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HYDRATION KINETICS OF CEMENT PASTE WITH SILICA FUME AND FLY ASH

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This research study investigates the effect of fly ash and silica fume on the cement paste hydration. A total of 350 samples of different percentages of each additive were tested and compared with the controlled cement paste without additives. Testing method includes water curing and vacuum curing conditions and involves the use of Forney Universal Testing Machine and MTS Landmark Servohydraulic Testing System (MTS) for compressive strength; Fourier Transfer Infrared Spectroscopy (FTIR) monitored the hydration with spectra; and Scanning Electron Microscope (SEM) generated images for regional analysis. Compressive strength testing demonstrated that silica fume replacement had the highest overall strength under water curing. Replacement of fly ash exhibited the highest overall strength under vacuum curing. The hydration process was monitored with the use of FTIR and SEM. Signatures of CSH which produce most of the concretes' strength, has been determined and examined from 3 to 56 days. FTIR and SEM testing showed an increase in the change of CSH area with age. SEM testing revealed the formation of pores, CSH, and CH in images at all ages. The area of CSH grows most in early ages and diminishes over time. It is clear that the method of curing makes a difference in hydration. Results indicated that the area at which the possible formation of CSH was determined from each sample, has increased with respect to time; signifying the increase in strength over the course of testing days.

Keywords: Mechanical properties, MTS testing, FTIR monitoring, SEM monitoring, CSH growth, Curing methods.

1 INTRODUCTION

From the hydration process of cement and water, several products are formed. The main four products are: calcium silicate hydrate, calcium hydroxide, calcium aluminates and calcium sulfoaluminates. Calcium Silicate Hydrate (CSH) is the main and most important constituent of cement paste. Its hydration forms most of the new solid phases that give hardened cement paste its strength. It is known that the addition of fly ash materials have an adverse effects on the compressive strength of the cement. The replacement of cement with fly ash by percentage affects the properties, those being both the filler and dilution effects. Fly ash contains pozzolans, a siliceous material possessing cementitious properties, and consumes CH in the pozzolanic reaction (Narmluk and Nawa 2011). Zhang (2000) found that less CH will decelerate the hydration reaction. On the other hand, silica fume additive contains pozzolans which are siliceous and aluminous material which have no cementitious properties. However it will react with calcium hydroxide once hydrated. A pozzolanic reaction between silica fume and lime formed during cement hydration does not occur during the early stages of hydration. A study by Zelic *et al.* (2000) shows that the pozzolanic reaction between silica fume and lime formed during cement hydration does not occur until three days of hydration (Zelic *et al.* 2000). The presence of silica fume slightly increases the rate of cement hydration during the first few hours of hydration. Likewise, this indicates that silica fume affects hydration by the nucleating effect of its surface when it still exists as chemically inert filler. After silica fume hydrates increase in strength and hydration heat, pozzolanic activity takes over (Kadri and Duval 2009).

2 EXPERIMENTAL PROGRAM

In an effort to better comprehend the mechanisms underlying cement hydration, the use of new technology is needed to enhance the prediction of properties. This present work investigates the mechanical properties of cement paste as it goes under several stages of hydration, monitored by SEM and FTIR. The objective is to investigate the effect on cement hydration of supplemental fly ash or silica fume on the mechanical properties of cement paste. The integration of these two additives were studied to analyze their effect in accelerating C3S. Percentages of each additive will replace the cement by volume at 5% and 10% to be studied at 3, 7, 14, 28, and 56 day ages. Testing were carried out on 350 samples using a Forney Universal Testing Machine, MTS Landmark Servohydraulic Testing System (MTS), Fourier Transfer Infrared Spectroscopy (FTIR), and Scanning Electron Microscope (SEM). The testing methods should portray the compressive strength, modulus of elasticity, spectra, and images of the samples. This study will provide an understanding and insight towards the roles of fly ash or silica fume in the hydration properties of cement paste at various stages of hydration. The cement used in this study was of Portland cement Type 1. There are two commonly used classifications of fly ash, Classification F and C. Class F fly ash has good susceptibility to reducing the alkali-silica reaction (ASR). This classification will mitigate this issue better than class C fly ash. Classification F was used in this research. Silica fume is very fine noncrystalline silica produced in electric arc furnaces as a byproduct of the production of elemental silicon or alloys containing silicon. Silicon dioxide makes up a large percentage of silica fume.

For the experimental setup, five (5) mix designs were created. The first mix, M1, was the control mix with cement and water. The next four mixes, M2, M3, M4, and M5, consisted of a 5 and 10 percent of cement replacement by volume of fly ash and silica fume respectively. The water to cement (w/c) ratio was 0.40 for all mixes. For all mixes, eight (8) cylinders and six cubes were created for each age (hydration stage). The cylinders were 4 inches in diameter and 8 inches in height, while the cubes were exactly 2 inches cubed. All cylinders and cubes were unmolded after 24 hours and then half were cured in water and the other half vacuum cured for 3, 7, 14, 28, and 56 days until age of testing. Water curing involved the placement of the cement paste specimen into a water tank, completely submerged in water. For vacuum curing, a FoodSaver appliance series 2200 was used. The cement paste specimens were incased in vacuum seal bags and remained completely sealed until age of testing. After curing, the cylinders and cubes were dried in air for approximately one hour before testing.

2.1 Mechanical Properties

The Forney Universal Testing Machine was used to carry out all cylinders testing for compression and modulus of elasticity. It has 400 kip load capacity and a loading rate of 12000 lbs./in. Cylinders were capped with either rubber pads or a capping compound in accordance to ASTM C-617. Forney captured the maximum peak load applied to each cylinder under testing. The MTS Landmark Servohydraulic Testing machine was used to carry-out compressive strength testing for 2 inch cement paste cubes and produce stress-strain curves for each test. The loading rate for the MTS machine was 0.01 in/s. The system includes MTS software, FlexTest controls, MTS servohydraulic technology, and a complete selection of accessories. Once each cube was tested till breakage, the data results were stored. Test results include displacement in inches, loading in pounds, and the time in seconds. The data was later transferred to Excel to calculate the stress and strain, and further portrayed in the results.

2.2 Scanning Electron Microscope (SEM)

The high definition SEM EVO LS 10 made by ZEISS, was used for microstructure characterization and analysis of the hardened cement paste specimens. EVO LS 10 has full environmental capabilities to capture nano scale interactions of samples under various pressures, temperatures, and humidities. It includes EVO HD, which further increases an image resolution and contrast using a high definition beam source technology with low acceleration voltages. During experimentation, the SEM was set into the environmental mode (EP) which allows atmosphere in the chamber since the sample is based on hydration. The scanning speed was set to four, which automatically changed the scanning cycle to 731 ms. The EP target set to 50 Pa, the KV value was set to 10 KV and the beam current to 46.0 μA. SEM testing revealed the formation of pores, CSH, and CH in images at all ages.

2.3 Fourier Transfer Infrared Spectroscopy (FTIR)

The Thermo Scientific Nicolet iS10 FT-IR Spectrometer was used herein. Its many features includes creating standard operating procedures (SOPs) and suitable tests, verifies the quality of materials, identifies unknowns or mixtures, and can quantify mixture ingredients. With the use of OMNIC Specta software, the Nicolet iS10 can manage results and provide accurate and valid answers. The Nicolet iS10 consists of System Performance Verification (SPV) which tests the instrument against ASTM E-1421 method to insure quality performance. SPV is a tool used to ensure the spectrometer is performing as expected, at all times. For this experimental testing the Nicolet iS10 FTIR Spectrometer was used to identify and compare the unknowns within the cement paste mixtures. The FTIR spectrometer was used to identify the chemical properties during the hydration process.

3 EXPERIMENTAL RESULTS

As aforementioned, the hydration process of Portland cement with additives of fly ash or silica fume silica has been monitored. With the use of FTIR and SEM, signatures of

CSH which produce most of the concretes' strength, has been determined and examined from 3 to 56 days. Also, using Forney and MTS testing equipment, the compressive strength of the hardened cement pastes at all testing ages were determined and recorded for analysis.

3.1 Compressive Strength

Figure 1(a) shows the average compressive strengths for specimens that were cured in water. This figure represents the 0%, 5% and 10% of fly ash and silica fume to cement replacements, against the 3, 7, 14, 28 and 56 day tests. As shown in the figure, the 10% of silica fume consistently outperforms the 5% silica fume at all ages except three days. Figure 1(b) show the average compressive strengths for all vacuum cured testing specimens. In both the water and vacuum curing, the compressive strength increased with age. As stated in the experimental procedure, each material was casted into three cubes; 0%, 5% and 10% of fly ash and silica fume to cement replacement for water and vacuum curing. The stress-strain curves created from the three cubes were averaged together to obtain a single averaged stress-strain curve for each material tested at each age. Sample of the stress-strain curves is shown in Figure 2.

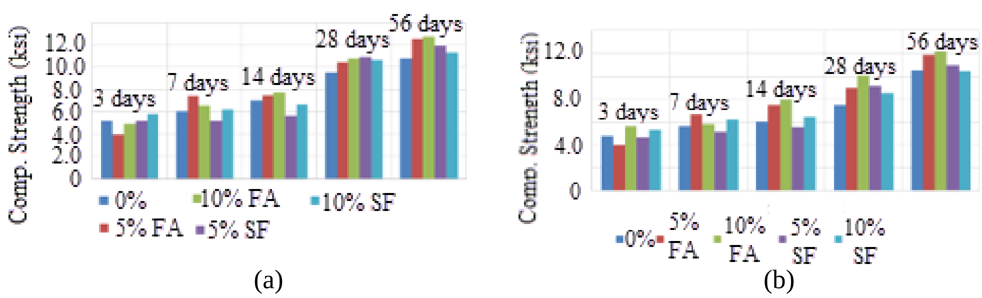
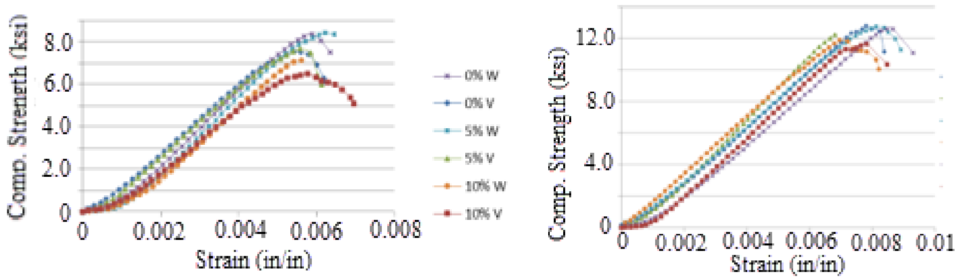


Figure 1. Average compressive strength: (a) water cured and (b) vacuum cured.

3.2 Scanning Electron Microscope (SEM)

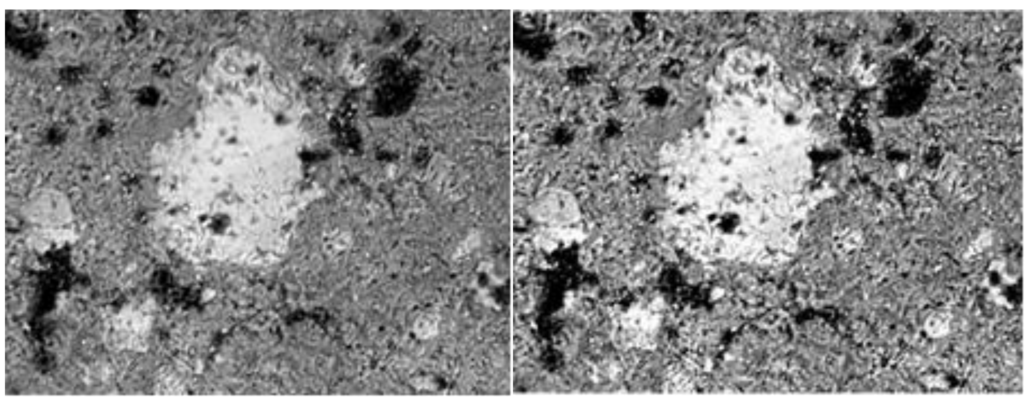
The images in Figure 3 illustrate the cement hydration of 28 day cement paste at 1300x magnification without and with a filter, respectively. The filtered image has gone through both the convolution and median filters.

Analyzing SEM images show that the 10% fly ash replacement has a higher percentage of porosity, 7% more CSH, but less CH than 5% replacement. Silica fume at 10% replacement has a higher percentage of CSH by two percentage and lower porosity and CH than 5% replacement. Comparing fly ash and silica fume averages at 10%, silica fume had lower porosity, CH, and higher CSH. The control specimen had lower porosity than fly ash and higher than silica fume at 14%. Control specimen had 65% CSH average which was lower than fly ash and silica fume. In case of vacuum cured specimens, fly ash of 10% replacement has lower percentage of porosity, higher CSH by 4% than 5% replacement but same CH. Silica fume 10% replacement has a higher percentage of CSH by 8% and lower porosity and CH than 5% replacement. Comparing fly ash and silica fume averages at 10%, silica fume had lower porosity, CH, and higher CSH. The control had higher porosity than fly ash and silica fume but silica fume at 5% was the same at 16%. The CH of the control was higher than silica fume but lower than fly ash averages. Overall areas for water and vacuum curing have CSH percentages that continually grow larger with age. Figure 4 shows percentage of CSH area for specimens cured in (a) water and (b) in vacuum.



(a) (b)

Figure 2. Stress-strain curves: (a) 7 days fly ash and (b) 56 days silica fume.



(a) Unfiltered SEM image (b) Filtered SEM image

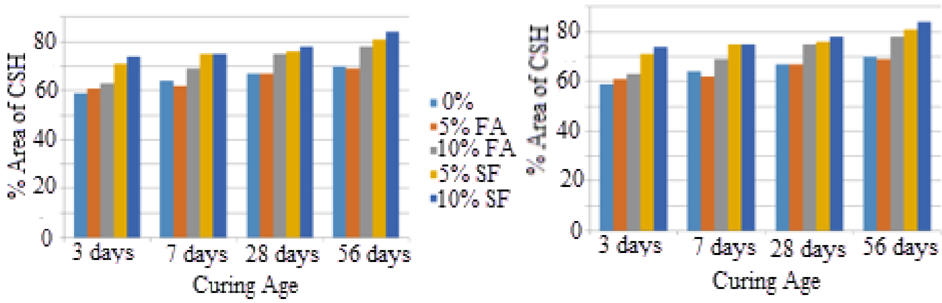
Figure 3. SEM image of a 28 day water cured control section.

3.3 Fourier Transfer Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to monitor the hydration process and to approximate the amount of CSH formation within all samples. In this study, the hydration process was monitored for 3, 7, 14, 28, and 56 days, by acquiring an FTIR spectrum for each sample cured under water and vacuum. Figure 5 shows the absorbance spectrum of the 5% silica fume of cement replacement hydrated for 3, 7, 28 and 56 days after water curing.

As seen in Figure 5, the two major peaks occur around the wavelength numbers of 877 cm^{-1} and 1100 cm^{-1}. From the chemical composition of Portland cement and from past literature for possible assignment for peaks observed on cement spectrum; the peaks can possibly be assigned to the CaO and the SiO_2 for the two peaks respectively. Also notice the large peak in the area of 3400 cm^{-1}, which can be associated with hydrogen bond (O-H) or capillary water within that region. It should be noted that

Calcium silicate hydrate is a weak bond structure which appears around 1100 cm^{-1} and can be associated with the peak in that region.



(a) Water cured specimens (b) Vacuum cured specimens

Figure 4. Growth of CSH with age.

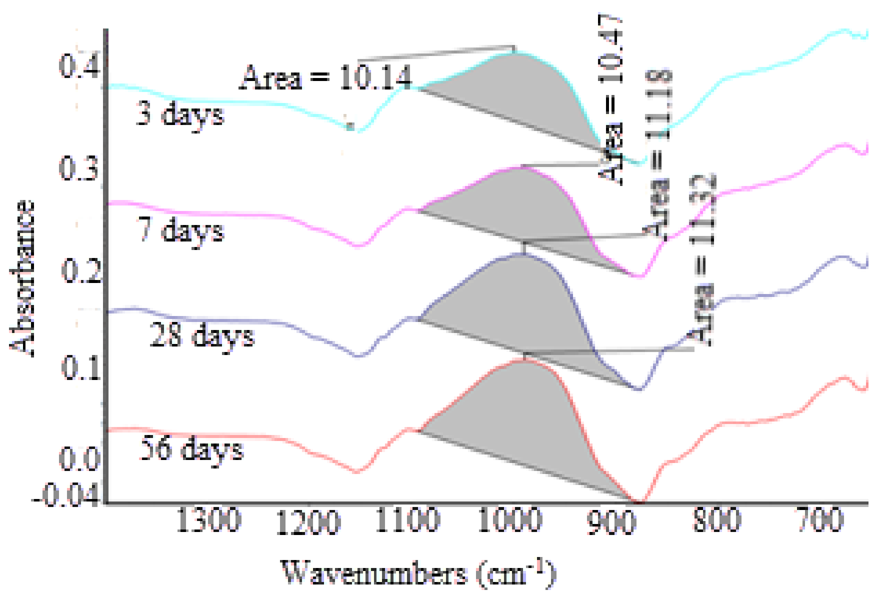


Figure 5. Absorbance of 5% silica fume spectra of water cured samples.

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