 79]. Due to the small particle size of silica fume, dispersion of the material prior to mixing is of key importance. If not properly dispersed, silica fume tends to agglomerate or clump together thus making the particle size significantly higher and eliminating the beneficial properties of the material.
Another supplementary cementitious material that has been used in UHPC is metakaolin. This material also shows improved performance in cementitious composites similar to silica fume, however, the particle size is larger and specific surface area is smaller. Despite of this, metakaolin can lead to increased strength up to the levels achieved with silica fume [81]. The use of other replacements for silica fume may also include pulverized fly ash, limestone microfiller, siliceous microfiller, micronized phonolith, or rice husk ash [82, 83].

Another type of cementitious material, although not commonly linked to concrete technology, is oil well cement. This cement is often used in slurries for placing barriers
with cementitious materials between well castings and geological formations surrounding the well [84]. The development of this type of cement was due to the requirement for oil wells to be protected from salt water, pressure due to extreme depths, and protection from corrosion. The requirement for the cement to remain fluid for an extended period of time also led to the need for oil well cement. Oil wells are often subjected to extreme temperatures and pressures at such great depths which would make ordinary portland cement difficult to perform adequately. These cements are often coarser ground so that the hydration is controlled at such temperatures and pressures. The properties of this material are much different from ordinary portland cements. The tricalcium aluminate (C₃A) content in oil well cements is drastically reduced which will lead to slower setting times and decrease in temperature rise during hydration. In this respect, some oil well cements are similar to Type IV portland cements. The reduced heat of hydration and increased particle size lead to lower autogenous shrinkage as less water is required for hydration and, therefore, these materials are less likely to form cracks from insufficient moisture supply. Additionally, because of the large particle sizes, the material would require less initial water to form the adequate strength. There may be larger volumes of dicalcium silicate (C₂S) in oil well cement which improve the later age strength.

2.2.2 Aggregate Properties of UHPC

Another important feature of UHPC is related to tailored aggregate proportions. UHPC does not include coarse aggregates and often utilizes sand particles on the lower end of what is considered to be fine aggregate. As in any cementitious material, the proper particle size distribution of aggregates must be considered to effectively fill as much space as possible without reducing the mechanical performance [85]. A proper size distribution
of aggregates can also lead to a sustainable cementitious material with reduced cement content without reduction in performance.

Finely graded silica or quartz sand is often used as filler and aggregates in UHPC. The inclusion of even finer aggregates such as glass powder or silica flour is often used [86]. Finely graded quartz sand is often used due to the small particle size [87].

Despite many researchers use of as many fine aggregate as possible, some researchers have found that the replacement of fine ground quartz sand with an equal volume of well-graded natural aggregate with a maximum size of 8 mm provided the same compressive strength when used at the same water to cement ratio [88].

2.2.3 Admixtures and Additives for UHPC

Ultra-high performance cementitious composites typically have a very low water to cement ratio, therefore in order to achieve the adequate workability, chemical admixtures such as high range water reducing agents or superplasticizers must be used. Plank et al. (2009) tested different polycarboxylate (PCE) based superplasticizers for their effect of dispersion of cement and silica fume particles in UHPC [76]. It was found that effective dispersion of silica fume is more essential than the dispersion of cement to achieve a highly workable UHPC because of the high surface area of the silica fume. Additionally, methacrylate based PCEs disperse cement particles well and allylether based PCEs perform well to disperse the silica fume. A combination of these two PCEs was proposed for applications in UHPC.

Other admixtures and additives were used in UHPC to achieve desired properties. UHPC may exhibit large amounts of shrinkage due to its high cement content; therefore, shrinkage reducing admixtures may be required [89]. Additionally, the viscosity of UHPC
may be modified to obtain the self-leveling properties without segregation of cement paste and aggregate with the use of viscosity modifying admixtures (VMA) such as nano-silica [90].

Nano-materials have also been used in UHPC to improve the strength and performance. Nano-clay and nano-silica have been added to improve the chloride permeability [91]. Other nano-materials can be used to provide a denser micro structure and thus higher strength and improved durability.

2.2.4 Curing of UHPC

Curing of UHPC is a critical aspect to assure that high strength is achieved. Inadequate curing conditions often reduce the performance of any cement-based composites due to shrinkage cracks and is detrimental for UHPC because of high cement content. UHPC often utilized increased temperatures and steam curing to achieve higher strength. Steam curing has been used to achieve higher compressive strength when applied for 48 hours starting at 24 hours after casting [92]. Heat curing can also be used and has shown to provide increased strength of up to 280 MPa when heated to 65 to 180°C compared with standard curing resulting in strength of 178-189 MPa [93].

2.2.5 Applications of UHPC

Although UHPC is a new and developing material, it has been commercially available for some time. The most notable product is Ductal from Lafarge. This product comes as a premixed powder along with metallic fibers and chemical admixtures. The Ductal based UHPC is often used in bridges. Since the material has such a high compressive strength and high shear resistance, it can be used to produce pre-stressed girders with longer spans compared to conventional concrete. In Canada, the first UHPC
bridge was constructed in 1997 and since several others have been created. In the United States, UHPC has also been used on bridges in Iowa and Virginia [94, 95]. The material has also been used in bridge decks to produce a lightweight, pre-cast waffle slab for faster construction [96]. UHPC can also be used to create unconventional slabs, roofs, and stairways for structures that otherwise could not be made with conventional concrete.

2.3 USE OF NANO MATERIALS IN CEMENTITIOUS COMPOSITES

The use of nano-materials in cementitious composites is another field that has gained much attention recently. When used in small quantities, nano-particles or nano-fibers can provide significantly improved performance. Because concrete is such a complex material whose properties are determined at the nano-level, the use of nano admixtures can generate improved performance. Nano-materials in concrete can be divided into two different categories. The first would be the bottom up approach introduced by Drexler et al. in 1991 [97]. Here, the materials are produced from the molecular components and formed through an assembly or self-assembly process. The other type is the top down approach where larger materials are broken down through milling or similar processes to materials of the nano-size. In this case, the materials would maintain their atomic properties, but due to their size and surface area, can have more efficient performance than at their original size. The types of commonly used nano-materials in concrete include nano-silica, nano-titanium oxide, nano-calcium carbonate, nano-clay, nano alumina, as well as others. Nano-carbon fibers or nano-carbon tubes have also been in cementitious materials for a number of different applications.

Nano-silica is one of the more common nano-materials that is used in concrete. It has been found to accelerate cement hydration by accelerating the formation of calcium-
silicate-hydrate (CSH) and the dissolution of tricalcium silicates (C₃S) [98]. It has been observed that the use of nano-silica in cementitious materials can generate a denser packing of hydration products, a refinement of the pore structure an improved interfacial transition zone [90, 99-101]. Nano-silica has higher pozzolanic reaction activity compared with silica fume [102]. The use of this type of nano-material accelerates the hydration of cementitious products by acting as a seed for the nucleation of CSH [103]. Nano-silica has often been recommended as a viscosity modifying admixture [90]. Here, the nano-particles allow for a good workability in high strength and highly flowable concrete without segregation because of the higher surface area of the nano-silica. This can be beneficial when a flowable concrete is desired; therefore larger quantities of superplasticizer (SP) can be used in such mixtures without having any segregation.

The uses of other nano-materials in concrete can also be very beneficial. Nano-titaniaum dioxide can been used for photocatalytic concrete [104, 105]. This can improve the quality of air by eliminating nitrogen oxide in the presence of ultra violet (UV) light. Nano-calcium carbonate can be used to accelerate the hydration of concrete [106, 107]. Nano-clays have been used to increase the formation of CSH [108]. Nano-clays have also been used to reduce the pressure on formworks in highly flowable concrete [109-111]. This is because the clay particles are hydrophilic and can attract water and hold the particulate cementitious material together. In some cases the use of clays can cause some expansion due to the hydrophilic effect of the material, especially if the water content is not controlled [112].

Carbon nanotubes (CNT) or carbon nanofibers (CNF) have been used beneficially in cementitious materials. Many applications use CNT/CNF for nano-reinforcements or
electrically conductive composites. Most of the research has focused on CNT instead of CNF and of these CNT, much research focus has been on multi-wall carbon nanotubes instead of single-wall CNT. These nano-materials, similarly to nano-particles, have been found to accelerate the hydration of cement-based materials by acting as nucleation sites for the formation of CSH [113, 114]. The CSH that is formed has also been found to be higher stiffness CSH [115-117]. CNT/CNF are also able to act as fillers to produce a more dense micro structure to mortars [118].

The use of CNT/CNF in electrically conductive composites is attractive because of the conductive properties of the carbon [119]. When cracks are formed in fiber reinforced cementitious composites, the electrical properties change and can be monitored [120]. This allows for cracks to be observed remotely and so such composites can be used in structural health monitoring. In terms of mechanical performance, research results are varied. In some research no beneficial properties have been found, whereas with others, significant improvements have been seen. This is most likely due to the use of different CNT/CNF products and method and duration of dispersion of the nano-materials [115]. Increases in compressive strength from CNT have been seen up to 30% to 43% [121] and increases in flexural strength have been seen up to 40% [116]. This is because the CNT reduce the amount of fine pores within the cementitious composite resulting in lower capillary stresses [117].

Little work with nano-alumina (nano-Al$_2$O$_3$) in cementitious materials has been reported, however, some data on the decrease the porosity of cement-based materials was reported. The use of these nano-particles have also been found to create a more dense interfacial transition zone [122]. The resulted modulus of elasticity was significantly
improved. However, the use of these nano-materials, even at quantities as high as 7%, were found to provide little to no increase in compressive strength. The use of nano-alumina was also found to reduce the workability of concrete [123]. In this same study, the compressive strengths of the cementitious composites were only slightly increased when an optimal dose of 1% nano-\(\text{Al}_2\text{O}_3\) was used. It has also been found that nano-\(\text{Al}_2\text{O}_3\) can reduce the amount of chloride penetration/diffusion; however, not to the same extent as nano-silica or nano clays [91]. Currently, there has been no work reported on the use of nano-\(\text{Al}_2\text{O}_3\) fibers in cementitious composites. However, these have been used in other industries for improving the ductility of ceramics, super-fine abrasives, engineered plastics, fiber reinforced composites, and polymer-based epoxies and coatings.

The nano-structured phase of concrete which is primarily responsible for the strength is calcium-silicate-hydrate (CSH). Nano-materials in cementitious systems act as nucleation sites for the formation of these CSH phases. When nano-fibers are used as a nucleation site, the CSH forms around the fibers which provides a nano-reinforcement. Therefore, when nano cracks begin to form at the CSH level, these can be arrested by the reinforcing effect of the nano-fibers.

The dispersion of nano-materials is a critical step that needs to be taken when adding these materials to composites. Differences in results from one research group to another can vary because of dispersion techniques. Nano-materials typically have high Van der Waals forces resulting in agglomeration. Agglomeration reduces the efficiency of nano-materials. Effective dispersion can often be realized with the use of ultrasonification and use of surfactants [115]. The use of sonification relies on mechanical vibrations that create high levels of energy (high frequency vibrations) to disperse the particles. The use
of surfactants increases the chemical repulsion between the particles and prevent the particles from reagglomerating. However, the surfactant can become attached to these nano particles resulting in consumed surfactant that would not be effective at the stage which cementitious materials are mixed. Furthermore, the ultrasonification of the surfactant may impact the change in the chemical and physical properties affecting the performance in a cement-based mixture.

2.4 DEVELOPMENT OF METHODS FOR AIR VOID ANALYSIS OF HARDENED CONCRETE

The current standard to analyze the air void structure of hardened concrete (ASTM C457) uses several assumptions to determine the spacing factor of air voids with a smaller value providing superior performance. The spacing factor is often used as a key parameter governing the response of concrete to freezing and thawing cycles. The most common equation to determine the spacing factor is Powers’ equation [59]. It is often believed that this equation is used to estimate the distance between air voids or the distance water in hardened concrete would have to travel to reach an air void. However, the equation estimates the fraction of paste within some distance of an air void [124]. This means that no measurements of actual distance between the voids are performed. The Powers spacing factor has been split into two equations depending on the paste to air ratio (p/A). For smaller values of p/A, Powers used the concept of spreading a uniform layer of paste over each air void with thickness proportional to the total surface area of the air voids. The calculation for spacing factor can then be determined as follows:

$$L = \frac{P}{\alpha A} : \frac{P}{A} < 4.342$$  \hspace{1cm} (Eq. 7)
Where $\alpha$ is the expected estimate of the specific surface for the population of air voids within concrete.

For higher value of $p/A$, a cubic lattice is generated to determine the distance from the center of a unit cell to the nearest air void surface. This lattice is comprised of monosized spheres so that the sum of specific surfaces is equal to the specific surface of the bulk and whose sum of air contents is equal to the bulk. The spacing factor for this case can be determined as follows:

$$L = \frac{3}{\alpha}\left[1.4\left(\frac{p}{A} + 1\right)^{1/3} - 1\right]; \frac{p}{A} \geq 4.342$$

(Eq. 8)

In the above equations, the specific surface ($\alpha$) can be calculated as 4 divided by the average chord length. For linear traverse methods, the average chord length is easy to determine; however, for the modified point count method, the average chord length is calculated based on the following equation:

$$\bar{l} = \frac{S_a \times I}{N}$$

(Eq. 9)

Where $S_a$ is the number of stops in air voids, $I$ is the translation distance between stops, and $N$ is the total number of air voids intersected.

According to standards, these values can be calculated using Linear Traverse Method (ASTM C457 Procedure A) or Modified Point-Count Method (ASTM C457 Procedure B) (Figure 19). In the case of the linear traverse method, a polished concrete sample is viewed under a stereological microscope by analyzing lines on the surface to determine the paste and air quantities as well as the chord lengths through voids. These values are then used to estimate the specific surface. In the case of the modified point count method, the fraction of paste and air to the volume is estimated by randomly selecting
and identifying points across a polished surface of concrete. The modified point count method also requires the distance between air voids to be calculated along the grid lines in order to estimate the chord lengths.

![Figure 19: Schematic of modified point count method (A) and linear traverse method (B) after [125]](image)

These two approaches use the stereological principles to estimate the size and volume of air voids (in the shape of spheres) from points (0 dimensional) or lines (1 dimensional) into a 3-D volume. This approach may lead to many uncertainties. Other researchers have attempted to redesign the equations for spacing factor; however, the Powers’ equation is still the most widely used. Philleo attempted to find an approximation for the paste-void for finite sized air voids [126]. Fagerlund used a similar approach as Philleo by introducing air voids with shells around them of a certain thickness [127]. When these shells begin to overlap, the width of the shells can be computed to determine the mean void spacing. Attiogbe attempted to measure the surface-surface distance between adjacent air voids to be used for the void spacing [128]. Pleau and Pigeon created spacing
equations by considering the air void size distribution and the distribution of distances points in the cement paste and an air void center [129].

Snyder et al. [125] discusses the ability to determine the specific surface of the air voids when additional dimensions are added. In standard air void tests (e.g., linear traverse or modified point count), the specific surface is estimated based on 1-dimensional data. Since the specific surface of an object is defined as the surface area divided by the volume resulting in a value of length$^{-1}$, any estimation would require at least two-dimensions to result in a value with the same dimensions. If 2-dimensional or 3-dimensional data are used as an input, a more accurate estimation of specific surface may be obtained. This can be realized when 2-D flatbed scanning or 3-D tomography methods are used to determine the air void properties. When using these approaches, Powers’ spacing factor equations can be still applicable so the comparisons between different methods can be made (since Powers’ methods do not actually calculate the distance between air voids). In terms of using a planar surface for air void analysis, the diameters of the circles can be used to calculate the specific surface. The calculations for determining the specific surface in ASTM C457 uses the ratio $X^2/X^3$ to formulate the expected values of the surface area over the expected value of the volume. For planar studies the moments of expected values of the diameter and diameter squared can be used to generate this ratio. The first three moments or expected values ($X^n$) of the distribution of the diameters can be calculated based on the average values [125] ($Y^n$) as follows [130, 131].

$$\langle Y^n \rangle = \begin{cases} 
\frac{\langle X^{n+1} \rangle}{\langle X \rangle} \frac{1 \cdot 3 \cdot 5 \cdots n \pi}{2 \cdot 4 \cdot 4 \cdots (n+1) \frac{\pi}{2}} & n \text{ is odd} \\
\frac{\langle X^{n+1} \rangle}{\langle X \rangle} \frac{2 \cdot 4 \cdot 6 \cdots n}{1 \cdot 3 \cdot 5 \cdots (n+1)} & n \text{ is even}
\end{cases} \quad (\text{Eq. 10})$$
\[ \langle Y^{-1} \rangle = \frac{\pi}{2 \langle X \rangle} \quad \text{(Eq. 11)} \]

\[ \langle X \rangle = \frac{\pi}{2} \frac{1}{\langle Y^{-1} \rangle} \quad \text{(Eq. 12)} \]

\[ \langle X^2 \rangle = 2 \frac{\langle Y \rangle}{\langle Y^{-1} \rangle} \quad \text{(Eq. 13)} \]

\[ \langle X^3 \rangle = \frac{3\pi}{4} \frac{\langle Y^2 \rangle}{\langle Y^{-1} \rangle} \quad \text{(Eq. 14)} \]

The equation for determining the specific surface of a sphere can be written as follows in terms of the diameter (d). Essentially, this equation could be simplified so only the diameter of the sphere is a variable; however for this purpose, the second and third moments are of importance and thus this equation can be only simplified down to the two variables of \( d^2 \) and \( d^3 \).

\[ \alpha = \frac{4\pi \left( \frac{d}{2} \right)^2}{4 \frac{d}{3} \pi \left( \frac{d}{2} \right)} \quad \text{(Eq. 15)} \]

The above equations can then be rewritten to the following equation:

\[ \alpha = \frac{\pi \langle X^2 \rangle}{\frac{6}{\pi} \langle X^3 \rangle} = \frac{16 \langle Y \rangle}{\pi \langle Y^2 \rangle} \quad \text{(Eq. 16)} \]

Here, the expected value of diameter and the expected value of the diameter squared can be directly used to solve the specific surface. This method can be used with 2-D flatbed scanning techniques with the help of image processing software.
3. MATERIALS AND METHODS

3.1 CEMENTITIOUS MATERIALS

Type I portland cement was used for many of the preliminary studies and some of the studies for mortar optimization. In this research, two types of portland cement were used. The first was commercially available Type I portland cement from Lafarge North America (referred to as LF in the following sections) and the second was commercially available Type I portland cements from Holcim (referred to as HO in the following sections). Chemical and physical properties of these Type I portland cements can be seen in Table 2 and Table 3, respectively. Type H oil well cement from Lafarge North America (referred to as OW in the following sections) was also used for the main research matrix. The chemical composition of Type H oil well cement is also reported in Table 2. All chemical compositions were determined using X-Ray Fluorescence techniques.
Table 2: Chemical Composition of Type I Portland Cements and Oil Well Cement

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ASTM C150 Limits*</th>
<th>LF</th>
<th>HO</th>
<th>OW</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂, %</td>
<td>-</td>
<td>19.8</td>
<td>19.4</td>
<td>21.8</td>
</tr>
<tr>
<td>Al₂O₃, %</td>
<td>-</td>
<td>4.9</td>
<td>5.3</td>
<td>3.1</td>
</tr>
<tr>
<td>Fe₂O₃, %</td>
<td>-</td>
<td>2.8</td>
<td>3</td>
<td>4.5</td>
</tr>
<tr>
<td>CaO, %</td>
<td>-</td>
<td>63.2</td>
<td>63.2</td>
<td>64.3</td>
</tr>
<tr>
<td>MgO, %</td>
<td>6.0 max</td>
<td>2.3</td>
<td>2.9</td>
<td>2.7</td>
</tr>
<tr>
<td>SO₃, %</td>
<td>3.0 max</td>
<td>2.9</td>
<td>3.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Na₂O, %</td>
<td>-</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂O, %</td>
<td>-</td>
<td>0.5</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Others, %</td>
<td>-</td>
<td>0.6</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>Ignition loss, %</td>
<td>3.0 max</td>
<td>2.8</td>
<td>1.1</td>
<td>-</td>
</tr>
</tbody>
</table>

*ASTM C150 Limits correspond to LF and HO only

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ / Fe₂O₃</td>
<td>1.8</td>
</tr>
<tr>
<td>C₄AF, %</td>
<td>8.5</td>
</tr>
<tr>
<td>C₃A, %</td>
<td>8.2</td>
</tr>
<tr>
<td>C₂S, %</td>
<td>10.3</td>
</tr>
<tr>
<td>C₃S, %</td>
<td>61.6</td>
</tr>
<tr>
<td>Na₂O&lt;sub&gt;equi&lt;/sub&gt;, %</td>
<td>0.6 max</td>
</tr>
</tbody>
</table>

Potential Composition

Along with Type I portland cement or Type H oil well cement, several supplementary cementitious materials were considered. Silica fume, metakaolin, Class F fly ash, and ground granulated blast furnace slag (slag cement) were among these.

Table 3: Physical Properties of Type I Portland Cements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ASTM C150 Limit</th>
<th>Test Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>-</td>
<td>3.13</td>
</tr>
<tr>
<td>Time of setting, minutes</td>
<td></td>
<td>3.08</td>
</tr>
<tr>
<td>Initial</td>
<td>45 min</td>
<td>103</td>
</tr>
<tr>
<td>Final</td>
<td>375 max</td>
<td>264</td>
</tr>
<tr>
<td>Compressive strength, MPa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 day</td>
<td>-</td>
<td>12.1</td>
</tr>
<tr>
<td>3 days</td>
<td>12.0 MPa</td>
<td>21.7</td>
</tr>
<tr>
<td>7 days</td>
<td>19.0 MPa</td>
<td>28.3</td>
</tr>
<tr>
<td>28 days</td>
<td>28.0 MPa</td>
<td>36.5</td>
</tr>
</tbody>
</table>

Along with Type I portland cement or Type H oil well cement, several supplementary cementitious materials were considered. Silica fume, metakaolin, Class F fly ash, and ground granulated blast furnace slag (slag cement) were among these.
Properties of these materials can be seen in Figure 105 of the Appendix. Silica fume was obtained through Elkem and was represented by spherical particles with sizes between 0.2 and 1 µm. Class F fly ash (FA F) from WE Energies, metakaolin from Burgess Optipozz represented by rough and flaky microparticles with sizes from 0.8 to 12 µm, and ground granulated blast furnace slag (GGBFS) from Lafarge North America were used in the experimental program. Scanning electron microscope (SEM) images were also taken for all cementitious materials and can be found in Appendix A.

3.2 CHEMICAL AND NANO-BASED ADMIXTURES

3.2.1 Chemical Admixtures

Commercially available polyacrilate/polycarboxylate superplasticizer (PCE-SP) with a 31% solid concentration was supplied by Handy Chemicals.

A viscosity modifying nano-silica (nano-SiO₂) admixture, Cembinder 8, was used in the preliminary study of the fiber reinforced composites under heat treatment. This admixture had a solid content and 52% and a Brunauer-Emmet-Teller (BET) surface area of 61.2 m²/g. In some studies, tributile phosphate (TBP) was used to reduce the entrapped air voids within cementitious materials. This admixture had an assay of 97% and a density of 0.979 g/mL (at 25°C).

The air entraining admixture that was used in the air void analysis section was commercially available Micro-Air with a 12.3% solid content. The admixture was composed of tall oil, fatty acids, and polyethylene glycol.

3.2.2 Nano-Materials

The nano-Al₂O₃ fibers used in this research to create dispersion are NAFEN Fibers from ANF Technology. These fibers are pure crystalline alumina with a surface area of
155 m\(^2\)/g. The single crystal tensile strength of the fiber is 12 GPa while the modulus is 400 GPa. They have a typical fiber diameter of 10-20 nm and come shipped in lengths of 50 mm (Figure 20). Upon dispersion, the fibers maintain their diameter but break down to lengths between 10 and 65 µm depending on the dispersion technique. The fibers are synthesized from liquid phase aluminum and then grown to the aforementioned lengths.

![Image of Al\(_2\)O\(_3\) nano-fibers](image)

*Figure 20: Al\(_2\)O\(_3\) nano-fibers prior to dispersion (left) and transmission electron microscope image of Al\(_2\)O\(_3\) nano-fibers (right)*

### 3.2.3 Superhydrophobic Admixtures

The hydrophobic or superhydrophobic admixtures (HAS) used polyvinyl alcohol surfactant (PVAS) from Across Chemicals and polymethyl hydrogen siloxane (XIAMETER MHX-1107) from Dow Corning as primary ingredients. The surfactant was 98% hydrolyzed PVA with a molecular weight of 16,000. The surfactant was used at a dosage of 3.5% by weight of the HSA. Polymethyl hydrogen siloxane (PMHS) with a specific gravity of 0.997 (at 25°C) and a viscosity of 30 cSt was used at a concentration of 25% by weight of the HSA. Commercially available metakaolin or silica fume (same
materials as described in the Cementitious Materials section) were used as microparticles. The nano-particles that were used within the emulsion were nano-SiO$_2$ (nano-silica, 99.5% SiO$_2$, MKN SiO2-015P) from MK Nano with an average particle size of 15 nm. The X-Ray Diffraction diagram of nano-SiO$_2$ is presented in Figure 107 of Appendix A. In the case of when only micro or nano particles were used, these were applied at a dosage of 0.5% by weight of the admixture. When micro and nano particles were used in combination, the micro particles were added at 0.4% by weight of the admixture and the nano-particles were added at a dosage of 0.1% by weight of the admixture.

3.2.4 Handling of Nano-Based Materials

Special precautions were taken when handling the nano-fibers for the dispersions and the nano-silica for the superhydrophobic admixtures. These materials are extremely small and light, therefore are prone to become airborne. These materials can also be hazardous to one’s health. To assure safety, the materials were weighed and added to liquid (the same liquid used for the admixtures or dispersions) in a glove box prior to mixing to assure no particles become airborne.

3.3 FIBERS

Polyvinyl alcohol fibers were used in the preliminary experiments. These fibers were RECS 15x12 mm Kuralon K-II PVA fibers from Kuraray, Japan. The fibers had a length of 12 mm, thickness of 15 dtex, diameter of 0.04 mm, Young’s Modulus of 40 GPa, and a tensile strength of 1.6 GPa.

Reinforcing fibers that were used in the main portion of the research include RECS 15x12 mm PVA fibers (same as above), RECS 15x8 mm PVA fibers from Kuraray Japan, hooked end steel fibers (32 mm long and 0.4 mm in diameter with a 4 mm hook), Sudaglass
brand basalt fibers from Advanced Filament Technologies, and polyethylene (PE) fibers from Eurofibers. The basalt fibers had a length of 12 mm, a diameter of 16 µm, a tensile strength of 4.8 GPa, and an elastic modulus of 89 GPa while the PE fibers have density of 970 kg/m³, a length of 12 mm, a diameter between 12 and 21 µm, an axial tensile strength of 3.6 GPa, and an axial tensile modulus of 116 GPa.

### 3.4 AGGREGATES

Standard graded silica sand conforming to ASTM C778 and AASHTO 106 was used for all research. This sand is graded so that the majority (96%) of the aggregates fall between the No. 30 and No. 100 sieves. Typical grading values for this silica sand are reported below (Table 4). This sand was purchased through US Silica Co.

<table>
<thead>
<tr>
<th>USA STD Sieve Size</th>
<th>ASTM C778 Limits</th>
<th>Typical Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh</td>
<td>Millimeters</td>
<td>% Passing Cumulative</td>
</tr>
<tr>
<td>16</td>
<td>1.180</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>0.600</td>
<td>96-100</td>
</tr>
<tr>
<td>40</td>
<td>0.425</td>
<td>65-75</td>
</tr>
<tr>
<td>50</td>
<td>0.300</td>
<td>20-30</td>
</tr>
<tr>
<td>100</td>
<td>0.150</td>
<td>0-4</td>
</tr>
<tr>
<td>Pan</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An additional type of sand was used for the preliminary experiment on the investigation of heat treatment of fiber reinforced cementitious composites. This sand (referred to in the text as quartz) was commercially available Granusil grade 4030 silica filler sand with a 99.692% SiO$_2$ content and typical particle sizes as seen in Table 5.
Table 5: Typical Particle Size Distribution of Granusil Grade 4030 Sand

<table>
<thead>
<tr>
<th>ASTM Sieve Size mesh opening (mm)</th>
<th>Typical Value</th>
<th>cumulative % retained</th>
<th>% passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 0.85</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>30 0.6</td>
<td>0.1</td>
<td>0.1</td>
<td>99.9</td>
</tr>
<tr>
<td>40 0.425</td>
<td>22.5</td>
<td>22.6</td>
<td>77.4</td>
</tr>
<tr>
<td>50 0.3</td>
<td>54.7</td>
<td>77.3</td>
<td>22.7</td>
</tr>
<tr>
<td>70 0.21</td>
<td>17.4</td>
<td>94.7</td>
<td>5.3</td>
</tr>
<tr>
<td>100 0.15</td>
<td>4.2</td>
<td>98.9</td>
<td>1.1</td>
</tr>
<tr>
<td>140 0.105</td>
<td>0.9</td>
<td>99.8</td>
<td>0.2</td>
</tr>
<tr>
<td>pan</td>
<td>0.2</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

3.5 PREPARATION OF HPC/UHPC

3.5.1 Preparation of Al₂O₃ Nano-Fiber Dispersions

For samples that included Al₂O₃ nano-fibers in the first preliminary studies, slurries were prepared to properly disperse the nano-material. To accomplish this, the nano-fibers, all superplasticizer, and 1% of supplementary cementitious material (metakaolin or silica fume) were mixed with distilled water at a 10 parts water to 1 part solid content ratio. Slurries were briefly premixed by hand to disperse large clumps of nano-fibers and then placed in an ultrasound bath at 85% intensity for 5 minutes. These slurries were then added into the mortar during the mixing process at the same time as the water.

This slurry preparation did not seem to adequately disperse the fibers, therefore a new procedure was created that tended to better disperse the nano-fibers. This method consisted of placing a full tablet of Al₂O₃ nano-fibers (typically between 35 to 45 grams) in a plastic container. A solution of de-ionized water with superplasticizer (the same SP as used in other parts of this research) was then added to the container. The solution with the nano-fibers was then hand mixed briefly using a stirring rod to break up any large agglomerates of fiber. The slurry was then dispersed using a T25 Ultra-Turrax high sped
mixin (HSM) from IKA at 8,000 rpm in combination with a 20 kHz ultrasound (UIP1000 from Hielscher Ultrasound Technology) at an amplitude of 85% (21.5 µm). Water and ice were used on the exterior of the container to keep the dispersion below 50°C. The water and ice were replaced regularly throughout the dispersion process. The slurry was then left to disperse for 1 or 3 hours.

3.5.2 Preparation of Superhydrophobic Admixtures

The hydrophobic or superhydrophobic admixtures were prepared by mixing polyvinyl alcohol surfactant (PVAS) with de-ionized water using a magnetic stirrer for 10 minutes at a temperature of 23±3°C while covered. The temperature was then increased to 90±5°C for 40 minutes while stirring the solution. The solution was then cooled to 23±3°C, at which point the PMHS was slowly added using a high speed mixer at 10,000 rpm for 10 minutes. The mass of the solution was recorded before and after mixing to assure no losses due to evaporation. In some cases where a simple approach was used (Air Void Structure of High Performance Fiber Reinforced Cementitious Composites section), this was the final step to the hydrophobic emulsions; however, in the case of the core or shell emulsions, micro-particles (metakaolin or silica fume) were slowly added and mixed at 5,000 rpm for 10 minutes. Finally, in the case of core or shell emulsions with micro and nano-particles, after the addition of the micro-particles, nano-particles (nano-SiO$_2$) were slowly added and mixed at 5,000 rpm for 10 minutes [58].

3.5.3 Preparation of Pastes/Mortars

The procedure to mix mortars without fibers in preliminary studies was modified from ASTM C305. The standard mixing procedure was not providing good results when such a low water to cement ratio was considered. The procedure used is as follows: all
drinking water and chemical admixtures were placed in the bowl followed by all sand and mixed for 30 seconds on low speed. Next, a 1/3 of the cementitious materials was added and mixed on low speed for 45 seconds. The second third of the cementitious materials was added and mixed for 45 seconds followed by the remaining cementitious materials and mixed for 60 seconds on low speed. The material was then mixed at medium speed for 30 seconds, tested for flow, and mixed for another 30 seconds before placing into the molds and compacting.

In the primary research investigating the properties of cement pastes and mortars, standard ASTM C305 procedures were used. In the cases where Al₂O₃ nano-fibers were used, the slurry with Al₂O₃ nano-fibers was added to the mix as part of the mixing water.

Diluted cement pastes for scanning electron microscope analysis were prepared in small high density polyethylene (HDPE) containers and mixed by hand for 1-2 minutes.

**3.5.4 Preparation of Composites**

Fiber reinforced cementitious composites for preliminary experiments and for air void analysis were created as follows: 75% of drinking water (at room temperature) was added along with all chemical admixtures (including the HSA). Next, standard graded silica sand was added and mixed at a low speed (107 rpm) for 30 seconds. Half of the PVA fibers were then added and mixed for 30 seconds followed by the remaining PVA fibers mixed for another 30 seconds. Next, half of the cementitious material was added and mixed for 1 minute, followed by the addition of the remainder of the cementitious materials mixed for another minute. Finally, the remainder of water was added and mixed at low speed for 1 minute, followed by 30 seconds of mixing on medium speed (198 rpm). The material
was then tested for flow, followed by mixing for 30 seconds at medium speed before being placed in the molds.

The fiber reinforced composites for the main phase of the research with oil well cement were mixed in a different way. Still, the FRC for the air void analysis were mixed in the same way as described in the preliminary research. For the main research phase, the composites were produced based on standard ASTM C305 (Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency) procedure. After this process, the fibers were slowly (over the course of 30-60 seconds) added to the mortar while mixing at medium speed and then mixed for an additional 90 seconds. A portion of the fresh composite was tested for flow and then placed back into the mix for additional mixing at medium speed for 30 seconds. The material was then ready for placing into the molds.

3.5.5 Compaction of HPC/UHPC

The materials were placed into 50.8 mm x 50.8 mm x 50.8 mm cube molds for compressive testing and 14 mm x 40 mm x 160 mm beam molds for 4-point flexural and tension testing. Cement pastes or mortars that were used for isothermal calorimetry were placed into 20 mL HDPE containers. Samples for X-Ray diffraction (XRD) were prepared by casting 1 cm x 1 cm x 0.5 cm tall tiles. For chemical shrinkage, cement pastes were placed in 20 mL glass containers. Samples for surface resistivity were placed in 10 cm diameter x 20 cm tall cylinders.

Before placing the material in the molds, each mold was sprayed with a release agent (WD-40) for ease of de-molding after 24 hours. Beam or cube molds were filled with cement-based composites in two layers, each being compacted using a standard hard
rubber tamper (13 x 25 x 152 mm) for mortars and levelled before placing in the curing chamber. The cube molds were compacted in accordance with ASTM C109 while the beam molds were compacted with 40 tamps (20 tamps on each layer). Fiber reinforced composites that were cast in cylinders for surface resistivity tests were cast in 4 layers. Each layer was compacted 20 times with a standard concrete tamping rod. The cylinders were cast in 4 layers (which is more than standard procedures indicate) because of the significantly smaller aggregates size used in composites to assure a good compaction. Cement pastes that were prepared for chemical shrinkage were placed in the 20 mL containers so that the paste filled approximately 5 to 10 mm in accordance with ASTM C1608. The containers were then gently tapped so that no paste remained on the walls of the containers and a leveled surface was created.

3.5.6 Curing of HPC/UHPC

After placing HPC/UHPC in the molds, the molds were covered with glass plates and placed in a curing room for curing at room temperature (20 ± 3°C) and a relative humidity of no less than 90% as per ASTM C192 standards. The specimens were then removed from the molds after 24 hours. One day tests were then performed on the appropriate specimens and the remaining specimens were placed in a lime water bath until the testing age.

Curing of cement pastes for X-Ray diffraction occurred the same way as mentioned above, while the pastes for heat flow were immediately placed in the isothermal calorimeter for evaluation. The pastes for SEM investigation were allowed to cure at room temperature in lab conditions because they were in a diluted state. Finally, pastes for chemical
shrinkage were placed in their glass containers for immediate evaluation in room temperature conditions.

3.6 EVALUATION OF HPC/UHPC

3.6.1 Evaluation of Al₂O₃ Nano-Fiber Dispersion

To evaluate the dispersion of nano-fibers in slurries, several different methods were used. First, the samples were observed under an optical microscope (Olympus BH-2) at 200x and 1000x magnification. Next, particle size and zeta potential were also determined using a Brookhaven Instruments Zeta PALS technique. Finally, the samples were observed using a scanning electron microscope (SEM) by placing a small drop of slurry on the sample holder. Then slurry was then allowed to dry for 1 hour in a 50°C oven. The sample was then coated in gold and observed through the SEM at 20,000x or 40,000x magnification at 10 kV.

3.6.2 Heat of Hydration of Cement Pastes and Mortars

Cement pastes and cement mortars were monitored for their exothermic reaction during the hydration. This was performed by placing 25 g of fresh cementitious material (for mortars) or 10 g fresh cement paste (for pastes) into a container and evaluating the heat of hydration using an isothermal calorimeter (TAM Air from TA Instruments) for a minimum of 72 hours at 25 ± 1°C in accordance with ASTM C1679.

3.6.3 Chemical Shrinkage of Cement Pastes

Chemical shrinkage tests on cement pastes were performed in accordance with ASTM C1608 Procedure A (volumetric method). The cement pastes were placed in 20 mL glass containers. The containers were weighed to the nearest 0.001 g before and after adding the paste so that an accurate mass of cement could be determined based on the water
to cement ratio. The containers were then filled with distilled water and a rubber stopper with a 1 mL graduated cylinder (with readings to 0.01 mL) through its opening was then placed in the glass container so that the distilled water would rise up through the graduated cylinder. This was done within 20 minutes after mixing of the cement paste and the initial reading was taken exactly 1 hour after the paste was first mixed (this allows time for the sample to achieve temperature equilibrium within the water bath) and then every 30-60 minutes for 8 hours and then approximately every 8 hours after that. The readings were observed to the nearest 0.0025 mL. The chemical shrinkage over time was then calculated as a function of sorbed water over mass of cement.

### 3.6.4 Scanning Electron Microscopy

Diluted samples for scanning electron microscope (SEM) analysis were prepared by mixing the slurries of Al₂O₃ nano-fibers with oil well cement at a 1:1 ratio. The diluted samples were placed in droplet on a glass slide and allowed to hydrate for 24 hours at which time hydration was halted by placing the sample in alcohol and after heating in an oven at 85°C for 30 minutes. Finally, the samples were observed using SEM to determine how the hydration products were forming around the nano-fibers.

### 3.6.5 X-Ray Diffraction of Cement Pastes

Samples for X-Ray Diffraction (XRD) were prepared in 1 cm x 1 cm x 0.5 cm tiles. After 24 hours of curing in the molds the samples were placed in a lime water bath until the age of testing. If the samples were not able to be tested for XRD that same day, they were placed in a 91% isopropyl alcohol to stop any hydration and stored until the testing. The alcohol within these baths was changed every 24-48 hours to assure that the small quantities of water from the isopropyl alcohol did not contribute to the hydration of cement.
The small tiles were then dried and crushed into a powder using a mortar and pestle. The powder specimens were placed into a sample holder and tested using a Bruker D8 Discovery X-Ray Diffractrometer between 2-theta angles of 5° and 60°.

3.6.6 Flow of HPC/UHPC

The flow of fresh HPC/UHPC was tested by using a 254 mm (10 inch) flow table \((Figure \ 21)\) as per ASTM C230 standards. The flow mold was in a form of a conical shape with the bottom base being 100 mm wide and a top surface of 70 mm in diameter. The height of the mold was 50.8 mm tall. The HPC/UHPC was placed in a flow mold in two layers. Each layer was compacted with a standard hard rubber tamper 20 times and then leveled to create a smooth top surface. After the top surface of the cementitious material was leveled the flow mold was removed and the flow table was dropped 25 times in 20 seconds (in very fluid mixtures, the table was not dropped and the spread due to lifting the flow mold was measured). The diameter of the flow was then recorded in order to compare the flow to other mixtures.

\[ Figure \ 21: \ 25.4 \text{ cm (10-inch) flow table} \]
3.6.7 Density of Fresh HPC/UHPC

The fresh density of HPC/UHPC was determined by filling a small container with fresh material. The volume of the container was known; therefore the mass of the material within the container divided by the volume of the container provided the density. Although different molds were used to determine the hardened air content, attention was paid to compact the material in a similar way.

3.6.8 Compressive Strength of HPC/UHPC

Compressive tests were performed on 50.8 x 50.8 x 50.8 mm cubes in accordance with ASTM C109. These specimens were tested with an ADR-Auto ELE compression machine and loaded at a rate of 1.4 kN/sec. The maximum load and maximum compressive stress were then recorded.

3.6.9 Air Void Analysis of Hardened HPC/UHPC

To measure the hardened air content and air void properties of HPC/UHPC, 160 mm x 40 mm x 14 mm beams were used. When performing conventional concrete air void analysis, one would typically use much larger samples cut to expose the middle portions (because edges are typically not a good representation of the air void structure). For the purposes of this study, the smooth edge (edge adjacent to the wall of the mold with 40 mm x 160 mm dimensions) was lapped to expose the inner air void structure. The entire lapping process decreased the height of the sample by about 5 to 7 mm or 35% to 50% of 14 mm height. This, along with the small aggregate size, was considered to provide a good representation of the inner structure.

The lapping process was performed using an automated grinding/lapping/polishing machine at 300 rpm. First, the surface was lapped using a No. 80 grit until about 3 to 5
mm of material were removed (typically 6 minutes of lapping time). This process then repeated using No. 120 grit, No. 220 grit, No. 500 grit, and finally No. 1200 grit polishing disks (typically 3 minutes of lapping time for each). Between lapping the sample on each grit size, a hardening solution was used to strengthen the surface of the cementitious material and ensure the rims of the air voids maintain their true shape. This hardening solution consisted of 10 parts of acetone and 1 part of oil-based lacquer. After each lapping sequence, the sample was cleaned using a soft brush and allowed to dry. The hardening solution was then painted onto the surface of the sample and again allowed to dry before starting the next lapping sequence. After the final lapping using a No. 1200 grit disk, the samples were briefly (3 to 5 minutes) placed in acetone to remove any leftover hardener. The samples were then cleaned and dried.

To prepare the polished/lapped sections for air void analysis, their surfaces were colored black using a broad tip marker pen by marking in parallel lines with slightly overlapping strokes. This layer was allowed to dry and a second coat of marker was applied with the strokes 90 degrees from the first. After the second coat was allowed to dry, a layer of white 99% pure barium sulfate with a typical particle size of 0.7 µm was placed on the surface of the sample. The barium sulfate was then pressed into the voids using a rubber stamper with sufficient force to ensure all voids have been filled. Excess powder was then brushed away using the palm of the hand until a sharp contrast between black paste and aggregate and white voids was achieved. The sample was then viewed through a stereomicroscope to ensure an adequate contrast. At this stage, careful attention was provided to blacken any fibers that appear white using a fine point marker. The samples were then tested using a Rapid Air C457 machine to calculate the air void properties using
ASTM C457 Procedure A – Linear Traverse Method. This method requires the paste content to calculate the specific surface and spacing factors of the samples. In conventional linear traverse air void analysis, this would be determined through testing what percentage of a line was paste, however this is a very time consuming process and Rapid Air machines require blackened paste and aggregate, therefore the paste content was assumed based on the mix design of the cementitious composite. While using the Rapid Air machine, a threshold of 174 was used to distinguish white and black portions of the sample. In this Rapid Air approach, the air void properties are determined by the chord lengths of air voids crossing the aforementioned lines. The calculations to determine these are void properties are further discussed in section 2.4 DEVELOPMENT OF METHODS FOR AIR VOID ANALYSIS OF HARDENED CONCRETE.

Air void analysis was also performed using flatbed scanner techniques. This approach used the same samples used for Rapid Air tests with the blackened paste and aggregate and white powdered air voids. The samples were laid flat on a scanner and scanned at 4800 dots per inch (DPI) with careful attention paid to cleaning the surface of the scanner between the scans so that no powder remained on the glass providing false air voids. The sizes of the samples were often too large for the scanner memory, therefore these were scanned in pieces and later stitched together using built in stitching software within Photoshop and then cropped so approximately 5 to 10 mm of the edge of the samples were disregarded as these portions would not provide an accurate representation of the air void structure. After this full image was obtained, it was converted to a binary image with a threshold of 174 to match the threshold used in Rapid Air tests. The image was then opened in an image processing software (ImageJ) where the binary image was converted
so that the paste and aggregate appeared white and the voids appeared black. The image
was then analyzed using the image processing software to find the number of voids,
percentage of voids space, and area of each individual void. When performing this image
analysis, attention was paid to avoid detection. Some small areas that are only comprised
of a few pixels were not considered as air voids; therefore, in order to be quantified for a
void, the area composed of a minimum of 5 pixels was considered. Additionally, the
circularity of the voids must be considered, because an elongated shape or irregular shape
should not be considered in an analysis. A minimum circularity of 0.2 was applied to
address this restriction.

After completion of the image processing, the area fraction of the voids was
recorded and the area of each individual void was plotted. In order to relate the areas to
conventional air void property calculations, circular air voids with equivalent areas were
generated for each void and their corresponding diameters were calculated. In order to use
methods for calculating the specific surface based on planar methods [125] as discussed in
section 2.4, the expected (taken as the average) value of the distribution of diameters and
the expected value of the distribution of diameters squared was required. The specific
surface was then calculated as follows where \(Y\) is the expected value of the distribution of
diameters and \(Y^2\) is the expected value of the distribution of diameters squared.

\[
\alpha = \frac{16(Y)}{\pi(Y^2)}
\]  
(Eq. 17)

Once the specific surface was determined, the spacing factor was determined using
the same procedure as the Rapid Air. Again, the paste contents had to be assumed based
on the mix proportions.
3.6.10 Surface Resistivity of HPC/UHPC

Surface resistivity readings were taken on 100 mm diameter by 200 mm tall cylinders using a Giatec Scientific Surf machine. Prior to testing, conductive gel was placed on the tips of the electrodes to ensure the electrical conductivity. The samples were then simply placed into the Surf machine and tested for ASTM standards. This device is used as an alternative to conventional ASTM C1202 Chloride Ion Penetration tests and uses the Wenner Four-Electrode Method of testing surface electrical resistivity of hardened concrete (Figure 22). The surface electrical resistivity readings of concrete using this method have also been shown to have good correlation with ASTM C1202 Chloride Ion Penetration tests (Table 6). The Surf machine uses this method in 4 evenly spaces locations around the concrete and repeats this process providing 8 total readings of which the average can be determined.
Figure 22: Setup of four-point Wenner Array Probe test [132]

Table 6: The Relationship Between the Rapid Chloride Permeability and Surface Resistivity Tests [132]

<table>
<thead>
<tr>
<th>ASTM C1202</th>
<th>Surface Resistivity, kΩ-cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Ion Permeability</td>
<td>Rapid Chloride Permeability Test Charge Passed, coulombs</td>
</tr>
<tr>
<td>High</td>
<td>&gt;4000</td>
</tr>
<tr>
<td>Moderate</td>
<td>2000-4000</td>
</tr>
<tr>
<td>Low</td>
<td>1000-2000</td>
</tr>
<tr>
<td>Very Low</td>
<td>100-1000</td>
</tr>
<tr>
<td>Negligible</td>
<td>&lt;100</td>
</tr>
</tbody>
</table>

3.6.11 Flexural Performance of HPC/UHPC

Four-point flexural testing was performed in order to determine the flexural behavior of HPC/UHPC. This test defines the material’s ability to withstand large
deformations while still maintaining a high load carrying capacity. This test was used for
most of the research since a material’s ability to withstand large deformations is vital for a
durable material. Flexural tests were performed on the 160 mm long x 14 mm tall x 40
mm wide beams using four-point (third point) bending test. The end supports were 120
mm apart with the middle loading supports 40 mm apart (Figure 23). The beams were then
loaded at a rate of 1.2 mm/min to observe the load-deflection (stress-strain) behavior after
initial cracking. The deflection at the top supports were recorded from the Instron testing
frame and used to interpolate the deflection at the midspan of the beam and ultimately
calculate the flexural strain of the composite using ASTM D7264.

![Figure 23: Set up for four point bending (third point) for HPC/UHPC](image)

3.6.12 Direct Tension of HPC/UHPC

Direct tension tests were performed on samples of the same 160 mm long x 14 mm
tall x 40 mm wide beams used for flexural behavior. These samples were then cut to form
a dog-bone shape to ensure that failure did not occur near the supports. This was done to
form a width of 34.5 mm and a gauge length of 76.2 mm. The samples were then carefully
measured for cross-sectional area in different locations and then the average values were
calculated to be used for stress values. The samples were then loaded into the Instron
testing frame and the initial gage length was measured which would later be used for strain values. The samples were then loaded at a rate of 0.2 mm/min until failure (or significant reduction in load carrying ability) and the load and deflection values for the entire curve were obtained from the Instron Bluehill software and used to calculated stresses and strains throughout loading.

### 3.7 EXPERIMENTAL APPROACH

The design of ultra-high performance concrete using a multi-scale approach was performed in this research (Figure 24). Additionally, the tests performed for each step are presented in Table 7. In terms of fiber reinforced cementitious composites, a multi-scale approach would ideally begin at the cement paste level, then move to the mortar level, and finally end at the fiber reinforced composite level. However, in this case, the compressive strength of the composite was of key importance. Testing the compressive strength of cement pastes is difficult, therefore the optimization of mortars (which are significantly easier to test for compression) was first studied to find the composite with the best compression strength. This was performed by testing different cement types, different additions of high range water reducing admixtures (HRWRA), different supplementary cementitious materials (SCM), and different nano-fiber quantities for compressive strength and heat of hydration to assure no detrimental effects are occurring due to the addition of certain materials. Next, cement pastes were monitored for heat of hydration, chemical shrinkage, X-Ray diffraction, and scanning electron microscopy to determine the underlying mechanisms leading to the improved performance in mortars. Different types of fiber reinforcement was then added to the optimal mortar and tested for flow, compression, and flexure to determine the best fiber to be used with the aforementioned
mortar. At the same time, different superhydrophobic admixtures were tested for air void analysis, fresh properties, and mechanical properties in high performance fiber reinforced composites to determine which admixture provides the best air void structure for durability and mechanical response. Finally, the optimal ultra-high performance fiber reinforced composite was combined with the optimal superhydrophobic admixture (obtained from high performance concrete testing) to determine if the combination is feasible. These samples were tested for compression, flow, flexure, and surface resistivity to provide some indication of the material’s mechanical and durability response. Additionally, select samples were tested for tension. This approach allows for conclusions to be drawn on the materials leading to improved performance, the mechanisms leading to this improved performance, and whether or not superhydrophobic admixtures can be beneficially used in ultra-high performance concrete.

Figure 24: Experimental approach to the design of ultra-high performance concrete
Table 7: Tests Performed for the Experimental Approach to the Design of Ultra-High Performance Concrete

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Section</th>
<th>Analysis</th>
<th>Tests Performed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mortar Optimization</td>
<td>5.1</td>
<td>Cement Type</td>
<td>Heat of Hydration, Compression, Flow</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>HRWRA Content</td>
<td>Heat of Hydration, Compression</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td>SCM Content</td>
<td>Heat of Hydration, Compression</td>
</tr>
<tr>
<td></td>
<td>5.4</td>
<td>Al₂O₃ Nano-Fiber Content</td>
<td>Heat of Hydration, Compression</td>
</tr>
<tr>
<td>Cement Pastes Verification</td>
<td>6.1</td>
<td>Effect of Composition</td>
<td>Heat of Hydration</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>Effect of Composition</td>
<td>Chemical Shrinkage</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>Effect of Composition</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>Effect of Composition</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Air Void Optimization</td>
<td>7.1</td>
<td>High Performance Fiber Reinforced Composites</td>
<td>Flow, Fresh Density, Heat of Hydration, Compression, Flexure, Air Void Analysis</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>High Performance Mortars</td>
<td>Flow, Fresh Density, Heat of Hydration, Compression, Flexure, Air Void Analysis</td>
</tr>
<tr>
<td>Fiber Reinforced UHPC</td>
<td>8</td>
<td>Effect of Fibers</td>
<td>Compression, Flexure, Flow</td>
</tr>
<tr>
<td>Superhydrophobic UHPC</td>
<td>9</td>
<td>Effect of superhydrophobic admixtures</td>
<td>Compression, Flexure, Flow, Tension, Surface Resistivity</td>
</tr>
</tbody>
</table>
4. PRELIMINARY EXPERIMENTS

4.1 USE OF ALUMINUM OXIDE NANO-FIBERS

The addition of Al$_2$O$_3$ nano-fibers was proposed to improve the mechanical properties of cementitious materials. These nano-fibers are not intended to be the main reinforcing material like the PVA fibers used in previous work, but rather to improve the compressive and splitting strengths of the material. The nano-fibers are intended to bridge the initial small (nano or micro) cracks that occur in the elastic region and just after the elastic region. Any crack larger than these would be too big for the nano-fibers to bridge and would need to be bridged by larger fibers such as PVA fibers.

An experimental matrix was created to test the effectiveness of Al$_2$O$_3$ nano-fibers. Supplementary cementitious materials (SCM) were considered at only a small (1%) amount of portland cement replacement in order to better understand the influence of the nano-fibers. The 1% of SCM was considered as this amount would be dispersed with the nano-fibers. Both metakaolin (MK) and silica fume (SF) were considered as the supplementary cementitious materials in this study because these materials are known to provide some additional strength to cementitious materials due to the small particle size. Additionally, metakaolin tends to have flakey particle shapes and thus may provide an additional contact area between the matrix and nano-fiber. There may also be an increased aluminate content from the combination of metakaolin and Al$_2$O$_3$ fibers that could increase the performance of the composite. A W/CM of 0.25 and a S/CM of 1.0 (with standard graded silica sand) were used along with a polycarboxylate ether superplasticizer (PCE-SP) (0.15% of solid content) dosed by weight of cementitious materials. The nano-fibers
were added at a dosage of 0.25% by weight of cementitious material. The experimental matrix is summarized in Table 8 below.

Table 8: Experimental Program for Tests with Al₂O₃ Nano-Fibers

<table>
<thead>
<tr>
<th>MIX ID</th>
<th>W/CM</th>
<th>S/CM</th>
<th>SCM</th>
<th>Nano-Al₂O₃ (by weight of CM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>0.25</td>
<td>1.0</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>MK</td>
<td>0.25</td>
<td>1.0</td>
<td>1% MK</td>
<td>None</td>
</tr>
<tr>
<td>SF</td>
<td>0.25</td>
<td>1.0</td>
<td>1% SF</td>
<td>None</td>
</tr>
<tr>
<td>MK + Nano Al₂O₃</td>
<td>0.25</td>
<td>1.0</td>
<td>1% MK</td>
<td>0.25%</td>
</tr>
<tr>
<td>SF + Nano Al₂O₃</td>
<td>0.25</td>
<td>1.0</td>
<td>1% SF</td>
<td>0.25%</td>
</tr>
</tbody>
</table>

To assure that the nano-fibers can be used effectively, proper dispersion of the material is required. To accomplish this, the fibers were dispersed along with the SCMs, water, and PCE/SP using an ultrasound for 5 minutes at 85% amplitude (21.25 µm). All the SP and SCMs were used for dispersion along with 10 parts of water to 1 part of SCM and Al₂O₃ nano-fibers while the remaining water was added at the stage of the final mixing of the mortar. Mixes MK and SF (without nano-fibers) were dispersed in the same way to assure consistency in testing. It is essential that nano and micro materials are properly dispersed; therefore, they were observed under an optical microscope to assure that no agglomeration of fibers is occurring. Prior to placing the material into the ultrasound chamber, agglomeration of the fibers was clearly seen, however after ultrasonification, little to no agglomeration was observed (Figure 25). In this image, no agglomeration can be observed meaning the fibers have been well dispersed.
The fresh properties of the mixes were also observed. Since the addition of nano-fibers reduces the flow and workability of composites, it is essential to have a high flow in a reference mortar. When comparing the reference to the samples without nano-fibers, the use of metakaolin slightly reduces the flow while the use of silica fume slightly increases the flow. When nano-fibers are added, the flow is drastically reduced; similar comparisons can be made with MK and SF mixtures as the samples with silica fume provide higher flow. The results of flow testing are reported in Figure 26.
Heat of hydration was monitored for these samples as well. This test provides a good indication of the early age hydration of the cementitious material. All investigated samples had an increased heat flow as compared with the reference sample indicating an acceleration of hydration and potential for additional early age strength. Comparing samples with nano-fibers to those without, a slight increase in heat flow can be observed due to the $\text{Al}_2\text{O}_3$ nano-fiber addition. All samples had a slightly faster hydration process when compared with the reference sample (REF). Since such a small amount of supplementary cementitious material was used in the study, it is doubtful that such acceleration could be attributed solely to silica fume or metakaolin, but is rather the synergetic effect of nano- and micro-particles. However, the main difference was that all samples except for the reference were placed in an ultrasound bath to disperse the micro-particles in water with superplasticizer. This bath may have affected the structure of superplasticizer which may have reduced its effectiveness in terms of fluidification. However, this reduction may not be detrimental in terms of hydration as the reference
sample experienced a slower hydration process, indicating excess superplasticizer in the mix.

![Heat Flow, mW/g by weight of cementitious material](chart)

**Figure 27: Heat of hydration of mortars with Al₂O₃ nano-fibers**

The compressive strength of mortars was also observed at 7- and 28-day age (Figure 28). At 7-day age, there was an increase in compressive strength when silica fume was used in combination with nano-fibers. However, at 28-day age the opposite trend was observed as there was a decrease in compressive strength when nano-fibers were added. The opposite was observed when metakaolin was used. Initially at the age of 7 days, the sample with metakaolin had a higher strength, but later, at 28-day age, the samples with nano-fibers demonstrated higher strength.
Despite the slight difference in the results, the deviation from the reference samples is not significant. This can be due to the small amount of nano-fibers used (0.25%). The use of small amounts of supplementary cementitious materials was intentionally used because the effects of the nano-fibers were intended to be observed and thus small amounts of supplementary cementitious materials was intended to be dispersed along with the nano-fibers. By using this approach, the exact mixing procedure including the creation of the slurry would be the same and the only difference would be the nano-fibers. The reference mixture (REF) was created without a slurry to determine the effect of superplasticizer when ultrasonification is used. However, based on the results of heat of hydration tests and compressive strengths, there does not seem to be a significant effect.

4.2 USE OF ALUMINUM OXIDE NANO-FIBERS WITH OIL WELL CEMENT

Another set of tests was performed with Al₂O₃ nano-fibers, although this time with oil well cement. The nano-fibers were still used at a low dosage for this initial trial and only silica fume was considered for supplementary cementitious composite. Again, the

Figure 28: Compressive strength of mortars with Al₂O₃ nano-fibers
silica fume was dispersed in a slurry with or without nano-fibers and the reference sample did not use ultrasonification of slurries. Table 9 below reports on the experimental matrix for this study where the reference sample (REF) was compared to a sample with 1% silica fume (OWSF) and a sample with 1% silica fume and 0.25% Al₂O₃ nano-fibers (OWNF).

Table 9: Experimental Matrix for the Preliminary Study of Al₂O₃ Nano-Fibers with Oil Well Cement

<table>
<thead>
<tr>
<th>MIX ID</th>
<th>W/CM</th>
<th>S/CM</th>
<th>SP (% CM)</th>
<th>Silica Fume %</th>
<th>Al₂O₃ Fibers %</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>0.165</td>
<td>1.0</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OWSF</td>
<td>0.165</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>OWNF</td>
<td>0.165</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The flow of the mortars with oil well cement was observed and is reported in Figure 29. The reference sample ended up being self-levelling as the material spread across the flow table without any drops of the table. The material was initially rather stiff and highly viscous, but slowly spread under its weight. The sample with silica fume (OWSF) also had a high flow, although not to the extent of the reference sample. The stiffness and viscosity was similar, however the standard procedure with 25 drops of the table was used to determine the flow. Despite this, the majority of the flow came for the spread of the material obtained under its own weight. The sample with nano-fibers had a significantly lower flow. This sample required additional effort when compacting in the molds. In this case, the nano-materials are utilizing a significant amount of superplasticizer for dispersion because of their high surface area. On the other hand, all samples were observed to have excess bubble formation. These bubbles are often the result of excessive superplasticizer (or insufficient dosage of air detrainer in the SP). Furthermore, 0.2% of SP is a relatively
high dosage for oil well cement, as the binder is more coarsely milled, has a very low C₃A content, and thus requires less superplasticizer for adequate dispersion.

Figure 29: Flow of mortars with Al₂O₃ nano-fibers and oil well cement

The results from the heat of hydration tests (Figure 30) tend to reinforce what was visually observed regarding the excess superplasticizer. This can be stated as the dormant period of the heat flow tends to be significantly longer than usual. It is known that in oil well cement hydration occurs at a significantly slower rate, however, some additional delay may be attributed to the excess superplasticizer. The peak heat flow was significantly reduced when compared to those tested with Type I portland cement. This is consistent with data reported in literature for oil well cement explained by the reduction of C₃A. The reference sample (REF) and sample with silica fume (OWSF) displayed similar results. The sample with nano-fibers began to hydrate prior to others. This may be an indication that some of the superplasticizer was consumed while dispersing the nano-fibers and there was not as much excess available to delay hydration.
For these materials, the 7-day compressive strength is between 112-125 MPa, while the 28-day compressive strengths were between 130-135 MPa (Figure 31). There also seemed to be a slight increase in compressive strength when silica fume was used. Although no significant increase was expected as only 1% silica fume replacement of portland cement was used, this improved the compressive strength. The reduction in flow was not to be expected with such a low addition of silica fume and may be the result of loss of active superplasticizer while creating the silica fume slurry. An additional minor increase in compressive strength was seen when silica fume was used in addition to Al₂O₃ nano-fibers; however, it may be assumed that the lack of significant increase is due to the reduced workability. Since the flow, and thus workability, was drastically reduced, voids can be entrapped thus reducing the compressive strength. These results demonstrated the need to rethink how the nano-fibers are added to the cementitious matrix.
Another experimental program was designed to observe the effects of Al₂O₃ nano-fibers on compressive strength. In the experiment, Type I portland cement was used, along with 1% replacement silica fume in each mix. Each mix also had a W/CM of 0.275, a SP content of 0.2% CM and a S/CM of 1.0. A tributyl phosphate at a dosage of 22% of the solid SP was also used to reduce the amount of entrapped air voids within the matrix. Al₂O₃ nano-fibers were used at dosages of 0.0, 0.10, 0.25, and 0.50% by weight of the cementitious material (Table 10).

These mortars were mixed in a similar fashion as reported in previous sections where a slurry was created to disperse the nano-fibers. The reference sample (SF_REF) used all of the superplasticizer in the mix while other samples used half of the SP in the mix and half to disperse the nano-fibers. The silica fume was also used in the slurry with the exception of the reference sample.
Table 10: Experimental Setup for Mortars with Varying Al₂O₃ Contents

<table>
<thead>
<tr>
<th>MIX ID</th>
<th>W/CM</th>
<th>S/CM</th>
<th>SP (% CM)</th>
<th>Silica Fume %</th>
<th>Al₂O₃ Fibers %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF_REF</td>
<td>0.275</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>SF_0.10</td>
<td>0.275</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
<td>0.10</td>
</tr>
<tr>
<td>SF_0.25</td>
<td>0.275</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
<td>0.25</td>
</tr>
<tr>
<td>SF_0.50</td>
<td>0.275</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Results from the heat flow curves (Figure 32) show similar behavior for all samples except for the sample with 0.50% nano-fibers (SF_0.50). This curve demonstrated a significantly faster hydration process with a higher peak heat flow. This may be due to the loss of active SP during the dispersion of the nano-fiber slurry or seed effect of the Al₂O₃ nano-fibers. Additionally, once this slurry was added to the mix, the higher surface area of all the components of the mix requires this additional SP. This may result in excess SP present in all other mixes without Al₂O₃ nano-fibers. Of the other three mixes, the addition of nano-fibers tended to provide a slight increase in the peak heat flow. This may be the sign of additional hydration products formed because of the nano-fibers (i.e., seed effect).

![Heat Flow, mW/g by weight of cementitious material](image)

*Figure 32: Heat flow of mortars with varying contents of Al₂O₃ nano-fibers*
The compressive strengths of samples with Al₂O₃ nano-fibers demonstrated some improvement. When 0.25% nano-fibers were used, there was a slight (7%) increase in compressive strength at 90-days, however, samples with 0.10 and 0.50% nano-fibers displayed little to no difference in compressive strength. Similar results were seen for 28-day specimens and all samples with nano-fibers actually displayed lower compressive strengths compared to the reference sample at 7-days. Again, it may have been expected that the addition of nano-fibers provide additional increases in compressive strength; however, this was not seen within this study. This may be due to the mixing procedure used to create the slurries and additional entrapped air voids generated from the lower workability.

**Figure 33: Compressive strength of mortars with varying contents of Al₂O₃ nano-fibers**

### 4.4 PREPARATION OF ALUMINUM OXIDE NANO-FIBER SLURRY

The addition of Al₂O₃ nano-fibers in the previous sections did not improve the strength. This would most likely be due to the procedure for dispersing the nano-fibers
and adding the slurry into the mixture. In all of the previous studies, some amount of SP that was to be used in the overall mix was used for dispersion of nano-fibers. This most likely would consume some of the effectiveness of the SP and reduce the workability of the mixtures. The addition of nano-fibers would also generate a higher surface area for all of the materials in the mixture; therefore, additional SP would be required. For this reason, a new procedure was created to disperse the fibers where the same amount of SP was added to each mixture and an additional SP was used to disperse the nano-fibers. This approach may lead to some uncertainties on whether or not active SP from fiber dispersion would then be added to the main mixture. Despite this being the case, it would be difficult to monitor and would be assumed that none of the SP is active and can later be analyzed to see if this is the case. The distilled water used for the dispersion of nano-fibers was still considered when determining W/CM in the full mixture proportions.

To produce the slurry, a full tablet of Al$_2$O$_3$ nano-fibers was dispersed using distilled water and SP. This full process was reported in the Preparation of Al$_2$O$_3$ Nano-Fibers Dispersions section. The final proportions of the nano-fiber slurry are 94.69% distilled water, 3.85% Al$_2$O$_3$ nano-fibers, and 1.46% SP. The slurries were prepared using an ultrasound mixer combined with a high speed mixer for either 1 or 3 hours. First, the dispersion was observed through an optical microscope at 200x magnification and 1000x magnification. As can be seen in the lower magnification (Figure 34), some agglomerates are still present when 1 hour a mixing is performed, while fewer agglomerates are seen after 3 hours of mixing. While observing the dispersion through higher magnification (Figure 35), the fibers tended to have shorter lengths. Prior to the slurry dispersion, the fibers were added as a full disk. This disk tended to have some agglomeration of adjacent
fibers, but still all fibers had the same width. This is evident with the lower magnification images as agglomeration was reduced with mixing time. Additionally, since the fibers are grown along the height of the disk (z coordinate), prior to dispersion are approximately 50 mm long. With dispersion, fibers break apart to form shorter lengths and with more dispersion, become even shorter. This process is evident from the higher magnification images. Although dimensions cannot be reported from optical microscope images, fibers ranged from 18 to 65 µm with 1 hour of dispersion and 10 to 23 µm with 3 hours of dispersion.

*Figure 34: Al₂O₃ fibers dispersed for 1 hour (left) and 3 hours (right) observed through an optical microscope at 200x magnification*

*Figure 35: Al₂O₃ fibers dispersed for 1 hour (left) and 3 hours (right) observed through an optical microscope at 1000x magnification*
The dispersions were all tested for the zeta potential (Z-Potential) and mobility mean (Table 11) to test their stability as a colloidal dispersion. The average diameter of the particles was also determined and as expected, smaller diameters are correlated with more dispersion time. Although all of the fibers are physically the same diameter, the results from this test demonstrate a higher diameter for less dispersion time due to the additional agglomerations. The zeta potential (calculated based on values from the mobility mean) for longer dispersions has a higher absolute value indicating a more stable dispersion resistant to sedimentation after initial dispersion.

Table 11: Characterization of Al₂O₃ Fiber Dispersion

<table>
<thead>
<tr>
<th>Dispersion Time, hours</th>
<th>Diameter mean, nm</th>
<th>Z-Potential, mV</th>
<th>Mobility Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>157.4±5.8</td>
<td>-15.17±1.05</td>
<td>-1.14±0.08</td>
</tr>
<tr>
<td>3</td>
<td>128±1.4</td>
<td>-26.4±5.33</td>
<td>-1.99±0.4</td>
</tr>
</tbody>
</table>

Finally, the dispersions were observed through a scanning electron microscope. A drop of each slurry was placed in an oven and as they dried, the fibers collapsed, and as further drying occurred some cracks formed between the fibers. The fibers between these cracks were then observed at 20,000x magnification and 40,000x magnification for dispersion of 1 hour (Figure 36) and 3 hours (Figure 37). Again, the longer dispersion time tended to have less agglomeration. The solid portions (left and right of images, outside of cracks) tended to be more uniform with a longer dispersion, again indicating less agglomeration as more agglomeration would result in bundles of fibers and additional void space within the solid portions. Based on these results, it is clear that 3 hours of dispersion time results in a more stable and better dispersed slurry. These slurries still need to be tested in mortars to prove the efficiency of dispersion process and contribution to strength.
Figure 36: SEM images of nano-fiber slurry dispersed for 1-hour at 20,000x magnification (left) and 40,000x magnification (right)

Figure 37: SEM images of nano-fiber slurry dispersed for 3-hours at 20,000x magnification (left) and 40,000x magnification (right)

Mortars with the above-mentioned slurries mixed for 3 hours were prepared for compressive strength tests. The experimental matrix (Table 12) for these mortars was prepared so that all samples had the same W/CM, S/CM, and SP. Additional SP was used in the slurry preparation meaning that more SP was used overall in all samples other than the reference (there is still a debate on whether this additional SP is active). The samples with Al₂O₃ nano-fibers were used without any additional SCM, or in combination with 1% silica fume or 1% metakaolin. Type I portland cement (HO) was also used for all mixes.
Table 12: Experimental Setup for Samples with Al₂O₃ Nano-Fibers Dispersed for 3 Hours

<table>
<thead>
<tr>
<th>MIX ID</th>
<th>W/CM</th>
<th>S/CM</th>
<th>SP (% CM)</th>
<th>SCM %</th>
<th>Al₂O₃ Fibers %</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>0.275</td>
<td>1.0</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.25Al</td>
<td>0.275</td>
<td>1.0</td>
<td>0.1</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>0.25Al+SF</td>
<td>0.275</td>
<td>1.0</td>
<td>0.1</td>
<td>1.0 SF</td>
<td>0.25</td>
</tr>
<tr>
<td>0.25Al+MK</td>
<td>0.275</td>
<td>1.0</td>
<td>0.1</td>
<td>1.0 MK</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The flow of the samples was much different from previous experiments in that with the addition of Al₂O₃ nano-fibers, there was an increase in flow. This would most likely be due to the additional SP used to disperse the nano-fibers. This may also give an indication that at least some of the SP is still active. With the addition of 1% silica fume and nano-fibers, there was a slight decrease in flow and an even further decrease with 1% metakaolin. Silica fume and metakaolin often result in lower flows and less workability because of their higher surface area, but in this case there is only a slight reduction because such a small quantity was used. If higher quantities of SCM are used, there would most likely be a significant reduction in flow, especially with metakaolin.

![Flow, %](image-url)

*Figure 38: Flow of mortars with Al₂O₃ fibers dispersed for 3 hours*
The heat flow of these samples also show results which are to be expected (Figure 39). All of the samples with the Al\textsubscript{2}O\textsubscript{3} nano-fibers had a slight delay which would most likely be due to the additional SP, although this delay is not that significant and would not negatively affect the setting. The sample with nano-fibers and the one with a nano-fibers and metakaolin combination displayed a higher peak heat release. This may be an indication that additional hydration products are being formed. The sample with nano-fibers and silica fume tends to show the same peak heat release as the reference; however, additional hydration products may still be forming in this system.

![Heat Flow, mW/g by weight of cementitious material](image)

*Figure 39: Heat flow of mortars with Al\textsubscript{2}O\textsubscript{3} fibers dispersed for 3 hours*

The compressive strength of samples with Al\textsubscript{2}O\textsubscript{3} nano-fibers that had been dispersed for three hours displayed promising results (Figure 40). The addition of these nano-fibers appears to increase the compressive strength. The 90-day compressive strength results of the sample with nano-fibers and no SCM had an increase in strength of 4%, the
sample with nano-fibers and metakaolin had an increase of 11%, and the sample with nano-fibers and silica fume had an increase of 17.5% compared to the reference. This shows that the nano-fibers may be contributing to the strengths when properly dispersed. It may be assumed that the addition of only 1% metakaolin or silica fume alone is not sufficient for increased compressive strength because such low quantities had been used. This may indicate that the combination of nano-fibers with these SCM results in additional hydration products and densification of the cementitious matrix that increase the compressive strength. Further work may need to be performed in order to determine the mechanisms contributing to the increase in strength. Another possibility that may be occurring is that the additional SP provides a more workable mixture than can be compacted more easily and thus result in fewer entrapped air voids leading to a more dense structure. If this is the case, the nano-fibers are then acting as a viscosity modifying admixture that allow additional SP to be used without resulting in segregation. It would most likely be the case that if this additional quantity of SP had been used without the nano-materials, and possibly these micro particles (silica fume or metakaolin), severe segregation would occur.

Figure 40: Compressive strength of mortars with Al₂O₃ fibers dispersed for 3 hours
4.5 HEAT TREATMENT OF FIBER REINFORCED CEMENTITIOUS COMPOSITES

Several different fiber reinforced cementitious composites were tested in an attempt to create an ultra-high performance cementitious composite. In this set of tests, 16 different mixes were created with varying W/CM, SCM quantities, and different sand types. Silica fume was used in all samples at different quantities while the second SCM varied between fly ash Type C (FA) and ground granulated blast furnace slag (slag). The two sands that were tested were standard graded silica sand (silica) conforming to ASTM C778 and commercially available Granusil grade 4030 silica filler sand (quartz) with a 99.7% SiO$_2$ content. All samples contained a polycarboxylate ether superplasticizer (PCE-SP) with solid content of 0.175% (by weight of cementitious material) and a viscosity modifying admixture (colloidal nano-SiO$_2$ based) with solid content of 0.15% (by weight of cementitious material). Additionally, the samples were cured in three different ways. First, a set of reference samples were cured at standard conditions, the next set was cured under standard conditions for 7 days, then placed in an oven ($130 \pm 10^\circ$C) for 24 hours and after conditioned in the curing room, while the 3$^{rd}$ set was processed similarly to the 2$^{nd}$, except that specimens were placed into the oven after 14 days. These samples were then tested for compressive strength and flexural behavior at 28-day ages. The experimental program for these tests is summarized in Table 13.
Table 13: Experimental Matrix for Fiber Reinforced Cementitious Composites Subjected to Heat Treatment

<table>
<thead>
<tr>
<th>MIX #</th>
<th>MIX ID</th>
<th>PVA Volume (%)</th>
<th>W/CM</th>
<th>S/CM</th>
<th>S.F. (%)</th>
<th>SCM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D1SS5</td>
<td>2.5</td>
<td>0.3</td>
<td>0.5 (silica)</td>
<td>5</td>
<td>45 (slag)</td>
</tr>
<tr>
<td>2</td>
<td>D1SS10</td>
<td>2.5</td>
<td>0.3</td>
<td>0.5 (silica)</td>
<td>10</td>
<td>40 (slag)</td>
</tr>
<tr>
<td>3</td>
<td>D1SS15</td>
<td>2.5</td>
<td>0.3</td>
<td>0.5 (silica)</td>
<td>15</td>
<td>35 (slag)</td>
</tr>
<tr>
<td>4</td>
<td>D1SS20</td>
<td>2.5</td>
<td>0.3</td>
<td>0.5 (silica)</td>
<td>20</td>
<td>30 (slag)</td>
</tr>
<tr>
<td>5</td>
<td>D2SS10</td>
<td>2.5</td>
<td>0.27</td>
<td>0.5 (silica)</td>
<td>10</td>
<td>40 (slag)</td>
</tr>
<tr>
<td>6</td>
<td>D2SS15</td>
<td>2.5</td>
<td>0.27</td>
<td>0.5 (silica)</td>
<td>15</td>
<td>40 (slag)</td>
</tr>
<tr>
<td>7</td>
<td>D2QS10</td>
<td>2.5</td>
<td>0.27</td>
<td>0.5 (quartz)</td>
<td>10</td>
<td>40 (slag)</td>
</tr>
<tr>
<td>8</td>
<td>D2QS15</td>
<td>2.5</td>
<td>0.27</td>
<td>0.5 (quartz)</td>
<td>15</td>
<td>40 (slag)</td>
</tr>
<tr>
<td>9</td>
<td>D3SSL35</td>
<td>2.25</td>
<td>0.27</td>
<td>0.5 (silica)</td>
<td>15</td>
<td>35 (slag)</td>
</tr>
<tr>
<td>10</td>
<td>D3SFA35</td>
<td>2.25</td>
<td>0.27</td>
<td>0.5 (silica)</td>
<td>15</td>
<td>35 (FA)</td>
</tr>
<tr>
<td>11</td>
<td>D3QLS35</td>
<td>2.25</td>
<td>0.27</td>
<td>0.5 (quartz)</td>
<td>15</td>
<td>35 (slag)</td>
</tr>
<tr>
<td>12</td>
<td>D3QFA35</td>
<td>2.25</td>
<td>0.27</td>
<td>0.5 (quartz)</td>
<td>15</td>
<td>35 (FA)</td>
</tr>
<tr>
<td>13</td>
<td>D4SSL35</td>
<td>2.25</td>
<td>0.25</td>
<td>0.5 (silica)</td>
<td>15</td>
<td>35 (slag)</td>
</tr>
<tr>
<td>14</td>
<td>D4SFA35</td>
<td>2.25</td>
<td>0.25</td>
<td>0.5 (silica)</td>
<td>15</td>
<td>35 (FA)</td>
</tr>
<tr>
<td>15</td>
<td>D4QLS35</td>
<td>2.25</td>
<td>0.25</td>
<td>0.5 (quartz)</td>
<td>15</td>
<td>35 (slag)</td>
</tr>
<tr>
<td>16</td>
<td>D4QFA35</td>
<td>2.25</td>
<td>0.25</td>
<td>0.5 (quartz)</td>
<td>15</td>
<td>35 (FA)</td>
</tr>
</tbody>
</table>

The flow of fresh cementitious composites is a good indication of how workable the material will be. This property is controlled by composition, dosage of SP, and W/CM. The higher the W/CM the higher the flow; however, such mixtures may also result in reduced strength. A highly workable material can also be achieved through the use of chemical admixtures such as high range water reducing admixtures (superplasticizers) which provide both high strengths (due to reduction of W/CM) and high workability. However, the use of excessive dosages of water reducing admixtures may result in segregation of cement paste from the sand, resulting in an undesirable mix. To account for this, viscosity modifying admixtures (VMA) can be used to allow for better workability at higher superplasticizer contents. Knowing this, it is still important to have a highly workable material to assure that the material can be placed and finished as easily as possible to ensure the quality and save labor resources in the field.
Results of the flow tests are reported in Figure 41. It can be observed that samples with fly ash tend to result in a better flow when compared to the mixtures of same composition with slag, especially in samples with a lower fiber volume. It can also be seen that with the additional quantities of silica fume, the flow is reduced (Mix 1-4). It is assumed that at lower W/CM ratios, the flow would be reduced; however, this is not seen in the results because all samples with a lower W/CM were tested at a reduced fiber volume.

![Flow of fiber reinforced cementitious composites](image)

*Figure 41: Flow of fiber reinforced cementitious composites*

The compressive strength of the samples is reported in Figure 42. These results indicate that samples made with fly ash demonstrate significantly lower strength. It was initially assumed that the use of higher quantities of silica fume would result in higher strength, but this was not realized (mixes 1-4). The reduction of W/CM also did not result
in significant increases in compressive strength when reference (series without heat treatment) samples were considered; however a drastic improvement was reported in the samples with a lower W/CM after heat treatment. This is especially evident when compositions with lower fiber volumes and silica sand were used. There also tends to be a slight decrease in strength when quartz sand is used. For samples with a higher volume of fibers and W/CM of 0.30, heat treatment results in lower compressive strength and for samples with a higher fiber volume and a W/CM of 0.27, heat treatment at 7-day age results in a reduction in strength, while heat treatment at 14 days was improving the strengths. This could be an indication that heat treatment has a negative effect on the fibers as the reduced compressive strengths are occurring when higher fiber volumes are used. The best compositions (Mixes 9 and 13) provided compressive strength of around 140 MPa, which is still not sufficient to qualify for ultra-high performance concrete.
Figure 42: 28-day compressive strength of fiber reinforced cementitious composites with heat treatment for mixes 1-8 (top) and mixes 9-16 (bottom)

The flexural behavior of fiber reinforced cementitious composites is essential to assure that the material provides the maximum durability. When performing these tests,
not only is the maximum flexural strength important, but the deflection and flexural strain are equally important. It would be difficult to compare the load vs. deflection curves of all samples in this study; therefore, the area under the load vs. deflection curve was calculated to better compare the overall flexural behavior of the samples (*Figure 43*). These results could then be correlated to the energy dissipated from the test, which is another important parameter. All load vs. deflection curves can be seen in Appendix B. For all samples with a lower W/CM, a reduction in flexural response can be seen when heat treatment is applied. Some samples (Mixes 9, 11, 13, and 15) that demonstrated a higher compressive strength after heat treatment displayed a loss in flexural properties after heat treatment. These results may indicate that heat may have a detrimental effect on the reinforcing PVA fibers. Despite this, when considering the samples without heat treatment, the sample with a low W/CM, silica sand, and fly ash (Mix 14) had the best results. The reason behind this was most likely due to the weaker bond between the matrix and the fibers because of the addition of fly ash. This would then allow for fiber pullout instead of fiber rupture and thus result in high ductility. However, when heat treatment was used, the properties were significantly reduced. Other samples that performed well were Mixes 3, 9, and 10. Mix 10 may have performed better because it also had fly ash. Mixes 3 and 9 had high quantities of silica fume and provided higher strength, but also resulted in superior flexural behavior. Mix 9 had a lower W/CM, provided high compressive strength, and demonstrated good flexural response. Since the heat treatment may not work well for samples with PVA fiber reinforcement, a material similar to Mix 9 may be further tailored to create an ultra-high performance cementitious composite.
To determine how PVA fibers are affected by higher temperatures, thermogravimetric analysis and differential thermal analysis (TG-DTA) tests were performed (Figure 44). As the temperature increased, the PVA fibers started to lose mass at around 60°C. This mass loss could have been due to moisture or loss of oiling agent from the sample. The oiling agent is a key factor when considering the fibers’ bond strength with the cementitious matrix to allow for fiber pullout instead of fiber rupture. Results have indicated a reduction in flexural behavior after being exposed to high temperatures; therefore, this loss in mass as seen in the thermogravimetric analysis could be an indication of loss in fiber bond properties. Additionally, this loss in mass (around 2% between 60°C and 120°C) is significant enough to suggest additional transformations
of the material. The differential thermal analysis revealed that there is a phase change at around 75°C. This corresponds to literature stating the glass transition temperature for PVA is around 85°C [133]. Therefore, it can be said that heat treatment would not be beneficial for PVA-based composites to improve the mechanical properties of a cementitious matrix.

*Figure 44: Thermogravimetric analysis-differential thermal analysis (TG-DTA) of PVA fibers*
5. OPTIMIZATION OF ULTRA-HIGH PERFORMANCE MORTARS

The development of mortars with compressive strengths of at least 150 MPa was considered in this study. This was approached by using Al₂O₃ nano-fibers with different types of cement. Next, different types and quantities of supplementary cementitious materials were considered and finally, the use of Al₂O₃ nano-fibers at different quantities was investigated.

The testing of mortars was performed prior to testing of cement pastes because the compressive strength was of the main importance. Since it is difficult to determine the compressive strengths of cement pastes, it was proposed that testing the compressive strength of mortars and monitoring the early hydration would be the most efficient way. After these experiments, investigation of selected compositions in the form of pastes would give an indication of the underlying mechanisms.

5.1 CEMENT TYPE

In this study, different types of cement were considered along with different types of supplementary cementitious materials and Al₂O₃ nano-fibers. The cements that were considered are Type I portland cement from Lafarge (LF), Type I portland cement from Holcim (HO), and Type H oil well cement from Lafarge (OW). Each group of cements was tested so that there was a reference (REF, no SCM nor nano-fibers added), 0.25% by weight of cementitious material nano-fibers without any SCM (0.25), 0.25% nano-fibers with metakaolin (0.25MK), and 0.25% nano-fibers with silica fume (0.25SF). For the samples that utilized either metakaolin or silica fume, only 1% replacement of cement by SCM was considered. A S/CM of 0.5 was used for all mixes. Due to the differences in cement type, different W/CM and SP contents had to be used. To generate some
consistency between the mixtures, these were designed so that the reference samples of each set had the same flow. These had flows of 117.6%, 116.8%, and 118.0% for LF, HO, and OW, respectively. An experimental program for this study is reported in Table 14. Even though similar samples were tested in the preliminary experiments, this experimental program was intended to investigate the effects of the addition of nano-fibers and compatibility with different types of cements affecting the compressive strength and heat of hydration for mixtures based on the new nano-fiber preparation method (as discussed in section 4.4). Additionally, only 1% replacement of cement was considered when adding either metakaolin or silica fume. The strength improvement due to these SCM’s should not be significant at such low quantities; however, any synergy which may be occurring between the nano-fibers and the micro SCM is of interest for this study.

Table 14: Experimental Program for Mortars with Varying Cements, SCM, and Nano-Fibers

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Cement type</th>
<th>W/CM</th>
<th>SP, % of CM</th>
<th>Al₂O₃ Fibers, %</th>
<th>SCM, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF_REF</td>
<td>LF</td>
<td>0.25</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LF_0.25</td>
<td>LF</td>
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<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>LF_0.25MK</td>
<td>LF</td>
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<td>0.15</td>
<td>0.25</td>
<td>1.0 MK</td>
</tr>
<tr>
<td>LF_0.25SF</td>
<td>LF</td>
<td>0.25</td>
<td>0.15</td>
<td>0.25</td>
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</tr>
<tr>
<td>HO_REF</td>
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<td>0.14</td>
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<tr>
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<td>0.14</td>
<td>0.25</td>
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<tr>
<td>HO_0.25MK</td>
<td>HO</td>
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<td>0.14</td>
<td>0.25</td>
<td>1.0 MK</td>
</tr>
<tr>
<td>HO_0.25SF</td>
<td>HO</td>
<td>0.23</td>
<td>0.14</td>
<td>0.25</td>
<td>1.0 SF</td>
</tr>
<tr>
<td>OW_REF</td>
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<td>0.10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OW_0.25</td>
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<td>0.10</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>OW_0.25MK</td>
<td>OW</td>
<td>0.173</td>
<td>0.10</td>
<td>0.25</td>
<td>1.0 MK</td>
</tr>
<tr>
<td>OW_0.25SF</td>
<td>OW</td>
<td>0.173</td>
<td>0.10</td>
<td>0.25</td>
<td>1.0 SF</td>
</tr>
</tbody>
</table>

The heat flow curves from the mortars based on LF cement \(\text{(Figure 45)}\), HO cement \(\text{(Figure 46)}\), and OW cement \(\text{(Figure 47)}\) generally have the same trends between the
reference samples and those with Al₂O₃ nano-fibers. There is, however, a significant difference between the heat flow curves of the different cements. The most significant difference was with the OW cement where the hydration process resulted in a delay with a much lower peak heat flow. This is to be expected as the OW cement has lower C₃A contents that would lead to both delayed hydration and setting time and lower heat generated. Additionally, OW cements are more coarsely ground which would lead to lower heat release during the hydration and a slower reaction time. When comparing LF cement with HO cement, the HO cement provides higher heat release along with a faster hydration process. Both cements have similar chemical characteristics, therefore the faster hydration process and higher peak heat release is most likely due to the smaller particle size of the HO cement. In most cement types, there are typically two distinct regions, a higher peak and an “elbow”, to the heat flow curves. In most cases the first peak is usually higher and corresponds to the hydration of C₃S and the second elbow is lower and corresponds to the hydration of C₃A. This is the case for the HO cement, but is not the case for the LF cement. In the LF cement, the first region is a lower “elbow” followed by a higher second peak. Since these two peaks often correspond to the C₃S and C₃A content, one would think that the two cements would have different C₃A and C₃S contents; however, these cements have similar compositions. One reason for this may be due to an adverse reaction between the cement and SP reducing the C₃S peak. In a previous study [134], the same type of cement was used with the same SP content and similar results were reported. In that same study, a reference sample was also produced without any SP and compared. It was determined that the second peak remained in the same location (this second peak was represented by an elbow in the reference sample and a peak in the sample with SP) and the first peak was
lowered. This would give some indication that the combination of LF cement and SP was having an adverse effect on the C₃S hydration as the first peak occurred at the same time with just lower heat flow while the second peak occurred at the same time with similar heat flow. Knowing this, the use of LF cement may not be advantageous when used in combination with the current SP used within this study.

While comparing the difference in heat flow curves between the samples with and without nano-fibers in with LF cement (Figure 45), it is clear that there is a delay in hydration with the addition of nano-fibers. This is most likely due to the additional SP that has been used to disperse the fibers resulting in a delay in hydration as well as lowering the peak heat flow. It would be expected that nano-fibers would initiate the formation of additional hydration products at a faster rate and then, therefore, result in a higher peak heat flow, but the additional SP is having some retardation effect on the hydration. Of the samples with nano-fibers, the one without any SCM (0.25) and the one with metakaolin (0.25MK) have very similar peaks while the one with silica fume (0.25SF) has a lower peak heat flow along with a slight delay in hydration. The use of silica fume can sometimes result in a lower peak heat release because when it is used as a replacement for cement (which is more reactive), however, in this case, it is being used at such a minor quantity that any reduction would be difficult to detect. Additionally, because of the smaller particle size of the silica fume, it may increase the speed of hydration, but this behavior was not observed within this study. Further tests may need to be performed to clarify this observation.
The heat flow curves of the HO cement (Figure 46) still have a delay in hydration due to the additional SP, but, in some cases, show an increase in peak heat flow. The silica fume (0.25SF) mixtures display a slightly lower peak heat flow which is similar to what was observed with the LF cement, while the metakaolin (0.25MK) had similar peak heat release and the reference nano-fiber sample (0.25) actually had the highest peak heat release. In this case, these minor reductions in peak heat release may be due to the fact that lesser cement is being used with the addition of these SCM, however, the fact that there is no significant reduction in peak heat flow as seen with the other types of cements is an indication that there is a good compatibility between the SP and HO cement. With that said, the increase in peak heat flow with nano-fibers may be due to a seed effect increasing the volume of hydration products and accelerating hydration.

*Figure 45: Heat flow of mortars with LF cement and Al₂O₃ nano-fibers*
Figure 46: Heat flow of mortars with HO cement and Al$_2$O$_3$ nano-fibers

The samples with nano-fibers produced a delay in hydration when used with OW cement (Figure 47). The delay is more significant in this case because of the slower hydration in OW cement. Additionally, the courser ground particles of OW cement require less SP, meaning that the additional SP from the dispersion of the nano-fibers induces an even further delay. Similar to the LF cement, the peak heat flows are lower vs. the reference indicating some retardation effects from the SP. Unlike the previous two cements, the addition of 1% silica fume (0.25SF) provides acceleration, as well as an increase in peak heat release. This may be an indication that the addition of only small amount of silica fume combined with Al$_2$O$_3$ nano-fibers in OW cement may indeed be resulting in the formation of additional hydration products causing such shift in the hydration whereas detrimental effects were seen with other cements.
The compressive strength of these mortars show promising results that can potentially be used in ultra-high performance concrete formulations (Figure 48). Early, 1-day strength from the HO group of mixes are quite high with compressive strengths just under 100 MPa. These values are typically around 20 to 35% higher than LF or OW samples. The C₃S content of this cement compared with LF is similar, therefore the contribution of additional C₃S, which is often responsible for early strength gain, cannot be a cause for the early strength gain. However, based on the heat flow curves, the C₃S peak is completely different between these two, meaning that something is altering it. Another reason for the early strength gain, may be that the HO cement is a finer material. This would accelerate the hydration process and provide higher early strength. This accelerated hydration process was also seen in the heat of hydration curves. The early age (1-day strength) of the OW group is also low. This is to be expected as the C₃A content is lower and the material is more course, slowing down the reaction. When considering the
early age strength contribution of nano-fibers and SCM, there is generally some improvement with the exception of the OW group. Here, the extended delay seen with the addition of nano-fibers is more than likely the contributing factor. In the LF and HO groups, where the hydration process is more complete, there is around a 15% improvement in compressive strength when nano-fibers are added. In most cases, there is not much difference between the samples without any SCM (0.25), samples with metakaolin (0.25MK), or samples with silica fume (0.25SF). Again, it is assumed that such small volumes of SCM cannot contribute to the strength development, but at an early age, strengths can be slightly reduced because of the SP. On the other hand, reactions between the nano-fibers and SCM may be increasing strength; therefore it is difficult to make any conclusions on the effect of SCM at these early ages.

When considering the compressive strength at later ages (28 and 90-days), it is clear that the OW group displays the best performance. For this group, the compressive strength, especially for ones including Al₂O₃ nano-fibers, were well above the minimum strength of 150 MPa required for ultra-high performance concrete. At 28 days, these values were around the 150 MPa threshold, whereas at 90 days, the values were well above that, approaching 190 MPa. Here, the addition of nano-fibers proved to show significant improvement in compressive strength. The sample with metakaolin had slightly lower compressive strengths, but this can be due to the deviations in testing, especially at higher strengths. The use of 1% silica fume actually displayed a lower compressive strength than the sample with nano-fibers and without any SCM (0.25). These results may not demonstrate any additional benefit of using metakaolin or silica fume along with Al₂O₃ nano-fibers in oil well cement systems.
Both at 28 and 90 days, the average compressive strength of samples with nano-fibers, regardless of whether they had SCM’s or not, provided a 15% increase in compressive strength when used with oil well cement. These later age results had a drastic difference from the lower compressive strengths observed in early age. This finding can be expected as oil well cement has an early delay in hydration and higher C₂S which is responsible for later age strength. Here, Al₂O₃ nano-fibers can actually accelerate (activate) the hydration of C₂S. Additionally, the more course ground particles allow less water to be used, which often leads to improved strengths.

The compressive strength of samples with nano-fibers used in the LF and HO groups were also improved. This was especially evident at 90 days with the LF group where the average increase in compressive strength among all of the samples with nano-fibers was 25% higher than the reference. In the HO group the improvement was only 8%. Additionally, the 28-day strengths provided a 19% and 14% improvement for the LF and HO groups, respectively. In the LF group, the use of SCM’s, especially silica fume, provided higher compressive strength. This was not the case in the OW group and in the HO group; metakaolin provided slightly higher compressive strengths while silica fume provided slightly lower values. The use of metakaolin and silica fume, even in small quantities, in combination with Al₂O₃ nano-fibers is provides around a 10% increase in strength whereas with other cements the difference was negligible.
Based on the results from the previous studies, it is clear that the addition of Al₂O₃ nano-fibers improves the compressive strength of mortars. However, it is unclear if this improvement is due to the nano-fibers or due to the contribution of superplasticizer producing a more workable mixture that is more easily compactable and denser. The reference samples in the above studies for OW cement had a SP dosage of 0.10% (by weight) of the cementitious material, while the samples with nano-fibers included additional SP used for dispersion. This additional SP would result in an overall dosage of 0.171% (by weight) of the cementitious material. Additionally, it is unclear if whether or not this SP that had been used for dispersion is active. To test if the additional SP was improving the compressive strengths, an experimental matrix was designed so that different quantities would be added to the mixture without being used to disperse nano-fibers (Table 15). Here, the SP was added to mortars with OW cement at different contents between 0.10 (content in reference samples) to 0.171 (content in nano-fiber samples) so
that 25%, 50%, 75%, and 100% of the difference was considered. These mixtures were also considered with and without 1% silica fume to determine if this SCM is affecting the strength when used in combination with additional SP. Another theory that may be proposed to explain the response of the samples with nano-fibers and additional SP is that the nano-fibers are acting as a viscosity modifying admixture and allow additional SP to be used effectively without hydration delays and by avoiding segregation. Although viscosity and flow were not measured within this study (flows were exceeding the diameter of the testing equipment), any segregation of paste and aggregate could be visually observed. The W/CM and S/CM remained the same as in the previous study for OW cement having ratios of 0.173 and 0.50, respectively.

Table 15: Experimental Setup for Mortars with Varying SP Contents

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>SP added from slurry, %</th>
<th>Total SP, % of CM</th>
<th>Silica Fume, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS-0.0</td>
<td>0</td>
<td>0.100</td>
<td>0</td>
</tr>
<tr>
<td>SPR-0.25</td>
<td>25</td>
<td>0.118</td>
<td>0</td>
</tr>
<tr>
<td>SPR-0.50</td>
<td>50</td>
<td>0.135</td>
<td>0</td>
</tr>
<tr>
<td>SPR-0.75</td>
<td>75</td>
<td>0.153</td>
<td>0</td>
</tr>
<tr>
<td>SPR-1.0</td>
<td>100</td>
<td>0.171</td>
<td>0</td>
</tr>
<tr>
<td>SPS-0.25</td>
<td>25</td>
<td>0.118</td>
<td>1.0</td>
</tr>
<tr>
<td>SPS-0.5</td>
<td>50</td>
<td>0.135</td>
<td>1.0</td>
</tr>
<tr>
<td>SPS-0.75</td>
<td>75</td>
<td>0.153</td>
<td>1.0</td>
</tr>
<tr>
<td>SPS-1.0</td>
<td>100</td>
<td>0.171</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Based on the results from the heat flow curves (Figure 49 and Figure 50), the addition of extra SP results in delays in hydration. In many cases, especially with higher quantities of SP, there is also a reduced peak heat flow. Here, the peak heat flow of the samples with the full SP content (SPR-1.0 and SPS-1.0) are around 4.5 to 5.0 mW/g which occur at around 17 to 18 hours. Previously, the peak heat flow for samples with nano-fibers (same overall SP content) occurred around 5 mW/g at 15 hours. Similar heat flows
to these samples with nano-fibers were observed for samples with 50% of the additional SP added. This could give an indication that around 50% of the SP from the slurry preparation may be active in the mix. It is clear with additional SP used, higher delays are expected. If the complete dosage was used without being utilized for dispersion, a drastic delay and slightly lower peak heat flow would be observed. This gives an indication that the nano-fibers are consuming some of the SP during the dispersion and can be acting as a viscosity modifying admixture. Additionally, the ultrasonification of the SP may be changing its properties.

Figure 49: Heat flow of mortars with varying SP contents without any SCM
The compressive strength of mortars with varying quantities of SP can be found in Figure 51. From this data it can be concluded that higher amounts of SP improve the compressive strength. This may be due to the additional SP allowing the mixture to be more workable and thus requiring less compaction. This would result in fewer entrapped air voids, thus increasing the compressive strength. The strength was also higher when comparing the samples without silica fume to those with 1% of silica fume. This is because silica fume is acting as a viscosity modifier. The addition of this silica fume reduces the flow allowing for more entrapped air voids to be formed. For the samples without silica fume there tended to be an increasing trend in the compressive strength with higher quantities of SP. This was not the case when the silica fume was used as there was no trend and seemed to be large deviations among the data. These large deviations were also present in the samples without silica fume and higher quantities of SP. This is expected as visual segregation was seen in these samples. It was observed that excess SP would result in bleeding and the formation of a whitish layer with bubble formations (Figure 52). This is
a clear indication that there is too much of SP in the system which results in segregation. This would also be the reason for high deviation in results. The high compressive strengths may also be misleading because the segregation would lead to higher paste contents in different portions of the sample leading to some eccentricities during the test. Despite the high strengths, the excess SP and segregation of the cement paste and aggregate would lead to several problems in terms of structural loading, durability, and shrinkage. The use of high quantities of SP also leads to significantly delayed hydration which would be unfavorable for many applications. It can be seen that the samples with lower quantities of SP did not exhibit any segregation. It can be concluded that the additional SP which is used for the dispersion of nano-fibers is not acting in this same way. This means that either the nano-fibers are acting as a viscosity modifier allowing additional quantities of SP to be used without segregation or the ultrasonification of the SP within the nano-fiber dispersion is changing its properties and not acting in the same way as if it were directly added to the mixture. Nevertheless, it is clear that such quantities of SP cannot be used to create an adequate mortar without being used for the dispersion of the nano-fibers. Even though there may be some detrimental effects of the additional SP within the dispersion such as delay in hydration and lower peak heat release, such dosage may be necessary for adequate dispersion of nano-fibers, as well as helping to provide a more workable mix without segregation.
5.3 SUPPLEMENTARY CEMENTITIOUS MATERIALS

An experimental program (Table 16) was designed to determine how the optimal mortar mixes from the previous studies performed with the addition of different types and quantities of supplementary cementitious composites. Here, the same W/CM of 0.173,
S/CM of 0.50, and SP content of 0.10% (by weight) of the cementitious material were used with oil well cement. It is often assumed that the addition of micro-particles such as silica fume or metakaolin will increase the compressive strength, but in some cases these may reduce the workability, resulting in difficulty during placement or compaction leaving large entrapped air voids ultimately reducing the compressive strength. Here, both silica fume and metakaolin were added at 1, 5, or 10% replacing the oil well cement. These were each added with and without 0.25% Al$_2$O$_3$ nano-fibers. As seen from the previous studies, the addition of only 1% of silica fume or metakaolin combined with the nano-fibers provided improved strengths. This may be an indication that small quantities of micro-particles can be effective when combined with nano-particles. For this study, larger quantities of these micro-particles were combined with and without nano-fibers to see if small volumes of metakaolin or silica fume combined with nano-fibers can be as effective as larger quantities of micro-particles alone. Additionally, larger quantities of micro-particles combined with nano-fibers were tested to see if they would provide an even further increase in strength.

In the following table, the Mix ID’s were set up so that the first letter is all S; the second letter is R for reference (without SCM’s), M for metakaolin, or S for silica fume; the following two digits refer to the percentage of micro-particles being added; and the last digit is labelled so that a 0 refers to no nano-fibers and a 1 refers to 0.25% nano-fibers. It should be noted that mix S_M100 was unmixable because the addition of such a high quantity of metakaolin resulted in an extremely dry mix. However, the same mix with the addition of nano-fibers (S_M101) was mixable because of the presence of SP in the nano-fiber slurry.
Table 16: Experimental Program for Mortars with Different Quantities of SCMs

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Al₂O₃ Fibers, %</th>
<th>SCM, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_R000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S_R001</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>S_M010</td>
<td>0</td>
<td>1.0 MK</td>
</tr>
<tr>
<td>S_M011</td>
<td>0.25</td>
<td>1.0 MK</td>
</tr>
<tr>
<td>S_M050</td>
<td>0</td>
<td>5.0 MK</td>
</tr>
<tr>
<td>S_M051</td>
<td>0.25</td>
<td>5.0 MK</td>
</tr>
<tr>
<td>S_M100*</td>
<td>0</td>
<td>10.0 MK</td>
</tr>
<tr>
<td>S_M101</td>
<td>0.25</td>
<td>10.0 MK</td>
</tr>
<tr>
<td>S_S010</td>
<td>0</td>
<td>1.0 SF</td>
</tr>
<tr>
<td>S_S011</td>
<td>0.25</td>
<td>1.0 SF</td>
</tr>
<tr>
<td>S_S050</td>
<td>0</td>
<td>5.0 SF</td>
</tr>
<tr>
<td>S_S051</td>
<td>0.25</td>
<td>5.0 SF</td>
</tr>
<tr>
<td>S_S100</td>
<td>0</td>
<td>10.0 SF</td>
</tr>
<tr>
<td>S_S101</td>
<td>0.25</td>
<td>10.0 SF</td>
</tr>
</tbody>
</table>

* Mix S_M100 was unmixable

The results from the heat flow curves (Figure 53 and Figure 54) show that with the addition of silica fume or metakaolin, the hydration process occurs faster. This may be due to the fact that the higher surface area of these materials would require larger quantities of SP and thus compensate for the delay produced. In many cases, the samples with metakaolin are hydrating slightly faster than those with silica fume. One reason for this is that metakaolin particles are flaky, requiring more SP for dispersion than the spherical silica fume particles. Additionally, the higher quantity of aluminate phases in metakaolin can speed up the reaction process. There also seems to be a trend that with the higher quantities of SCM’s being considered, there is a lower peak heat flow. This is to be expected as metakaolin and silica fume, or many other supplementary cementitious materials for that matter, are pozzolanic materials that do not produce large quantities of heat during hydration. These materials are siliceous or have aluminous silicate...
components, and in the presence of water react with calcium hydrates to form calcium silicate hydrates (CSH). These CSH’s are similar to the ones formed from the hydration of C2S and C3S, thus these pozzolans demonstrate excellent cementitious properties. The addition of these pozzolans typically produce slower hydration and increased CSH, resulting in increased later age strengths. Here, metakaolin and silica fume are very fine particles with high surface areas, thus can tend to be more reactive than most pozzolans. This would increase the speed at which these reactions are occurring and significant improvements in early age strength may be observed. In many cases the peak heat release of the samples with metakaolin is higher than the peak heat release of the samples with silica fume. This is because the metakaolin has aluminate phases resulting in the acceleration of hydration and higher heat releases. When comparing the samples with and without the nano-fibers, the hydration process typically occurs later when the nano-fibers are added. This is most likely due to the additional SP required for the dispersion of the nano-fibers delaying hydration. The samples with lower quantities of supplementary cementitious materials often see a more significant delay when nano-fibers are present, however this delay is minor in mixtures with higher volumes of SCM. This means at these higher quantities of SCM, much of the SP is being consumed and no excess is available to delay the hydration. Here, the workability and fluidity is more dependent on the use of metakaolin or silica fume than it is on the use of nano-fibers meaning that the additional SP present from the dispersion of nano-fibers may be necessary when higher quantities of supplementary cementitious materials are used. The samples with nano-fibers also tend to have slightly lower peak heat flows. It would be expected that the addition of nano-fibers would result in higher peak heat flows because of additional hydration products being
formed at a faster rate, but this was not the case. This is consistent with previous data on oil well cement (in the cement type study) and may be an indication that the ultrasonification of the SP is changing its properties.

Figure 53: Heat flow of mortars with varying quantities of metakaolin and silica fume

Figure 54: Heat flow of mortars with varying quantities of metakaolin and silica fume with $\text{Al}_2\text{O}_3$ nano-fibers
The compressive strength of samples with varying types and quantities of supplementary cementitious materials is reported in Figure 55. It is observed that many of the samples at 28-days reached the minimum required 150 MPa compressive strength. When comparing samples without Al₂O₃ nano-fibers, the ones without any SCM displayed relatively low compressive strengths compared to those with SCMs. These same samples without any SCM then demonstrated reductions in compressive strength when larger quantities of SCM were used. This was seen with 5% metakaolin, 5% silica fume, and 10%, silica fume. This is most likely due to the fact that these micro-particles were acting as viscosity modifying admixtures reducing the workability of the mixtures and generating higher quantities of entrapped air voids. The reduction in compressive strength was more prevalent in the samples with 5% metakaolin than with 5% or 10% silica fume. This is due to the shapes of these micro-particles. The silica fume particles have a spherical shape, whereas the metakaolin particles are more flat and angular resulting in a more significant reduction in compressive strength. When comparing samples with Al₂O₃ nano-fibers, it is clear that the addition of SCMs improves their compressive strength (which is in agreement with previous studies). For the samples with metakaolin, 1% replacement of cement provides the best strengths, while a reduction in compressive strength was observed at 5% replacement. For the samples with silica fume, 1% and 5% replacement of cement performed the best. When 10% of silica fume was used in combination with Al₂O₃ nano-fibers, the compressive strength was reduced because of the additional entrapped air voids and reduced workability. When comparing 1% and 5% silica fume mixtures, the 5% mix had approximately 8% increase in compressive strength at 28-days whereas these two were comparable at 90-days. This allows some flexibility in designing. If strength is required
at 28 days, 5% silica fume may be beneficial; however, at 90-days the use of only small quantities of SCMs such as silica fume in combination with Al₂O₃ nano-fibers can be beneficial. In many cases of UHPC, high quantities of silica fume are required to achieve the desired strength. Here, the same desired strength can be obtained with small quantities of silica fume in combination with nano-fibers.

**Compressive Strength, MPa**

![Compressive Strength Chart]

*Figure 55: Compressive strength of mortars with Al₂O₃ nano-fibers and varying SCM*

### 5.4 AL₂O₃ NANO-FIBER TYPE AND QUANTITY

Another study was performed to test the performance of mortars using different quantities of Al₂O₃ nano-fibers (Table 17). These nano-fibers were added at quantities of 0.10, 0.25, and 0.50% by weight of the cementitious material. These quantities are small, but nano-fibers are often effective at these small quantities. This experimental program helped to determine the feasibility of using smaller quantities of nano-fibers. Here, the maximum nano-fiber content was held at 0.50% (by weight) of the cementitious material
because a certain amount of water is required for dispersion of nano-fibers (which counts towards the W/CM) and any additional nano-fibers would result in a water demand greater than used to satisfy the W/CM. Along with different fiber quantities, fibers that had been dispersed for 1 and 3 hours were also used. In the preliminary work, it was determined that dispersing the nano-fibers for 3 hours provides shorter fiber lengths and a better dispersion and stability to the slurry. Based on these findings, the following studies used the nano-fibers that had been dispersed for 3 hours. Here, nano-fibers dispersed for only 1 hour were also used to determine if an additional dispersion time is necessary in terms of strength. This study used the same W/CM, S/CM, and SP contents as in previous work (having values of 0.173, 0.50, and 0.10% by weight of cementitious material, respectively). Additionally, oil well cement was used in all mixtures along with 1% silica fume.

Table 17: Experimental Program for Mortars with Different Quantities of Al₂O₃ Nano-Fibers Dispersed at 1 or 3 Hours

<table>
<thead>
<tr>
<th>MIX ID</th>
<th>Fiber Type</th>
<th>Al₂O₃ Fibers, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-REF</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>F1-0.10</td>
<td>1 hour</td>
<td>0.10</td>
</tr>
<tr>
<td>F1-0.25</td>
<td>1 hour</td>
<td>0.25</td>
</tr>
<tr>
<td>F1-0.50</td>
<td>1 hour</td>
<td>0.50</td>
</tr>
<tr>
<td>F3-0.10</td>
<td>3 hour</td>
<td>0.10</td>
</tr>
<tr>
<td>F3-0.25</td>
<td>3 hour</td>
<td>0.25</td>
</tr>
<tr>
<td>F3-0.50</td>
<td>3 hour</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Based on the heat flow curves (Figure 56 and Figure 57), the difference in hydration between the samples with nano-fibers dispersed for 1-hour and nano-fibers dispersed for 3 hours seems to be negligible. It was earlier determined the longer dispersion time results in a better dispersion. One would think that this longer dispersion time would require more SP as this would become less effective during the dispersion process and less
active SP would be present; however, this idea cannot be supported from the heat flow curves. If this had been the case, the samples with nano-fibers dispersed for longer periods of time would have less active SP and thus there would be less of a delay in hydration. Again, the peak heat flow of the reference sample was slightly higher than that for the samples with nano-fibers which would most likely be due to the additional SP. Also, the differences in peak heat flow for all samples with nano-fibers were negligible. Even though it was assumed that the additional SP may be leading to lower heat flow, the samples with higher quantities of nano-fibers had higher quantities of SP and thus also should have lower peak heat flows. Although this was not the case which may be an indication that the additional SP is not resulting in a decrease of the peak heat flow, but rather the ultrasonification that the SP is exposed to is changing its properties. This was not the case in the previous study where additional quantities of SP without the addition of nano-fibers displayed a decreasing trend in peak heat flow.

A delay in the hydration can also be seen with increasing amount of nano-fibers. The proportion of nano-fibers to SP was the same for all dispersions; therefore higher quantities of nano-fibers would require higher quantities of SP. With these higher quantities in the system, a larger delay can be expected.
The compressive strength of mortars with different quantities of Al$_2$O$_3$ nano-fibers as well as nano-fibers dispersed for different periods of time are reported in Figure 58. Again, it is clear that the addition of Al$_2$O$_3$ nano-fibers provides a significant improvement in compressive strength. When comparing different quantities of nano-fibers dispersed for 1 hour, there seems to be no trend in compressive strengths with all of the values being
similar. This may be due to the longer nano-fibers becoming more agglomerated and becoming tangled as reported in the preliminary work. This higher degree of agglomeration would make the nano-fibers less effective which is the reason for no significant improvement observed with higher quantities. The only trend that can be reported with the nano-fibers dispersed for 1 hour is that 1-day compressive strengths tend to be reduced as higher quantities are used. This is because the higher quantities require additional SP for the dispersion. This higher quantity of SP triggers a delay in hydration as supported by the heat flow curves and thus lower early age compressive strengths. This same decreasing trend was seen in the nano-fiber samples that were dispersed for 3 hours. However at later ages, it is clear that the addition of higher quantities of nano-fibers provide increased compressive strength. Here, the dispersion allows for less agglomeration and thus the fibers are more effective. The 90-day compressive strengths are encouraging with 0.5% nano-fibers having an increase of 17% compressive strength compared to mixtures with 0.1%. The samples with 0.25% nano-fibers had an increase of 14%, which was slightly lower than that for mixtures with 0.50%. Later, when macro/micro fibers are added to FRC, it may be assumed that the strength will be reduced because of entrapped air voids created due to the incorporation of fibers. Here, it may be feasible to use 0.50% nano-fibers instead of 0.25% to achieve the desired strength even though the difference between the two is minor. From these results, it may be evident that the higher quantities of well-dispersed nano-fibers result in higher compressive strength.
Figure 58: Compressive strength of mortars with Al$_2$O$_3$ nano-fibers dispersed for 1 or 3 hours
6. CEMENT PASTES WITH ALUMINUM OXIDE NANO-FIBERS

Based on the results of the previous section optimizing the performance of mortars, it is clear that the addition of Al₂O₃ nano-fibers provides improved compressive strengths. However, the mechanisms underlying such improvements are still not clear. Possible mechanisms are as follows. First, the nano-fibers could be acting as a viscosity modifying admixture, allowing an additional SP to be used without segregation and, in turn, resulting in a denser cementitious matrix. Next, the nano-fibers could be acting as seeds to promote the formation of hydration products. This would mean that the hydration products are formed around the fibers and the fibers are acting as a reinforcement for the CSH providing a stiffer cementitious matrix that would increase the resistance of the formation of micro-cracks and drying-swelling deformations at the level of CSH. This concept can explain the production of more hydration products at a faster rate because of the higher surface area of the nano-fibers. Another suggestion explaining the increased strength is that the ultrasonification of the SP may change its structure resulting in the enhancement of performance by the addition of accelerating functionality.

To test these theories, cement pastes were made and tested for heat flow, chemical shrinkage (up to 7 days), X-Ray diffraction at 1, 3, 7, and 28 days, and were observed under SEM at 24 hours after mixing. The samples created for the SEM were made of diluted samples so that the morphology of the hydration products would be easier to detect. All other tests were performed using the same W/CM and SP content as reported for the mortar study (Table 18). The only differences are that in the mortar study, an additional SP was used for the dispersion of nano-fibers while a content of 0.10% (by weight of solid) of SP to cementitious material was used in the mix (totaling around 0.17%). Here, in the cement
paste mixtures, the SP used for dispersion of the nano-fibers was also considered for the mix so that the total SP content (in the mix and dispersion) totaled 0.10%. This approach (although may not be as beneficial for strength) was considered to realize the true improvements from the nano-fibers and can also help to detect if the structure of the SP is being altered during the ultrasonification. Additionally, the experimental matrix for these tests was designed so that the benefits of both silica fume and Al₂O₃ nano-fibers can be evaluated. Therefore, based on this study, the major contributors (addition of silica fume, Al₂O₃ nano-fibers, or a combination of the two) to improved performance were expected to be determined.

Table 18: Experimental Setup for Cement Pastes with Silica Fume and Al₂O₃ Nano-Fibers

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>W/CM</th>
<th>SP, % of CM</th>
<th>Silica Fume, % of CM</th>
<th>Al₂O₃ Nano-Fibers, % of CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>0.173</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nano</td>
<td>0.173</td>
<td>0.1 (0.04% dispersion, 0.06% mix)</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>SF</td>
<td>0.173</td>
<td>0.1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Nano+SF</td>
<td>0.173</td>
<td>0.1 (0.04% dispersion, 0.06% mix)</td>
<td>1</td>
<td>0.25</td>
</tr>
</tbody>
</table>

6.1 HEAT FLOW OF CEMENT PASTES

The results of the heat flow of the cement pastes are reported in Figure 59. Here, it is observed that the addition of only 1% silica fume provides a significant increase in peak heat flow. There is also a slight acceleration of the hydration. On the other hand, the addition of Al₂O₃ nano-fibers resulted in a delay of hydration. One would expect that this addition would lead to an acceleration because of the increased surface area of the nano-fibers; however, this is not the case. This delay can be an indication that the physical properties of the SP are being altered during the ultrasonification. The chemical properties
of the Al₂O₃ cannot be contributing to the delay as it is an inert material and the increased surface area would likely result in a faster hydration, therefore the only explanation for the delay can be the alteration of the SP. The addition of these nano-fibers also results in an increased peak heat flow compared to the reference; however, not to the same extent as observed for silica fume. The combination of silica fume and nano-fibers results in an acceleration of hydration compared to the mix with only nano-fibers and a slight decrease in peak heat flow. The heat flow from the combination of silica fume and nano-fibers is interesting because one would expect that since both silica fume and nano-fibers alone resulted in increased peak heat flow, the combination would result in an even higher peak heat flow. Despite this, the cumulative heat for the two samples with Al₂O₃ nano-fibers were the same indicating that they had similar overall degrees of hydration. Therefore, even though it is clear that the addition of silica fume alone provides the best acceleration of hydration, as seen from previous studies, the addition of the nano-fibers results in a significant improvement in strength. Based on this data, it appears as though the addition of nano-fibers can provide an increase in overall hydration compared with the reference; however, not to the same extent as silica fume. This indicates that the nano-fibers are providing some seeding action, but this phenomenon may not be the only reason for the significant improvements in compressive strength.
6.2 CHEMICAL SHRINKAGE OF CEMENT PASTES

The chemical shrinkage of the same set of cement pastes were tested for 7 days. The results of these tests are reported in Figure 60. The results demonstrate that there is not much deviation between the mixtures. The deviations that do occur show that both silica fume and nano-fibers generate less chemical shrinkage than the reference sample. The addition of the silica fume is generating a denser cementitious matrix which restricts the deformations of the sample. The addition of nano-fibers to the material provides even less chemical shrinkage. This is especially beneficial because the chemical shrinkage can often be correlated with the overall hydration of a cement-based material [135]. This being said, the curves for chemical shrinkage should match the results from the cumulative heat from Figure 59 above. Since these results do not match, it may be concluded that the nano-fibers are providing a reinforcing effect to the CSH which is the reason for reduced...
chemical shrinkage. Despite the fact that the use of only 1% silica fume on its own provides a more dense structure resulting in a lower chemical shrinkage, the combination of 1% silica fume with nano-fibers does not provide much of an improvement compared to the sample with only nano-fibers. The same can be said about the degree of hydration in the previous figure. Furthermore, the compressive strength between similar mortars with nano-fibers with and without 1% silica fume do not display many differences. These results may indicate the nano-fibers are the main contributor to the compressive strength while the use of 1% silica fume has only a minor contribution. It appears as though the use of silica fume in combination with nano-fibers has little effect on the long term benefits; however, the addition of even small quantities of silica fume can help with early age properties as seen with the compressive strength values in the supplementary cementitious materials section, as well as faster hydration process in the above section.

**Chemical Shrinkage, mL/g**

*Figure 60: Chemical shrinkage of cement pastes with silica fume and Al₂O₃ nano-fibers*
The chemical shrinkage was also plotted vs. the estimated degree of hydration (Figure 61). Here, it was estimated that the theoretical degree of hydration of the reference sample was 30% at 40 hours of hydration. Theoretically, this value could be calculated based on the mineral composition of the paste, but in this case the value is arbitrary. The remaining samples were then standardized to the time in which the same degree of hydration was observed and presented as the degree of hydration. Based off of these results, the sample with only silica fume provides the lowest chemical shrinkage. The samples with nano-fibers also show reduced chemical shrinkage compared to the reference. This may be an indication that the silica fume is providing a denser structure reducing the amount of shrinkage. However, this figure only represents the chemical shrinkage and hydration up to 30 hours. Based on the previous figure where chemical shrinkage was tested for 7 days and the degrees of hydration may be assumed to be similar, the use of nano-fibers provides the best restraint for chemical shrinkage.

![Chemical shrinkage compared to the theoretical degree of hydration](image)

*Figure 61: Chemical shrinkage compared to the theoretical degree of hydration*
6.3 INVESTIGATION OF CEMENT PASTE HYDRATION BY X-RAY DIFFRACTION

The X-Ray Diffraction results of hydrating cement pastes (as tested in the previous sections) are reported in *Figure 62, Figure 63, Figure 64, and Figure 65* for hydration times of 1-day, 3-day, 7-day, and 28-day, respectively. This study can evaluate the formation of different products of the hydration and the effects of Al$_2$O$_3$ nano-fibers and silica fume on the hydration, which can be monitored by the change of C$_3$S, C$_3$A, and Ca(OH)$_2$ (CH) intensities. In the 1 day sample with the combination of silica fume and Al$_2$O$_3$ nano-fibers the formation of additional CH was detected. The increase in CH is not as present in the sample with only nanofibers; however, it appears as though slightly higher quantities of CSH may have formed in this sample. This is especially beneficial because for this composition, the heat flow results demonstrated a delay in hydration. These results demonstrate that the additional hydration products formed within the first 24 hours of hydration due to the addition of nano-fibers. Additionally, the increased CH observed for the combination of nano-fibers and silica fume is an indication of the formation of CSH and, therefore, a more dense structure. At 3 days, the addition of silica fume resulted in a formation of higher quantities of CSH and CH. This observation is even more evident at 7 days when both the samples with nano-fibers and in combination with silica fume provided higher quantities of CH. At 28 days, the CSH content of the sample with nano-fibers and silica fume appears to be significantly higher. This higher CSH content was also seen in the sample with only nano-fibers; however, this composition displayed lower quantities of CH. With the combination of the silica fume and nano-fibers, both CH and CSH contents are proportionally higher. These results demonstrate that the use of nano-
fibers result in higher quantities of CSH and thus stronger composites as demonstrated by the superior compressive strengths reported in the previous sections. However, this increase in CSH content may not be as prevalent at earlier ages.

Figure 62: The 1-day XRD results of cement pastes (A=Ettringite, B=CH, C=CSH, D=C₃S, E=C₆S, F=C₄AF)
Figure 63: The 3-day XRD results of cement pastes (A=Ettringite, B=CH, C=CSH, D=C_3S, E=C_2S, F=C_4AF)

Figure 64: The 7-day XRD results of cement pastes (A=Ettringite, B=CH, C=CSH, D=C_3S, E=C_2S, F=C_4AF)
6.4 INVESTIGATION OF CEMENT PASTES BY SCANNING ELECTRON MICROSCOPY

The cement pastes were also observed using a scanning electron microscope to determine if products of the cement hydration of forming around the fibers. Here, cements pastes were created in diluted samples where the quantity of nano-fibers was equivalent to the cement content. The same fiber dispersions were used for this, meaning that the amount of water required for dispersion was equal to the amount of water within this cement paste. This equates to a W/CM of 25. This was performed in order to better visualize the nano-fibers within this system. The nano-fibers in the diluted cement paste can be observed in Figure 66. The magnification may not be high enough in order to see if the hydration products are forming around the fibers; however, from these images it appears as though...
this is occurring, but cannot be verified. In the higher magnification image on the left, it appears as though some hydration products have formed around the nano-fibers, but still higher magnification may be required.

Figure 66: Scanning electron microscope images of diluted cement pastes with Al$_2$O$_3$ nano-fibers at 20,000x magnification (left) and 9,000x magnification (right)
7. FORMATION OF “ENGINEERED” AIR VOID STRUCTURE IN MORTARS AND FIBER REINFORCED CEMENTITIOUS COMPOSITES

The air void structure created with polymethyl hydrogen siloxane (PMHS) based admixtures was studied in this section to tune this approach to the best properties. This was performed by testing several different PMHS-based admixtures in fiber reinforced composites and comparing with a commercially available air entraining admixture. Selective fiber reinforced composites were also compared with mortars to determine the additional quantity of entrapped air voids generated through the use of fiber reinforcement. Here, the use air void structure of samples with tributyl phosphate (intended to eliminate any entrapped air voids) were also analyzed. These tests were performed using both Rapid Air and flatbed scanning techniques as discussed in the Evaluation of HPC/UHPC section. Additionally, void size distributions were provided based on flatbed scanning testing.

7.1 AIR VOID STRUCTURE OF FIBER REINFORCED CEMENTITIOUS COMPOSITES

To test the air void structure created by polymethyl hydrogen siloxane (PMHS) based admixtures, several high performance fiber reinforced cementitious composites were created. The fresh properties as well as the hardened properties of these materials were analyzed to see if there is any correlation with air void structure and the mechanical response present as well as to determine which samples provide the best properties to resist against freezing and thawing. To test these, several different PMHS admixtures were created and compared with a commercially available air entraining admixture and a reference (no air entraining admixture). All of the these mixes used Type I portland cement (LF), a S/CM of 0.5, a W/CM of 0.30, 2% (by volume) of PVA RECS 15 x 12 mm fibers,
and 0.125% SP (as solid content, by weight) of the cementitious material. Each of the PMHS-based admixtures were applied at a single dose defined as an admixture containing 0.25 g of PMHS for 1 L of cement-based composite. Each PMHS-based admixture was composed of 25% PMHS along with 4.4% PVA emulsifier, and different micro or nano-particles. These particles were applied at a total quantity of 0.5% of the PMHS-based admixture and consisted of metakaolin, silica fume, nano-silica, or a combination of these. The experimental matrix for this study is reported in Table 19. The admixtures were also created in such a way to provide the products with different properties (Figure 67). Here, the simple mix concept represents an admixture with no micro or nano-particles. The shell mix concept represents an air void bubble that is formed with the micro or nano-particles on the exterior of the bubble, and the core concept represents an air void bubble that has the particles on the interior surface of the bubble. The commercially available air entraining admixture was used at a dosage of 0.005% which was intended to provide similar air content. The air void properties were also determined using two different techniques. The first is conventional ASTM C457 Procedure A Rapid Air method, while the second used the flatbed scanning technique. Additionally, the fresh and early age properties of the admixtures were analyzed to quantify the effect of the PMHS-based admixtures as the bubble formation is achieved in a different way than as with conventional air entraining admixtures.
Water (dispersion medium) | PVA as film (surfactant) | Siloxane drops (dispersed phase) | Water (dispersion medium) | PVA as film (surfactant) | Siloxane drops (dispersed phase) | Water (dispersion medium) | PVA as film (surfactant) | Siloxane drops (dispersed phase) + particles

Shell Theory Core Theory Simple Theory

Figure 67: Concept of simple, shell, and core emulsion [58]

Table 19: Experimental Setup for Investigation of High Performance Fiber Reinforced Cementitious Composites with Different Air Void Structures

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Admixture Type</th>
<th>Quantity of particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-REF</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2-AEMA</td>
<td>Commercial AE</td>
<td>0.005% of cementitious weight</td>
</tr>
<tr>
<td>3-ECSF</td>
<td>Core</td>
<td>0.5% of silica fume</td>
</tr>
<tr>
<td>4-ECMK</td>
<td>Core</td>
<td>0.5% of metakaolin</td>
</tr>
<tr>
<td>5-ECNS</td>
<td>Core</td>
<td>0.5% of nano-silica</td>
</tr>
<tr>
<td>6-ECR</td>
<td>Simple</td>
<td>None</td>
</tr>
<tr>
<td>7-ESSF</td>
<td>Shell</td>
<td>0.5% of silica fume</td>
</tr>
<tr>
<td>8-ESMK</td>
<td>Shell</td>
<td>0.5% of metakaolin</td>
</tr>
<tr>
<td>9-ESNS</td>
<td>Shell</td>
<td>0.5% of nano-silica</td>
</tr>
<tr>
<td>10-ECNMK</td>
<td>Core</td>
<td>0.1% of nano-silica, 0.4% of metakaolin</td>
</tr>
</tbody>
</table>

The flow of the fiber reinforced composites with different air entraining admixtures is reported in Figure 68. It is observed that the sample with the conventional air entraining admixture provided the best properties. This is because, upon mixing, the formation of air bubbles occurs immediately with conventional air entraining admixtures, while the formation of the air bubbles with the PMHS-based admixtures typically occurs several hours after mixing. This additional air content that was present upon testing of the flow,
provided for a greater workability. In general, the flow of PMHS-based mortars was lower than the reference and mortars with conventional air entraining admixture. One would expect these values to be similar to the reference (as no entrained air is present at the time); however, the results were still similar.

![Flow, %](image)

*Figure 68: Flow of high performance fiber reinforced cementitious composites with PMHS-based admixtures (vs. reference and air entrained samples)*

The fresh density of these fiber reinforced composites is reported in *Figure 69*. The fresh density of the reference sample is the highest, which is to be expected because there is no intentionally added air within the system. The sample with the commercially available air entraining admixture provided the lowest fresh density which also was expected. This air entraining admixture is intended to produce the air bubbles during the mixing, therefore reducing the density. Comparing this to the samples with PMHS-based admixtures demonstrates that the conventional air entraining admixture produces the air bubbles immediately whereas the PMHS-based admixtures generate the air bubbles at later times. This is especially evident when the hardened air contents are the same. Here, it was
expected that the PMHS reacts with lime from the cement paste releasing the hydrogen and, in turn, forming the required air void structure. This demonstrates that at the time the flow was tested (typically within 5 to 10 minutes of mixing) a few of the air voids have formed in PMHS mixtures, but many have yet to be formed. This is evident as the total hardened air content of the conventional air entrained mixtures and many of the PMHS-based admixtures were similar. Of the PMHS-based admixtures, the admixture incorporating silica fume for a core type emulsion provided the highest density indicating the smallest amount of bubbles have formed while the core emulsion with both metakaolin and nano-silica provided the lowest density. It should be noted that the core admixture using both nano-silica and metakaolin displayed lower hardened air content; therefore a comparison on the quantity of air voids that have formed is difficult. Of the other PMHS-based admixtures, it appears as though the shell emulsions typically provide a lower density than the core type emulsions.

Figure 69: Fresh density of high performance fiber reinforced cementitious composites with PMHS-based admixtures.
The analysis of the heat flow of the fiber reinforced composites with different air entraining admixtures reveals that the PMHS-based admixtures cause a delay in hydration (Figure 70 and Figure 71). This delay is rather consistent between different types of PMHS-based admixtures. The use of conventional air entraining admixtures displays little difference in hydration compared to the reference samples. In general, the core type emulsions display a slightly lower peak heat flow than the reference with the exception of the core emulsion with silica fume and core emulsion with metakaolin and nano-silica combined. The shell emulsions typically display a slightly higher peak heat flow. This may be due to the micro and nano-particles present on the exterior of the air void bubbles. In this case, the particles may be migrating to the cement paste and acting as seeds that promote the formation of hydration products. This is also the case when the nano-silica is used as shell emulsion where both an increase in peak heat flow and an acceleration of hydration is detected. These are both indicative of the seeding action and the formation of “additional” hydration products. Although this may be beneficial in some cases, the intent of the nano and micro particles is to provide a certain degree of surface roughness on the surface of air voids. If hydration products are formed in the bulk, the surface roughness can be compromised reducing the hydrophobicity of the surface. If this indeed is occurring, the use of core emulsions may be more beneficial to the hydrophobicity of the air voids. For the core emulsions that displayed a higher peak heat flow, the droplet sizes of the emulsion were smaller resulting in smaller air voids and thus less interaction with the bulk of cement paste and higher peak heat flows.
The compressive strength of the samples with PMHS-based materials is promising as in many cases the compressive strength of these samples is higher than the compressive strength of the reference and conventional air entraining admixtures. However, the early
The compressive strength of the samples with PMHS-based admixtures is typically lower. This is consistent with the heat flow curves as a delay in hydration is present. This is especially evident in the samples that used the shell concept to create the admixtures. These compressive strength values are then improved at later ages. As known for the use of conventional air-entraining admixtures, the compressive strength of air entrained materials is reduced when compared to the reference, non-air entrained sample. The reason for this is because the air void bubbles that are typically entrained are larger and not as well distributed. This results in higher stress concentrations and thus the lower compressive strength. The PMHS-based admixtures are intended to provide smaller, better dispersed air voids which upon loading result in lower levels of stress. Due to this, it may be expected that some of these samples result in similar compressive strength values as the reference; however, in some cases the compressive strength was actually improved. The reason for this may be because of the compaction of the material due to gas release and also that micro or nano-particles from the emulsions promote the formation of a denser CSH around the air voids, ultimately strengthening the composites. This may be evident as the two samples that displayed the highest compressive strength, the core sample with nano-silica and metakaolin and the core sample with silica fume, also displayed a high peak heat flow which may indicate the particles are acting as a seed to form CSH. However, the likelihood of the seeding action is low because small quantities are used in proportion to the cementitious materials. Typically, silica fume or nano-silica can be effective at even small quantities. Of the PMHS-based admixtures, the ones using the shell concept typically have lower compressive strengths. This may be an indication that the shell emulsions are
producing larger air voids which would have more of an impact on reduction in compressive strength.

**Compressive Strength, MPa**

![Compressive Strength Graph](image)

*Figure 72: Compressive strength of fiber reinforced cementitious composites with PMHS-based admixtures*

The area under the flexural stress vs. strain curves is presented in *Figure 73* while the full stress-strain curves for each sample can be seen in Appendix C. It can be seen that in many cases there is quite a significant deviation among the flexural curves. In many cases, the PMHS-based admixtures provided a better flexural response compared with the reference. Additionally, many of these PMHS-based admixtures provided a better response than the conventional air-entrained sample. Few mixtures, such as FRC with core emulsion with nano-silica and the simple emulsions appeared to have less energy dissipation. There also appears to be no clear indication of strength improvement after 28-day age. This may be due to the large deviations in results. When analyzing the stress-strain curves (Appendix C), it can be concluded that the reference sample provides a relatively high flexural strain and flexural stress. The air-entrained FRC provided similar results with slightly lower peak
stress and reduced ductility. This may be due to the presence of larger air voids resulting in higher stress concentrations and thus lower ductility. The sample with a core emulsion with silica fume resulted in similar initial crack stress, but provided significant post-first crack behavior with comparable peak stresses and higher ductility. Such behavior was also observed in the sample with a core emulsion combined with metakaolin and nano-silica although it had a slightly lower peak stress. In general, the samples that used shell and simple type emulsions did not provide a significant ductility with the exception of a single specimen (7-ESSF) which resulted in significant deviation. This may be an indication that the core emulsions provide an air void structure that results in superior flexural behavior. Of these core emulsions, the use of silica fume or metakaolin as micro particles provided a good combination of peak stress and ductility, while the sample with both metakaolin and nano-silica provided the best ductility with a lower peak stress. Conversely, the core sample with only nano-silica resulted in a similar behavior as many of the shell emulsions. These results indicate that the emulsion with a combination of micro and nano-particles (which was previously seen to provide a better distribution of droplet sizes) is capable of providing better air void distributions resulting in higher ductility of FRC.
Figure 73: The area under the flexural stress-strain curve for fiber reinforced cementitious composites with PMHS-based admixtures

The hardened air content using both Rapid Air techniques and flatbed scanner is reported in Figure 74. Here it can be observed that the reference sample provides the lowest hardened air content (which was expected because there is no intentionally placed air voids within the material). The conventional air entraining admixture provided consistent air contents as many of the PMHS-based admixtures. Of these PMHS-based admixtures the simple concept provides lower air content indicating that the addition of micro or nano-particles results in higher volume of air voids. The use of admixtures based on the core concept typically have provided consistent values when analyzed using the Rapid Air technique; however, had higher variability when tested using the flatbed scanner method. It may be assumed that the proposed flatbed scanner method (based on 2-D image analysis vs. the 1-D method used by Rapid Air) is more accurate and may give a better depiction of the true air void structure. The Rapid Air technique uses chord intersects as per ASTM C457 while the flatbed scanner was adopted to use the entire 2-D data of the
cross-section. Statistically, the sample should be good enough to represent the whole, however since the Rapid Air machine only measures chord lengths of air voids, the chords that are being measured provide lesser information to estimate the 3D air void structure. The proposed flatbed scanner approach considers the circularity of the voids when considering to count it as a void. Knowing this and analyzing the results based on the flatbed scanner technique, there tends to be a good deal of variance between different PMHS-based admixtures, especially in the case of the shell emulsions where the ones with silica fume and nano-silica displayed around twice as much air content as the one with metakaolin. The opposite trend was observed in the core emulsions where the one with metakaolin had higher air content than the ones with silica fume or nano-silica. In general, the core emulsions tended to provide more consistent results, again demonstrating their excellent compatibility with cementitious composites.

![Air, %](image)

**Figure 74:** Hardened air content of fiber reinforced cementitious composites using Rapid Air and flatbed scanner techniques

The following figures analyze the air void properties in terms of quantity and size, which are ultimately used to calculate the spacing factor of the voids. The specific surface
(Figure 75), average chord length (Figure 76), void frequency (Figure 77), and spacing factor (Figure 78) are presented here. The spacing factor was calculated using both the Rapid Air and flatbed scanner techniques, however not all of the values represented below are required for calculating the spacing factor via the flatbed scanner approach. Here, the deviations between the values determined using the Rapid Air technique and flatbed scanner technique are lower. The specific surface of the samples is an indication of the surface area of the voids to volume of the voids. A larger specific surface will represent a sample with larger amount of voids. It can be observed that in most cases the PMHS-based admixtures had a higher specific surface. Even though the conventional air entraining admixture specimen had a higher air content, other samples still displayed a higher specific surface. Of these samples, the core emulsion with silica fume and the core emulsion with nano-silica and metakaolin displayed promising values. The latter sample is especially impressive considering it had a lower air content compared with other PMHS-based admixtures. When considering the size of the air voids, results from average chord length and specific surface can be monitored. Again, both the core emulsion with silica fume and the core emulsion with nano-silica and metakaolin displayed good results. Both of these samples displayed the lowest average chord length indicating the presence of smaller air voids and both displayed exceptional void frequency indicating larger quantities of voids. Again, the ability of the admixture with metakaolin and nano-silica to provide a high void frequency with smaller air content is beneficial. A cementitious composite is often tested solely for air content to determine if it is adequate to resist against freezing and thawing. However, a better indication of its ability to resist against freezing and thawing is the spacing factor. Therefore, even though the core emulsion with both metakaolin and silica
fume resulted in lower air content, the spacing factor is comparable to other samples. The two samples with metakaolin using as a shell and core emulsion proved to have higher spacing factors than those obtained with conventional air entraining admixtures. Samples with silica fume or nano-silica displayed lower spacing factors indicating that these may be beneficial to provide a better freeze-thaw resistance. Even though both the core type emulsions and shell emulsions with metakaolin did not display the best performance, the addition of small amounts of nano-silica in combination with metakaolin (when used in a core emulsion) displayed similar performance to the samples with silica fume or nano-silica. Furthermore, this admixture is intended to form the voids where micro and nano-particles cover the interior surface. In this case, the hierarchical surface roughness of this admixture is assumed to provide a better hydrophobicity for the void compared to the other core admixtures. These results indicate that the use of PMHS-based admixtures can provide exceptional air void properties for cementitious composites even at smaller air contents.

**Figure 75: Specific surface of fiber reinforced cementitious composites**
Figure 76: Average chord length of fiber reinforced cementitious composites

Figure 77: Void frequency of fiber reinforced cementitious composites
Figure 78: Spacing factor of fiber reinforced cementitious composites

7.2 AIR VOID STRUCTURE OF MORTARS

The air void properties of three fiber reinforced cementitious composites (FRC) were compared against three mortars (M) in this study. Each set (mortar or fiber reinforced composite) contained a reference sample and a sample with a PMHS-based emulsion and tributyl phosphate (TBP). Additionally, the set of FRC’s had a sample with only a PMHS-based admixture while the set of mortars had a sample with only TBP. The optimized PMHS-based emulsion that incorporated both nano-silica (NS) and metakaolin (MK) was used. The TBP was used at a quantity of 22.5% of the solid SP and was intended to reduce the quantity of entrapped air voids or reduce the quantity of voids formed by the SP. By testing samples with TBP, conclusions regarding the effects of unwanted voids and “pure” effects of the engineered air void structure can be drafted. Furthermore, testing the differences in air void properties between the fiber reinforced composites and mortars can help to provide an indication of the contribution of additional entrapped air formed by the fibers. It is also important to ensure that TBP is not eliminating the air altering engineered
air voids from air-entraining and PMHS-based admixtures. All of the samples were based on the same mix proportions with the only exception being the difference in the experimental design as seen in Table 20. The mix proportions are also the same as the previous study.

Table 20: Experimental Matrix for Fiber Reinforced Cementitious Composites and Mortars

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Fibers, %</th>
<th>Emulsion</th>
<th>TBP, % of solid SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRC</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>FRC-E</td>
<td>2</td>
<td>MK+NS</td>
<td>0</td>
</tr>
<tr>
<td>FRC-E-TBP</td>
<td>2</td>
<td>MK+NS</td>
<td>22.5</td>
</tr>
<tr>
<td>M</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M-TBP</td>
<td>0</td>
<td>0</td>
<td>22.5</td>
</tr>
<tr>
<td>M-E-TBP</td>
<td>0</td>
<td>MK+NS</td>
<td>22.5</td>
</tr>
</tbody>
</table>

The flow of fresh mixtures are reported in Figure 79. It is clear that the flow of the fiber reinforced samples is significantly reduced vs. the flow of the corresponding mortars. This is expected as the high aspect ratio of the fibers that are used typically results in less workability. When considering the fiber reinforced samples, all provided a similar flow. However, the mortar samples displayed significant differences between the reference, TBP, and TBP with emulsions. The reference mortar sample provided the lowest flow followed by the TBP and then the sample with TBP and emulsion. It would be expected that the TBP would reduce the flow because it was intended to eliminate the air voids which would reduce the workability, however, this was not the case. The mortar sample with both TBP and a PMHS-based emulsion displayed the highest flow. Here, the addition of the emulsion may help to provide a slight increase in workability because of the hydrophobic properties of the admixture. Only small-size air voids may have formed to this point which would slightly increase the flow, but it is assumed that bulk of the voids forms several hours (2-
4) later. The hydrophobic admixtures in the mix can act as a retarder complementing the effect of water reducing admixtures and resulting in the higher flow. This hypothesis is also consistent with the delayed hydration as seen in the previous study.

The density of the fiber reinforced cementitious composites along with mortars that were used for air void testing are reported in Figure 80. The mortar with TBP provides the highest density (as would be expected) because of elimination of entrapped air voids. Interestingly, the plain mortar sample provided the lowest density. It may be assumed that the fiber reinforced composites would have reduced density; however, this was not the case. The reason for this may be due to high workability and the use of SP that would have been beneficial for the dispersion of fibers. Of the fiber reinforced composites, the reference had the highest density, followed by the FRC with a PMHS-based emulsion and TBP, and, finally, the FRC with PMHS based admixture alone. These results were expected as some additional void space is produced by hydrophobic emulsions and some of the entrapped air voids may have been eliminated from the TBP based mixture.

Figure 79: Flow of FRC and mortars samples used for air void analysis
The released heat flow of FRC samples had similar results as previously reported for mixtures with PMHS-based admixtures resulting in a delay of hydration (Figure 81). This is especially evident in the case of the mortar samples. The TBP tends to slightly delay the hydration as well as providing a slightly lower peak of heat release. This could be an indication that the TBP may have a negative effect on the cement hydration process.

In general, the hydration of mortars is accelerated as compared to the FRC. The additional entrapped air voids formed by the fibers may reduce the contact area that cement particles have with one another and thus be the reason for the delayed hydration. Despite the delayed hydration due to the PMHS-based admixtures, in the case of the FRC, the peak heat flow was actually increased. Later, the voids would form by the PMHS-based admixtures and result in a higher hardened air content.
It was observed that the mortar samples typically have higher compressive strength values than the FRC (Figure 81). This was to be expected as additional entrapped air voids would form due to the fibers, thus resulting in a lower compressive strength. The PMHS-based admixtures did not cause the reduction of compressive strength when FRC are considered; however, when emulsions were combined with TBP in the mortars, a significant reduction in compressive strength was observed. The TBP did not have much of an effect on compressive strength when used alone in the mortar samples, but when combined with a PMHS-based emulsion in the FRC samples an increase in strength was observed indicating the positive contribution of TBP eliminating some of the undesired entrapped air voids. Similar to previous observations, the early age strength of the samples with PMHS-based admixtures was lower.
The area under the flexural curves for both mortars and FRC that were used for air void analysis are presented in Figure 83 while the corresponding stress-strain curves are available in Appendix C. Clearly, the energy dissipation of mortars is significantly lower because there are no fibers to provide any post-first crack flexural response. This means that when the first crack appears, the sample fails. Of the FRC samples, again, there tends to be a significant deviation between the results. Both FRC samples with a PMHS-based emulsions provided lower peak stress, but higher ductility as seen in Appendix C, which may not be visible from the results presented in Figure 83. This supports the hypothesis that the emulsions are capable of providing a more ductile composite. There also seems to be no significant difference between the FRC samples with TBP indicating that the use of this admixture may not be beneficial. When comparing the stress-strain curves of the mortar samples, no significant differences can be detected. In this case, the samples with TBP were able to provide a slightly higher first crack stress which may be a result of the reduction in entrapped air voids. However, the average void size of this sample is higher
(as reported in Figure 87), indicating a larger overall number of voids, but the maximum size of the voids may be reduced which would provide a lesser stress concentration resulting in the higher first crack stress.

The hardened air content of the FRC and mortars is reported in Figure 84. The reference samples had the lowest air content which was expected because there were no intentionally placed air. The sample with TBP used in a mortar actually displayed a higher hardened air content than the reference mortar. In the sample with both TBP and a PMHS-based emulsion, a higher air content was especially evident when using the Rapid Air technique, whereas only a slightly higher air content was reported when the flatbed scanner technique was used. It would be expected that TBP would eliminate the excess air voids formed by the SP or entrapped air voids, however this was not the case. The differences between the flatbed scanner and Rapid Air techniques with this sample may be that the Rapid Air method is counting air voids that are irregularly shaped. One hypothesis may
be that as the TBP is eliminating the voids, it may not be able to remove these completely leaving “elongated” voids. Since the circularity of the voids in the flatbed scanner technique is a parameter, it may not be capturing the same set of voids. In the case of the FRC, the TBP was able to reduce the air content in the samples with a PMHS-based emulsion; however, the total air content was still higher than that observed for the reference FRC. It was visually observed that large air voids were present near the top (edge near the top surface during the first 24 hours of curing) of the mortar samples with TBP. This may be an indication that the TBP is attempting to eliminate some of the voids, but this air is becoming trapped near the surface of the sample and forming even larger voids. This result, along with the increased air content detected in the mortar samples demonstrates that the use of TBP may not be beneficial. The reference FRC had around a 50% higher air content than the reference mortar. This demonstrates that the larger amount of entrapped air voids is produced due to the addition of fibers.

![Figure 84: Hardened air content of FRC and mortar samples](image)

The air void properties defined by the specific surface (Figure 85), spacing factor (Figure 86), average chord length (Figure 87), and void frequency (Figure 88) are reported
The spacing factor of the FRC samples with PMHS-based emulsions had the lowest values indicating that these can provide the best resistance against freezing and thawing. There tends to be no difference in spacing factor between the FRC with PMHS-based emulsions and the same composition with the addition of TBP. However, the sample without TBP resulted in a higher hardened air content, but the same spacing factor indicating there are more voids that have a smaller size. This finding is supported by the average chord length results. Interestingly, the average chord length of the mortar samples was smaller than that observed for the FRC. It may often be assumed that the entrapped air voids created by the addition of fibers are larger, but these results indicate otherwise. Again, the results of the air void properties of the mortars with TBP had unexpected outcomes as high spacing factors and large voids (indicated by the average chord length) were detected. This may lead to the conclusion that the use of TBP in mortars may not be applicable; however, when used in FRC, these were effective to reduce the size of entrapped air voids. Despite this, the TBP effect may not be significant enough to justify the use of this admixture in all fiber reinforced composites.

Figure 85: Specific surface of FRC and mortar samples
Figure 86: Spacing factor of FRC and mortar samples

Figure 87: Average chord length of FRC and mortar samples

Figure 88: Void frequency of FRC and mortar samples
An additional benefit of using flatbed scanning techniques for air void analysis is that the void size distributions can be observed (Figure 89). Here, the diameters of void sizes are presented for FRC and mortar samples. Most of the voids in the samples are not spherical (circular in the 2-dimensional scan); therefore, the area of each void was determined and an equivalent circle of the same area was calculated with their diameters presented below. Surprisingly, the mortar samples with TBP had the largest voids. This is because it was visually observed that large voids formed near the top of the mortar samples with TBP. These large voids may be the result of the TBP attempting to eliminate some voids; however, when the air from these voids tries to escape, it becomes trapped. Larger voids were also observed in the FRC with TBP as well, but not to the same extent. The maximum void size between the reference FRC and reference mortar are the same indicating that even though there may be additional entrapped air void due to the addition of fibers, the maximum void size is the same. This is important to note, because the largest voids will be provide higher degrees of stress concentrations and therefore be the critical factor for first crack flexural or tensile stresses. The addition of a PMHS-based admixture to FRC results in a larger maximum size void; however, the overall distribution of voids tends to be more gap graded with higher quantities of smaller voids. This may be the reason for the lower first crack stresses but improved flexural performance as the smaller voids will help to prolong the multi-cracking behavior after the first few cracks have formed.
Figure 89: Void size distribution of FRC and mortar samples based on flatbed scanner measurements
8. FIBER REINFORCED ULTRA-HIGH PERFORMANCE CEMENTITIOUS COMPOSITES

The mechanical performance of ultra-high performance cementitious composites was evaluated using the optimal cementitious matrix reported for previous studies using different types of fiber reinforcement. From previous sections, the minimum compressive strength required for ultra-high performance concrete of 150 MPa was observed. However, the addition of fibers can result in the formation of additional entrapped air voids producing a less dense cementitious matrix and thus a weaker cementitious material. Here, it is important to maintain a high workability so that the fiber reinforced composite can be easily compacted to the state with minimal entrapped air voids. In this study, several different types of fibers were considered at 2% by volume. These fibers include two types of PVA, steel, basalt, and polyethylene (PE). The experimental matrix for these mixtures is reported in Table 21 along with the dimensions of the fibers. Other physical properties of fibers were reported in the Materials and Methods section. It should be noted that a second type of steel fiber (29 mm long by 0.35 mm in diameter) was attempted to be used but the tested mortar displayed an extreme segregation from the fibers as observed in Figure 90. The first type of steel fibers also displayed some segregation, but not to the same extent. Due to such segregation, the results from steel fiber reinforced composites may demonstrate some variability, especially, the results from flow tests. The cementitious matrix used for this study had a W/CM of 0.173, a S/CM of 0.50, a SP dosage of 0.10 % of the cementitious material (and additional SP was used for the dispersion of nano-fibers), a silica fume content of 5% (as a replacement of oil well cement), and a Al₂O₃ nano-fiber content of 0.5% as this was determined to be the optimal mixture from previous work. It
should be noted that in previous studies, 5% silica fume was found to have a superior 28-day compressive strength compared with only 1%, while 90-day compressive strength values were similar. Due to this, 5% silica fume was used in this study to provide better compressive strength at 28 days.

Table 21: Fibers Used for Mechanical Testing of Ultra-High Performance Cementitious Composites

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Fiber Type</th>
<th>Length, mm</th>
<th>Diameter, mm</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 mm PVA</td>
<td>Polyvinyl alcohol</td>
<td>12</td>
<td>0.04</td>
<td>300</td>
</tr>
<tr>
<td>8 mm PVA</td>
<td>Polyvinyl alcohol</td>
<td>8</td>
<td>0.04</td>
<td>200</td>
</tr>
<tr>
<td>Steel</td>
<td>Hooked End Steel</td>
<td>32*</td>
<td>0.4</td>
<td>80*</td>
</tr>
<tr>
<td>Basalt</td>
<td>Basalt</td>
<td>12</td>
<td>0.016</td>
<td>750</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
<td>12</td>
<td>0.012-0.021</td>
<td>1000-570</td>
</tr>
</tbody>
</table>

*The measured length of the hooked end steel fibers was 32 mm (from end to end) with a hook length of 4 mm

Figure 90: Segregation of mortar from clump formed by steel fibers

The flow of the fiber reinforced composites can be seen in Figure 91. All of the fibers other than steel remained within a close band between 31% and 43%. The steel fibers provided significantly higher flow of around 100%. However, these results for steel FRC may be misleading. The aforementioned smaller-size steel fibers resulted in
significant segregation. The larger steel fibers also resulted in some segregation, but not to the same extent as the smaller ones. This would mean that the fibers dispersion throughout the composite would not be uniform and, therefore, not be expected to provide adequate performance. Of the other fibers, the 8 mm PVA fibers provided the best flow. This is most likely due to the shorter length of the fibers. Fibers that are longer and have a higher aspect ratio are more likely to ball together which can significantly reduce the flow or workability. When comparing fibers that are 12 mm long, both PVA and PE fiber reinforced composites displayed similar behavior while basalt fibers displayed slightly lower flows.

![Flow, %](image)

*Figure 91: Flow of fiber reinforced ultra-high performance cementitious composite mixtures*

The compressive strength of the fiber reinforced composites is reported in *Figure 92*. The 7-day and 28-day strength differ for different types of fibers. The lowest compressive strength was found for 8 mm PVA fibers. One would think that since these fibers are the shortest, they would be less likely to ball together which would result in fewer
entrapped air voids and thus in a greater compressive strength. Conversely, because the fibers are shorter and applied at a constant volume, there are more individual fibers within the mix which could also lead to the formation of additional entrapped air voids or more porous space around the fibers. All other fiber types provided a compressive strength between 156 to 166 MPa which is sufficient to qualify for ultra-high performance. However, when comparing the compressive strength to the corresponding values of mortars, the FRC test results are relatively lower. Based on the previous results, a similar cementitious matrix should provide a 28-day compressive strength of around 185 MPa. In this way, the addition of the fibers tends to reduce the compressive strength by around 10%. This can be explained by heterogeneity including the additional entrapped air voids formed by the fibers.

![Compressive Strength, MPa](image)

**Figure 92: Compressive strength of fiber reinforced ultra-high performance cementitious composites**

The 7-day and 28-day flexural results are reported in *Figure 93* and *Figure 94*, respectively. Based on these results it is clear that the polyethylene fibers provide the best
performance. These not only provide the best flexural strength, but maintain the best load carrying ability upon initial cracking. These fibers also provide an excellent multi-cracking behavior as it was visually observed and recorded on the flexural curves with drops and recoveries in flexural stress. The 28-day flexural strength of the polyethylene fibers was significantly higher than the 7-day flexural strength while at the same time, there was no reduction in flexural strain between the ages. This is a unique feature attributed to PE fibers as higher strength composites typically become more brittle, whereas in this case similar ductility is observed. The use of other types of fibers also have promising flexural behavior, however, not to the same extent as the polyethylene fibers. Despite possessing reduced ductility, most fibers were able to withstand increased loads after first crack. When comparing the two different types of PVA fibers, there was little difference in overall performance. At 7 days, the ultimate flexural strength and modulus of the 12 mm PVA fiber reinforced composites were slightly higher. At 28 days, the ultimate flexural strength, modulus, and flexural strain were comparable. The basalt fibers provided similar behavior as the 8 mm PVA fibers at 7 days. These results (7-day 8 mm PVA, 7-day 12 mm PVA, 7-day basalt, 28-day 8 mm PVA, and 28-day 12 mm PVA) provide some improvement for post first crack behavior, but it is clear from the flexural curves that only a few cracks have formed. This is because the high strength cementitious matrix is capable of withstanding higher tensile loads which results in the formation of fewer cracks. Additionally, the stresses that are carried by the fibers across the cracks that have formed are high enough that fiber rupture occurs more suddenly. At 28-day age, these same FRC display no improved flexural strength, whereas the steel any polyethylene based FRC had improved strength. Contrary to the 7-day results, the 28-day flexural behavior of the basalt fibers
displayed no post-first crack response as these fibers are very brittle and rupture at the higher stress levels achieved at 28 days. The 7-day behavior of the steel FRC had the lowest first crack strength, and also did not provide the increased load carrying ability after this first crack. However, the ductility of the material is respectable, even though the flexural strength is low. At 28 days, the first crack flexural strength was comparable with that demonstrated by other fibers, but the crack behavior is significantly improved providing higher ultimate flexural strength and strain-hardening and multi-cracking behavior. After the ultimate flexural stress was achieved in the steel fibers, decent ductility was still observed despite the lower load carrying capabilities. These steel FRC results may be somewhat misleading at it was visually observed that the crack sizes were large and significant spalling occurred in the flexural region between the fibers. Here, the stiffness of the steel fibers contributed to the flexural behavior as the larger cracks formed. Another inconsistency with the use of the steel fibers is that they are longer than the depth of the samples being produced and tested; therefore, they would then be aligned in a 2-D preferable pattern and so to withstand higher stresses. The other types of fibers may also be likely to align due to the depth of the samples, however because of their shorter length and higher aspect ratio, these would be more likely to curve and form a more random distribution.
Figure 93: The 7-day flexural behavior of UHPC with different types of fibers

28-Day Flexural Stress, MPa

Figure 94: The 28-day flexural behavior of UHPC with different types of fibers
9. MECHANICAL AND DURABILITY PROPERTIES OF FIBER REINFORCED ULTRA-HIGH PERFORMANCE CEMENTITIOUS COMPOSITES WITH CONTROLLED AIR VOID STRUCTURES

Mechanical and durability properties were performed on samples that incorporate findings from previous sections. These mixtures were intended to determine the differences in mechanical and durability properties due to the inclusion of Al₂O₃ nano-fibers, PMHS-based admixtures, and a combination of the two. Additionally, these parameters were tested using two different types of fibers, 8 mm PVA fibers and PE fibers (both used at 2% by volume). These two types of fibers were considered because it is intended that the addition of PMHS-based admixtures will provide improved ductility; however, it was unknown if this same improvement can be seen in FRC samples that utilize fibers that already provide superior ductility (PE fibers). Additionally, the PMHS-based admixtures are capable of providing increased ductility in high performance composites, but was unknown if they can increase the ductility in ultra-high performance composites (with the addition of Al₂O₃ nano-fibers). To test these concepts, compressive strength, flexural behavior, and surface resistivity tests were performed at 7 and 28 days while tension tests were performed on select samples at 28 days. The samples used the optimal mortar mix design determined in the previous sections which include a W/CM of 0.173, S/CM of 0.5, and a SP dosage of 0.10 (by weight of cementitious material). For samples that included the PMHS-based admixture, the admixture was included at a dosage of 0.25 g of PMHS per liter of mix. The composition of this admixture is the same as the core emulsion with metakaolin and nano-silica as discussed in the previous sections. All samples also included a silica fume content of 1% replacement of oil well cement. It was
previously stated that the addition of 5% silica fume increases the 28-day strength, but shows comparable strength at 90 days. Here, it may be assumed that the 1% of silica fume will have slightly lower 28-day strength, but should provide higher strength at 90 days. For the samples that used Al$_2$O$_3$ nano-fibers, a dosage of 0.5% (by weight of the cementitious material) was used. Again, the samples that included the nano-fibers had additional SP for the dispersion of the slurry. A summary of the experimental matrix is reported in Table 22.

Table 22: Experimental Matrix for FRC with Al$_2$O$_3$ Nano-Fibers and PMHS-Based Admixtures

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>SF, %</th>
<th>Fibers</th>
<th>PMHS, g/L</th>
<th>Al$_2$O$_3$ nano-fibers, % of CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA-REF</td>
<td>1</td>
<td>2% PVA</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PVA-Al$_2$O$_3$</td>
<td>1</td>
<td>2% PVA</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>PVA-PMHS</td>
<td>1</td>
<td>2% PVA</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>PVA-PMHS+Al$_2$O$_3$</td>
<td>1</td>
<td>2% PVA</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>PE-REF</td>
<td>1</td>
<td>2% PE</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PE-Al$_2$O$_3$</td>
<td>1</td>
<td>2% PE</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>PE-PMHS</td>
<td>1</td>
<td>2% PE</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>PE-PMHS+Al$_2$O$_3$</td>
<td>1</td>
<td>2% PE</td>
<td>0.25</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The fresh flow of these samples was also tested and is reported in Figure 95. These results demonstrate that with the addition of nano-fibers, the flow is increased. This can be attributed to the additional SP used for the dispersion of the nano-fibers allowing for additional workability. It was also observed that these samples with nano-fibers provided significantly easier compaction, at a much greater level than recorded from flow readings. The use of PMHS-based admixtures typically did not result in any differences in flow. In general, the PVA fibers resulted in slightly higher flow than the PE fibers. This may be attributed to the higher aspect ratio and lower specific gravity of the PE fibers resulting in
higher numbers of fibers to obtain the same volume. This higher number of fibers would thus result in lower workability and lower flow readings.

**Figure 95**: Fresh flow of FRC with PMHS-based admixtures and Al₂O₃ nano-fibers

The compressive strength of the samples tested within this study is presented in **Figure 96**. The samples that performed the best tended to be the samples with Al₂O₃ nano-fibers. This is consistent with previous studies as it was determined that these nano-fibers are able to increase compressive strength. In general, the FRC with PE fibers tended to provide slightly higher compressive strengths than those with PVA fibers. This may be a result of the PE fibers restricting micro-cracks from forming and thus providing additional load carrying ability. The samples with PMHS-based admixtures provided desired results when used with PVA fibers (as the compressive strength of the sample with a PMHS-based admixture provided the same compressive strength as the reference sample); however, provided a decrease in strength when used with PE fibers. It was intended that this admixture would produce small air voids that would results in minimal stress.
concentrations and therefore not reduce the compressive strength. The sample with a PMHS-based admixture used in the PE fibers still provides comparable strength to the same sample used with PVA fibers. The reference FRC used with PE fibers provided exceptional compressive strength; therefore, one hypothesis may be that the PE fibers are resulting in a fewer entrapped air voids and thus the air voids generated by the PMHS-based admixtures are more likely to have a more significant impact on the compressive strength, whereas in the case of the PVA fibers, the compressive strength is controlled by the entrapped air voids. The samples with a combination of PMHS-based admixtures and nano-fibers tended to provide a significant decrease in compressive strength, especially when used with PVA fibers. This may be due to the combination of delayed hydration time due to the hydrophobic admixtures along with the delay in hydration due to the additional SP used in the nano-fiber slurry. In this case, the delay could be significant enough to result in detrimental effects and reduce the overall hydration of the composite. Again, it is clear that the addition of Al₂O₃ nano-fibers is capable of providing improved compressive strength with FRC. However, the compressive strength observed within this study is slightly lower than the 150 MPa required for ultra-high performance concrete. In previous studies, it was determined that the use of 0.5% nano-fibers with only 1% silica fume can result in compressive strength of around 175 MPa, therefore the addition of PE fibers resulted in a 15% decrease in compressive strength. In the previous study where FRC’s were created with 0.5% nano-fibers and 5% silica fume, the reduction due to the addition of fibers was only 10%. Additionally, it was previously determined that the use of 5% silica fume provides comparable compressive strengths at 90 days and around a 8% increase in compressive strength (compared against 1% silica fume) at 28 days, it may be
safe to assume that if tested at 90 days, the compressive strength will reach the required 150 MPa threshold. If, the minimum compressive strength of 150 MPa is required at 28 days, the addition of 5% silica fume will help to achieve these strengths as demonstrated in the previous study. These results also indicate that the compressive strength of samples with PMHS-based admixtures in ultra-high performance materials may result in significant reductions, whereas in lower strength, but still high performance composites, the reduction in compressive strength is minimal.

![Compressive Strength, MPa](image)

**Figure 96: Compressive strength of FRC with PMHS-based admixtures and Al₂O₃ nano-fibers**

In order to determine some durability aspects of the samples tested within this study, surface resistivity readings were taken at 7 and 28 days (**Figure 97**). Here, all surface resistivity values are above 50 kΩ*cm indicating “very low” permeability (minimum 34 kΩ*cm required for “very low” permeability) if the surface resistivity readings are converted to rapid chloride permeability readings. As expected, these samples provide
exceptional permeability properties which may result in exceptional durability properties. The 7-day results demonstrate some variability; however, the reference samples provide good results. Additionally, the sample with nano-fibers and PE fibers also shows superior results at 7 days. These results may provide some indication of the density of the samples at this age. However, at 28 days, the samples with nano-fibers and PE fibers provide the best results. It is intended that the addition of the nano-fibers results in a denser CSH, which contributes to these higher surface resistivity values and thus should have superior durability properties. In general, the samples with PMHS-based admixtures provide lower values. This is a result of the additional void space created within the sample as the surface resistivity readings depend greatly on the porosity of the composite. These voids are intended to have hydrophobic features that would increase the durability; therefore, results from surface resistivity readings from samples with PMHS-based admixtures may not provide a direct correlation with durability.

\[\text{Surface Resistivity, } k\Omega \cdot \text{cm}\]

**Figure 97:** Surface resistivity of FRC with PMHS-based admixtures and Al\(_2\)O\(_3\) nano-fibers
The flexural behavior comparing samples with PMHS-based admixtures and Al₂O₃ nano-fibers is reported in *Figure 98, Figure 99, Figure 100, and Figure 101* for 7-day PVA fibers, 28-day PVA fibers, 7-day PE fibers, and 28-day PE fiber, respectively. It is clear that the PE fibers outperformed the PVA fibers in these high performance mixtures (Note, the scales of these charts are not the same because of the drastic differences in performance). The use of PE fibers not only results in better ultimate flexural stress behavior, but provides additional ductility. This is consistent with the results from the previous section by demonstrating that PE fibers outperform PVA fibers in higher strength matrices. The results with PVA fibers show that the addition of nano-fibers provides superior performance at 7 days. Additionally, the samples with nano-fibers and PMHS-based admixture also display good performance with slightly reduced peak flexural stresses compared against the sample with only nano-fibers. At 28 days, the samples with combined PMHS-based admixtures and nano-fibers outperforms the sample with only nano-fibers. These results indicate that with lower ductility samples, the post-first crack flexural behavior can be improved with the use of an “engineered” air void system. However, the use of PMHS-based admixtures without nano-fibers results in composites with reduced performance. This may be because the lower workability of the samples without nano-fibers results in higher quantities of entrapped air voids and the addition of the PMHS-based admixtures even further increases the void space. Additionally, the admixtures may have some detrimental effects on the hydration in these samples. When nano-fibers are used, a denser matrix is formed and this may lead to lesser detrimental effects on hydration and the ability of the voids to act as artificial flaws to promote multi-cracking behavior instead of the entrapped air voids initiating cracking. The PE fibers
show similar results. In general the samples with nano-fibers perform the best and the samples with nano-fibers and PMHS-based admixtures have slightly lesser performance at both 7 and 28 days. In the case of PVA fibers, the ductility remained the same between 7 and 28 days, but the flexural stress was increased. Typically, with stronger matrices, a reduction in ductility is observed. However, the PE fibers show both improved flexural stress and flexural strain at 28 days compared with 7 days. These results show that as the strength of the composite becomes greater, the PE fibers are capable of providing even better ductility. This may be due to the bond of the cementitious matrix with the fibers being strong combined with the ductility of the fibers. Here, once a crack forms, the fibers are able to adequately bridge the crack and maintain their bond with the matrix while at the same time elongate so that fiber rupture does not occur. At lower matrix strengths, the bond may be lesser, thus not providing the same load transferring ability. These results also indicate that the use of PMHS-based admixture alone in this matrix may not perform as well as they did in previous sections with lower strength matrices. However, they are capable of providing adequate performance when combined with nano-fibers, but still there is a slight reduction in behavior when compared against the samples only nano-fibers. It may be concluded that unlike previous work with lower strength matrices, the use of PMHS-based admixtures in higher strength matrices does not provide improved performance in terms of flexural behavior.
Figure 98: The 7-day flexural behavior for PVA-FRC samples with Al$_2$O$_3$ nano-fibers and PMHS-based admixtures

Figure 99: The 28-day flexural behavior for PVA-FRC samples with Al$_2$O$_3$ nano-fibers and PMHS-based admixtures
Figure 100: The 7-day flexural behavior for PE-FRC samples with Al₂O₃ nano-fibers and PMHS-based admixtures

Figure 101: The 28-day flexural behavior of PE-FRC samples with Al₂O₃ nano-fibers and PMHS-based admixtures
The tensile behavior of selected PE-FRC is presented in Figure 102. Here, the samples with only Al₂O₃ nano-fibers and the samples with Al₂O₃ nano-fibers and PMHS-based emulsions were tested. Only these selected samples were tested because of the difficulty to run tension tests on fiber reinforced cementitious composites. It is critical to assure proper grip between the supports and the sample so that slippage of the sample does not occur and that frictional forces between the sample and the supports are not observed. Additionally, any eccentricities that are present would result in inaccurate results. Finally, it is critical to assure that cracks do not form near the supports which would lead to false data. To account for this, the samples were cut into coupon shapes so that the area being tested was narrower than at the supports to assure that cracks would not appear near the supports. After these tests were performed, it was observed that no cracks appeared near the supports indicating results from these tests can be confidently used.

These results indicate that similar to the flexural behavior, the samples without the PMHS-based admixtures provide superior performance. These samples not only provided a higher tensile stress but a higher tensile strain. Again, this may be an indication that the use of PMHS-based admixtures in ultra-high strength matrices results in detrimental effects. The samples that provided the best performance (sample with only Al₂O₃ nano-fibers) maintained high ductility; however, the first crack tensile stress was slightly below 4 MPa, while the maximum tensile stress was around 5 MPa. The requirements for UHPC indicate that the sample must have first crack and sustained tensile stresses of at least 5 MPa. Despite the samples tested within this study not reaching that requirement, it may be assumed that had 5% silica fume been used, the tensile stresses would be higher. Additionally, if tested at 90 days, similar increased performance may be observed.
Figure 102: The 28-day tensile behavior of PE-FRC samples with Al$_2$O$_3$ nano-fibers and PMHS based admixtures.
10. CONCLUSIONS

High performance and ultra-high performance cementitious composites were created within this research using a multi-scale approach. These materials can serve as alternatives to conventional concrete in critical sections of infrastructure that require superior durability. Here, the denser matrices can result in lower absorption, lower permeability, and thus better durability. Additionally, the use of superhydrophobic admixtures in high performance cementitious composites results in a water repellant air void system that can reduce the permeability even further while at the same time act as “engineered” artificial flaws to promote multi-cracking and strain hardening behavior resulting in a more ductile material. In ultra-high performance cementitious composites, the matrices become even denser resulting in desirable durability and mechanical properties without the need for superhydrophobic admixtures.

In high performance cementitious composites reinforced with polyvinyl alcohol (PVA) fibers, an optimal air void structure was produced by the use of “core” type emulsions using nano-silica and metakaolin particles. This was apparent because of the exceptional air void properties and high ductility of these composites. However, the use of these admixtures tends to delay the hydration process, resulting in a lower strength of early age samples. When comparing the air void structure of fiber reinforced composites with mortars, it becomes apparent that the fibers result in composites with higher quantities of entrapped air voids.

Mortars with compressive strengths just under 200 MPa were created with the use of oil well cement in combination with Al₂O₃ nano-fibers. Here, it was found that the adequate dispersion (3 hours) of nano-fibers at the optimal dosage 0.5% (by weight of the
cementitious material) provides over a 55% improvement in compressive strength as compared with the reference. Greater quantities of nano-fibers may even further increase the strength; however, would require the usage of additional water (beyond what is required for mixing) for adequate dispersion. It was also determined that small quantities of silica fume (1-5%) combined with the nano-fibers can be used to achieve the desired strength and reach the ultra-high performance benchmark of 150 MPa. Previous research has used significantly more (20% or more) silica fume to achieve this same strength. The use of 5% silica fume can provide high compressive strength at the age of 28 days; however, comparable compressive strength can be observed in samples using only 1% of silica fume and Al₂O₃ nano-fibers at 90 days. It was also determined that the ultrasonification of the superplasticizer during the dispersion of the nano-fibers changes its properties resulting in a nano-fiber slurry that is favorable for using in cementitious composites. This additional superplasticizer from the slurry allows for a more workable mixture without significant detrimental effects on hydration.

The characterization of the cement pastes demonstrates that the use of only 1% silica fume can result in better hydration of the paste. Additionally, the use of nano-fibers results in improved hydration when compared against the reference. When comparing these results to chemical shrinkage (as there is a correlation between the chemical shrinkage and total hydration) and, in spite of higher degree of hydration, the samples with nano-fibers displayed a better performance. This is a result of the nano-fibers acting as nucleation sites for the formation of high density calcium silicate hydrate (CSH). Furthermore, as the CSH forms around the nano-fibers, the nano-fibers are able to provide
some reinforcement from the deformations of the CSH during hydration, ultimately resulting in a denser structure and improved strength.

The addition of fibers to optimal ultra-high performance mortars did result in 10 to 15% reduction of compressive strength. However, the use of polyethylene fibers (PE) was able to result in an exceptional flexural behavior while still maintaining the compressive strength of 150 MPa required for ultra-high performance concrete. Here, the PE fibers were able to provide a sufficient bond with the strong cementitious matrix while also having controllable slip from the matrix, high ductility when bridging cracks resulting in multi-cracking, and strain hardening behavior. Additionally, the use of these fibers in combination with Al₂O₃ nano-fibers resulted in exceptional surface resistivity values. Other fibers that were used were not able to provide the same ductility, while some produced comparable flexural strength. Ultra-high performance concrete often utilizes steel fibers as reinforcement; however, when combined with the cementitious material of the proposed composition, some segregation occurred.

Finally, the use of superhydrophobic admixtures in combination with the ultra-high performance cementitious composite based on high ductility PE fibers and relatively low ductility PVA fibers were tested. It was hypothesized that the addition of the “engineered” air void system would be able to increase the ductility in these ultra-high performance composites; however, this was not the case. The use of these admixture resulted in reduced compressive strength, reduced surface resistivity, and only comparable ductility. These results indicate that the use of superhydrophobic admixtures in ultra-high performance cementitious composites (e.g., based on oil well cement), may not be beneficial whereas these were found to improve the performance of high performance composites.
11. FUTURE WORK

Future work that can be performed to complement this research may include several steps:

- Characterization of the superplasticizer after ultrasonification can be performed to determine what is occurring to the admixture during the dispersion of the nano-fibers.
- Additional work may be required to further investigate the quantities and types of the hydration products that are formed due to the presence of Al\(_2\)O\(_3\) nano-fibers.
- Mechanics-based models comparing the flexural or tensile properties of fiber reinforced composites with “engineered” air void systems can be created.
- The optimization of the cementitious matrix to include steel fiber reinforcement without segregation would result in a more economical material as the cost of PE fibers is significant.
- It is often assumed that ultra-high performance cementitious composites provide exceptional durability; however, additional tests on the durability of the composites discussed in this research may be required to have a better understanding of the service life of the material.
- Finally, the structural testing and analysis of the material could be performed to allow for the use of this ultra-high performance cementitious composite in structural codes and ultimately in field applications.
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Figure 103: X-Ray diffraction for ordinary Type I portland cement (LF)
Figure 104: 2000x magnification SEM image of ordinary Type I portland cement (LF) particles

Figure 105: X-Ray diffraction diagram of ground granulated blast furnace slag, silica fume, and Class F fly ash
Figure 106: SEM images taken at 2000x magnification of: a) metakaolin; b) silica fume; c) Class F fly ash; and d) ground granulated blast furnace slag

Figure 107: X-Ray diffraction diagram of nano-SiO$_2$
APPENDIX B: FLEXURAL RESULTS OF FIBER REINFORCED CEMENTITIOUS COMPOSITES FOR HEAT TREATMENT

Figure 108: Load vs. deflection curves for M1 with heat treatment

Figure 109: Load vs. deflection curves for M2 with heat treatment
Figure 110: Load vs. deflection curves for M3 with heat treatment

Figure 111: Load vs. deflection curves for M4 with heat treatment
Figure 112: Load vs. deflection curves for M5 with heat treatment

Figure 113: Load vs. deflection curves for M6 with heat treatment
Figure 114: Load vs. deflection curves for M7 with heat treatment

Figure 115: Load vs. deflection curves for M8 with heat treatment
Figure 116: Load vs. deflection curves for M9 with heat treatment

Figure 117: Load vs. deflection curves for M10 with heat treatment
Figure 118: Load vs. deflection curves for M11 with heat treatment

Figure 119: Load vs. deflection curves for M12 with heat treatment
**Figure 120:** Load vs. deflection curves for M13 with heat treatment

**Figure 121:** Load vs. deflection curves for M14 with heat treatment
Figure 122: Load vs. deflection curves for M15 with heat treatment

Figure 123: Load vs. deflection curves for M16 with heat treatment
APPENDIX C: FLEXURAL RESULTS OF FIBER REINFORCED CEMENTITIOUS COMPOSITES FOR AIR VOID ANALYSIS

Figure 124: Flexural behavior of 1-REF

Figure 125: Flexural behavior of 2-AEMA
Figure 126: Flexural behavior of 3-ECSF

Figure 127: Flexural behavior of 4-ECMK
Figure 128: Flexural behavior of 5-ECNS

Figure 129: Flexural behavior of 6-ECR
Figure 130: Flexural behavior of 7-ESSF

Figure 131: Flexural behavior of 8-ESMK
Figure 132: Flexural behavior of 9-ESNS

Figure 133: Flexural behavior of 10-ECNMK
Figure 134: Flexural behavior of FRC-E-TBP

Figure 135: Flexural behavior of M
Figure 136: Flexural behavior of MTBP

Figure 137: Flexural behavior of METBP
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**Peer Reviewed Conference Proceedings**


Muzenski, Scott, Ismael Flores-Vivian, and Konstantin Sobolev. “The Development of Hydrophobic and Superhydrophobic Cementitious Composites.” In 4th International Conference on the Durability of Concrete Structures, July 24-26, 2014 Purdue University, West Lafayette, Indiana, USA

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Reports

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Presentations

**Presenter:** Transportation Research Board 95th Annual Meeting (January 2015, Washington D.C.), Emerging and Implementation-Ready Technologies to Control Cracking of Concrete Transportation Infrastructure, Part 2, “Hydrophobic Concrete”


**Presenter:** Alaska Concrete Summit (November 2014, Anchorage, AK), “Superhydrophobic Engineered Cementitious Composites”

**Presenter:** Ohio Transportation Engineering Conference (October 2014, Columbus, OH), “Flexible Waterproof Concrete – Superhydrophobic Engineered Cementitious Composites”

**Presenter:** UWM Research Foundation Breakfast Research Talk (September 2014, Milwaukee, WI) “The Development of Hydrophobic and Superhydrophobic Cementitious Composites”


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**Presenter**: ACI Fall Convention (October 2012, Toronto, Canada): Committee 236D (Material Science-Nanotechnology of Concrete), “The Use of Superhydrophobic Admixtures with Nanoparticles in Engineered Cementitious Composites”

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