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# Influence of carbon nanofiber clustering in cement pastes exposed to sulfate attack

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## HIGHLIGHTS

- Sulfate attack of cement paste with carbon nanofibers investigated over 550 days.
- Pore refinement with carbon nanofibers slows sulfate-induced microstructure changes.
- Nanofiber clusters provide a reinforcing network that delays cracking and spalling.
- Less sulfate-induced changes in flexural strength with carbon nanofibers.

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## ABSTRACT

The effects of CNFs and CNF clustering on the microstructural evolution and mechanical response of cement pastes subjected to sulfate attack were studied. Portland cement pastes with and without 0.5% CNFs were exposed to sodium sulfate for a total duration of 550 days. The presence of CNFs and CNF clusters led to pore refinement, limited sulfate-induced microstructural changes, and provided a reinforcing network that delayed the onset of cracking and spalling and increased the cement paste expansion capacity. At all stages of exposure, the cement paste with CNFs experienced less sulfate-induced changes in flexural strength than the reference cement paste.



## 1. Introduction

Sulfate attack of cementitious materials typically occurs due to exposure to sulfate (e.g. seawater, groundwater, sewage water, or saturated sulfate-rich soils), which leads to a chemical alteration of the cement paste (i.e. formation of gypsum and ettringite) as well as expansion, spalling, and cracking that eventually leads to a loss of cohesion in the material and a decrease in mechanical properties [1,2]. Carbon nanofibers (CNFs) have been shown in the literature to refine the pore network of the cement paste [3–8], slow crack propagation [9–15], and increase failure strain and post-cracking structural integrity [5,15–21], which are expected to be beneficial during sulfate attack. However, proper dispersion of CNFs in cementitious matrices has proven difficult [22], and a non-uniform dispersion of CNFs may impact the reinforcing ability of the fibers. Some studies suggest that the CNFs, even in clustered form, are capable of providing positive impacts on the cementitious matrix [22–24], yet limited research has been done on the durability of cementitious materials containing CNFs [24], and the influence of the CNFs and CNF clustering on the reinforcing ability of cement pastes during sulfate attack is not clear. Therefore, this study seeks to determine the influence of CNFs and CNF clustering on the physical, chemical, and macromechanical properties of cement pastes subjected to sodium sulfate attack.

Portland cement pastes with and without CNFs were exposed to a sodium sulfate ($Na_2SO_4$) solution for a total duration of 550 days (1.5 years). To the best of the authors' knowledge, this study is one of the few to report on the effect of CNFs in cement pastes during extended exposure to sulfate attack. Physical changes, such as expansion and spalling, were monitored periodically throughout the exposure duration. Microstructural changes were also examined as a function of exposure duration. Changes in the flexural and compressive response of the cement paste with CNFs were studied and reviewed in relation to CNF clustering and microstructural evolution. Results showed a strong coupling between CNF clustering, sulfate-induced microstructural evolution, and the flexural properties of the cement paste. The presence of CNFs and CNF

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clusters in the cement paste were found to interfere with the sulfate-induced microstructural evolution of the cement paste and provide a reinforcing network, which helped delay cracking and spalling, increased the expansion capacity of the cement paste, and generally improved the cohesion of the cement paste.

## 2. Materials and methods

### 2.1. Materials and specimen preparation

Two types of paste were prepared: a plain Portland cement paste (reference cement paste) and a Portland cement paste containing 0.5% CNFs per mass of cement (cement paste with CNFs). Type I/II Portland cement (Lafarge, Nashville, Tennessee) conforming to ASTM C150 [25] was used as the cementitious material, and vapor-grown Pyrograf® -III PR-19-LHT CNFs (Applied Sciences, Inc., Cedarville, Ohio) that were commercially available were used as received from the manufacturer. Glenium 7500 (BASF, Ludwigshafen, Germany), a polycarboxylate-based high range water reducer (HRWR), was used at a loading of 1% per mass of cement to promote the dispersion of the CNFs in the cement paste [26,27]. A water to cement ratio of 0.28 was used for all mixes. The water, HRWR, and CNFs (where applicable) were combined and sonicated with a bath sonicator (Aquasonic model 250D) for 30 min before mixing with the cement powder. After mixing, the pastes were poured into 2.54 cm × 2.54 cm × 69 cm (height × width × length) beam molds and compacted by hand. The beams were then cured at room temperature under 100% relative humidity for a minimum of 28 days and sectioned into shorter beams with a length of 11.5 cm prior to exposure to sulfate attack.

### 2.2. Sulfate exposure conditions

After curing, four specimens of each paste were immersed in an enclosed plastic container containing 4 L of sodium sulfate ($Na_2SO_4$) solution at a concentration of 50 g/L for 60, 120, and 550 days following a modified ASTM C1012 [28]. The first exposure duration (60 days) was selected in order to test the samples after exposure to sulfate, but before any noticeable spalling occurred. The second exposure duration (120 days) was selected based on the initiation of spalling of the reference cement paste. The final exposure duration (550 days) was selected to evaluate the samples after cracking and spalling had initiated but prior to complete sulfate-induced failure/cracking (i.e. prior to extensive cracking/loss of integrity that would have made physical mechanical testing of the sample difficult). The solution was renewed every two weeks. At the end of each exposure period, the specimens were stored under 100% relative humidity until further testing.

### 2.3. Characterization

#### 2.3.1. Visual inspection, mass loss, and expansion monitoring

The mass of each specimen was measured prior to exposure to $Na_2SO_4$ solution and at periodic intervals during the exposure duration. Each specimen was removed from the $Na_2SO_4$ solution, surface-dried, and weighed. Immediately after measuring the mass, expansion measurements were collected. A micrometer was used to take three measurements each of specimen length, width, and height at predetermined locations. The measurements were then averaged together to determine the final length, width, and height of the specimen at a given exposure duration. The specimen was then immediately returned to the $Na_2SO_4$ solution so as to limit the exposure to ambient conditions. During the mass and expansion measurements, the specimens were also visually inspected for any change in surface texture as well as any indications of spalling and cracking. When noticeable changes had occurred, the specimens were photographed to allow for comparison between the reference cement paste and the cement paste with CNFs.

#### 2.3.2. Microstructural and morphological analysis

An environmental FEI Quanta FEG 650 high resolution scanning electron microscope equipped with a Schottky field emission gun, digital imaging, and an energy dispersive X-ray spectrometer was used to evaluate the microstructure and morphology of the cement pastes before and after sulfate attack. Typical operating conditions included a working distance of 10.5 mm, spot size of 3.5, pressure of 130 Pa, and an accelerating voltage that was varied from 10 to 20 kV when collecting high resolution backscatter electron images in order to optimize imaging quality.

The 2D spatial and size distributions of the CNF clusters were characterized using the image mapping system of a New Wave UP-213 Laser Ablation System. A total of 1350 images (27.6 × 20.6 pixels each) were collected and assembled into a single image, which represented the entire cross-section of the cement paste. A combination of thresholding techniques and visual inspection was used to create a binary image showing only clusters of CNFs in the cement pastes. Careful identification of the clusters was performed with adequate checks using optical microscopy (i.e. comparison to what was expected in the reference cement paste with no CNFs) as well as using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) mapping to confirm the presence of carbon. The resulting images showing only CNF clusters were analyzed using ImageJ software (a Java-based, open source, digital image processing software, National Institute of Health, Bethesda, Maryland, USA) and in-house developed Matlab codes to determine the size distribution, area fraction, and spatial distribution of the CNF clusters in the cement paste. The area fraction was defined as the ratio of the area covered by CNF clusters to the total area of the cement paste section analyzed. The histogram of the spatial distribution of the CNF clusters in a given cement paste cross-section was generated from the distance to the five closest neighboring CNF clusters. Only CNF clusters of size area greater than 0.007 $mm^2$ were considered in the analysis due to limitations in the imaging resolution of the optical mapping tool.

#### 2.3.3. Porosity distribution

The SEM counting technique outlined in [24] was utilized to determine the 2D porosity (areal porosity) distribution of the cement pastes prior to exposure to sulfate attack. The areal porosity determined by the SEM image method only accounts for part of the total porosity given the limitations of the SEM image resolution and the grid collecting technique and should only be used to compare datasets that were analyzed using the same method.

Nitrogen adsorption/desorption was also used to analyze the pore size distribution of cement pastes with and without CNFs prior to sulfate attack, specifically the mesopore (i.e. pores < 50 nm in diameter) and lower macropore region (i.e. pores 50–200 nm in diameter) that is difficult to measure by the SEM porosity method. All samples were degassed at 110 °C prior to testing. Testing was performed at 77.4 K using a 2010 Accelerated Surface Area and Porosimetry System from Micromeritics. The Barret, Joyner, and Halenda (BJH) model [29] was applied to the desorption branch of the nitrogen isotherm to calculate the pore size distribution of the cement pastes.

#### 2.3.4. Macromechanical testing

A Tinius Olsen Super L 60 K (300 kN) universal testing machine (Tinius Olsen, Inc., Horsham, PA, USA) was used to determine the flexural and compressive properties of the cement pastes. A three-point bending test (modified ASTM C293 [30]) with a loading