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Investigating the Effect of Nanosilica on Compressive Strength of Hard Concrete by Considering Atomic Force Microscopy (AFM) Examinations

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Abstract: This study investigated the compressive strength of hardened concrete and the formation of Calcium Silicate Hydrate (C-S-H) with the addition of nanosilica (SiO2). Compressive strength testing was performed using ASTM C496 to determine stress-strain curves and compressive strength of the materials. The hydration process and formation of C-S-H and Calcium Hydroxide (CH) were examined using Atomic Force Microscopy (AFM) and Fourier Transform Infrared Spectroscopy (FTIR). Results indicate an increase in compressive strength using 1, 3, and 5% of nanosilica to concrete replacement by volume in comparison to the control mix (without nanosilica). The optimum concrete replacement to yield maximum strength was of the 5% nanosilica content. Comparing the 56-day results for the 3 and 5% of nanosilica replacement samples shows the same percentage of C-S-H formation of 83 and 85%, respectively.

Keywords: AFM, Compressive Strength, Concrete, FTIR, NanoSilica

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Research paper

1 INTRODUCTION

A series of chemical reactions takes place during the hydration process of concrete paste. Once water is added to the cement, the tricalcium aluminate reacts with the gypsum to produce ettringite and heat. Next, the tricalcium silicate is hydrated to produce the C-S-H, lime and heat. Once the gypsum is gone, the ettringite becomes unstable and begins to react with the remaining tricalcium aluminate to form monosulfate aluminate hydrate crystals [1].

During a sulfate deficient solution, the monosulfate crystals become unstable. The crystals then resort back into ettringite during the presence of sulfates. The increase in the crystal size is what causes the cement to crack when subjected to sulfate attack. The belite hydrates to form C-S-H and heat. The C-S-H during this phase generates strength within the concrete. This process has a very slow rate; however, this compound produces the long-term strength of cement concrete. The ferrite goes through two progressive reactions with the gypsum. The first reaction is when the ettringite reacts with the water and gypsum to form ettringite, lime, and alumina hydroxides.

The second reaction occurs when the ferrite further reacts with the ettringite that was formed during the first reaction in order to produce garnets. Hydration kinetics has been modeled by several researchers to better understand the reactions and changes that Portland cement undergoes during the hydration process. Lin and Meyer [2] developed a hydration kinetic model for Portland cement based on the thermodynamics of multiphase porous media. Their model considered the effects of cement fineness, chemical composition, water-cement ratio, pressure, and curing temperature, to analyze the ultimate degree of hydration and develop a corresponding formula. They concluded that their proposed model adequately demonstrates the different experimental results for cement hydration at high pressures and elevated temperatures. Trapote-Barreira [3] conducted a research dissertation on the dissolution kinetics of calcium silicate hydrate gel and the durability of mortar. Examinations were carried out using AFM and Force Microprobe Analyzer (EPMA). Zaki and Ragab [4] conducted testing using 0, 0.5, 0.7, and 1% of nanosilica in concrete along with 20% of silica fume in all mixes. They concluded the optimum amount of nanosilica was 0.5% by weight of cementitious material. Gopinath et al. [5] investigated the effects of nanosilica in normal-strength concrete using 1.5 and 3% of nanosilica to cement replacement by weight; compared to concrete without nanosilica. Their findings portrayed varying results with greater earlier 3-day strength results with 3% of nanosilica and higher 28-day results with 1.5% of nanosilica. Salkhordeh et al. [6] investigated the effects of recycled concrete as an aggregate and nanosilica as cement replacement in Self-Consolidating Concrete (SCC) for 28-day compressive strength. With different percentages of recycled concrete aggregates ranging from 0 to 100 in 20% intervals and nanosilica replacing 10% of cement weight; they found that adding nanosilica to all samples leads to an increase in compressive strength. Elkady et al. [7] investigated the reasons for the inconsistencies in the workability and compressive strength of nanosilica concrete. The research investigated how agglomeration can affect the compressive strength and workability of normal strength concrete due to different methods of deagglomeration. Results showed that sonication proved to be the most significant de-agglomeration method as it enhanced the gain in compressive strength of concrete by 23% using only 1% nanosilica to cement substitution. Givi et al. [8] studied the size effects of SiO2 nanoparticles on compressive, flexural, and tensile strength of binary blended concrete. They specified that the rate of the pozzolanic reaction is related to the surface area existing during the reaction. Thus, it is feasible to add high purity (99.9%) nanosilica with a high Blaine fineness value (60 m2 /g) in order to improve the characteristics of cement. Their results showed that nanoparticles blended with concrete increased the compressive, flexural, and tensile strength at all curing ages. Belkowita and Armentrout [9] also studied the relationships of using different sizes of nanosilica in cement paste. They measured the heat of hydration, the concentration of CH through X-ray diffraction, grain structures through AFM, and compressive strength. Their experimental results showed an increase in compressive strength as the C-S-H became more rigid when the nanosilica particles decreased in size and their size distribution broadened. Bi et al. [10] tested nanosilica in concrete for compressive strength and durability. The nanosilica used was a powder obtained from an extraction process of silica sand. Their results indicated that the combined use of nanosilica with silica fume effectively increases the compressive strength and durability of the concrete. Quercia et al. [11] studied two different types of nanosilica in Self-Compacting Concrete (SCC). Both types of nanosilica, fumed powder silica, and precipitated silica in colloidal suspension have similar particle size distributions; yet, both were produced in different processes. Their results demonstrated that the use of nanosilica in SCC can improve the mechanical properties and durability of concrete. Spectroscopic methods have commonly been used to study the chemistry behind the hydration process of Portland cement. However, the study of cement hydration with the incorporation of nanosilica is an uncommon area of study. The main objective of this study is to investigate the effect of nanosilica in

cement on the hydration process of concrete over 56 days. Fourier Transform Infrared Spectroscopy (FTIR) was used to study the complexity of the hydration chemistry of the Portland cement with the addition of nanosilica content. This study investigated the hydration process of Portland cement with increments of nanosilica addition by cement replacement, monitored by FTIR and AFM. The results of FTIR spectroscopic signatures were compared to the represented samples examined under AFM. An attempt to correlate the spectroscopic features to the development of concrete strength is also determined. Strength testing was carried out by using Forney Universal Testing and MTS machines for compressive strength and stress-strain. This investigation also studied the effects of water curing in comparison to vacuum curing. Concrete cured in airless environments or vacuum curing, is a new area of interest.

2 EXPERIMENTAL METHOD

2.1. Methodology

This experimental study investigated the strength and hydration of Portland cement with nanosilica compared to cement paste without nanoparticles. Compressive testing was carried out using Forney and MTS testing machines. FTIR and AFM were used to monitor and portray the chemical transformations of the cement paste. Approximately 25 specimens were prepared to conduct several tests using 4 in. by 8 in. cylinders and 2 in. cubes. Four (4) mix designs were created. The first mix, M1, was the control mix of the cement paste. The next three mixes, M2, M3, and M4, consisted of 1, 3, and 5% nanosilica by volume of cement, respectively. Nearly half of the specimens created from each mix were cured in water and the other half in the vacuum seal.

$$Fcm = fc + 1.34s + 1.5 \text{ M Pa} \quad (1)$$

$$Fcm = fc + 2.33s - 4 \text{ M Pa} \quad (2)$$

Where, f is pressure strength [2].

2.2. Materials

The materials used in this study were Portland cement Type 1, nanosilica and Polycarboxilate polymer-based superplasticizer. The nanosilica is silicon oxide nanoparticles (SiO_2) synthetic product of porous and nearly spherical particles. The particle size ranges from 15-20 nm, consisting mainly of pure silica (>99%). Figure 1 shows the physical properties of the nanosilica used herein. The nanosilica was obtained from Sky Spring Nanomaterials, Inc., Houston, Texas, while the polycarboxylate was provided by Handy Chemicals Limited, located in Beachwood, Ohio. The Polycarboxylate, also referred to as Megapol is a high performance acrylic based polymer. It's specifically was developed to improve the workability, strength, flexibility, modulus of elasticity, and durability of concrete properties. It is an effective dispersant and High Range Water Reducer (HRWR). The water to cement (w/c) ratio was 0.27 using a superplasticizer. The cement and nanosilica were measured and dry mixed together by hand to reduce the loss of nanoparticles. The polycarboxylate and water were both measured and mixed together. Next, following ASTM Standard C-305, the water with superplasticizer was poured into a rotary mixer bowl (Hobart HL 200, 20-quart mixer). The dry mix of cement and nanosilica was then added to the mixer bowl. Once the materials were in the bowl, they were mixed at a low rate (59 agitator rpm) for 30 sec. After mixing at low speed, the mixing rate was increased to Level 1 (107 agitator rpm) for one minute. After the mixing process concluded, the mixture was carefully poured into cylinder and cube molds. The cylinders and cubes were then ridden, vibrated, and leveled before being stored away for curing. One cylinder from each batch mixture was weighed and measured to obtain the unit weight after mixing. For this experiment, a total of 12 cubes and 13 cylinders, totaling 25 samples, were manufactured for testing. Half of the manufactured specimens were cured in water while the other half were cured in vacuum curing. The cylinders were comprised of plastic molds, 4 inches in diameter and 8 inches in depth, in compliance with ASTM C-470. The cube molds were comprised of brass, exactly 2 inches in size, and able to form three cubic specimens within each mold. Physical properties of the nanosilica are Particle Size (nm): 15-20, Surface Area (m^2 /g): 640, Bulk Density (g/cm^3): 0.08-0.10, Molecular SiO_2, Molecular Weight: 60.08, Porosity (ml/g): 0.6, Morphology: Porous and nearly spherical. Several testing machines were used throughout this experimental study to obtain the required data. The compressive strength data was obtained. The AFM and FTIR were used to analyze the chemistry and microstructure of the testing specimens. The MTS 810 Landmark Servo hydraulic Testing system was used to determine compressive strength and stress-strain curves obtained from testing. These systems include MTS software; Flex Test controls, MTS servo hydraulic technology, and a complete selection of accessories. The testing machine was used to carry out all cylinder testing, including compression and modulus of elasticity. The machine has a 400-kip load capacity and a load rate of 12,000 lbs/min. The high-definition Atomic Force Microscope (AFM EVO LS) made by ZEISS, was used for microstructure characterization and analysis of the hardened concrete specimens. EVO LS has full environmental capabilities

to capture nanoscale interactions of samples under various pressures, temperatures, and humidity. The Fourier Transform Infrared Spectroscopy- FTIR (Thermo Scientific Nicolet iS10 FT-IR Spectrometer) was used to monitor the changes in C-S-H as the hydration of cement paste takes place. This FTIR Spectrometer delivers the highest confidence in the verification and identification of materials. With the use of OMNIC Spectra software, the Nicolet iS10 can manage results and provide accurate and valid answers.

3 RESULTS

3.1. Compressive Strength and Stress-Strain

The Zwick/Roell Z250 Testing Machine was used to conduct all cylinder compressive strength tests. The results from testing are displayed by column graphs in "Figs. 1 and 2". Figure 1 shows the average compressive strengths for all water cured testing cylinders. This figure represents the control, 1 and 3% of nanosilica to cement. As shown, both the 1 and 3% nanosilica samples performed significantly higher than that of the controlled. To compare the cylinder compressive strengths of the reference curing methods, a separate column graph was created to represent the comparison.

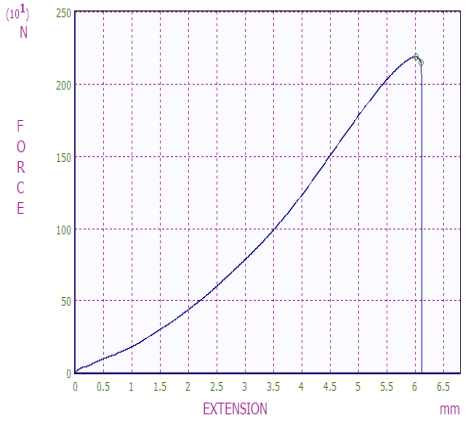

Fig. 1 The average cylinder strength of the 0% controlled samples.

The stress-strain curves display partial results, while the graphs displaying the methods with the change in nanosilica content were developed but not shown here due to page limitations of the manuscript. Figure 2 displays the stress-strain curves for the control samples. As seen the stresses were around 405 Mpa for the reference samples and over 480 Mpa for the control samples. This Figure also shows the stress-strain relationship of the samples for all testing. However, with the incorporation of nanosilica, the stresses at all testing are shown to be much greater than that of the control samples. The stresses for the 5% nanosilica samples range between 480 Mpa.

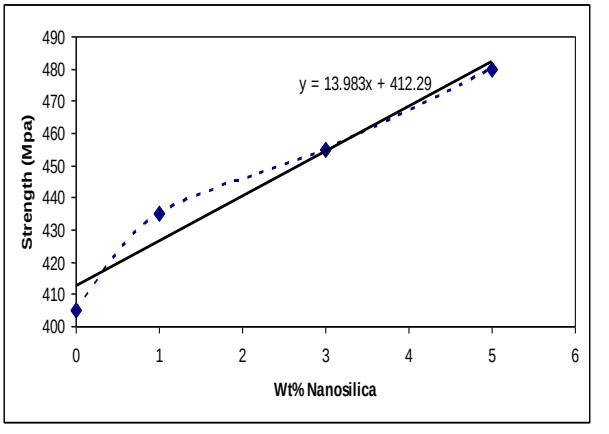

Fig. 2 Compressive strength for different curing methods.

3.2. Atomic Force Microscope (AFM)

The AFM was used to obtain microscopic images of the tested specimens during all testing. From the images obtained, a further analysis using MATLAB was conducted to filter the images using a Gaussian filter and to determine the percentages of chemical products for which that image portrays. The MATLAB program was used to filter the AFM images and generate histograms outlying the major constituents of the hydrated cement. Backscatter used in AFM allows grey-level identification of the chemical elements. This grey-level identification will distinguish the different phases of the hydrated cement products. Four main phases can be identified, which are: Porosity (P), Calcium Hydroxide (CH), Calcium Silicate Hydrate (C-S-H), and Unhydrated Products (UP). Other products such as limestone and other hydrated products were not distinguished. Using the MATLAB analysis, it was expected to produce histograms with three or more peaks for all testing samples. The various peaks help distinguish the thresholds that separate the phases from the grey-level images. Once the grey-level images were filtered, a colored image was generated portraying each phase with a specific color. For this study, the following phases were assigned with the specified color: P-Blue, C-S-H-Green, CH-Red, and UP-Black. Changes to the thresholds were expected to be seen in the adjusted histogram after running the MATLAB script once again. Figure 3 shows the original AFM image of the hardened cement paste sample containing 1% nanosilica after water curing and testing. Figure 3, shows the same sample after filtered using the Gaussian filter. Features from this image are lighter and more distinguished.

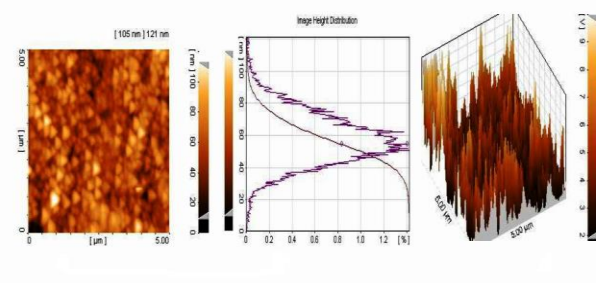

Fig. 3 AFM image-colored phases.

From the results gathered from the MATLAB analysis of all samples, a figure was generated to portray the results obtained. Figure 2 shows the water cured averages of porosity, calcium silicate hydrate and calcium hydroxide for all testing days under changes in nanosilica content. Results from "Fig. 2" show an increase in C-S-H formation from 3-day to 56-day results for the control and all nanosilica mixtures. Results show a maximum amount of C-S-H formation in the 5% nanosilica samples than that of the 1 and 3% nanosilica samples. Also, at all testing ages, samples with nanosilica outperformed or contained more C-S-H content than the control. The 14-day test results performed poorly due to an experimental error, resulting in obscure data results that do not follow the trend of the results obtained. For this reason, several of the 14-day results collected were removed from the analysis and figures thereof. For data that has been removed from the following figures, the cell block will display "OUT". Similar results were obtained for vacuum curing.

3.3. Fourier Transform Infrared Spectroscopy (FTIR)

In this study, FTIR spectrum was used for each sample under water and vacuum curing and for each percentage of nanosilica. The process starts with displaying the reference spectrum for the anhydrate dry cement. It was observed two major peaks occur around the wavelength numbers of 877 and 1100 cm^{-1}. From the chemical composition of Portland cement and from past literature for possible assignment for peaks observed on the cement spectrum; the peaks can possibly be assigned to the CaO and the SiO_2 for the two peaks respectively. There was a large peak in the area of 3400 cm^{-1}, which can be associated with hydrogen bond (O-H) or capillary water within that region. This comparison shows that the optimum nanosilica to cement replacement for curing is 1%. Results also indicate about a 5% difference in the control mix compressive strength. When comparing the control samples to that of the samples containing nanosilica, a significant increase in C-S-H formation during all testing days with all additions of nanosilica was noticed. With the increase in C-S-H formation, results signify an increase in strength with the hardened cement samples containing nanosilica than the control samples without nanosilica. Also, AFM results show a greater increase in C-S-H formation in the samples containing 5% nanosilica to cement replacement in comparison to the 1 and 3% nanosilica samples. The percentage of C-S-H found in the 5% nanosilica samples was slightly higher than the 3% nanosilica samples through both methods of curing. These results should indicate a greater increase in compressive strength with the 5% nanosilica samples; however, the compressive strength results show the 5% nanosilica samples portraying lower strength values when compared to the 1 and 3% nanosilica tests. The reasoning behind the dissimilarities could be due to the area in which the AFM image data was gathered and collected to determine the amount of C-S-H or hydrated products. The AFM images only look into one location under 1300 x magnification within a specific sample. Thus, the area examined under the AFM is a small representation of the sample and therefore provides an estimate of the full sample strength. When comparing the water and vacuum curing methods of the AFM results, the percentage of C-S-H within the samples is very similar for each testing day. For instance, when looking into the 56-day results, the control water and vacuum samples show approximately 70 percent C-S-H formation. Similarly, when comparing the 56-day results for the 3 and 5% of nanosilica replacement samples shows the same percentage of C-S-H formation of 83 and 85%, respectively. From these results, the curing methods performed identically in the curing of the samples and formation of C-S-H.

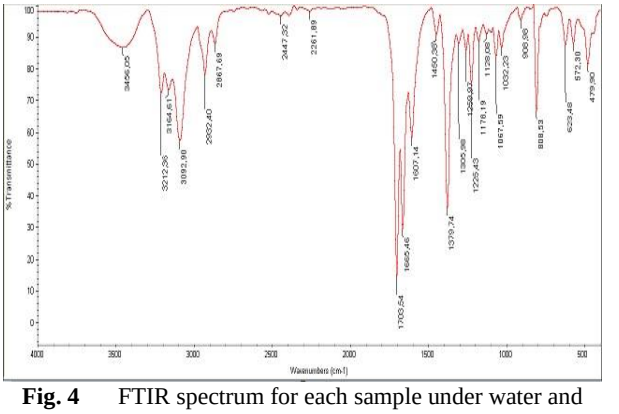

Fig. 4 FTIR spectrum for each sample under water and vacuum curing and each percentage of nanosilica.

4 CONCLUSIONS

In this study, the hydration process of Portland cement with additives of nanosilica has been monitored. With the use of AFM and FTIR, signatures of C-S-H which

produce most of the concretes' strength, have been determined and examined with age. Also, using Forney and MTS testing equipment, the overall strength of the hardened cement pastes was determined and recorded for analysis. The objective of this report was to demonstrate how FTIR and AFM can give more insight into the hydration of cement, with and without the incorporation of nanosilica, during the later ages or stages of hydration. From this study and the results obtained, several conclusions have been drawn:

• The area of possible formation of C-S-H was determined to show an increase with respect to time; signifying the increase in strength with age
• In comparing water and vacuum curing methods, the vacuum cured samples perform identically to that the water cured when monitoring the hydration. Results indicate similar increases with age between both methods
• Nanosilica in all percentages of cement replacements showed a significant increase in compressive strength in all ages of testing. When comparing the amount of nanosilica replacement, results show the optimal percentage of cement replacement is 1%, followed closely by 3% nanosilica addition. 5% nanosilica replacement results portrayed a decrease in strength in comparison to the 1 and 3% additions.
• Water curing proved to be a beneficial form of curing by displaying higher overall strength values than that of the vacuum cured method. Yet, the compressive strength of vacuum cured specimens showed a small reduction in compressive strength (usually within 5%), when compared to the water cured samples

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