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

Jon S. Belkowitz[1], WhitneyLe B. Belkowitz[2], Kamil Nawrocki[3] and Frank T. Fisher[4]

Biography:

Jon S. Belkowitz – ACI Member Jon Belkowitz is a Ph D Student at Stevens Institute of Technology in Hoboken, NJ. He received a BS in Civil Engineering from Colorado School of Mines and Technology in Golden Colorado in 2006. He received an MS from the University of Denver in 2009. His research interests include nanotechnology of concrete and sustainable concrete solutions.

WhitneyLe B. Belkowitz – ACI Member WhitneyLe Belkowitz is the Vice President of Intelligent Concrete, LLC in Freehold, NJ. WhitneyLe manages the research and development team at Intelligent Concrete, LLC bringing new technologies to the concrete industry. Her research interests include nanotechnology of concrete and sustainable concrete solutions.

Kamil Nawrocki – ACI Student Member Kamil Nawrocki is an undergraduate student, class of 2016, at Harvard University in Cambridge, MA. He is majoring in Government with a focus in International Relations. In the summer of 2011, he worked as an intern researcher with Jonathan Belkowitz and Intelligent Concrete at Stevens Institute of Technology in Hoboken, NJ. His research interests span all academic fields, including cement and concrete.

Frank. T. Fisher – Frank Fisher is an Associate Professor in the Department of Mechanical Engineering and co-Director of the Nanotechnology Graduate Program at Stevens. His research interests span advanced material systems at the nanoscale, including polymer and cement-based nanocomposites. He has been awarded the National Science Foundation's CAREER award, the American Society of Engineering Education (ASEE) Mechanics Division Beer and Johnson Outstanding New Educator Award, and the 2009 Outstanding Teacher Award from the Stevens Alumni Association.

[1] Corresponding Author – JBelkowi@stevens.edu
[2] Whitney@Intelligent-Concrete.com
[3] Kamil.nawrocki@harvard.edu
[4] Frank.Fisher@stevens.edu

1   **ABSTRACT**

2   In this work, the impact of nano silica particles in grouts and concrete samples were

3   measured to identify the change to temperature of cement hydration, strength and density.

4   The compressive strength and modulus of elasticity were also evaluated as a means to

5   understand the impact that the nano silica size and surface area had on the macroscopic

6   properties traditionally used in the concrete industry. Finally, electrical resistivity was

7   measured as a means to understand how the pore connectivity and density of the concrete

8   specimens were manipulated by nano silica addition. Three types of nano silica dispersions

9   (3-6 nm, 15-17 nm and 45-47 nm) were added to cement composites and examined over short

10   and long curing times. All three different sized nano particles were added to have an equal

11   surface area of silica. The larger particles exhibited higher levels of enhancement on the

12   cement composite showing increased compressive and modulus of elasticity by more than

13   20% over the reference mixtures. The finest nano silica particle exhibited a 20% increase in

14   compressive strength at its lowest dosages and a 14% reduction in compressive strength at its

15   highest dosage. These results illustrate a limitation when using the finest nano silica particle.

16   Finally, the addition of all nano silica particles proved to increase the electrical resistivity of

17   the concrete by 30% for the smallest nano silica particles and 700% for the largest nano silica

18   particle. This increase could be attributed to a reduction in permeability and a denser concrete

19   specimen.

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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

1   out of dispersion. The tendency for agglomeration of neighboring nano silica particles in the

2   cement paste is higher, as the cement paste has a higher viscosity than the nano silica in a

3   dispersion alone. If agglomeration is allowed to occur in the fluid cement paste of the

4   concrete composite, these same agglomerates could possibly cause large pores or voids

5   within the hydrated cement matrix of fluid and cured concrete. Large pores and voids within

6   the cured concrete would lead to a reduction in strength, the migration of aggressive

7   materials, and eventually cause degradation of the concrete, as shown by Belkowitz *et al.* (J.

8   Belkowitz 2010).

9   Nano silica has been shown by a number of scientists to increase the strength of concrete.

10   Bjornstrom, *et al* showed that due to the size of the nano silica particle (3-6 nm), there was an

11   increased rate of accelerated cement dissolution in cement composites (J. Bjornstrom 2004).

12   Where the smaller sized nano silica particle will have a higher amount of monomeric silica

13   units on its surface. This higher surface area of condensation sites for pozzolanic reaction are

14   what generate the accelerated cement dissolution and increased rate of pozzolanic reaction.

15   Land*, et al* showed similar results when using nano silica in cement composites and grout

16   specimens and added that there was an increased rate of pozzolanic reaction as well as a

17   higher degree of cement hydration (Land 2012). Land, *et al* attribute these enhancements to

18   the size of the nano silica particle and the accompanying heterogeneous nucleation effect.

19   Belkowitz, *et al* also showed that an increased rate of reaction and compressive strength

20   when using the same nano silica particles as used in this research (J. Belkowitz 2010). Below

21   are the proposed mechanisms, quantitative and qualitative experiments were used to

22   distinguish the impact that the nano silica had on the cement composites, grout and concrete

23   specimens in conjunction with the aforementioned mechanisms.

24   **Increased rate of pozzolanic reaction** - Nano silica is similar to silica-based materials

1 of larger particle-size (such as Class F Fly Ash) in that nano silica provides SiO_2 to combine

2 with calcium hydroxide (the by-product of the cement hydration reaction) to form more C-S-

3 H (Qing 2006), the back-bone of concrete strength. Excess calcium hydroxide, which is

4 normally found in pores and voids, neither bonds to itself nor anything else, and in the

5 presence of water will dissolve back into solution (Mindess 2003). This unstable crystal

6 offers little-to-no strength to the concrete composite. Moreover, when calcium hydroxide

7 dissolves, it leaves behind a pore or void, which can allow to the transport of more aggressive

8 materials (Mindess 2003). Through pozzolanic reaction, the silica (from either nano silica or

9 Class F Fly Ash) combines with the calcium hydroxide in solution to form a super-saturated

10 gel. As the ratio of calcium oxide, CaO, (Ca) to silica, SiO2 (Si) increases in this gel, excess

11 calcium-silicate-hydrates (C-S-H) start to polymerize into a hardened microstructure with a

12 varying degree of internal connectivity. Pellenq *et al,* proposed that reacting excess silica

13 with calcium-hydroxide (pozzolanic reaction) would cause a reduction in the pore structure of

14 the C-S-H microstructure, effectively reducing the fibril and porous structure to a globular

15 and denser C-S-H gel (Pellenq 2007). This excess formation of C-S-Hs effectively reduces

16 the pore distribution and increases the strength of the hydrated cement matrix. Therefore, like

17 Class F Fly Ash, nano silica increases the density of the hydrated cement matrix to increase

18 the strength and durability of concrete.

19 The nano silica is unlike the more mature concrete mineral additives, in that it is an

20 extremely small particle – 1000 times smaller than Class Fly Ash (silica purity, 36.0%) – that

21 has an increased surface area available for immediate pozzolanic reaction in the cement

22 hydration process. Nano silica also has a higher purity of silica, 99.9%. Land *et al*, showed

23 through heat flow calorimetry that nano silica particles lead to an instantaneous pozzolanic

24 reaction in hydrating cement paste, densifying the cement matrix (Land 2012). Bjornstrom *et*

25 *al* showed*,* and confirmed by Qing *et al*, this instantaneous pozzolanic reaction would create

1 a denser foundation within the hydrated cement matrix of the concrete composite for later

2 stages of cement hydration to build upon (J. M. Bjornstrom 2003, Qing 2006). Bentz, *et al*

3 showed that by increasing the rate of pozzolanic reaction early on during the cement

4 hydration process, there is an increase in the hydrated cement matrix density and therefore an

5 increase in concrete strength (D. Bentz 1994).

6 **Accelerated Cement Dissolution** – Pellenq *et al,* hypothesized that during standard

7 cement hydration (without any pozzolanic material or nano silica) a cement particle

8 undergoes hydration until the hydrated products create a diffusion barrier that covers the

9 unhydrated portion of the cement particle, impeding continued hydration (Pellenq 2007).

10 Even with the use of mature mineral additives, the ultimate degree of hydration (percent of

11 cement particle that has reacted) is limited because of the formation of the diffusion barrier.

12 Bjornstrom *et al.* found, through analysis of cement pastes with nano silica using diffuse

13 reflectance FTIR (DR-FTIR) spectroscopy, that nano silica accelerated the dissolution of

14 cement (J. Bjornstrom 2004). This accelerated dissolution ultimately leads to a greater

15 consumption of the cement particle. As with the pozzolanic reaction, the accelerated cement

16 dissolution densifies the hydrated cement matrix of concrete and leads to increased strength.

17 Bjornstrom found through the use of DR-FTIR that the acceleration of cement dissolution

18 was linked to the highly reactive surface of the nano silica particle. Specifically, the higher

19 reactivity is due to a greater amount of monomeric silica units at the surface of the nano silica

20 particle surface and constitute condensation sites for cementitious components (C_3S and C_2S)

21 (J. Bjornstrom 2000). Due to the nano silica size, there is an increased amount of these

22 condensation sites that effectively increase the amount of cement consumed (compared to

23 cement alone) in both the aforementioned cementitious and pozzolanic reactions. Therefore,

24 the use of nano silica particles can increase the efficiency of OPC (degree of cement

1   hydration), leading to a denser hydrated cement matrix and stronger concrete composite.

2   **Heterogeneous nucleation** - The final proposed mechanism is heterogeneous nucleation

3   or the building of distinct phases on a localized surface. Due to the smaller size of the nano

4   silica particles, there is a lower surface potential or smaller electrical double layer at the nano

5   silica particle surface (Wise 1990, Luo 2006). This lower surface potential increases the

6   affinity for heterogonous nucleation, specifically the growth of C-S-Hs, on the surface of

7   nano silica particles. Jayalapan showed, through iso-thermal calorimetry, that an increased

8   amount of nano-TiO_2 and a smaller diameter nano-TiO_2 (an inert material when introduced

9   into cement hydration) increased the degree of hydration for cement composites,

10 hypothesizing that the heterogeneous nucleation was the most probable cause (Jayapalan

11 2009). Land *et al.* showed similar findings when using nano silica, identifying that the

12 nucleation processes and the large number of seeds caused an acceleration of cement

13 hydration, and ultimately leads to a denser concrete (Land 2012). Furthermore, Hou *et al.*

14 showed that nano silica increases the production of stiffer C-S-H gels and increases the

15 density of the hydrated cement matrix through a preferred hydrate formation and

16 heterogeneous nucleation (P. W. Hou 2012, P. K. Hou 2013). Therefore, nano silica has the

17 potential to enhance the HCM through its physical spherical shape and size as well as the

18 chemical reactions that it accelerates. It should be noted that these proposed mechanisms are

19 not singular events occurring at precise times but more of a family of events that occur with

20 some degree of predictability throughout the hydration process. While these mechanisms do

21 occur, to some degree, in standard cement hydration, and even with mature pozzolanic

22 additives such as Class F Fly Ash, it is proposed that they are more likely to occur (and

23 enhance the concrete) when using nano silica particles.

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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 (m^2/g) was used as the primary cementitious material for experimentation. The composition of the cement was: SiO_2, 19.9; CaO, 63.9%; Al_2O_3, 4.8%; Fe_2O_3, 3.2%; C3S, 57%; C2S, 13%; and C3A, 7%. A Class F Fly Ash with a fineness of 0.420 m^2/g was used as a replacement pozzolanic material, with a chemical composition of: SiO_2, 51%; CaO, 13.7%; Al_2O_3, 21%; Fe_2O_3, 6.4%; and Na_2O, 1.2%. The three colloidal nano silica particle dispersions had a silica purity of 99.9% and surface areas (m^2/g) of: 5 nm, 500 m^2/g (hereafter known as NS1); 16 nm, 190 m^2/g (NS2); and 46 nm, 80.0 m^2/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/m^3), for a total Class F Fly Ash mass of 84 kg/m^3. The total free silica surface area brought to the concrete composite by the Class

1 F Fly Ash (with a surface area of 0.42 m^2/g and a silica purity of 36%) was calculated, based

2 on aforementioned cementitious mass, to be approximately 14,000 m^2 per batch (m^2/bt). This

3 surface area, 14,000 m^2/bt, represented the initial dosage for the three different nano silica

4 dispersions discussed earlier. Nano silica replacement dosages for OPC by mass, listed in

5 Table 1 , were changed for each nano silica size distribution to keep the amount of free silica

6 surface constant between sample sets. Each successive dosage represented an increase by one

7 order of magnitude of the silica surface area. The fourth and final dosage (DOS 4) was for a

8 free silica surface area of approximately 280,000 m^2/bt. The amount of Class F Fly Ash that

9 would be needed to equal the different amount of nano silica surface areas are also listed in

10 Table 1 but were not used during experimentation and only serve as a reference.

11   The nano silica distributions and the respective replacement for OPC are listed according

12 to the amount of silica surface area that the nano silica brought to the concrete mixtures in

13 **Table 1**. The smaller nano silica particles required a smaller replacement of the OPC to reach

14 the same silica surface area as the larger particles. The requirement for less material was due

15 to the larger surface area of reactive silica that the smaller particle had when compared to the

16 larger particle. This smaller dosage also reduced the total mass of silica (compared to the

17 larger nano silica particles and Class F Fly Ash), which could be consumed in pozzolanic

18 reaction during later ages of cement hydration.

19   Table 1 - Nano silica percent replacement of Portland cement by mass. The two reference

20   mixtures used had 100% OPC (OPC) and 20% Class F Fly Ash (20% F Ash)

Nano Silica Replacement by mass of OPC (%)			
	NS1, 500 m^2/g	NS2, 190 m^2/g	NS3, 80 m^2/g	Class F Fly Ash, 0.42 m^2/g
Dosage (DOS) 1	0.009%	0.02%	0.05%	20%
DOS 2	0.09%	0.23%	0.55%	200%
DOS 3	0.87%	2.30%	5.46%	2000%
DOS 4	1.75%	4.60%	10.92%	4000%

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

1 depending on the test. For the semi-adiabatic temperature readings, the grout samples were

2 mixed with potable tap water and a fine aggregate with procedures conforming to ASTM C

3 305 (ASTM C305-12 2012). For the concrete samples, concrete sand and crushed granite

4 with a 57/67 gradation were used to make concrete samples. Concrete was mixed in 3.0 cubic

5 foot capacity rotary mixer per ASTM C 192 (ASTM C192-12a 2012). Table 2 lists the

6 mixture constituents for the grout and concrete used throughout the experiments. For all

7 mixes the amount of water that was brought by the nano silica solution was subtracted from

8 the grout or concrete batch water in order to keep the water-to-cementitious ratio consistent

9 between mixes.

10 All samples were prepared according to ASTM C 305 or ASTM C 192, where the fresh

11 grout and concrete, after thoroughly being mixed, were cast into non-absorbent cylindrical

12 molds (ASTM C305-12 2012, ASTM C192-12a 2012). The fluid mix was cast in two lifts of

13 equal volume. Each lift was consolidated 25 times with a metal rod. The cylindrical samples

14 were then tamped 10-15 times lightly on the outside of the mold in the same area of the

15 consolidated lift. After the final lift, the grout and concrete samples were finished with a steel

16 trowel. The samples were allowed to cure for 24 hours in an environmentally controlled

17 laboratory at 21 C. After 24 hours, the cylindrical molds were stripped, the samples were

18 marked, and then placed in a temperature controlled lime-water bath at 21 C.

19 Table 2 - Grout and Concrete Mixtures Proportions

Material Type	Concrete (kg/m3)	Grout (kg/m3)
Type I/II OPC	420	420
67 / 57 Crushed Rock	931	-
Concrete Sand	848	1186
Water-to-Cementitious Ratio	0.47	0.47

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21 **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 H_2O 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.
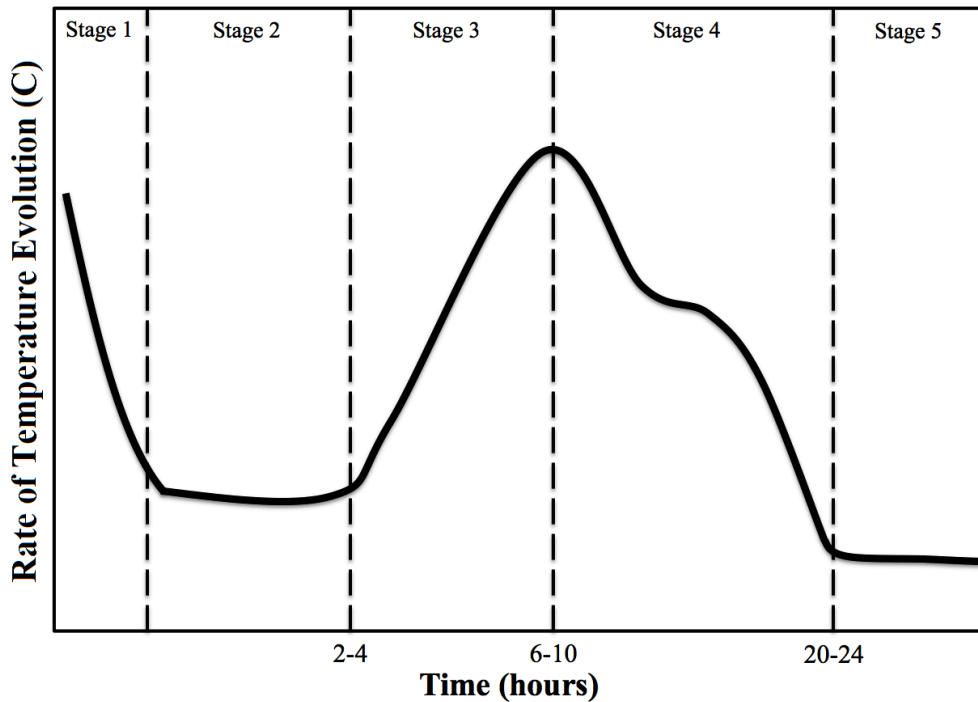
Figure 1 - The 5 stages of the cement hydration process: Stage 1, Mixing; Stage 2,

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

1   equation (1) with the applied load and longitudinal strain. At the point when the longitudinal

2   strain was 50 millionths the load was recorded (S1). The strain (ε2) was then recorded when

3   the applied load was equal to 40 % of the ultimate load (S2).

4   **Electrical Resistivity:** The electrical resistivity of the concrete specimens was measured at

5   28 days, as shown in Figure 2, as a means to identify how the nano silica size and surface

6   area impacted the density of the HCM. A higher density HCM has lower porosity and pore

7   connectivity. Shane *et al,* showed through the use of chloride ion permeability (a test used to

8   measure durability of concrete) and electrical resistivity that as permeability decreased,

9   electrical resistivity increased (Shane 1999). The electrical resistivity was used as a means of

10   measuring the impact of nano silica size and surface area on the pore connectivity and density

11   of concrete.

12   This test method consists of measuring the bulk resistivity of water-saturated concrete

13   cylinders by the use of two plate electrodes in contact with the end surfaces of the specimen.

14   An alternating electrical current was applied through the concrete specimen by the resistivity

15   meter. The apparatus measured the resistance of a concrete specimen. The resistance,

16   measured in ohms (Ω), is the raw data measured and used to determine the electrical

17   resistivity. It has been shown by Shane *et al*, that electrical resistivity can be related to the

18   permeability and density of concrete (Shane 1999). Specifically the concrete specimen's

19   ability to resist to fluid penetration, due to a reduction in pore connectivity. Resistivity is

20   expressed in Equation 3, where L is the specimen length (cm), A is the specimen cross-

21   sectional area (cm^2) and Ω is the resistance of the specimen.

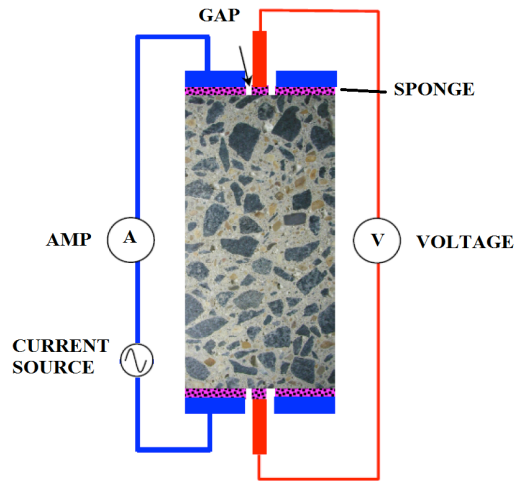22 $$\rho = (\Omega)\left(\frac{A}{L}\right) \tag{3}$$

Figure 2 - Electrical Resistivity of concrete specimen (Shane 1999)

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5 **ANALYTICAL INVESTIGATION**

6   The measured modulus of elasticity was compared to the modulus of elasticity calculated

7 (Ecalculated) by the equation (2) using compressive strength (f'c) from ACI 318, 8.5.1 (318-

8 08 2008). The given equation for modulus determination is the standard used for reinforced

9 concrete design. The mathematical model reduces the modulus to a function of compressive

10 strength. While newer models have been suggested this is the standard used to make

11 decisions for commercial job-site specifications. The current model published in ACI 318

12 grossly under-estimates the modulus for non-standard concrete – this could lead to over-

13 designed concrete and waste of materials in different applications. The measured and

14 calculated moduli of elasticity values were compared in order to highlight the impact that

15 these new nano materials have on the standard concrete practices. Where it is proposed that

16 the nano silica could effectively increase the strength and other engineering properties (such

17 as modulus of elasticity) of concrete in a manner not covered by standardized models.

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$$E_{measured} = \frac{(S_2 - S_1)}{(\varepsilon_2 - 0.000050)} \quad (1)$$

$$E_{calculated} = 57,000(\sqrt{f'c}) \quad (2)$$

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

1   exposed and bound in agglomerates.

2   The decrease of the time in the dormancy stage and the increase in temperature of the

3   acceleration stage can be clearly observed for the NS1 DOS mixture, occurring due to the

4   pozzolanic effect, accelerated OPC dissolution, and nucleation. Figure 3 illustrates that the

5   higher surface area of the nano silica advances the hydration reactions during the dormancy

6   stage, when compared to the reference mixtures. Bjornstrom *et al.* showed in their research

7   that nano silica provides additional surface area for the pozzolanic reaction but also causes

8   the C_3S and C_2S to dissolve faster, thus rendering a more rapid formation of C–S–H and

9   thereby releasing more energy in the form of heat and thus increasing the temperature (J.

10   Bjornstrom 2004). Land *et al.* confirmed these findings, suggesting that in addition to

11   accelerated cement dissolution, an instantaneous pozzolanic reaction occurred developing a

12   C-S-H kernel for nucleation (Land 2012) and also contributed to this rise in heat and

13   temperature.
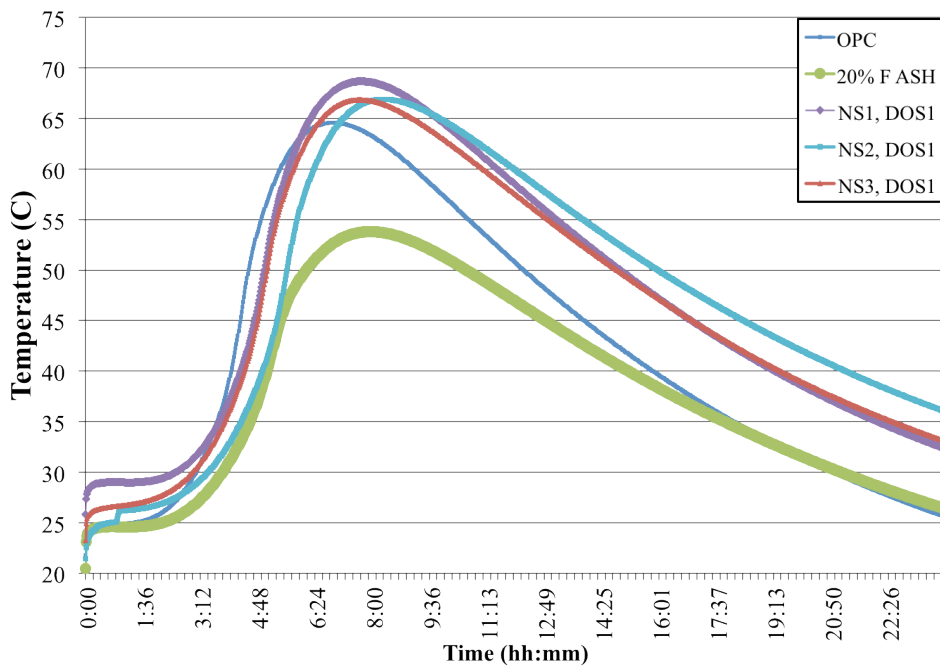
14
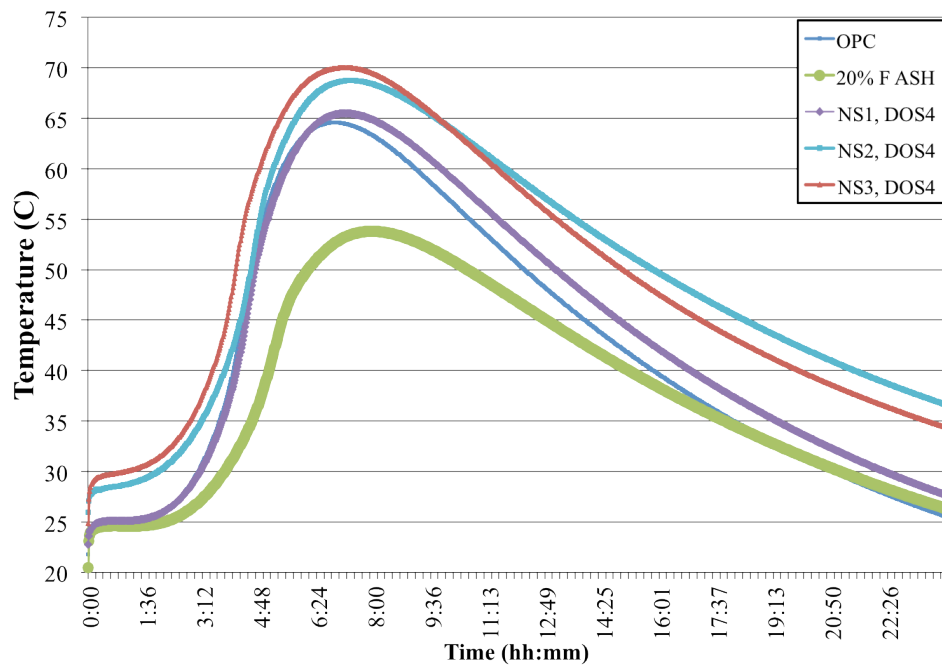15   Figure 3 - Semi-adiabatic temperature curves for dosage one (DOS 1) of the nano silica,
16   measured over 24 hours.

17   Despite the lower temperature curves for NS2 DOS 1 and NS3 DOS 1in 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.
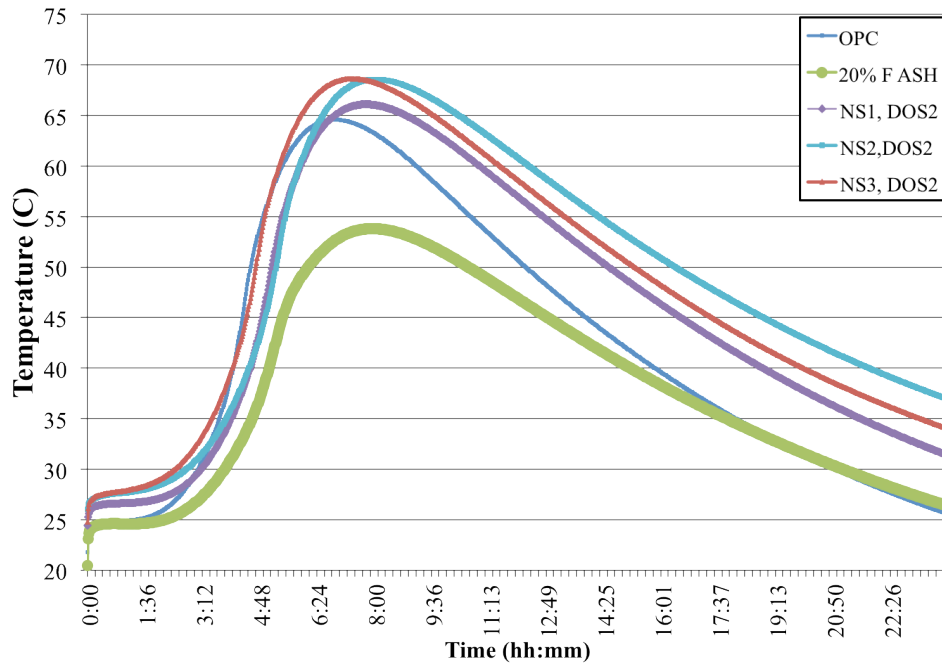
Figure 4 - Semi-adiabatic temperature curves for dosage two (DOS 2) of the nano silica, measured over 24 hours.

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.
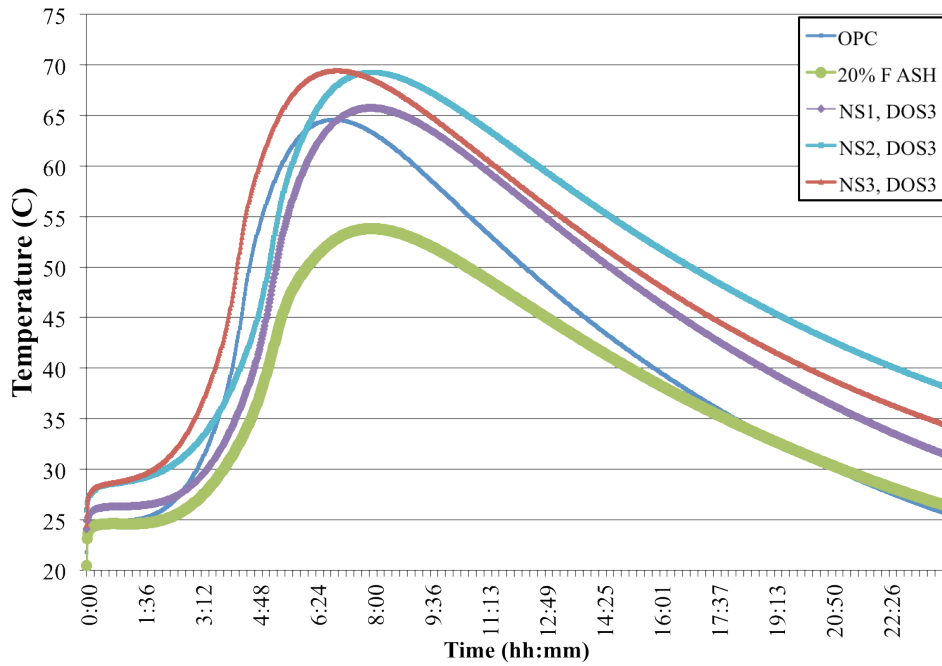
Figure 5 - Semi-adiabatic temperature curves for dosage three (DOS 3) of the nano silica,
measured over 24 hours.

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

1 discussed earlier, the tendency for the nano silica in solution to agglomerate is dependent on

2 the surface potential of said particle and the type of medium it is in. Once the nano silica

3 dispersion is added to the concrete mixture it will immediately have the inclination to

4 agglomerate due to the chemical environment and the viscosity of the cement paste. At

5 higher dosages where a smaller particle might agglomerate the larger nano silica particle is

6 more stable in the cement paste, and therefore has a greater impact on the thermokinetics of

7 cement hydration.

8 **Compressive Strength**

9 The change in compressive strengths (compared to the reference mixtures, OPC and

10 20% F Ash)of the cast specimens after 24 hours, 7 days, 14 days, and 28 days of curing are

11 listed in **Table 3**. For the tested samples, all results conformed to the standard deviation

12 guidelines as stipulated in ASTM C 39 (ASTM C39-12a 2012). All four figures show the

13 typical compressive strength development for the reference mixtures (OPC and 20% F Ash),

14 as well as the mixtures with the nano silica dispersions, over 28 days. As stated in earlier

15 sections, the compressive strength development is dependent on the HCM, aggregate and

16 interfacial zone between the HCM and the aggregate. Upon combining with water, the OPC

17 dissolves and chemically reacts to form the C_3Ss and C_2Ss, a porous network of C-S-Hs – the

18 backbone of the HCM and concrete compressive strength. As time progresses and the OPC

19 cures in the lime-water bath, there is an increase in compressive strength. The increase in

20 compressive strength for the reference mixtures (and nano silica mixtures) are expected for

21 cement composites made with OPC due to the high concentration of water and soluble salts

22 to keep the cement hydration process active. As time progresses the development of

23 compressive strength slows due to a reduction in the availability of anhydrous cement

24 particles caused by a formation of a diffusion barrier at the surface of the cement particle.

25 Belkowitz, *et al* showed that excess free silica content, from the introduction of nano silica

1   particles would increase the rate of OPC dissolution and C-S-H polymerization; thereby

2   increasing early and late compressive strength (J. Belkowitz 2010).

3   There is a distinct increase in compressive strength for the lowest dosage of the NS1

4   mixture (DOS 1) over the reference mixtures and other nano silica mixtures (NS2 DOS 1 and

5   NS3 DOS 1) as listed in **Table 3**. The increase in early and late compressive strength of the

6   NS1 DOS1 mixtures occurred due to the pozzolanic effect, accelerated dissolution and

7   heterogeneous nucleation. The NS2 and NS3 mixtures at the same dosage (DOS 1) have a

8   lower impact on compressive strength development when compared to the NS1, which is due

9   to the lower reactive surface than the NS1 dispersion.

10
11 Table 3 - Percent Change of the Compression Specimens with Colloidal Silica (CS) compared to the reference mixtures (OPC and 20% F Ash).

Mix ID	Break Date	% Change		Mix ID	% Change		Mix ID	% Change	
		OPC	FAsh		OPC	FAsh		OPC	FAsh
NS1 DOS 1	24 Hour	84%	142%	NS2 DOS 1	47%	94%	NS3 DOS 1	9%	43%
	7 Day	22%	61%		20%	58%		6%	40%
	14 Day	19%	36%		20%	37%		8%	23%
	28 Day	20%	13%		18%	12%		6%	0%
NS1 DOS 2	24 Hour	77%	132%	NS2 DOS 2	36%	78%	NS3 DOS 2	32%	73%
	7 Day	17%	55%		17%	55%		11%	46%
	14 Day	15%	31%		15%	31%		21%	38%
	28 Day	15%	8%		15%	8%		16%	9%
NS1 DOS 3	24 Hour	57%	107%	NS2 DOS 3	25%	64%	NS3 DOS 3	66%	117%
	7 Day	5%	38%		13%	49%		12%	48%
	14 Day	5%	19%		14%	30%		22%	40%
	28 Day	5%	-1%		14%	8%		25%	18%
NS1 DOS 4	24 Hour	-27%	-5%	NS2 DOS 4	13%	49%	NS3 DOS 4	83%	141%
	7 Day	-7%	22%		7%	41%		19%	57%
	14 Day	-8%	6%		8%	23%		36%	56%
	28 Day	-14%	-19%		4%	-2%		39%	31%

12

13   An increase in early and late strength can be clearly observed, the higher dosages of the

14   NS2 and NS3 (DOS 2) mixtures, occurring due to a higher degree of the aforementioned

15   mechanisms due to a greater amount of silica surface area. At the same surface area as the

1   NS1, the higher dosages of NS2 and NS3 do not bring an excessive amount of nano silica

2   particles to the fresh concrete that would cause over-saturation and compressive strength

3   reduction, as shown in Table 4. **Table 4** lists the amount of nano silica particles based on

4   percent replacement, by mass, of OPC. It should be noted that number of particles listed in

5   **Table 4** represents the approximate number of nano silica particles based on the nano silica

6   sizes and dosages and should not be taken as an exact number of particles. The number of

7   particles was used to identify the cause of agglomeration and compressive strength reduction

8   when using nano silica. Due to the lower amount of particles and the size of the larger

9   particles, NS2 and NS3 are more stable than the NS1 DOS 2 (which has a lower increase in

10   compressive strength when compared to NS1 DOS 1) and therefore did not have a tendency

11   to agglomerate and cause a compressive strength reduction.

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

No. of Nano Silica Particles per cubic meter (cm)			
DOS 1	1.78E+08	3.02E+07	2.57E+07
DOS 2	1.78E+09	3.02E+08	2.57E+08
DOS 3	1.78E+10	3.02E+09	2.57E+09
DOS 4	3.57E+10	6.04E+09	5.14E+09

16

17   The same phenomena for the higher dosage (DOS 3) of both the smaller and larger nano

18   silica particles hold true for the compressive strength illustrated in **Table 3**. While there is

19   still some early compressive strength increase for the NS1 DOS 3 mixture, the later strengths

20   (specifically the 28 day compressive strength and listed in **Table 3**) shows a reduction of

21   strength over the 20% F Ash mixture (-1%) and a moderate increase in strength when

22   compared to the OPC mixture (5%). This lack of early and later compressive strength gain is

23   a by-product of an over-saturation of the NS1 dispersion. Similar to the NS1 DOS, the NS2

1   DOS 3 has no change in compressive strength compared to the lower dosages of the same

2   dispersion as listed in **Table 3**. This suggests that like the NS1, there is a limitation on the

3   amount of NS2 used. Conversely to the NS1 and NS2 (DOS 3) mixtures, the NS3 DOS 3

4   mixture leads to a steady increase in strength. This consecutive increase in strength for the

5   NS3 DOS 3 would be the result of a higher stability to resist agglomeration and therefore a

6   higher degree of efficiency.

7   A severe decrease in strength, relative to the control, is apparent for the higher dosage of

8   NS1 (DOS4) in **Table 3**, with a decrease in strength occurring due to an over-saturation

9   effect (more nano silica particles give rise to a greater number of agglomerated sites and

10   voids). Nazari *et al,* showed similar results (when using 5% percent mass of 12-18 nm nano

11   silica) in their investigation of nano silica in self compacting concrete. Nazari *et al,* attributed

12   the reduction in strength to a reduction in C-S-Hs growth and density; this inevitably led to a

13   weaker cement matrix (Nazari 2011). The cause for the reduced compressive strength noted

14   by Nazari was the super-saturation of Si in relation to the amount of available Ca for

15   pozzolanic reaction (Nazari 2011). Nazari, *et al,* also hypothesized that the higher dosages of

16   the nano silica caused the development of nano silica particle agglomerates, rounded masses

17   of collected nano silica particles, in the hardened HCM. These agglomerates, which offer no

18   resistance to compressive loads, softened the HCM and led to a reduction in the compressive

19   strength. By this logic, the NS1 effectively brought an excessive amount of nano silica

20   particles to the fresh concrete mixture, listed in **Table 4**, compared to the other nano silica

21   dispersions at the same dosage. The excessive particle content in the highly viscous fresh

22   concrete would agglomerate and create voids in the hardened state. These voids would act as

23   crack propagation sites during the loading of the sample, causing a decrease in strength.

24   As the dosage of the nano silica increased (and number of particles) there was a greater

1   likelihood for these particles to agglomerate, soften the HCM and reduce compressive

2   strength, referred to as over-saturation of nano silica. This phenomenon would be most

3   prevalent, illustrated by the percent change in **Table 3**, with the smallest nano silica particle

4   distribution used, NS1, due to a lower surface potential of the NS1 particle, when compared

5   to the other distributions used in these tests. Just like the NS1 DOS 4, the highest dosage of

6   NS2 (DOS 4) was negatively impacted by over-saturation or agglomeration. This dosage of

7   NS2 had a reduction in early and later strength, when compared to the reference mixtures and

8   the other nano silica mixtures. It is hypothesized that this amount of nano silica caused a

9   similar phenomenon that occurred in the NS1 DOS 4 mixture but to lesser degree as found by

10 the change in strength listed in **Table 3**. For the highest dosage of the NS3 (DOS 4) mixture,

11 an increase in early and late strength can be clearly observed. No decrease in strength was

12 found for dosages of NS3, suggesting that the largest nano silica (with the largest surface

13 potential) is less sensitive to over-saturation when compared to the smaller nano silica

14 particles.

15   Two key components identified for the use of nano silica to increase compressive

16 strength focus on the relationship between the size of the nano silica particle and its tendency

17 to agglomerate in the HCM. First, the use of a larger nano silica particle seemed more

18 effective due to a greater stability against over-saturation. The controlled use of the larger

19 nano silica particles allowed for a higher degree of the aforementioned mechanisms

20 (increased rate of pozzolanic reaction, accelerated cement dissolution and heterogeneous

21 nucleation) to increase the compressive strength. The second component is the limitation of

22 the amount of nano silica that can be used to enhance compressive strength. This limitation,

23 referred to as over-saturation, is dependent on the size, surface area (accompanying surface

24 potential) of the nano silica particle as well as the number of the nano silica particles in the

25 HCM.   Specifically, the smaller nano silica particles inherently have a smaller surface

1 potential, and therefore have a higher propensity for agglomeration. The larger nano silica

2 particles, particularly the NS3, have a larger surface area and therefore a lower inclination for

3 agglomeration and compressive strength loss. The data presented illustrates the potential that

4 nano silica has on compressive strength development in concrete as well as some of its

5 limitations.

6 **Modulus of Elasticity**

7   Bentz *et al,* showed through concrete modeling and simulation that just like the

8 compressive strength, the modulus of concrete is dependent on the modulus of the aggregate,

9 hydrated cement matrix and the strength of the interfacial zone between the aggregate and the

10 hydrated cement matrix (D. Bentz 1991). Both the reference mixtures have lower values for

11 measured modulus than a majority of the mixtures with nano silica (excluding NS1 DOS 4).

12 As with the previously recorded data for the reference mixtures, over the first day of

13 hydration both the reference mixtures showed a lower rate and a shorter duration of cement

14 hydration. Furthermore, the rate of compressive strength gain and the ultimate compressive

15 strength was lower for both the reference mixtures when compared to the nano silica mixtures

16 (excluding NS1 DOS 4). Both of these data sets support the lower modulus values measured

17 for the reference mixtures. The reasoning for this lower measured modulus is due in full to

18 the lack of nano silica, which enhances both the hydrated cement matrix and concrete.

19   At the same dosage all three nano silica dispersions show an increase in modulus over

20 the reference mixtures. The lowest dosage of NS1 (DOS 1) generates the highest modulus

21 when compared to the other nano silica mixtures at the same dosage (NS2 DOS 1 and NS3

22 DOS 1) in **Table 5**. The increase in the nano silica mixtures are listed in **Table 5** and show

23 that the NS1 generates a 20% increase over the OPC and 22% increase over the 20% F Ash.

24 This higher measurement is due to the higher surface area (and a lower surface potential),

25 which ultimately causes an increase in the modulus through an increase in pozzolanic

1 reaction, accelerated cement dissolution and heterogeneous nucleation. The lower modulus

2 values for the NS2 and NS3 mixtures in **Table 5**, at the same dosage, would be due to the

3 lower amount of reactive silica surface area and therefore a lower degree of enhancement.

4 Table 5 – Percent Change of the Modulus of Elasticity for the Nano Silica mixtures when

5 compared to the reference mixtures.

Mix ID	20% F Ash	OPC
NS3 DOS 4	29%	30%
NS2 DOS 4	16%	17%
NS1 DOS 4	-7%	-6%
NS3 DOS 3	17%	18%
NS2 DOS 3	10%	11%
NS1 DOS 3	5%	6%
NS3 DOS 2	16%	17%
NS2 DOS 2	9%	10%
NS1 DOS 2	9%	10%
NS3 DOS 1	14%	15%
NS2 DOS 1	6%	7%
NS1 DOS 1	20%	22%

6
7 As the dosages of nano silica are increased in DOS 2 and DOS 3 it is evident that the

8 NS1 is starting to soften as shown through the reduction in percent increase over the

9 reference mixtures in Table 5. This softening is due to the over-saturation that was found to

10 have occurred with the compression strength specimens. As with the compression it is

11 hypothesized that this over-saturation of the nano silica is causing the formation of voids with

12 nano silica agglomerates that offer little to no strength to the concrete. The larger NS2 and

13 NS3, which have been shown to be more stable at higher dosages than the NS1, are more

14 effective at increasing the modulus of the specimens as shown in **Table 5** for DOS 2 and

15 DOS 3. The larger nano silica particles have a larger surface potential at their surface, which

16 keeps the particles more stable (less likely to agglomerate) at higher dosages. These higher

17 and more stable dosages of nano silica also provide more residual silica for pozzolanic

18 reactions at later ages.

1	The final collection of data, from the highest dosage of nano silica (DOS 4) supports the

2	hypotheses for the over-saturation of the smaller nano silica and the stability of the larger

3	particle. At the highest dosage for the NS1 the modulus is lower that of both of the reference

4	mixtures (6% and 7% reduction when compared to the 20% F Ash and OPC mixtures). Both

5	the NS2 (greater than 15% increase) and NS3 (greater than 29% increase) dosages exhibit a

6	significant increase in modulus over the reference mixtures. Ultimately this data illustrates

7	the sensitivity on the amount of nano silica used in relation to its size and surface area to

8	over-saturation; smaller particles with a higher surface area have a higher sensitivity to over-

9	saturate and agglomerate than larger particles with a smaller surface area.

10	As previously stated ACI 318 reduces the modulus of concrete to a factor of the

11	compressive strength. The calculated percent changes from the reference mixtures, in **Table 5**,

12	demonstrate that for the standard concrete (OPC) the measured modulus and calculated

13	modulus are similar, less than 2% change between the two values. The modulus calculated

14	for the performance based concrete (20% F Ash and nano silica) mixtures is grossly

15	underestimated. For the lower dosages of the NS1 (DOS 1 and DOS 2) the calculated

16	modulus is 13% and 8% lower than the measured modulus. The higher dosages of NS1 have

17	a percent change between the calculated and measured at 6% and -6%. While the values for

18	the calculated and measured modulus for the NS2 mixtures are closer (less than 10% change),

19	the change for the values of the NS3 mixtures is between 5% and 13%. These values

20	discussed are evidence that the current equation employed in ACI 318 to predict modulus is

21	obsolete and future research should be used to identify alternative standard procedures to

22	determine modulus of elasticity for non-standard concrete.

23	**Electrical Resistivity**

24	The average electrical resistivities of the concrete specimens were measured after 28

25	days of curing. The electrical resistivity experiment determines the bulk electrical resistivity

1   of water-saturated concrete, and provides an indication of its resistance to the penetration of

2   fluids and aggressive ions. Furthermore, the electrical resistivity of a saturated concrete

3   sample directly correlates to the durability of concrete – a denser concrete relates to lower

4   porosity and pore connectivity, and leads to a higher resistivity.

5   As discussed in previous sections, the cement hydration process is triggered when OPC

6   and water are mixed. Concrete electrical resistivity, just like strength development, is

7   dependent on porosity and pore connectivity. As cement hydration commences and the HCM

8   matrix densifies, a higher degree of cement hydration normally yields a decrease in voids and

9   pores (both in size and population). This ultimately reduces the connectivity between pores

10   and thus increases the density of the HCM and the concrete composite. Under the

11   circumstances for these materials and methods, the electrical resistivity increases with

12   increasing density, and therefore correlates to the strength of concrete. Electrical resistivity,

13   therefore, provides a good indication of the extent of the pore structure, permeability and the

14   impact that nano silica has on the densification of the hydrated cement matrix.

15   The percent change in electrical resistivity measurements (compared to the reference

16   mixtures) for DOS 1 through DOS 4 are listed in **Table 6**. Similar to the compressive

17   strength and modulus, the increase in electrical resistivity and the densification of the

18   concrete for all the nano silica mixtures was caused by an increased cement dissolution,

19   pozzolanic reaction and heterogeneous nucleation. Just like previous results, the NS1 is most

20   efficient at its lowest dosage when compared to the reference mixtures and NS2 and NS3 at

21   DOS 1 and NS1 at higher dosages. This higher reading for the NS1, at its lowest dosage,

22   illustrates how the nano silica dispersion can effectively enhance concrete when used at a

23   stable dosage. Both the NS2 and NS3 have a lower reading at the same dosage (DOS 1) due

24   to a lower reactivity and therefore lower degree of enhancements.

Table 6 – Percent change of Electrical Resistivity compared to the reference mixtures

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

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

1   that the higher particle content of NS1 creates a hydrating environment less conducive to an

2   enhanced microstructure.

3   While the highest dosage of the NS1 (DOS 4), did not have a severe decrease in

4   electrical resistivity (like the decrease in compressive strength and modulus), the values did

5   not increase as with the NS2 and NS3 mixtures. The lack of increase in the NS1 mixture at

6   DOS 4 is occurring due to an over-saturation effect or agglomeration discussed in previous

7   sections. The highest dosage for NS2 and NS3 yields a 122% to 770% increase over the

8   reference mixtures, listed in **Table 6**. Just like the compressive strength and modulus, these

9   higher values indicate that the larger particles are more efficient at reducing the pore

10   connectivity of the concrete due to their stability and larger total mass of silica for later aged

11   enhancements.

12   The data shows that an effective dosage of both the small and large nano silica particles

13   can manipulate the HCM in order to yield a denser concrete composite. Bjornstrom *et al,*

14   shows that increasing cement dissolution would reduce the size and amount of anhydrous

15   cement, which would normally act as large voids in concrete (J. Bjornstrom 2004). Land

16   hypothesized that the accelerated pozzolanic reaction of nano silica could possibly create a C-

17   S-H kernel for nucleation of excess C-S-Hs and densification of the HCM (Land 2012).

18   Therefore, this decrease in voids and increase the density would increase the electrical

19   resistivity of concrete. Furthermore, instantaneous pozzolanic reaction would also facilitate

20   an increased rate and total polymerization of C-S-H gel, reducing the pore connectivity

21   within the C-S-H microstructure, which would not normally occur in concrete without nano

22   silica. Overall, the electrical resistivity data presented and discussed support the use of nano

23   silica (at a stable, non-agglomerated dosage) to densify the HCM of concrete.

1 **SUMMARY AND CONCLUSIONS**

2 In the present work, three nano silica dispersions were added to grout and concrete specimens

3 to understand the impact of nano silica size and surface area on the temperature curves

4 associated with cement hydration, compressive strength, the modulus of elasticity and

5 electrical resistivity. Originally it was hypothesized that the larger the surface area (i.e. the

6 smaller the nano silica particle diameter), the greater the probability of enhancing the degree

7 of cement hydration, the microstructure, and the macroscopic properties. When comparing

8 the changes in the battery of experiments conducted, it was shown that when using the nano

9 silica there is a sensitivity to size, surface area and the amount of nano silica employed.

10 Nano silica has been shown to increase the temperature of hydrating cement specifically

11 during the acceleration, deceleration, and the early portion of the densification stages of

12 cement hydration. The temperature curves illustrate the impact the nano silica has on the rate

13 of reactions and consumption of cement. The grout specimen with the largest nano silica

14 (NS3) had the highest temperature output. As the particle size was decreased, so did the

15 temperature output. This phenomenon would be a product of the greater stability and higher

16 effectiveness of the larger nano silica particle. While the smallest nano silica particle (NS1)

17 does show a small increase in temperature for the highest dosage (which normally alludes to

18 an increase in strength), a decrease in compressive strength was found. It could be concluded

19 that despite an increase in the temperature and degree of cement hydration, a reduction in

20 compressive strength was caused by over-saturation, or large voids of agglomerates of nano

21 silica in the concrete. The present experimental study shows that, by introducing the smaller

22 nano silica diameters, the hydrated cement matrix can be produces a softer backbone for the

23 concrete composite. Current research suggests the possibility of an over-saturation threshold,

24 but more work needs to be conducted to better understand this phenomenon.

1 Like the compressive strength, the modulus of elasticity of the concrete was found to

2 increase with the inclusion of nano silica. The highest modulus values were achieved by

3 using the smaller nano silica at lower dosages, and the larger particles at higher dosages. As

4 noted earlier these results point to a threshold when using nano silica particles in concrete

5 that is dependent on the size, surface area and amount of nano silica used in the concrete.

6 Where using nano silica past this threshold could create agglomerates of nano silica (voids),

7 which ultimately soften the concrete specimens. Furthermore, the measured modulus from

8 the nano silica mixtures showed significant inconsistencies over the calculated modulus of

9 elasticity from ACI 318, suggesting that the ACI 318 equation for modulus grossly

10 undervalues the impact that the nano silica (as well as other concrete additives) has on a non-

11 standard concrete mixture.

12 The electrical resistivity is indicative of pore structure of the concrete composite. When

13 the nano silica was used at a stable dosage it was shown to successfully increase the electrical

14 resistivity of the concrete. In doing so, this effectively decreased the pore connectivity of the

15 HCM and concrete composite. Even when over-saturated (NS1 at the highest dosage), nano

16 silica enhanced concrete showed a level of electrical resistivity that was comparable to the

17 reference mixtures. Ultimately, the electrical resistivity illustrated how nano silica when used

18 successfully decreased the pore connectivity and increased the density of the HCM and

19 concrete composite.

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