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Laboratory Investigation of Nanomaterials to Improve the Permeability and Strength of Concrete

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16. Abstract:

Concretes containing various supplementary cementitious materials (SCMs) such as silica fume, fly ash, and slag have improved properties. Nanomaterials (a nanometer, nm, is 10^{-9} m), new SCMs with possible applications in concrete, have the smallest particle size that is less than 100 nm. Nanomaterials are very reactive because of the particles' small size and large surface area and have great potential in improving concrete properties such as compressive strength and permeability. This study evaluated the use of a variety of nanomaterials in concrete compared with conventional concrete and concrete containing common SCMs. The potential benefits of using nanomaterials over other SCMs are their high reactivity; the need for smaller amounts, resulting in less cement replacement; and cost-effectiveness.

Concretes containing nanosilica and nanoclay were prepared in the laboratory and compared to concretes containing silica fume, fly ash, slag, or only portland cement. Specimens were tested for compressive strength and permeability. The microstructure of selected concretes with improved compressive strength and permeability were analyzed using an atomic force microscope and nanoindenter to determine the reason for the improvements.

The microstructure of the nanosilica concrete was denser and more uniform than that of the conventional concrete microstructure. In addition, the nanosilica had the largest improvement in both compressive strength and permeability among the nanomaterials tested.

The results of this study indicate that some of the nanomaterials tested have potential in concrete applications. However, further evaluation is required before nanomaterials can be used in concrete. Specifically, they should be evaluated for improved dispersion to achieve uniformity, optimized amounts of ingredients, and cost-effectiveness.

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FINAL REPORT

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ABSTRACT

Concretes containing various supplementary cementitious materials (SCMs) such as silica fume, fly ash, and slag have improved properties. Nanomaterials (a nanometer, nm, is 10^{-9} m), new SCMs with possible applications in concrete, have the smallest particle size that is less than 100 nm. Nanomaterials are very reactive because of the particles' small size and large surface area and have great potential in improving concrete properties such as compressive strength and permeability. This study evaluated the use of a variety of nanomaterials in concrete compared with conventional concrete and concrete containing common SCMs. The potential benefits of using nanomaterials over other SCMs are their high reactivity; the need for smaller amounts, resulting in less cement replacement; and cost-effectiveness.

Concretes containing nanosilica and nanoclay were prepared in the laboratory and compared to concretes containing silica fume, fly ash, slag, or only portland cement. Specimens were tested for compressive strength and permeability. The microstructure of selected concretes with improved compressive strength and permeability were analyzed using an atomic force microscope and nanoindenter to determine the reason for the improvements.

The microstructure of the nanosilica concrete was denser and more uniform than that of the conventional concrete microstructure. In addition, the nanosilica had the largest improvement in both compressive strength and permeability among the nanomaterials tested.

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INTRODUCTION

Concrete durability is very important, especially when concretes are exposed to the outdoors. Therefore, many new ways to improve concrete properties to ensure longevity are being investigated. Nanotechnology is a relatively new technology that is being integrated into many applications including electronics, telecommunications, and biomedicine. Manipulation at the nanoscale can change chemical reactions, temperature, electricity, and magnetism (Birgisson, 2006). Nanotechnology deals with particles having at least one dimension between approximately 1 and 100 nm (ASTM E2456) (ASTM International, 2006). Recently, nanotechnology has been applied in the production of concrete to reduce permeability, which is essential in extending service life (He and Shi, 2008). In addition, the nanomodification can result in improvements in strength, shrinkage, ductility, and impact resistance (Birgisson, 2006).

When used as supplementary cementitious material (SCM) in concrete, various nanoparticles can improve and densify the cement matrix, leading to improved permeability and strength. The nanoparticles act as “nuclei” of hydration (Li et al., 2004), possess pozzolanic behavior (Li et al., 2004), and can fill the voids in the cement matrix (Shih et al., 2006). Pozzolans chemically react with calcium hydroxide liberated during hydration to form cementitious compounds (Kosmatka et al., 2002). The large surface area of nanoparticles and their abundance because of their small size can facilitate the chemical reactions necessary to produce a dense cement matrix with more calcium silicate hydrate (C-S-H) and less calcium hydroxide. This, in turn, will enhance the overall concrete performance. Nanoparticles are, in general, smaller than the commonly used SCMs, making them more reactive and effective. Different forms of nanosilica (NS) and nanoclays (NC) in cement paste have been shown to increase compressive strength, reduce permeability, and cause a denser microstructure (He and Shi, 2008). Nanoparticles can also strengthen the interfacial transition zone between the cement paste and the aggregate, which would lead to improved strength and permeability. For nanoparticles to be a substitute for other SCMs of larger particle size, equal or better performance at lower or equal cost is needed. This may be achieved by using lower dosages of nanoparticles.

Some nanomaterials for use in concrete include NS (nano-SiO_2), NCs, nanotubes, nanocomposites (e.g., NCs), and nano-titanium dioxide (nano-TiO_2) (He and Shi, 2008).

Various nanoproducts are available from different companies, and it is unknown which nanoproducts will improve the properties of concrete.

PURPOSE AND SCOPE

The purpose of this study was to determine the effect of the use of nanomaterials in concrete. Specifically, the objective of the study was to determine if nanomaterials can increase strength, decrease permeability, and cause a denser cement matrix. The study focused on air-entrained concrete.

The study was conducted with 26 batches of concrete, including an NS, six NCs, common SCMs (silica fume [SF], Class F fly ash, and slag), and only portland cement, that were made in the laboratory.

METHODS

Overview

Twenty-six batches of concrete with various amounts and types of SCMs, as described in Table 1, were prepared in the laboratory, and specimens were cast for tests. Fresh and hardened concrete properties were determined. Selected concretes that exhibited improvements in strength and permeability were evaluated at the nanoscale using the atomic force microscope (AFM) and the nanoindenter.

For fresh concrete properties, the air content and slump were determined. For hardened concrete properties, compressive strength, modulus of elasticity, permeability, and length change were determined.

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Table 1. Supplementary Cementitious Materials Used in This Study

SCM	Designation	Average Particle Size	Material Form	Replacement (%)
Class F fly ash	FA	~25 µm	Powder	21
Slag	S	<45 µm	Powder	40
Silica fume	SF	0.15 µm	Densified powder	7
Nanosilica	NS	22 nm	Slurry with water	3
NC vermiculite	NC1	<33% more than 45 µm; thickness in nm	Clay dispersed in water	3
NC hydrophobic nano montmorillonite synthetic	NC2	Sieve residue (63 µm): maximum 55%; thickness in nm	Powder	0.5
NC nanoparticle	NC3	2 µm long, diameter 30 Å	Rod-shaped particles	0.5, 2, 4
NC synthetic nanoparticle or colloid	NC4	100 nm	Powder	0.25, 0.5, 2
NC hydrophilic nano montmorillonite	NC5	Length and width 100s of nanometers, thickness 1 nm	Powder	0.5, 1, 3
NC surface modified nano montmorillonite	NC6	15-20 µm, thickness in nm	Powder	0.5, 1, 3

SCM = supplementary cementitious material; NC = nanoclay.

Mixture Proportions and Batches

Concretes were mixed in the laboratory in 0.75-ft^3 batches. A total cementitious material of 635 lb/yd^3 was used at two water–cementitious material ratios (w/cm). The w/cm of 0.38 was chosen to represent high-strength concretes (greater than 6,000 psi at 28 days) mainly used in beams; the w/cm of 0.45 was chosen to represent deck concrete (strengths exceeding 4,000 psi at 28 days). Two batches with two other w/cms are included in the table to provide additional information.

The replacement rates of the SCMs are given in Table 1. Some of the SCM was used only at the w/cm of 0.45 since this w/cm is more common in bridge structures and there were not enough nanomaterials to make additional batches at the other w/cms.

All mixtures contained the same materials except for the addition of the SCMs. The coarse aggregate used was granite gneiss with a nominal maximum size of 1 in. Natural sand was used for the fine aggregate. The portland cement was Type I/II. All concretes contained a commercially available air-entraining admixture, and all concretes except for the ones with NC4 contained a polycarboxylate-based high-range water-reducing admixture.

The mixtures with the promising strength and permeability values were selected for microstructure analysis. Table 2 is a summary of the mixture proportions for the selected concretes that represent conventional concrete (control concrete with only portland cement), concrete containing an SCM with a particle size of microns (SF), and an SCM with a particle size of nanometers (NS), respectively.

Table 2. Mixture Proportions (lb/yd^3)

Ingredient	Control	Silica Fume	Nanosilica
Cement	635	591	616
Coarse aggregate	1804	1804	1804
Fine aggregate	1148	1131	1145
Water	286	286	286
SCM	0	43	19
w/cm	0.45	0.45	0.45

SCM = supplementary cementitious materials; w/cm = water–cementitious materials ratio.

Testing for Concrete Properties

Concrete specimens were made in accordance with ASTM C192. Specimens were cured for 28 days at room temperature in the moist room except for the permeability specimens, which also included accelerated curing (moist cured for 1 week at 73 ºF and 3 weeks at 100 ºF). Results with the accelerated cure indicate the long-term permeability (6 months and beyond) at 28 days (Ozyildirim, 1998). Fresh concrete tests included density (ASTM C138), air content (ASTM C231), and slump (ASTM C143). Hardened concrete tests are listed in Table 3 with the specimen sizes.

Table 3. Hardened Concrete Tests and Specimen Sizes

Test	Specification	Size (in)
Compressive strength	ASTM C39	4 by 8
Elastic modulus	ASTM C469	4 by 8
Permeability[a]	ASTM C1202	2 by 4
Length change	ASTM C157	3 by 3 by 11

[a] Two curing methods were used: a standard moist cure and an accelerated cure (moist cured 1 week at 73 °F and 3 weeks at 100 °F).

Microstructure Testing

Atomic Force Microscope

The AFM was used to observe visually the microstructure and to generate information on roughness (lack of uniformity) of the paste. Concrete samples for AFM imaging were polished using various diamond disks. Initially, an 80 grit disk was used. This was followed by a 220 grit, a 600 grit, and then a 1,200 grit disk. Once the concrete was polished, it was cut down to samples approximately 5 mm by 5 mm by 2 mm for use in the AFM. AFM height and deflection images were made in the contact mode where the tip of the AFM stays in contact with the sample while moving across it.

Roughness measurements were made by performing a power spectral density (PSD). The software used along with the Veeco AFM executed a PSD on whole images (Digital Instruments, 1990). A root mean square (RMS) roughness value is obtained by integrating the PSD over a frequency and then taking the square root (Digital Instruments, 1990). The RMS roughness value takes into account the more than 200,000 data points in a randomly produced image. The images were 35.8 micron by 35.8 micron in size.

The roughness test enables the analysis of the uniformity of the microstructure. A more uniform and dense microstructure (lower roughness value) should relate to a concrete with higher compressive strength, higher elastic modulus, and lower permeability. Since all samples were polished in the same manner, the roughness values were expected to indicate the relative impacts the different SCMs had on the cement paste structures.

Nanoindentation

Nanoindentation was also performed on the polished samples. Two methods were used. First, the samples were indented elastically using the ramping mode of the AFM. However, the probes used were not stiff enough (k = 0.06 N/m) for the hardened concrete. The cantilever to which the tip is attached was bending instead of flexing. Since the cantilever was not strong enough, the data did not accurately represent the indenting process because the tip deflection was not measured. The tip that performed the best had a spring constant of 40 N/m, and it indented up to only 40 nm before bending. This did not provide enough data to determine the modulus of elasticity. A tip with a spring constant on the order of 100 N/m (which was not available) would allow more data to be collected from indentation.

Second, the samples were tested by applying loads to a three-sided pyramid (Berkovich) tip. In this study, the pyramid tip was pushed 5 μm into each concrete sample, causing permanent deformation. The nanoindenter graphs load applied versus the displacement of the tip. A curve is created during loading, and another curve is produced in unloading. A schematic of the indentation process is shown in the loading and unloading curves in Figure 1. The stiffness, S, which is equal to dP/dh (P = load and h = displacement), is used to find the elastic modulus of the indented surface (Oliver and Pharr, 1992).

Nanoindentation is important because of its ability to calculate the microscale modulus of elasticity, stiffness, and paste uniformity. The nanoindentation results were obtained by indenting three different paste areas on each sample. Four to seven indents were performed on each of the three paste areas. All indentation data for an individual concrete sample were put into one file and averaged. The average microscale E values for each type of concrete were compared to determine the relation among the different microstructures. In addition, the macroscale and nanoscale values found for E were compared and analyzed.

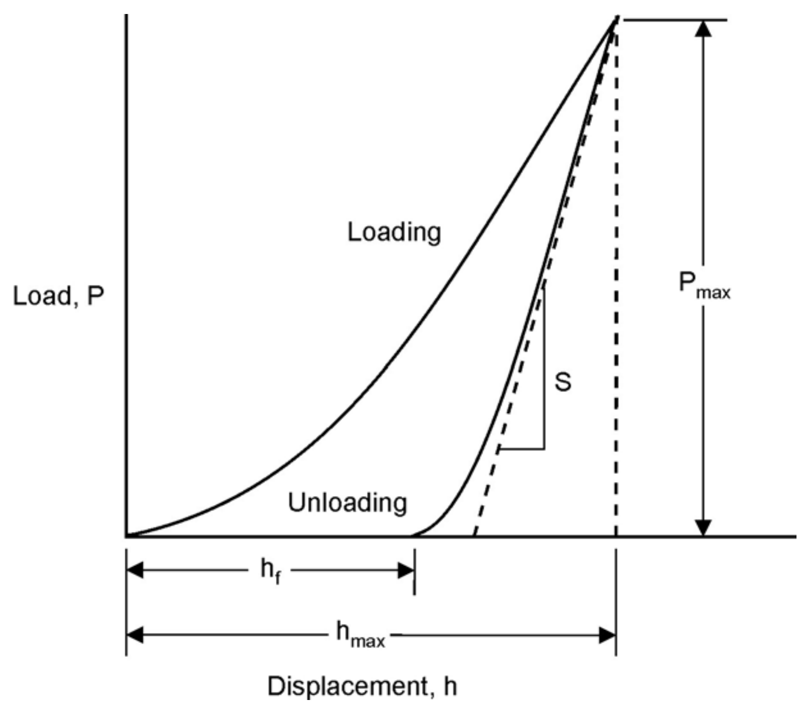


Figure 1. Determination of Elastic Modulus (Adapted from Oliver and Pharr, 1992)

RESULTS AND DISCUSSION

Concrete Properties

Fresh and Hardened Concrete Properties

The concretes containing nanomaterials were expected to have a significantly increased compressive strength and lower permeability because of the pozzolanic activity and the densification of the cement matrix. The fresh concrete properties of the 26 mixtures are listed in Table 4, and the hardened concrete properties are in Tables 5 and 6. The information in the tables is grouped in terms of the w/cm. The compressive strength of many of the concretes containing nanomaterials was increased as compared to that of the control concrete. The results are an average of two samples. The compressive strength of concretes with a w/cm of 0.38 ranged from 6,610 to 8,600 psi; that of concretes with a w/cm of 0.45 ranged from 4,420 to 7,080 psi. All values were satisfactory.

Permeability samples at 28 days subjected to accelerated curing had a lower permeability than those subjected to standard curing. SCMs take time to contribute to lowering permeability since they react after hydration reactions. Therefore, the comparison of results of accelerated curing versus standard curing at 28 days indicated the contribution of the SCMs as summarized in Table 5 and displayed in Figure 2. Based on accelerated curing, the control concrete with a w/cm of 0.45 had a high permeability (exceeding 4,000 coulombs). The concrete with SF had very low permeability (<1,000 coulombs), and the concretes with fly ash or slag had low permeability (1,000 to 2,000 coulombs). The concretes containing nanomaterials had moderate (2,000-4,000 coulombs) to high (>4,000 coulombs) permeability. The nanomaterial concrete with the lowest permeability (2280 coulombs) contained NS. The six concretes with a w/cm of 0.38 all had moderate permeability. In NCs at the w/cm of 0.45, going to a higher percentage of

Table 4. Fresh Concrete Properties

Material	Percentage[a]	w/cm	Air (%)	Slump (in)
Control	0	0.38	5.8	2.75
NC1	3	0.38	6.8	9.25
NC5	0.5	0.38	2.8	2.5
NC5	1	0.38	3.2	0.75
NC6	0.5	0.38	2.7	3.5
NC6	1	0.38	4.5	2.25
NC3	4	0.40	5.5	3.25
Nanosilica	1.8	0.41	9.5	1.5
Control	0	0.45	6.6	3.75
Fly ash	21	0.45	6.9	4
Slag	40	0.45	6.7	5
Silica fume	7	0.45	8.4	4.5
Nanosilica	3	0.45	6.8	2.75
NC1	3	0.45	5.4	9.3
NC2	0.5	0.45	3.3	2
NC3	0.5	0.45	7.4	2.25
NC3	2	0.45	8	2.25
NC4	0.25	0.45	4.7	2.5
NC4	0.5	0.45	7.5	4.5
NC4	2	0.45	4.9	8
NC5	0.5	0.45	8.5	4
NC5	1	0.45	5.8	2.5
NC5	3	0.45	2.5	3
NC6	0.5	0.45	2.3	5.5
NC6	1	0.45	3	4
NC6	3	0.45	8	4.5

w/cm = water–cementitious materials ratio; NC = nanoclay
[a] By weight of cementitious materials.

Table 5. Hardened Concrete Properties at 28 Days

Material	Percentage[a]	w/cm	Compressive Strength (psi)	E (ksi)	Permeability (coulombs)	Accelerated Permeability (coulombs)
Control	0	0.38	7710	3955	3300	2656
NC1	3	0.38	6610	3685	3200	2665
NC5	0.5	0.38	7430	3800	4158	3784
NC5	1	0.38	8080	4270	3770	3024
NC6	0.5	0.38	7870	4095	3887	2761
NC6	1	0.38	8600	4095	3889	2743
NC3	4	0.4	8380	3515	3795	3042
Nanosilica	1.8	0.41	7290	3520	2606	2312
Control	0	0.45	5620	3550	5319	4225
Fly ash	21	0.45	4420	3255	5516	1517
Slag	40	0.45	6020	3330	2614	1151
Silica fume	7	0.45	5920	3265	2456	865
Nanosilica	3	0.45	7080	3595	3004	2280
NC1	3	0.45	5580	3520	5086	4055
NC2	0.5	0.45	6230	3525	5988	5417
NC3	0.5	0.45	5950	3515	3394	3038
NC3	2	0.45	6040	3330	3960	2791
NC4	0.25	0.45	5450	3620	3909	3338
NC4	0.5	0.45	4800	3350	5849	4326
NC4	2	0.45	5170	3010	6613	5994
NC5	0.5	0.45	5220	3500	5057	4188
NC5	1	0.45	5960	3580	5319	4163
NC5	3	0.45	6420	3415	6858	5424
NC6	0.5	0.45	6450	3910	6754	5020
NC6	1	0.45	6810	3695	5941	4395
NC6	3	0.45	4610	3085	5082	4479

w/cm = water–cementitious materials ratio; NC = nanoclay
[a] By weight of cementitious materials.

addition resulted in an increase in permeability for NC3 and NC4 and no change in permeability for NC5 and NC6. This behavior can be attributed to the existence of an optimum replacement rate and possibly to the inefficient mixing and high variability. Mixing was performed in a conventional 1.75-ft^3 (0.05-m^3) pan mixer, which has a low shearing action. There are high-intensity, high-shear mixers that can provide more thorough and uniform mixing. In addition, the selection of the proper dispersant would help in obtaining the desired mixing. The lack of improvement with a higher percentage of the nanomaterial was also seen with the NC6 mixtures at the w/cm of 0.38.

Among the concretes with a w/cm of 0.45, the NS concrete had the highest compressive strength. The SF concrete had the lowest permeability. They were selected with the control concrete for the microstructure evaluation. Figure 3 shows the air content, slump, and compressive strength of the three mixtures. They had similar workability, indicated by the slump value, but the air content of the SF concrete was higher than in the others.

An increase in air content of 1% by volume typically relates to a drop in compressive strength on the order of about 5% (Whiting and Nagi, 1998). The concrete with NS had a higher compressive strength than the SF concrete but also had a lower air content. Concretes with NS

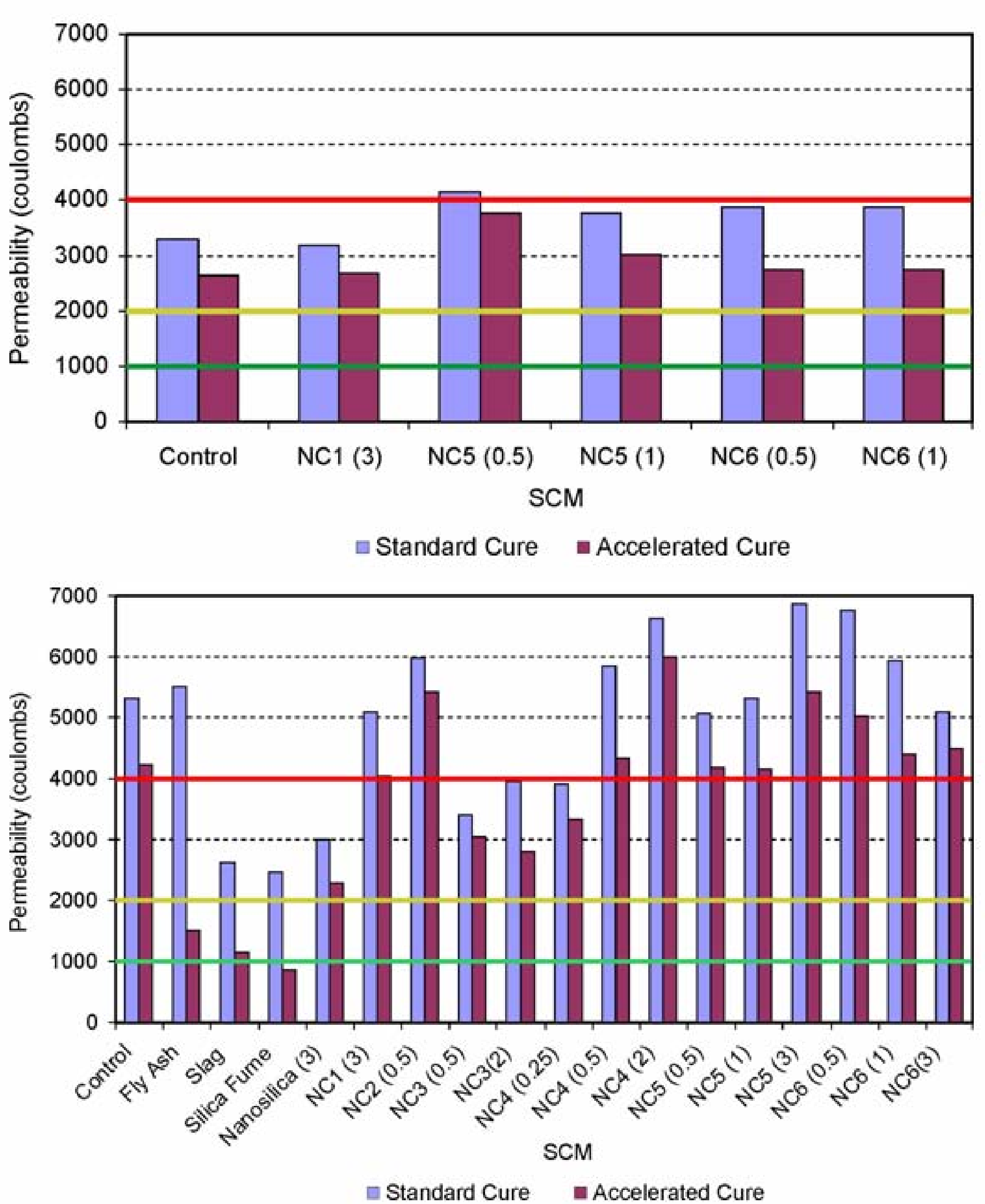


Figure 2. Contribution of SCMs to Concrete Permeability for w/cm = 0.38 (top) and w/cm = 0.45 (bottom). The percentage of nanomaterial is given in parenthesis. NC = nanoclay.

or SF had a higher strength than the control even though the control had the lowest air content. The size of the nanoparticle and the chemicals used in the slurry are expected to affect the air-entrainment. The effect of the nanomaterials on the air content and air-void parameters should be explored.

The elastic modulus values for all of the concrete mixes are listed in Table 5. The values are for an average of two test specimens. They ranged between 3,010 and 4,270 ksi.

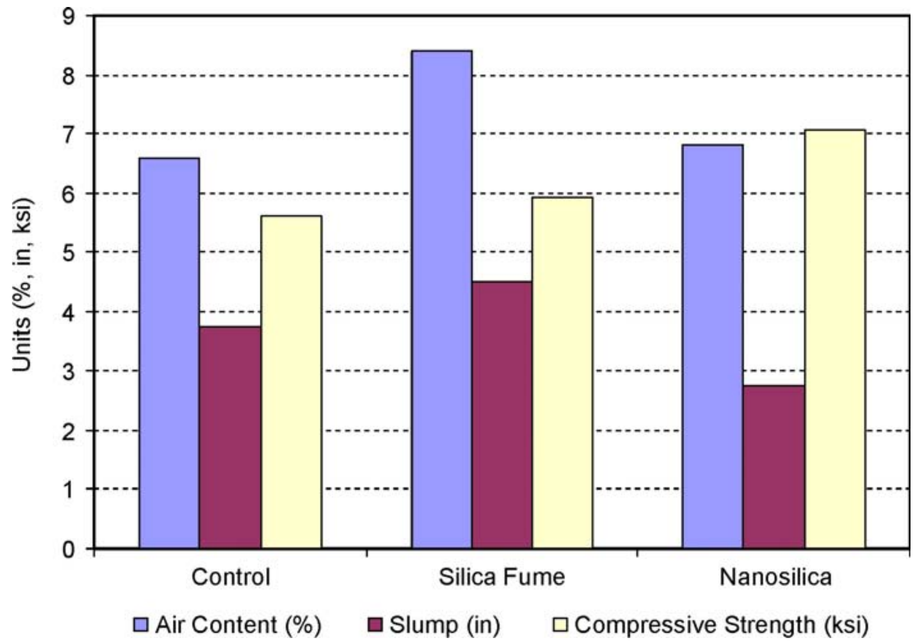


Figure 3. Air Content and Slump for Selected Mixtures

Correlation of Elastic Modulus and Compressive Strength

The elastic modulus is related to the square root of the compressive strength (Kosmatka et al., 2002). The elastic modulus was plotted and found to be correlated with the square root of the compressive strength as shown in Figure 4. The measured variations in the square root of the compressive strength predicted 70% of the measured variations in elastic modulus.

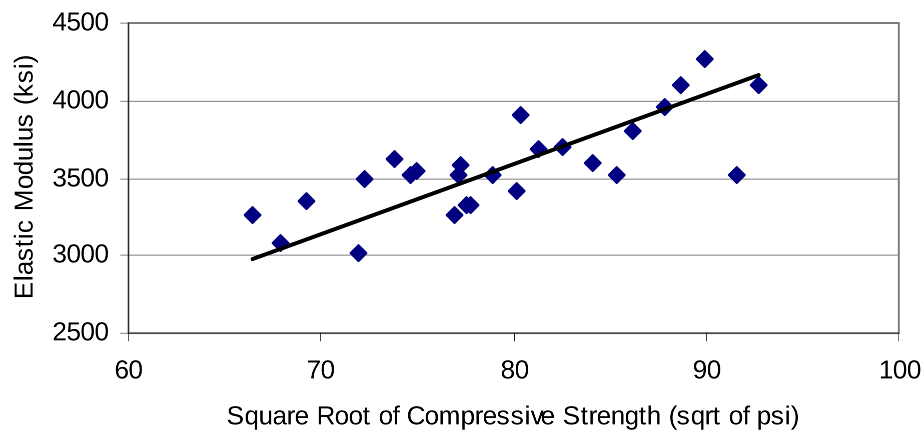


Figure 4. Relationship Between Compressive Strength and Elastic Modulus

Length Change

The length change data are shown in Table 6 for 28 days, 16 weeks, and 32 weeks after 28 days of moist curing. The values indicate drying shrinkage. Concretes made with the same

Table 6. Shrinkage Data in Microstrain

SCM	Percentage[a]	w/cm	28 days	16 weeks	32 weeks
Control	0	0.38	340	470	560
NC1	3	0.38	300	460	515
NC5	0.5	0.38	385	605	600
NC5	1	0.38	315	525	530
NC6	0.5	0.38	280	490	485
NC6	1	0.38	360	540	530
NC3	4	0.40	400	465	505
Nanosilica	1.8	0.41	315	395	460
Control	0	0.45	420	580	690
Fly ash	21	0.45	390	530	630
Slag	40	0.45	350	475	590
Silica fume	7	0.45	375	480	575
Nanosilica	3	0.45	355	490	590
NC1	3	0.45	320	515	575
NC2	0.5	0.45	440	650	650
NC3	0.5	0.45	355	495	510
NC3	2	0.45	385	500	500
NC4	0.25	0.45	335	445	440
NC4	0.5	0.45	410	590	595
NC4	2	0.45	485	695	685
NC5	0.5	0.45	410	605	625
NC5	1	0.45	390	585	600
NC5	3	0.45	515	720	720
NC6	0.5	0.45	410	620	645
NC6	1	0.45	385	565	580
NC6	3	0.45	370	580	610

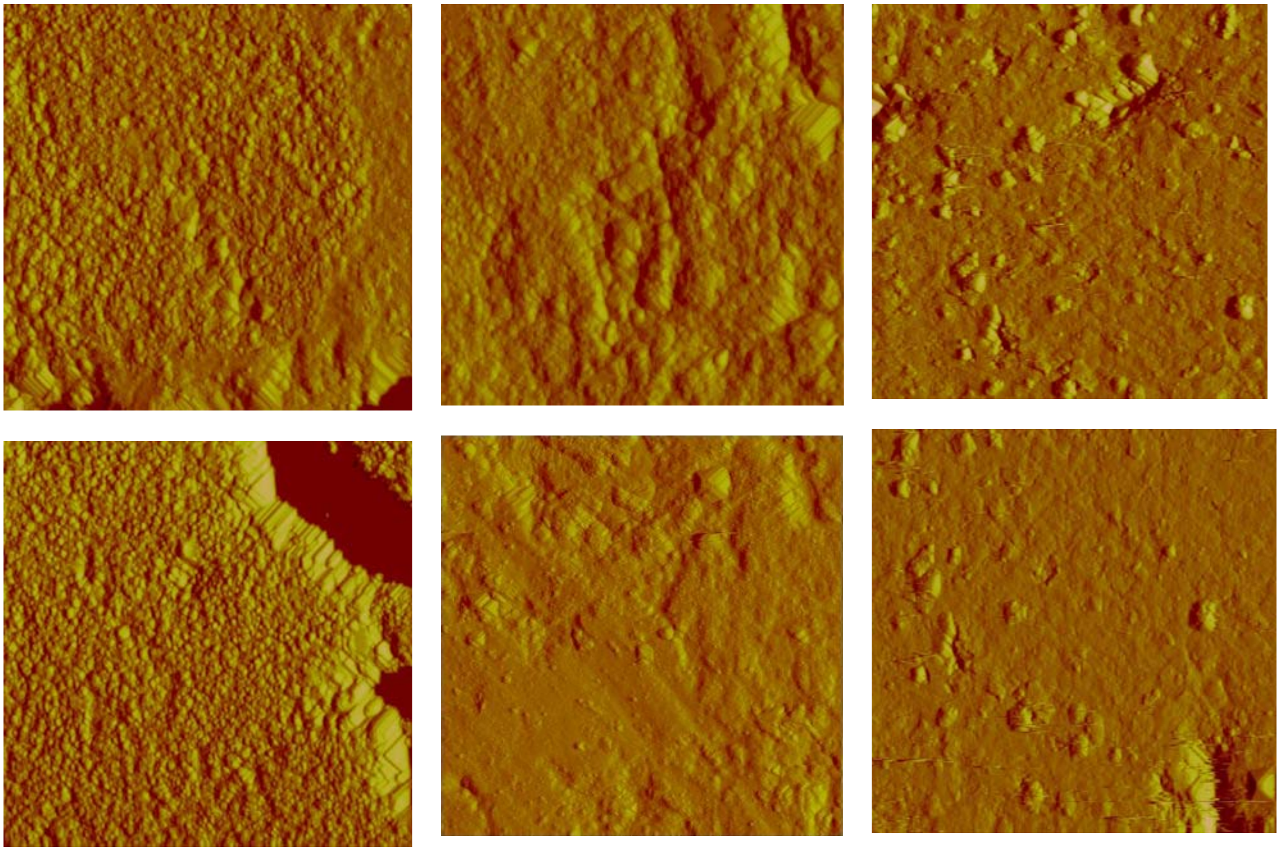
SCM = supplementary cementitious materials; w/cm = water–cementitious materials ratio; NC = nanoclay
[a] By weight of cementitious materials.

materials had less shrinkage in the lower w/cm since they had a lower water content. Shrinkage is primarily related to the water content of the mixture if the other ingredients are kept constant. At 16 weeks, only the NS (1.8%) with a w/cm of 0.41 had the drying shrinkage below 400 microstrain. It has been recommended that 28-day shrinkage be limited to 400 microstrain to prevent unacceptable shrinkage-induced transverse cracking (Babaei and Fouladgar, 1997). NS meets this even at 16 weeks. At 32 weeks, concretes with SCMs at a w/cm of 0.45 had less shrinkage than the control except for the NC5 (3%). Similarly at a w/cm of 0.38, SCM concretes had less shrinkage than the control concrete except for the NC5 (0.5%).

Microstructure Testing

AFM Images

AFM images of regular concrete, SF concrete, and NS concrete were analyzed for the different characteristics of the microstructures. Based on visual observation, the regular concrete microstructure was very gritty in nature (Figure 5a). The SF concrete microstructure appeared to be more mountainous (Figure 5b). In general, the flattest, most uniform microstructure visually was that of the NS concrete (Figure 5c).



(a) (b) (c)

Figure 5. AFM images (35.8 μm by 35.8 μm) of (a) Control Concrete, (b) Silica Fume Concrete, and (c) Nanosilica Concrete

AFM images measuring 35.8 μm by 35.8 μm were analyzed for roughness. Before the analysis, each image was plane fitted and flattened to eliminate image distortion from the microscope. The Nanoscope software that is used along with the Veeco Instruments AFM has plane fit and flatten options that will remove the bow and tilt from images. The third order plane fit was used to perform a plane fit of the entire image about the x axis. It is subtracted from the image to remove the bow and tilt (Digital Instruments, 2004). The third order flatten was used to perform least-squares fits to each scan line and subtract the fit from the scan line to remove the bow and tilt. It also accounts for the Z offset between the scan lines (Digital Instruments, 2004). Once the image distortion was removed, a PSD was performed and RMS roughness values were calculated. A higher roughness value represents a less uniform paste surface. The results are shown in Figure 6. The NS concrete had the overall lowest roughness values, and the SF concrete the overall highest roughness values. Lower roughness values correspond to a more uniform cement paste. The high values for the SF concrete might be caused by the agglomeration of the SF particles because of the difficulty of separating the densified SF particles during mixing.

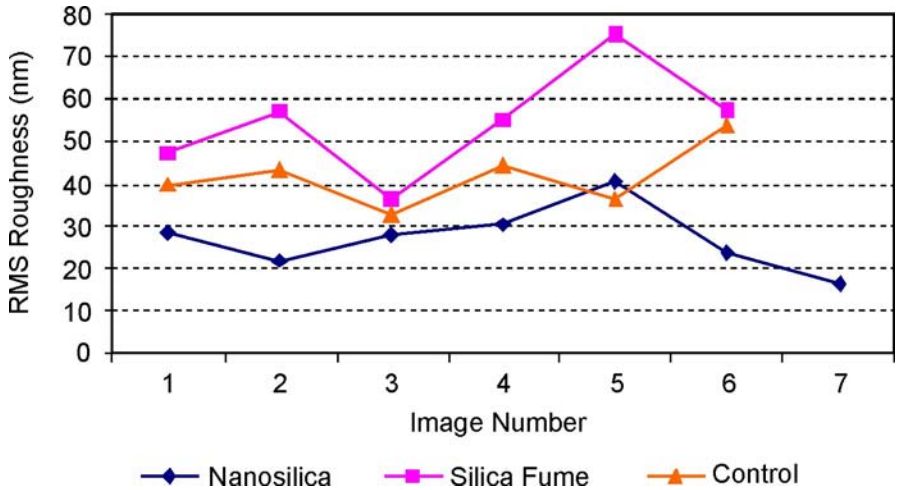


Figure 6. Roughness Values of Three Concretes

Nanoindentation

Four to seven indents were performed on each of the three paste areas on each sample using the nanoindenter. E values (elastic modulus of concrete) were calculated from the following equations (Oliver and Pharr, 1992):

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \qquad \text{[Eq. 1]}$$

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \qquad \text{[Eq. 2]}$$

where

S = experimentally measured stiffness of the upper portion of the unloading curve
A = projected area of the elastic contact
P = load
H = displacement
E_r= reduced elastic modulus defined in Equation 2
ν = Poisson's ratio
i = indicates that the values are for the indenter tip.

A total of 15 indents were performed on the SF concrete, 17 indents on the NS concrete, and 20 indents on the regular concrete sample. All runs for an individual concrete sample were put into one file and averaged. The E values given in Table 7 represent the average values. Table 7 also includes elastic modulus values determined using the standard elastic modulus test on the concrete cylinders (Macroscale E). Both tests show the same trend in elastic modulus values. The nanoindentation values are averages of three paste areas in each sample, and the macroscale values are averages of two cylinders. The NS concrete had the highest E values, and the SF concrete the lowest. The macroscale values of E were lower than the microscale values.

This is attributed to the averaging value in the macroscale E, which includes the interfacial transition zone (weak zone).

Table 7. Microscale and Macroscale Elastic Modulus Values

Type of Concrete	Microscale E (ksi)	Macroscale E (ksi)
Control	4080	3550
Silica fume	4060	3260
Nanosilica	4930	3600

SUMMARY OF FINDINGS

- When added to concrete mixtures, many of the types of nanomaterials improved the compressive strength and permeability of the concrete as compared to the control mix. In this study, NS was the nanomaterial with the best impact on concrete performance, and the NS (1.8%) has the highest potential to reduce drying shrinkage cracking. Some NCs had a negative effect compared to the control concrete. However, the results for the concretes containing these NCs were in the same range as the results for the control concrete.

- Concrete containing NS exhibited improvements in compressive strength compared to the concrete containing SF, but NS was not as effective in lowering permeability. The nanoindentation and roughness results indicated that the NS paste is stronger (highest E value) and has a more uniform microstructure (lowest roughness value) than the SF paste and regular concrete paste. However, the amount and size of NS may not be sufficient to fill in pores and reduce transport of fluids within the concrete. Three percent NS was used, which may not be enough or may not be well dispersed. High-intensity, high-shear mixing with the use of a proper dispersant would be helpful in thorough mixing with minimal clumping. The lack of NS in some areas could lead to places with voids that are not filled, which provide easy transport of fluids, affecting permeability.

- The AFM images of regular concrete, NS concrete, and SF concrete were analyzed for roughness. A lower roughness value correlates to a more uniform microstructure. According to the roughness results and visual observation of the AFM images, the NS concrete has the most uniform microstructure, followed by the regular concrete, and the SF concrete has the least uniform microstructure. The SF concrete may have dispersion issues, and the densified SF particles may have formed agglomerates that are difficult to break.

- The trend in elastic modulus values corresponds to the trend in roughness values. Since a lower roughness or more uniform paste corresponds to a higher strength, the elastic modulus should be higher for more uniform paste structures. As expected, the NS concrete had the lowest roughness value and the highest elastic modulus.

CONCLUSIONS

- Nanomaterials added in small quantities can improve the strength, permeability, and shrinkage of concrete.

- Although some of the nanomaterials tested have potential in concrete applications, further evaluation is required before nanomaterials can be used in concrete. Specifically, they should be evaluated further for improved dispersion to achieve uniformity, optimized amounts of ingredients, and cost-effectiveness.

- AFM can provide information on roughness, which correlates with the uniformity and density of the microstructure. Increase in the uniformity and density indicates improved strength.

- Nanoindentation provides information on elastic modulus, which can be used to explain the changes in the microstructure of the concrete and to verify the results of the AFM.

RECOMMENDATION

1. Although VDOT's Materials Division and Structure & Bridge Division can potentially benefit from the use of nanomaterials in concrete, the following should be addressed before nanomaterials are used in concrete for VDOT structures:

    - Determine the optimum amount of nanomaterials in trial batches.

    - Determine whether nanomaterials should be used in a slurry form for better dispersion of particles.

    - For cost-effectiveness, evaluate the combination of NS with different amounts of slag and fly ash to evaluate the concrete performance pertaining to compressive strength, permeability, and length change for future application for bridge deck concretes.

    - Verify the benefits of nanomaterials with proper tests regarding their microstructure. Perform other testing along with the AFM testing to delineate the microstructure, including pore size and distribution. Tests would include nanoindentations to provide additional information on the elastic modulus; mercury intrusion testing to enable the measurement of pores in the concrete; and scanning electron microscopy to provide images of the microstructure.

BENEFITS AND IMPLEMENTATION PROSPECTS

Very small amounts of nanomaterials in concrete can improve the cement paste and interfacial transition zone. These improvements benefit the compressive strength and permeability of the concrete. By adding only small amounts of the nanomaterials, there is minimal cement replacement, which could be more cost-effective than adding larger percentages of other conventional pozzolans for improved concrete properties, especially in cold weather.

Pozzolans are routinely used in concrete in the field to improve durability. Nanomaterials can be implemented immediately provided they are well dispersed for uniformity of the mixture and optimum amounts are determined and are deemed cost-effective. It is necessary for the technology to develop to a stage where nanomaterials that can benefit concrete can be selected and applied in well-dispersed non-powder forms without coagulation. This may be possible by using an effective dispersant that will keep the nanomaterials separate in suspension and the proper mixing equipment.

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