THE IMPACT OF NANO SILICA SIZE AND SURFACE AREA ON CONCRETE PROPERTIES

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Biography:

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ABSTRACT

In this work, the impact of nano silica particles in grouts and concrete samples were measured to identify the change to temperature of cement hydration, strength and density. The compressive strength and modulus of elasticity were also evaluated as a means to understand the impact that the nano silica size and surface area had on the macroscopic properties traditionally used in the concrete industry. Finally, electrical resistivity was measured as a means to understand how the pore connectivity and density of the concrete specimens were manipulated by nano silica addition. Three types of nano silica dispersions (3-6 nm, 15-17 nm and 45-47 nm) were added to cement composites and examined over short and long curing times. All three different sized nano particles were added to have an equal surface area of silica. The larger particles exhibited higher levels of enhancement on the cement composite showing increased compressive and modulus of elasticity by more than 20% over the reference mixtures. The finest nano silica particle exhibited a 20% increase in compressive strength at its lowest dosages and a 14% reduction in compressive strength at its highest dosage. These results illustrate a limitation when using the finest nano silica particle. Finally, the addition of all nano silica particles proved to increase the electrical resistivity of the concrete by 30% for the smallest nano silica particles and 700% for the largest nano silica particle. This increase could be attributed to a reduction in permeability and a denser concrete specimen.

Keywords: cement, concrete, compressive strength, bulk electrical resistivity, modulus, nano silica
INTRODUCTION

Current state of the art research has shown that there is untapped potential to improve the strength and durability of grout and concrete by adopting the use of the nanoparticles (Sanchez 2009). The advent and use of these novel technologies in the last decade has given engineers and materials scientists the ability to use concrete in more innovative applications.

Current research has focused on the impact of nano particles on cement hydration and engineering properties. It has been shown that nano particles, for example nano silica, can increase the early strength of performance-based concrete while maintaining and enhancing the resistance to chemical degradation. Said et al, showed through their research with nano silica in concrete that the hydrated cement matrix of the concrete was densified upon the addition of nano silica (Said 2012). These additions were found to increase strength and durability of the concrete. Furthermore, Hou et al, combined the nano silica particles with secondary cementitious materials in order to increase the strength of the concrete and resistance to chemical attack (P. W. Hou 2012, P. K. Hou 2013). Both Said et al, and Hou et al, attribute the enhancement of the concrete strength and durability to the effective manipulation of hydrated cement by: an increase in the degree of cement hydration, a reduction in pore structure from pozzolanic reaction and heterogeneous nucleation.

Nano silica refers to a liquid dispersion of ultra-fine amorphous colloidal silica. Colloidal silica, which measures on the nano scale (1 to 100 nanometers), is suspended in a solution of water and soluble alkalis (Kobler 2008). These soluble alkalis act as dispersing agents, which increase the surface potential of the nano silica (Wise 1990, Iijima 2009). Normally, the nano silica particle has a lower surface potential in a dispersion and has a higher propensity to agglomerate due to Van Der Waal (VDW) forces, resulting Brownian motion and the collisions of adjacent nano silica particles. If this agglomeration occurs in the nano silica dispersion, nano silica will normally just agglomerate into nano silica aggregates and drop
out of dispersion. The tendency for agglomeration of neighboring nano silica particles in the cement paste is higher, as the cement paste has a higher viscosity than the nano silica in a dispersion alone. If agglomeration is allowed to occur in the fluid cement paste of the concrete composite, these same agglomerates could possibly cause large pores or voids within the hydrated cement matrix of fluid and cured concrete. Large pores and voids within the cured concrete would lead to a reduction in strength, the migration of aggressive materials, and eventually cause degradation of the concrete, as shown by Belkowitz et al. (J. Belkowitz 2010).

Nano silica has been shown by a number of scientists to increase the strength of concrete. Bjornstrom, et al showed that due to the size of the nano silica particle (3-6 nm), there was an increased rate of accelerated cement dissolution in cement composites (J. Bjornstrom 2004). Where the smaller sized nano silica particle will have a higher amount of monomeric silica units on its surface. This higher surface area of condensation sites for pozzolanic reaction are what generate the accelerated cement dissolution and increased rate of pozzolanic reaction. Land, et al showed similar results when using nano silica in cement composites and grout specimens and added that there was an increased rate of pozzolanic reaction as well as a higher degree of cement hydration (Land 2012). Land, et al attribute these enhancements to the size of the nano silica particle and the accompanying heterogeneous nucleation effect. Belkowitz, et al also showed that an increased rate of reaction and compressive strength when using the same nano silica particles as used in this research (J. Belkowitz 2010). Below are the proposed mechanisms, quantitative and qualitative experiments were used to distinguish the impact that the nano silica had on the cement composites, grout and concrete specimens in conjunction with the aforementioned mechanisms.

**Increased rate of pozzolanic reaction** - Nano silica is similar to silica-based materials
of larger particle-size (such as Class F Fly Ash) in that nano silica provides SiO$_2$ to combine
with calcium hydroxide (the by-product of the cement hydration reaction) to form more C-S-H (Qing 2006), the back-bone of concrete strength. Excess calcium hydroxide, which is
normally found in pores and voids, neither bonds to itself nor anything else, and in the
presence of water will dissolve back into solution (Mindess 2003). This unstable crystal
offers little-to-no strength to the concrete composite. Moreover, when calcium hydroxide
dissolves, it leaves behind a pore or void, which can allow to the transport of more aggressive
materials (Mindess 2003). Through pozzolanic reaction, the silica (from either nano silica or
Class F Fly Ash) combines with the calcium hydroxide in solution to form a super-saturated
gel. As the ratio of calcium oxide, CaO, (Ca) to silica, SiO$_2$ (Si) increases in this gel, excess
calcium-silicate-hydrates (C-S-H) start to polymerize into a hardened microstructure with a
varying degree of internal connectivity. Pellenq et al, proposed that reacting excess silica
with calcium-hydroxide (pozzolanic reaction) would cause a reduction in the pore structure of
the C-S-H microstructure, effectively reducing the fibril and porous structure to a globular
and denser C-S-H gel (Pellenq 2007). This excess formation of C-S-Hs effectively reduces
the pore distribution and increases the strength of the hydrated cement matrix. Therefore, like
Class F Fly Ash, nano silica increases the density of the hydrated cement matrix to increase
the strength and durability of concrete.

The nano silica is unlike the more mature concrete mineral additives, in that it is an
extremely small particle – 1000 times smaller than Class Fly Ash (silica purity, 36.0%) – that
has an increased surface area available for immediate pozzolanic reaction in the cement
hydration process. Nano silica also has a higher purity of silica, 99.9%. Land et al, showed
through heat flow calorimetry that nano silica particles lead to an instantaneous pozzolanic
reaction in hydrating cement paste, densifying the cement matrix (Land 2012). Bjornstrom et
al showed, and confirmed by Qing et al, this instantaneous pozzolanic reaction would create
a denser foundation within the hydrated cement matrix of the concrete composite for later
stages of cement hydration to build upon (J. M. Bjornstrom 2003, Qing 2006). Bentz, et al
showed that by increasing the rate of pozzolanic reaction early on during the cement
hydration process, there is an increase in the hydrated cement matrix density and therefore an
increase in concrete strength (D. Bentz 1994).

**Accelerated Cement Dissolution** – Pellenq et al, hypothesized that during standard
cement hydration (without any pozzolanic material or nano silica) a cement particle
undergoes hydration until the hydrated products create a diffusion barrier that covers the
unhydrated portion of the cement particle, impeding continued hydration (Pellenq 2007).
Even with the use of mature mineral additives, the ultimate degree of hydration (percent of
cement particle that has reacted) is limited because of the formation of the diffusion barrier.

Bjornstrom et al. found, through analysis of cement pastes with nano silica using diffuse
reflectance FTIR (DR-FTIR) spectroscopy, that nano silica accelerated the dissolution of
cement (J. Bjornstrom 2004). This accelerated dissolution ultimately leads to a greater
consumption of the cement particle. As with the pozzolanic reaction, the accelerated cement
dissolution densifies the hydrated cement matrix of concrete and leads to increased strength.
Bjornstrom found through the use of DR-FTIR that the acceleration of cement dissolution
was linked to the highly reactive surface of the nano silica particle. Specifically, the higher
reactivity is due to a greater amount of monomeric silica units at the surface of the nano silica
particle surface and constitute condensation sites for cementitious components (C₃S and C₂S)
(J. Bjornstrom 2000). Due to the nano silica size, there is an increased amount of these
condensation sites that effectively increase the amount of cement consumed (compared to
cement alone) in both the aforementioned cementitious and pozzolanic reactions. Therefore,
the use of nano silica particles can increase the efficiency of OPC (degree of cement
hydration), leading to a denser hydrated cement matrix and stronger concrete composite.

**Heterogeneous nucleation** - The final proposed mechanism is heterogeneous nucleation or the building of distinct phases on a localized surface. Due to the smaller size of the nano silica particles, there is a lower surface potential or smaller electrical double layer at the nano silica particle surface (Wise 1990, Luo 2006). This lower surface potential increases the affinity for heterogeneous nucleation, specifically the growth of C-S-Hs, on the surface of nano silica particles. Jayalapan showed, through iso-thermal calorimetry, that an increased amount of nano-TiO$_2$ and a smaller diameter nano-TiO$_2$ (an inert material when introduced into cement hydration) increased the degree of hydration for cement composites, hypothesizing that the heterogeneous nucleation was the most probable cause (Jayapalan 2009). Land *et al.* showed similar findings when using nano silica, identifying that the nucleation processes and the large number of seeds caused an acceleration of cement hydration, and ultimately leads to a denser concrete (Land 2012). Furthermore, Hou *et al.* showed that nano silica increases the production of stiffer C-S-H gels and increases the density of the hydrated cement matrix through a preferred hydrate formation and heterogeneous nucleation (P. W. Hou 2012, P. K. Hou 2013). Therefore, nano silica has the potential to enhance the HCM through its physical spherical shape and size as well as the chemical reactions that it accelerates. It should be noted that these proposed mechanisms are not singular events occurring at precise times but more of a family of events that occur with some degree of predictability throughout the hydration process. While these mechanisms do occur, to some degree, in standard cement hydration, and even with mature pozzolanic additives such as Class F Fly Ash, it is proposed that they are more likely to occur (and enhance the concrete) when using nano silica particles.
RESEARCH SIGNIFICANCE

The goal of this research is to enhance the scientific understanding and add to the state-of-the-art on the use of nano particles in concrete. It has been hypothesized that nano silica particles can manipulate the thermokinetics of cement hydration, based on the aforementioned mechanisms, to increase the strength of concrete. What makes this research unique is the identification and understanding of the impact of nano silica size and surface area on strength. The specific experiments analyzed were used to identify how different sized nano silica particles, dosed to have the same free silica surface area, would impact cement hydration and the hardened properties of cured cement composites and concrete. The goal of this work is ultimately directed towards the potential commercial use of nano silica in the concrete industry in order to facilitate a stronger and more durable concrete.

MATERIALS AND EXPERIMENTAL PROCEDURE

A Type I/II ordinary Portland cement (OPC) with a Blaine fineness of 0.345 meters squared per gram (m²/g) was used as the primary cementitious material for experimentation. The composition of the cement was: SiO₂, 19.9%; CaO, 63.9%; Al₂O₃, 4.8%; Fe₂O₃, 3.2%; C3S, 57%; C2S, 13%; and C3A, 7%. A Class F Fly Ash with a fineness of 0.420 m²/g was used as a replacement pozzolanic material, with a chemical composition of: SiO₂, 51%; CaO, 13.7%; Al₂O₃, 21%; Fe₂O₃, 6.4%; and Na₂O, 1.2%. The three colloidal nano silica particle dispersions had a silica purity of 99.9% and surface areas (m²/g) of: 5 nm, 500 m²/g (hereafter known as NS1); 16 nm, 190 m²/g (NS2); and 46 nm, 80.0 m²/g (NS3).

The initial dosages of the nano silica were designed to equal the amount of silica surface area supplied by a 20% replacement of OPC by Class F Fly Ash, assuming a total cementitious mass of 420 kilograms per cubic meter (kg/m³), for a total Class F Fly Ash mass of 84 kg/m³. The total free silica surface area brought to the concrete composite by the Class
F Fly Ash (with a surface area of 0.42 m²/g and a silica purity of 36%) was calculated, based on aforementioned cementitious mass, to be approximately 14,000 m² per batch (m²/bt). This surface area, 14,000 m²/bt, represented the initial dosage for the three different nano silica dispersions discussed earlier. Nano silica replacement dosages for OPC by mass, listed in Table 1, were changed for each nano silica size distribution to keep the amount of free silica surface constant between sample sets. Each successive dosage represented an increase by one order of magnitude of the silica surface area. The fourth and final dosage (DOS 4) was for a free silica surface area of approximately 280,000 m²/bt. The amount of Class F Fly Ash that would be needed to equal the different amount of nano silica surface areas are also listed in Table 1 but were not used during experimentation and only serve as a reference.

The nano silica distributions and the respective replacement for OPC are listed according to the amount of silica surface area that the nano silica brought to the concrete mixtures in Table 1. The smaller nano silica particles required a smaller replacement of the OPC to reach the same silica surface area as the larger particles. The requirement for less material was due to the larger surface area of reactive silica that the smaller particle had when compared to the larger particle. This smaller dosage also reduced the total mass of silica (compared to the larger nano silica particles and Class F Fly Ash), which could be consumed in pozzolanic reaction during later ages of cement hydration.

All the samples tested were mixed with potable water and coarse and/or fine aggregate

<table>
<thead>
<tr>
<th>Nano Silica Replacement by mass of OPC (%)</th>
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</thead>
<tbody>
<tr>
<td>NS1, 500 m²/g</td>
</tr>
<tr>
<td>Dosage (DOS) 1</td>
</tr>
<tr>
<td>DOS 2</td>
</tr>
<tr>
<td>DOS 3</td>
</tr>
<tr>
<td>DOS 4</td>
</tr>
</tbody>
</table>

Table 1 - Nano silica percent replacement of Portland cement by mass. The two reference mixtures used had 100% OPC (OPC) and 20% Class F Fly Ash (20% F Ash)
depending on the test. For the semi-adiabatic temperature readings, the grout samples were mixed with potable tap water and a fine aggregate with procedures conforming to ASTM C 305 (ASTM C305-12 2012). For the concrete samples, concrete sand and crushed granite with a 57/67 gradation were used to make concrete samples. Concrete was mixed in 3.0 cubic foot capacity rotary mixer per ASTM C 192 (ASTM C192-12a 2012). Table 2 lists the mixture constituents for the grout and concrete used throughout the experiments. For all mixes the amount of water that was brought by the nano silica solution was subtracted from the grout or concrete batch water in order to keep the water-to-cementitious ratio consistent between mixes.

All samples were prepared according to ASTM C 305 or ASTM C 192, where the fresh grout and concrete, after thoroughly being mixed, were cast into non-absorbent cylindrical molds (ASTM C305-12 2012, ASTM C192-12a 2012). The fluid mix was cast in two lifts of equal volume. Each lift was consolidated 25 times with a metal rod. The cylindrical samples were then tamped 10-15 times lightly on the outside of the mold in the same area of the consolidated lift. After the final lift, the grout and concrete samples were finished with a steel trowel. The samples were allowed to cure for 24 hours in an environmentally controlled laboratory at 21 C. After 24 hours, the cylindrical molds were stripped, the samples were marked, and then placed in a temperature controlled lime-water bath at 21 C.

Table 2 - Grout and Concrete Mixtures Proportions

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Concrete (kg/m3)</th>
<th>Grout (kg/m3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I/II OPC</td>
<td>420</td>
<td>420</td>
</tr>
<tr>
<td>67 / 57 Crushed Rock</td>
<td>931</td>
<td>-</td>
</tr>
<tr>
<td>Concrete Sand</td>
<td>848</td>
<td>1186</td>
</tr>
<tr>
<td>Water-to-Cementitious Ratio</td>
<td>0.47</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Semi-Adiabatic Temperature test: The semi-adiabatic temperature test (SATT) was used to
measure the effect of nano silica on the temperature evolution of hydrated grout specimens. The semi-adiabatic chamber and software package were programmed to record changes in temperature for 24 hours, with readings taken every 0.2 seconds. The temperature was reported in Celsius (°C) to the 0.01 °C. The thermal-couple was located underneath the sample. The SATT was built with 203 mm of thermal insulation surrounding all sides of each sample to ensure that minimal energy in the form of heat was lost to the surrounding environment.

Cement strength is based on reactions between H₂O and the several successive cementitious phases that occur during hydration. To understand the importance of these reactions, it is first important to identify the stages at which these reactions take place in the cement hydration process. The time to reach those stages, and length of time in those stages varies between cement compositions and additives used. The development of crystal structures and C-S-H gels correlates closely with the changes in temperature that occur over time during cement hydration. An examples of a semi-adiabatic temperature curve for the cement hydration process is illustrated in Figure 1.
Figure 1 - The 5 stages of the cement hydration process: Stage 1, Mixing; Stage 2, Dormancy; Stage 3, Acceleration; Stage 4, Deceleration; Stage 5, Densification.

**Compressive Strength:** On the specimen break date three, 101.6 mm diameter by 203.2 mm tall cylindrical samples were taken out of the temperature controlled water bath. For purposes of stress calculations, the diameters of the specimens were measured in one direction, and then the second diameter was measured at a 90 degree rotation from the orientation of the first measurement, at about mid-height of the specimen; in one place on the sample as per ASTM C 39 (ASTM C39-12a 2012). As per ASTM C 39, the specimens were centered in the closed loop hydraulic press and crushed under a metered load (ASTM C39-12a 2012).

**Modulus of Elasticity:** Fourteen days before the specimens were tested, the ends were coated with a sulfur cap to increase the flatness as the samples as per ASTM C 469 (ASTM C469 / C469M-10 2010). The samples were then cured until the 28 day break date as per ASTM C 469.

The load was applied smoothly and increased continuously at a nominal rate within the range 20 to 40 kPa/sec. The measured modulus of elasticity (E_{measured}) was determined by
equation (1) with the applied load and longitudinal strain. At the point when the longitudinal
strain was 50 millionths the load was recorded (S1). The strain ($\varepsilon_2$) was then recorded when
the applied load was equal to 40 % of the ultimate load (S2).

**Electrical Resistivity:** The electrical resistivity of the concrete specimens was measured at
28 days, as shown in Figure 2, as a means to identify how the nano silica size and surface
area impacted the density of the HCM. A higher density HCM has lower porosity and pore
connectivity. Shane *et al,* showed through the use of chloride ion permeability (a test used to
measure durability of concrete) and electrical resistivity that as permeability decreased,
electrical resistivity increased (Shane 1999). The electrical resistivity was used as a means of
measuring the impact of nano silica size and surface area on the pore connectivity and density
of concrete.

This test method consists of measuring the bulk resistivity of water-saturated concrete
cylinders by the use of two plate electrodes in contact with the end surfaces of the specimen.
An alternating electrical current was applied through the concrete specimen by the resistivity
meter. The apparatus measured the resistance of a concrete specimen. The resistance,
measured in ohms ($\Omega$), is the raw data measured and used to determine the electrical
resistivity. It has been shown by Shane *et al,* that electrical resistivity can be related to the
permeability and density of concrete (Shane 1999). Specifically the concrete specimen’s
ability to resist to fluid penetration, due to a reduction in pore connectivity. Resistivity is
expressed in Equation 3, where L is the specimen length (cm), A is the specimen cross-
sectional area (cm$^2$) and $\Omega$ is the resistance of the specimen.

$$\rho = \frac{\Omega}{L} \left(\frac{A}{L}\right)$$  (3)
ANALYTICAL INVESTIGATION

The measured modulus of elasticity was compared to the modulus of elasticity calculated (E_calculated) by the equation (2) using compressive strength (f’c) from ACI 318, 8.5.1 (318-08 2008). The given equation for modulus determination is the standard used for reinforced concrete design. The mathematical model reduces the modulus to a function of compressive strength. While newer models have been suggested this is the standard used to make decisions for commercial job-site specifications. The current model published in ACI 318 grossly under-estimates the modulus for non-standard concrete – this could lead to over-designed concrete and waste of materials in different applications. The measured and calculated moduli of elasticity values were compared in order to highlight the impact that these new nano materials have on the standard concrete practices. Where it is proposed that the nano silica could effectively increase the strength and other engineering properties (such as modulus of elasticity) of concrete in a manner not covered by standardized models.

\[
E_{\text{measured}} = \frac{(S_2 - S_1)18}{(\varepsilon_2 - 0.000050)}
\]  
\[
E_{\text{calculated}} = 57,000(\varepsilon')
\]

Figure 2 - Electrical Resistivity of concrete specimen (Shane 1999)
EXPERIMENTAL RESULTS AND DISCUSSION

The strength and densification of the grout and concrete, prepared through mechanical mixing, were investigated as a function of nano silica particle size and surface area. As described below, the change in temperature of cement hydration, strength, and density of the grout and concrete specimens were predominately enhanced by the smaller nano silica particles at a lower surface area, and by the larger nano silica particles at a higher surface area. Furthermore, a limitation for nano silica dosage was discovered for the smaller particles, and compressive strength and modulus of elasticity degradation was identified when that limit of nano silica surface area was exceeded.

Semi Adiabatic Temperature Curves

The semi-adiabatic temperature curves of the concrete specimens over 24 hours of hydration are illustrated in Figure 3, 5, 6 and 7. Each figure represents a successive dosage of nano silica. These dosages correspond to the mixture proportions in Table 2. All four figures illustrate the typical temperature curves for the reference mixtures (OPC and 20% F Ash) over 24 hours. Upon combining with water, OPC dissolves and chemically reacts to release energy in the form of heat to the surrounding environment. As time progresses the OPC in the concrete hydrates (similarly to Figure 1) and the temperature transitions from a dormancy stage, through an acceleration and deceleration stage, into a plateau that begins to occur at 24 hours. The variation in these four stages can be attributed to the change in reaction type and rate of reactions, which can be correlated to strength development. Nazari et al, and Said et al, hypothesized that excess free silica content would increase the rate of OPC dissolution and C-S-H polymerization, thereby increasing heat and temperature output (Nazari 2011, Said 2012). The change in semi-adiabatic temperature curves of the different nano silica mixtures compared to the reference mixtures in Figure 3 through 7 would be the result of the amount of silica available (from the nano silica) and the amount of the added silica that is
exposed and bound in agglomerates.

The decrease of the time in the dormancy stage and the increase in temperature of the acceleration stage can be clearly observed for the NS1 DOS mixture, occurring due to the pozzolanic effect, accelerated OPC dissolution, and nucleation. Figure 3 illustrates that the higher surface area of the nano silica advances the hydration reactions during the dormancy stage, when compared to the reference mixtures. Bjornstrom et al. showed in their research that nano silica provides additional surface area for the pozzolanic reaction but also causes the C₃S and C₂S to dissolve faster, thus rendering a more rapid formation of C–S–H and thereby releasing more energy in the form of heat and thus increasing the temperature (J. Bjornstrom 2004). Land et al. confirmed these findings, suggesting that in addition to accelerated cement dissolution, an instantaneous pozzolanic reaction occurred developing a C-S-H kernel for nucleation (Land 2012) and also contributed to this rise in heat and temperature.

Figure 3 - Semi-adiabatic temperature curves for dosage one (DOS 1) of the nano silica, measured over 24 hours.

Despite the lower temperature curves for NS2 DOS 1 and NS3 DOS 1 in Figure 3, there
is a distinct widening of the curves supporting the hypotheses proposed by Bjornstrom et al. and Land et al. Both showed that nano silica has the potential for manipulating the total amount of cementitious and pozzolanic materials consumed and the degree of cement hydration. Despite a minor decrease in temperature during the initial portion of the acceleration stage (2.5 hour to 5 hour), there is a moderate increase of temperature for the NS2 and NS3 mixtures at the peak of acceleration stage (6 hours to 9.5 hours), which leads to a significant increase in temperature (over the reference mixtures) in the deceleration stage. These changes in temperature imply that there are different reactions that are occurring in the nano silica mixtures than in the reference mixtures and at a higher rate.

As the dosage of the NS1 is increased (DOS 2), in Figure 4, there is a reduction in temperature suggesting a reduction in reactive surface area. An increase in temperature for the NS2 DOS 2 and NS3 DOS 2, also illustrated in Figure 4, during the dormancy period and acceleration period. Furthermore, the peak temperatures for the NS2 DOS 2 and NS3 DOS 2 mixtures are greater than that of the NS1 DOS 2 mixture illustrated in Figure 4. The larger nano silica particles seem to be more stable a the higher dosages when compared to the NS1 at the same dosage.
The NS1 dispersion loses efficiency as the dosage is increased. This lose in efficiency of the NS1 continues for the next dosage (DOS 3) in Figure 5. For the higher dosages (DOS 3) of NS2 and NS3 mixtures, an increase in temperature for the dormancy, acceleration and deceleration stages can be clearly observed. The larger nano silica particles with the lower surface area have more of an impact on increasing the temperature of the hydrating cement when compared to the smaller nano silica particles with the higher surface area. This phenomenon is exemplified with the highest dosages for all the nano silica particles in Figure 6. A moderate increase in temperature for the NS1 DOS 4 curve is overcome by both the temperature curves for the NS2 DOS 4 and NS3 DOS 4. It is hypothesized that the largest nano silica particle, NS3, is the most efficient nano silica at this dosage due to its size and surface potential.
Figure 5 - Semi-adiabatic temperature curves for dosage three (DOS 3) of the nano silica, measured over 24 hours.

Figure 6 - Semi-adiabatic temperature curves for dosage four (DOS 4) of the nano silica, measured over 24 hours.

While the larger nano silica particles (NS3) require a greater amount of the nano silica to attain the same surface area, they are less likely to agglomerate than the smaller particles. As
discussed earlier, the tendency for the nano silica in solution to agglomerate is dependent on
the surface potential of said particle and the type of medium it is in. Once the nano silica
dispersion is added to the concrete mixture it will immediately have the inclination to
agglomerate due to the chemical environment and the viscosity of the cement paste. At
higher dosages where a smaller particle might agglomerate the larger nano silica particle is
more stable in the cement paste, and therefore has a greater impact on the thermokinetics of
cement hydration.

Compressive Strength

The change in compressive strengths (compared to the reference mixtures, OPC and
20% F Ash) of the cast specimens after 24 hours, 7 days, 14 days, and 28 days of curing are
listed in Table 3. For the tested samples, all results conformed to the standard deviation
guidelines as stipulated in ASTM C 39 (ASTM C39-12a 2012). All four figures show the
typical compressive strength development for the reference mixtures (OPC and 20% F Ash),
as well as the mixtures with the nano silica dispersions, over 28 days. As stated in earlier
sections, the compressive strength development is dependent on the HCM, aggregate and
interfacial zone between the HCM and the aggregate. Upon combining with water, the OPC
dissolves and chemically reacts to form the $C_3S$ and $C_2S$, a porous network of C-S-Hs – the
backbone of the HCM and concrete compressive strength. As time progresses and the OPC
cures in the lime-water bath, there is an increase in compressive strength. The increase in
compressive strength for the reference mixtures (and nano silica mixtures) are expected for
cement composites made with OPC due to the high concentration of water and soluble salts
to keep the cement hydration process active. As time progresses the development of
compressive strength slows due to a reduction in the availability of anhydrous cement
particles caused by a formation of a diffusion barrier at the surface of the cement particle.
Belkowitz, et al showed that excess free silica content, from the introduction of nano silica
particles would increase the rate of OPC dissolution and C-S-H polymerization; thereby increasing early and late compressive strength (J. Belkowitz 2010).

There is a distinct increase in compressive strength for the lowest dosage of the NS1 mixture (DOS 1) over the reference mixtures and other nano silica mixtures (NS2 DOS 1 and NS3 DOS 1) as listed in Table 3. The increase in early and late compressive strength of the NS1 DOS1 mixtures occurred due to the pozzolanic effect, accelerated dissolution and heterogeneous nucleation. The NS2 and NS3 mixtures at the same dosage (DOS 1) have a lower impact on compressive strength development when compared to the NS1, which is due to the lower reactive surface than the NS1 dispersion.

Table 3 - Percent Change of the Compression Specimens with Colloidal Silica (CS) compared to the reference mixtures (OPC and 20% F Ash).

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Break Date</th>
<th>% Change</th>
<th>Mix ID</th>
<th>% Change</th>
<th>Mix ID</th>
<th>% Change</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>OPC</td>
<td>FAsh</td>
<td></td>
<td>OPC</td>
<td>FAsh</td>
</tr>
<tr>
<td>NS1</td>
<td></td>
<td></td>
<td></td>
<td>NS2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOS 1</td>
<td>24 Hour</td>
<td>84%</td>
<td>142%</td>
<td>DOS 1</td>
<td></td>
<td>47%</td>
</tr>
<tr>
<td></td>
<td>7 Day</td>
<td>22%</td>
<td>61%</td>
<td></td>
<td>20%</td>
<td>58%</td>
</tr>
<tr>
<td></td>
<td>14 Day</td>
<td>19%</td>
<td>36%</td>
<td></td>
<td>20%</td>
<td>37%</td>
</tr>
<tr>
<td></td>
<td>28 Day</td>
<td>20%</td>
<td>13%</td>
<td></td>
<td>18%</td>
<td>12%</td>
</tr>
<tr>
<td>NS1</td>
<td></td>
<td></td>
<td></td>
<td>DOS 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOS 2</td>
<td>24 Hour</td>
<td>77%</td>
<td>132%</td>
<td>DOS 2</td>
<td></td>
<td>36%</td>
</tr>
<tr>
<td></td>
<td>7 Day</td>
<td>17%</td>
<td>55%</td>
<td></td>
<td>17%</td>
<td>55%</td>
</tr>
<tr>
<td></td>
<td>14 Day</td>
<td>15%</td>
<td>31%</td>
<td></td>
<td>15%</td>
<td>31%</td>
</tr>
<tr>
<td></td>
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<td>15%</td>
<td>8%</td>
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<td>15%</td>
<td>8%</td>
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<tr>
<td>NS1</td>
<td></td>
<td></td>
<td></td>
<td>DOS 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOS 3</td>
<td>24 Hour</td>
<td>57%</td>
<td>107%</td>
<td>DOS 3</td>
<td></td>
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<td>7 Day</td>
<td>5%</td>
<td>38%</td>
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<td>13%</td>
<td>49%</td>
</tr>
<tr>
<td></td>
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<td>5%</td>
<td>19%</td>
<td></td>
<td>14%</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td>28 Day</td>
<td>5%</td>
<td>-1%</td>
<td></td>
<td>14%</td>
<td>8%</td>
</tr>
<tr>
<td>NS1</td>
<td></td>
<td></td>
<td></td>
<td>DOS 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOS 4</td>
<td>24 Hour</td>
<td>-27%</td>
<td>-5%</td>
<td>DOS 4</td>
<td></td>
<td>13%</td>
</tr>
<tr>
<td></td>
<td>7 Day</td>
<td>-7%</td>
<td>22%</td>
<td></td>
<td>7%</td>
<td>41%</td>
</tr>
<tr>
<td></td>
<td>14 Day</td>
<td>-8%</td>
<td>6%</td>
<td></td>
<td>8%</td>
<td>23%</td>
</tr>
<tr>
<td></td>
<td>28 Day</td>
<td>-14%</td>
<td>-19%</td>
<td></td>
<td>4%</td>
<td>-2%</td>
</tr>
</tbody>
</table>

An increase in early and late strength can be clearly observed, the higher dosages of the NS2 and NS3 (DOS 2) mixtures, occurring due to a higher degree of the aforementioned mechanisms due to a greater amount of silica surface area. At the same surface area as the
NS1, the higher dosages of NS2 and NS3 do not bring an excessive amount of nano silica particles to the fresh concrete that would cause over-saturation and compressive strength reduction, as shown in Table 4. Table 4 lists the amount of nano silica particles based on percent replacement, by mass, of OPC. It should be noted that number of particles listed in Table 4 represents the approximate number of nano silica particles based on the nano silica sizes and dosages and should not be taken as an exact number of particles. The number of particles was used to identify the cause of agglomeration and compressive strength reduction when using nano silica. Due to the lower amount of particles and the size of the larger particles, NS2 and NS3 are more stable than the NS1 DOS 2 (which has a lower increase in compressive strength when compared to NS1 DOS 1) and therefore did not have a tendency to agglomerate and cause a compressive strength reduction.

Table 4 - Approximate Number of Nano Silica per cubic yard of Concrete calculated by determining the volume of one particle from the average diameter. Then the approximate number of particles was calculated using the specific gravity of the dispersion, solid content and the amount or dosage of nano silica.

<table>
<thead>
<tr>
<th>No. of Nano Silica Particles per cubic meter (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOS 1</td>
</tr>
<tr>
<td>DOS 2</td>
</tr>
<tr>
<td>DOS 3</td>
</tr>
<tr>
<td>DOS 4</td>
</tr>
</tbody>
</table>

The same phenomena for the higher dosage (DOS 3) of both the smaller and larger nano silica particles hold true for the compressive strength illustrated in Table 3. While there is still some early compressive strength increase for the NS1 DOS 3 mixture, the later strengths (specifically the 28 day compressive strength and listed in Table 3) shows a reduction of strength over the 20% F Ash mixture (-1%) and a moderate increase in strength when compared to the OPC mixture (5%). This lack of early and later compressive strength gain is a by-product of an over-saturation of the NS1 dispersion. Similar to the NS1 DOS, the NS2
DOS 3 has no change in compressive strength compared to the lower dosages of the same dispersion as listed in Table 3. This suggests that like the NS1, there is a limitation on the amount of NS2 used. Conversely to the NS1 and NS2 (DOS 3) mixtures, the NS3 DOS 3 mixture leads to a steady increase in strength. This consecutive increase in strength for the NS3 DOS 3 would be the result of a higher stability to resist agglomeration and therefore a higher degree of efficiency.

A severe decrease in strength, relative to the control, is apparent for the higher dosage of NS1 (DOS4) in Table 3, with a decrease in strength occurring due to an over-saturation effect (more nano silica particles give rise to a greater number of agglomerated sites and voids). Nazari et al, showed similar results (when using 5% percent mass of 12-18 nm nano silica) in their investigation of nano silica in self compacting concrete. Nazari et al, attributed the reduction in strength to a reduction in C-S-Hs growth and density; this inevitably led to a weaker cement matrix (Nazari 2011). The cause for the reduced compressive strength noted by Nazari was the super-saturation of Si in relation to the amount of available Ca for pozzolanic reaction (Nazari 2011). Nazari, et al, also hypothesized that the higher dosages of the nano silica caused the development of nano silica particle agglomerates, rounded masses of collected nano silica particles, in the hardened HCM. These agglomerates, which offer no resistance to compressive loads, softened the HCM and led to a reduction in the compressive strength. By this logic, the NS1 effectively brought an excessive amount of nano silica particles to the fresh concrete mixture, listed in Table 4, compared to the other nano silica dispersions at the same dosage. The excessive particle content in the highly viscous fresh concrete would agglomerate and create voids in the hardened state. These voids would act as crack propagation sites during the loading of the sample, causing a decrease in strength.

As the dosage of the nano silica increased (and number of particles) there was a greater
likelihood for these particles to agglomerate, soften the HCM and reduce compressive strength, referred to as over-saturation of nano silica. This phenomenon would be most prevalent, illustrated by the percent change in Table 3, with the smallest nano silica particle distribution used, NS1, due to a lower surface potential of the NS1 particle, when compared to the other distributions used in these tests. Just like the NS1 DOS 4, the highest dosage of NS2 (DOS 4) was negatively impacted by over-saturation or agglomeration. This dosage of NS2 had a reduction in early and later strength, when compared to the reference mixtures and the other nano silica mixtures. It is hypothesized that this amount of nano silica caused a similar phenomenon that occurred in the NS1 DOS 4 mixture but to lesser degree as found by the change in strength listed in Table 3. For the highest dosage of the NS3 (DOS 4) mixture, an increase in early and late strength can be clearly observed. No decrease in strength was found for dosages of NS3, suggesting that the largest nano silica (with the largest surface potential) is less sensitive to over-saturation when compared to the smaller nano silica particles.

Two key components identified for the use of nano silica to increase compressive strength focus on the relationship between the size of the nano silica particle and its tendency to agglomerate in the HCM. First, the use of a larger nano silica particle seemed more effective due to a greater stability against over-saturation. The controlled use of the larger nano silica particles allowed for a higher degree of the aforementioned mechanisms (increased rate of pozzolanic reaction, accelerated cement dissolution and heterogeneous nucleation) to increase the compressive strength. The second component is the limitation of the amount of nano silica that can be used to enhance compressive strength. This limitation, referred to as over-saturation, is dependent on the size, surface area (accompanying surface potential) of the nano silica particle as well as the number of the nano silica particles in the HCM. Specifically, the smaller nano silica particles inherently have a smaller surface
potential, and therefore have a higher propensity for agglomeration. The larger nano silica particles, particularly the NS3, have a larger surface area and therefore a lower inclination for agglomeration and compressive strength loss. The data presented illustrates the potential that nano silica has on compressive strength development in concrete as well as some of its limitations.

**Modulus of Elasticity**

Bentz *et al.* showed through concrete modeling and simulation that just like the compressive strength, the modulus of concrete is dependent on the modulus of the aggregate, hydrated cement matrix and the strength of the interfacial zone between the aggregate and the hydrated cement matrix (D. Bentz 1991). Both the reference mixtures have lower values for measured modulus than a majority of the mixtures with nano silica (excluding NS1 DOS 4). As with the previously recorded data for the reference mixtures, over the first day of hydration both the reference mixtures showed a lower rate and a shorter duration of cement hydration. Furthermore, the rate of compressive strength gain and the ultimate compressive strength was lower for both the reference mixtures when compared to the nano silica mixtures (excluding NS1 DOS 4). Both of these data sets support the lower modulus values measured for the reference mixtures. The reasoning for this lower measured modulus is due in full to the lack of nano silica, which enhances both the hydrated cement matrix and concrete.

At the same dosage all three nano silica dispersions show an increase in modulus over the reference mixtures. The lowest dosage of NS1 (DOS 1) generates the highest modulus when compared to the other nano silica mixtures at the same dosage (NS2 DOS 1 and NS3 DOS 1) in Table 5. The increase in the nano silica mixtures are listed in Table 5 and show that the NS1 generates a 20% increase over the OPC and 22% increase over the 20% F Ash. This higher measurement is due to the higher surface area (and a lower surface potential), which ultimately causes an increase in the modulus through an increase in pozzolanic
reaction, accelerated cement dissolution and heterogeneous nucleation. The lower modulus values for the NS2 and NS3 mixtures in Table 5, at the same dosage, would be due to the lower amount of reactive silica surface area and therefore a lower degree of enhancement.

Table 5 – Percent Change of the Modulus of Elasticity for the Nano Silica mixtures when compared to the reference mixtures.

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>20% F Ash</th>
<th>OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS3 DOS 4</td>
<td>29%</td>
<td>30%</td>
</tr>
<tr>
<td>NS2 DOS 4</td>
<td>16%</td>
<td>17%</td>
</tr>
<tr>
<td>NS1 DOS 4</td>
<td>-7%</td>
<td>-6%</td>
</tr>
<tr>
<td>NS3 DOS 3</td>
<td>17%</td>
<td>18%</td>
</tr>
<tr>
<td>NS2 DOS 3</td>
<td>10%</td>
<td>11%</td>
</tr>
<tr>
<td>NS1 DOS 3</td>
<td>5%</td>
<td>6%</td>
</tr>
<tr>
<td>NS3 DOS 2</td>
<td>16%</td>
<td>17%</td>
</tr>
<tr>
<td>NS2 DOS 2</td>
<td>9%</td>
<td>10%</td>
</tr>
<tr>
<td>NS1 DOS 2</td>
<td>9%</td>
<td>10%</td>
</tr>
<tr>
<td>NS3 DOS 1</td>
<td>14%</td>
<td>15%</td>
</tr>
<tr>
<td>NS2 DOS 1</td>
<td>6%</td>
<td>7%</td>
</tr>
<tr>
<td>NS1 DOS 1</td>
<td>20%</td>
<td>22%</td>
</tr>
</tbody>
</table>

As the dosages of nano silica are increased in DOS 2 and DOS 3 it is evident that the NS1 is starting to soften as shown through the reduction in percent increase over the reference mixtures in Table 5. This softening is due to the over-saturation that was found to have occurred with the compression strength specimens. As with the compression it is hypothesized that this over-saturation of the nano silica is causing the formation of voids with nano silica agglomerates that offer little to no strength to the concrete. The larger NS2 and NS3, which have been shown to be more stable at higher dosages than the NS1, are more effective at increasing the modulus of the specimens as shown in Table 5 for DOS 2 and DOS 3. The larger nano silica particles have a larger surface potential at their surface, which keeps the particles more stable (less likely to agglomerate) at higher dosages. These higher and more stable dosages of nano silica also provide more residual silica for pozzolanic reactions at later ages.
The final collection of data, from the highest dosage of nano silica (DOS 4) supports the hypotheses for the over-saturation of the smaller nano silica and the stability of the larger particle. At the highest dosage for the NS1 the modulus is lower that of both of the reference mixtures (6% and 7% reduction when compared to the 20% F Ash and OPC mixtures). Both the NS2 (greater than 15% increase) and NS3 (greater than 29% increase) dosages exhibit a significant increase in modulus over the reference mixtures. Ultimately this data illustrates the sensitivity on the amount of nano silica used in relation to its size and surface area to over-saturation; smaller particles with a higher surface area have a higher sensitivity to over-saturate and agglomerate than larger particles with a smaller surface area.

As previously stated ACI 318 reduces the modulus of concrete to a factor of the compressive strength. The calculated percent changes from the reference mixtures, in Table 5, demonstrate that for the standard concrete (OPC) the measured modulus and calculated modulus are similar, less than 2% change between the two values. The modulus calculated for the performance based concrete (20% F Ash and nano silica) mixtures is grossly underestimated. For the lower dosages of the NS1 (DOS 1 and DOS 2) the calculated modulus is 13% and 8% lower than the measured modulus. The higher dosages of NS1 have a percent change between the calculated and measured at 6% and -6%. While the values for the calculated and measured modulus for the NS2 mixtures are closer (less than 10% change), the change for the values of the NS3 mixtures is between 5% and 13%. These values discussed are evidence that the current equation employed in ACI 318 to predict modulus is obsolete and future research should be used to identify alternative standard procedures to determine modulus of elasticity for non-standard concrete.

**Electrical Resistivity**

The average electrical resistivities of the concrete specimens were measured after 28 days of curing. The electrical resistivity experiment determines the bulk electrical resistivity
of water-saturated concrete, and provides an indication of its resistance to the penetration of fluids and aggressive ions. Furthermore, the electrical resistivity of a saturated concrete sample directly correlates to the durability of concrete – a denser concrete relates to lower porosity and pore connectivity, and leads to a higher resistivity.

As discussed in previous sections, the cement hydration process is triggered when OPC and water are mixed. Concrete electrical resistivity, just like strength development, is dependent on porosity and pore connectivity. As cement hydration commences and the HCM matrix densifies, a higher degree of cement hydration normally yields a decrease in voids and pores (both in size and population). This ultimately reduces the connectivity between pores and thus increases the density of the HCM and the concrete composite. Under the circumstances for these materials and methods, the electrical resistivity increases with increasing density, and therefore correlates to the strength of concrete. Electrical resistivity, therefore, provides a good indication of the extent of the pore structure, permeability and the impact that nano silica has on the densification of the hydrated cement matrix.

The percent change in electrical resistivity measurements (compared to the reference mixtures) for DOS 1 through DOS 4 are listed in Table 6. Similar to the compressive strength and modulus, the increase in electrical resistivity and the densification of the concrete for all the nano silica mixtures was caused by an increased cement dissolution, pozzolanic reaction and heterogeneous nucleation. Just like previous results, the NS1 is most efficient at its lowest dosage when compared to the reference mixtures and NS2 and NS3 at DOS 1 and NS1 at higher dosages. This higher reading for the NS1, at its lowest dosage, illustrates how the nano silica dispersion can effectively enhance concrete when used at a stable dosage. Both the NS2 and NS3 have a lower reading at the same dosage (DOS 1) due to a lower reactivity and therefore lower degree of enhancements.
Table 6 – Percent change of Electrical Resistivity compared to the reference mixtures

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>20% F Ash</th>
<th>OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS3 DOS 4</td>
<td>770%</td>
<td>579%</td>
</tr>
<tr>
<td>NS2 DOS 4</td>
<td>184%</td>
<td>122%</td>
</tr>
<tr>
<td>NS1 DOS 4</td>
<td>52%</td>
<td>18%</td>
</tr>
<tr>
<td>NS3 DOS 3</td>
<td>349%</td>
<td>251%</td>
</tr>
<tr>
<td>NS2 DOS 3</td>
<td>74%</td>
<td>36%</td>
</tr>
<tr>
<td>NS1 DOS 3</td>
<td>48%</td>
<td>16%</td>
</tr>
<tr>
<td>NS3 DOS 2</td>
<td>60%</td>
<td>25%</td>
</tr>
<tr>
<td>NS2 DOS 2</td>
<td>71%</td>
<td>34%</td>
</tr>
<tr>
<td>NS1 DOS 2</td>
<td>54%</td>
<td>20%</td>
</tr>
<tr>
<td>NS3 DOS 1</td>
<td>59%</td>
<td>24%</td>
</tr>
<tr>
<td>NS2 DOS 1</td>
<td>51%</td>
<td>18%</td>
</tr>
<tr>
<td>NS1 DOS 1</td>
<td>69%</td>
<td>32%</td>
</tr>
</tbody>
</table>

As the dosage of the nano silica is increased, a gradual decrease (relative to the other nano silica dosages) in the electrical resistivity is apparent for the higher dosages in NS1 (DOS2 and DOS 3). Both of the higher dosages of the NS1 still yielded increased values when compared to the reference mixtures in Table 6. This reduction in the electrical resistivity reading alludes to the over-saturation and agglomeration issued discussed in previous sections. The agglomerated voids of nano silica would act as large pores, increasing the pore connectivity between adjacent voids within the HCM of concrete. This over-saturation (instability and agglomeration) phenomenon was not found to have the same effect for the NS2 and NS3 at higher dosages. As these dispersions were increased, the electrical resistivity readings increased. The percent change of the NS2 and NS3 mixtures (DOS 2 and DOS 3) show a 30% to 70% increase over the reference mixtures in Table 6. This change stems from the greater stability that the larger nano silica particles exhibit. This greater stability in solution and in the cement paste yields a higher degree of enhancements (due to a greater amount of exposed silica surface area and residual silica) to the hydrated cement matrix and thus yields a concrete with a lower pore connectivity. It could be hypothesized
that the higher particle content of NS1 creates a hydrating environment less conducive to an enhanced microstructure.

While the highest dosage of the NS1 (DOS 4), did not have a severe decrease in electrical resistivity (like the decrease in compressive strength and modulus), the values did not increase as with the NS2 and NS3 mixtures. The lack of increase in the NS1 mixture at DOS 4 is occurring due to an over-saturation effect or agglomeration discussed in previous sections. The highest dosage for NS2 and NS3 yields a 122% to 770% increase over the reference mixtures, listed in Table 6. Just like the compressive strength and modulus, these higher values indicate that the larger particles are more efficient at reducing the pore connectivity of the concrete due to their stability and larger total mass of silica for later aged enhancements.

The data shows that an effective dosage of both the small and large nano silica particles can manipulate the HCM in order to yield a denser concrete composite. Bjornstrom et al, shows that increasing cement dissolution would reduce the size and amount of anhydrous cement, which would normally act as large voids in concrete (J. Bjornstrom 2004). Land hypothesized that the accelerated pozzolanic reaction of nano silica could possibly create a C-S-H kernel for nucleation of excess C-S-Hs and densification of the HCM (Land 2012). Therefore, this decrease in voids and increase the density would increase the electrical resistivity of concrete. Furthermore, instantaneous pozzolanic reaction would also facilitate an increased rate and total polymerization of C-S-H gel, reducing the pore connectivity within the C-S-H microstructure, which would not normally occur in concrete without nano silica. Overall, the electrical resistivity data presented and discussed support the use of nano silica (at a stable, non-agglomerated dosage) to densify the HCM of concrete.
SUMMARY AND CONCLUSIONS

In the present work, three nano silica dispersions were added to grout and concrete specimens to understand the impact of nano silica size and surface area on the temperature curves associated with cement hydration, compressive strength, the modulus of elasticity and electrical resistivity. Originally it was hypothesized that the larger the surface area (i.e. the smaller the nano silica particle diameter), the greater the probability of enhancing the degree of cement hydration, the microstructure, and the macroscopic properties. When comparing the changes in the battery of experiments conducted, it was shown that when using the nano silica there is a sensitivity to size, surface area and the amount of nano silica employed.

Nano silica has been shown to increase the temperature of hydrating cement specifically during the acceleration, deceleration, and the early portion of the densification stages of cement hydration. The temperature curves illustrate the impact the nano silica has on the rate of reactions and consumption of cement. The grout specimen with the largest nano silica (NS3) had the highest temperature output. As the particle size was decreased, so did the temperature output. This phenomenon would be a product of the greater stability and higher effectiveness of the larger nano silica particle. While the smallest nano silica particle (NS1) does show a small increase in temperature for the highest dosage (which normally alludes to an increase in strength), a decrease in compressive strength was found. It could be concluded that despite an increase in the temperature and degree of cement hydration, a reduction in compressive strength was caused by over-saturation, or large voids of agglomerates of nano silica in the concrete. The present experimental study shows that, by introducing the smaller nano silica diameters, the hydrated cement matrix can be produces a softer backbone for the concrete composite. Current research suggests the possibility of an over-saturation threshold, but more work needs to be conducted to better understand this phenomenon.
Like the compressive strength, the modulus of elasticity of the concrete was found to increase with the inclusion of nano silica. The highest modulus values were achieved by using the smaller nano silica at lower dosages, and the larger particles at higher dosages. As noted earlier these results point to a threshold when using nano silica particles in concrete that is dependent on the size, surface area and amount of nano silica used in the concrete. Where using nano silica past this threshold could create agglomerates of nano silica (voids), which ultimately soften the concrete specimens. Furthermore, the measured modulus from the nano silica mixtures showed significant inconsistencies over the calculated modulus of elasticity from ACI 318, suggesting that the ACI 318 equation for modulus grossly undervalues the impact that the nano silica (as well as other concrete additives) has on a non-standard concrete mixture.

The electrical resistivity is indicative of pore structure of the concrete composite. When the nano silica was used at a stable dosage it was shown to successfully increase the electrical resistivity of the concrete. In doing so, this effectively decreased the pore connectivity of the HCM and concrete composite. Even when over-saturated (NS1 at the highest dosage), nano silica enhanced concrete showed a level of electrical resistivity that was comparable to the reference mixtures. Ultimately, the electrical resistivity illustrated how nano silica when used successfully decreased the pore connectivity and increased the density of the HCM and concrete composite.

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