

Effect of Nanocellulose Materials on Cement Hydration

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Abstract

Nanocellulose materials, including cellulose nanofibers and cellulose nanocrystals have demonstrated the ability to improve structural properties of cement pastes, such as flexural strength [1,2]. Though these improvements have been observed at a macroscopic scale, little research has been done to understand the mechanism by which these improvements occur. Here, isothermal calorimetry, *in situ* x-ray diffraction, thermogravimetric analysis, and scanning electron microscopy are used to gain insights into the effect these nanocellulose materials have on cement hydration. It was found that these materials seem to have a significant impact on hydration kinetics, but do not significantly affect the final composition of cement microstructures.

1. Introduction

Concrete is the most commonly used construction material in the world and the second most consumed material, after water. Due to its prevalence, a major goal of concrete research focuses on methods of improving its structural properties. Often, this is achieved by adding supplementary materials, or admixtures, to cement mixes. In recent years, emphasis has been placed on the usage of biomaterials for these applications, as these are more environmentally friendly than conventional synthetic admixtures. Nanocellulose materials is a class of biomaterials that has been shown to improve mechanical properties, like flexural strength, of cement pastes [1, 2]. Though the effect of nanocellulose on the structural properties of cements has been observed at a macroscopic scale, the mechanism by which these improvements occur is not yet well understood.

This study aims to investigate the effect of nanocellulose materials on the hydration mechanism of cement pastes and provide reasoning for the structural improvements observed at the macroscopic scale. Through a combination of several techniques, a multifaceted understanding of the effect of nanocellulose materials on cement hydration can be realized.

2. Materials and Methods

Two types of nanocellulose materials were used in this study: cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs). CNF lengths fall in the range of several hundred microns, while those of CNCs range between 0.1-0.15 microns. Additionally, CNFs have a diameter of approximately 50 nm, while CNC diameters range between 9-14 nm. To study the effects of CNFs and CNCs on cement hydration, samples of white ordinary Portland cement (OPC) pastes were dosed with each of the nanocellulose materials at levels of 0.2%, 0.5%, and 1.0% by volume of cement. One control sample containing no nanocellulose materials was also prepared. Each of these samples was investigated using isothermal calorimetry, *in situ* x-ray diffraction (XRD), and thermogravimetric analysis (TGA) to understand various aspects of the hydration mechanism. Isothermal calorimetry was employed to understand the extent of reaction occurring in each of the samples over a period of 5 days by analyzing the amount of heat released due to the hydration reaction. XRD was used as a complimentary technique

to isothermal calorimetry to understand what crystal structures formed in the samples over the first 48 hours of hydration. TGA was used to quantify the amount of portlandite and bound water present in the samples after 28 days of hydration. Finally, scanning electron microscopy (SEM) was used to capture microscopic images of CNF-containing samples to gain a qualitative understanding of CNF arrangement within the cement paste microstructure.

2.1 Sample Preparation

Cement paste samples were mixed at a 0.4 water-binder ratio (w/b) in a Fann Constant Speed Mixer Model 686CS. White OPC powder was mixed at room temperature with deionized water and nanocellulose materials at the specified w/b for 60 s at 4,000 rpm, followed by 30 s at 10,000 rpm. The mix was allowed to rest for 150 s, after which it was mixed once more for 30 s at 10,000 rpm.

2.2 Isothermal Calorimetry

Isothermal calorimetry measurements were performed using a TAM Air Isothermal Calorimeter. Samples were loaded into the calorimeter as quickly as possible after mixing, falling in the range of 9-13 min after initial contact between binder and water. 5 ± 0.5 g of each cement paste sample was loaded into the calorimeter, and measurements were taken for the first 5 days of hydration at a temperature of 23°C.

2.3 In Situ X-Ray Diffraction (XRD)

In situ XRD measurements were performed using a PANalytical Empyrean X-Ray Diffractometer with Bragg-Brentano HD X-ray mirror and goniometer radius of 240 mm. All seven samples were loaded into the diffractometer simultaneously, and measurements were automated using an autosampler. After mixing the paste samples, the pastes were loaded into the sample holder of diameter 27 mm and the exposed sample surface is covered with a low-permeability thin film made of polyethylene terephthalate of thickness 6 μ m to prevent evaporation of mix water and carbonation of hydrating paste. The sample was incident with $\text{CuK}\alpha$ X-rays generated using Empyrean Cu LFF HR X-ray tube at 45 kV and 40 mA operating conditions. Soller slits of 0.04 rad and the fixed Mask, anti-scatter, and divergence slits of 10 mm, $\frac{1}{2}^\circ$, and $\frac{1}{8}^\circ$ were used

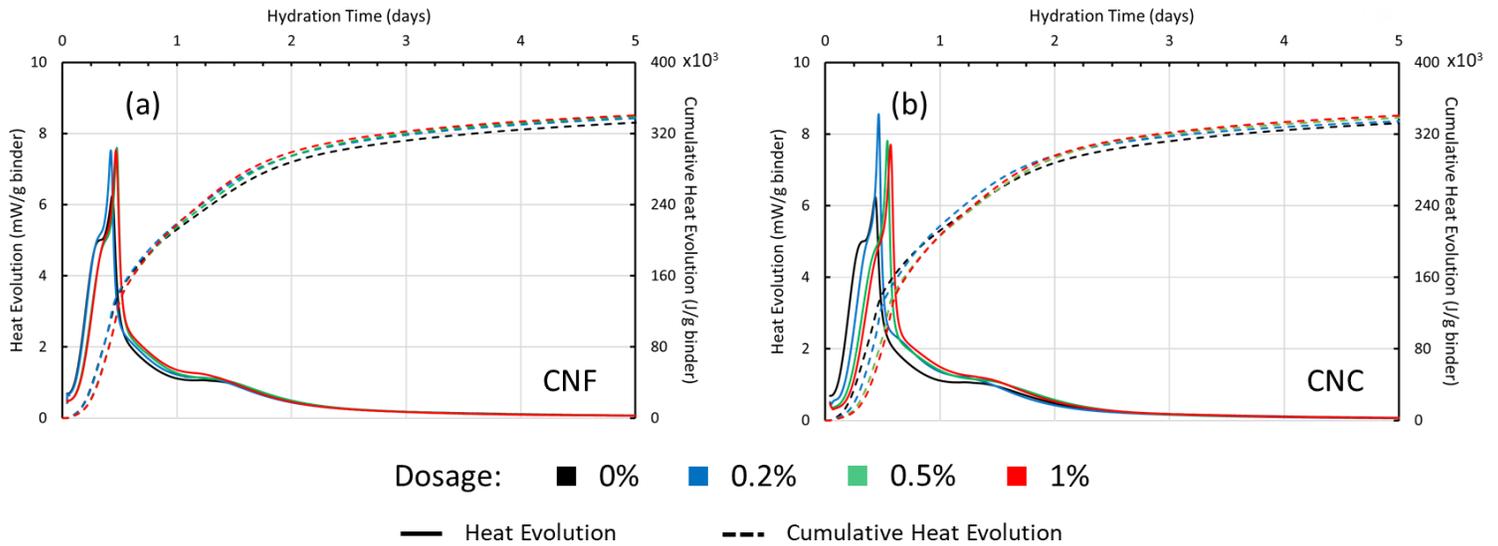


Fig. 1. Rate of heat evolution and cumulative heat evolution over 5 days of hydration for samples dosed with a) CNFs and b) CNCs.

in the incident beam path. In the diffracted beam path, a fixed anti-scatter slit of 7.5 mm and soller slits of 0.04 rad were used. A PIXcel3D-Medipix3 1x1 area detector with an active length of 3.347° was used for data acquisition. Data was collected over an angular range of 5° to 60° with a step size and counting time of 0.013° and 23.97 s, respectively, resulting in a total measurement time of approximately 8 min. The first measurement was taken at 2 h after mixing, and subsequent measurements were taken each hour afterward until 48 h after mixing.

2.4 Thermogravimetric Analysis (TGA)

After 28 days of hydration, samples were crushed and sieved through a No. 50 sieve (300 μm). The sieved powder was then dried through a two-step solvent exchange procedure using isopropanol and diethyl ether. 5 g of powder was soaked in isopropanol for 15 min to remove pore water, then vacuum dried under N_2 for 5 min to remove isopropanol. Diethyl ether was then added to the product, mixed, and left for 1 min to remove any remaining isopropanol, after which the sample was again vacuum dried under N_2 for 5 min to remove all diethyl ether. This method has been shown to sufficiently dry crushed cement pastes while avoiding sorption of alcohol to hydrates or breakdown of hydrates [3].

After drying, powders were sieved through a No. 200 sieve (75 μm) in preparation for TGA measurements. For each sample, 20 ± 1 mg of powder was loaded into a Hitachi TG/DTA 7300 and measurements were recorded across a temperature range of 40-1,000°C. During measurements, powders were contained in open, aluminum (III) oxide (Al_2O_3) crucibles under N_2 gas flow.

3. Results and Discussion

Several techniques were used in combination to understand the effect that nanocellulose materials have on the cement hydration process. Isothermal calorimetry and XRD provide information on reaction kinetics through data on reaction thermodynamics and crystal formation, respectively. These two techniques can be used as complements to one another to form a better picture of the hydration kinetics. TGA is used to analyze

the final microstructure composition of cement pastes after the hydration process is allowed to proceed for a given length of time. This allows for an understanding of how nanocellulose materials affect the final composition of cement pastes.

3.1 Reaction Kinetics

The hydration reaction that cement paste undergoes as it sets is an exothermic reaction. This indicates that a higher heat evolution from a sample correlates with a larger extent of reaction. Isothermal calorimetry was used in this study to determine how the addition of CNFs and CNCs affects reaction timing and overall reaction extent.

Fig. 1 shows the rate of heat evolution and cumulative heat evolution for each of the samples investigated in this study. Examination of the curves representing rate of heat evolution reveals that, for both CNFs and CNCs, the rate of heat evolution peaks later for samples dosed with nanocellulose materials in all but one case (0.2% CNF). Because the rate of heat evolution corresponds with the rate of reaction, this indicates that the addition of nanocellulose materials to a cement mix delays the initial hydration reaction.

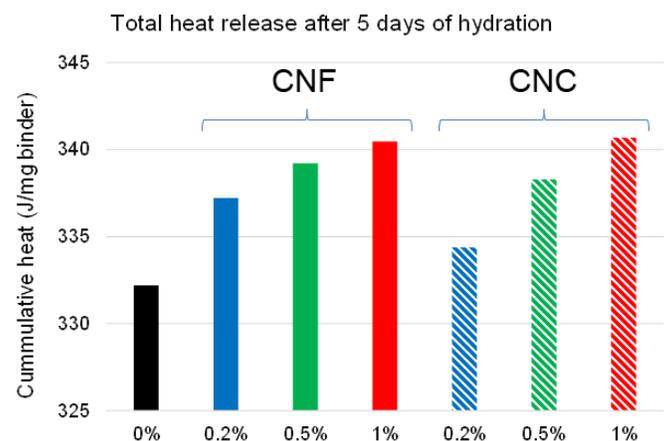


Fig. 2. Cumulative heat release after 5 days of hydration.

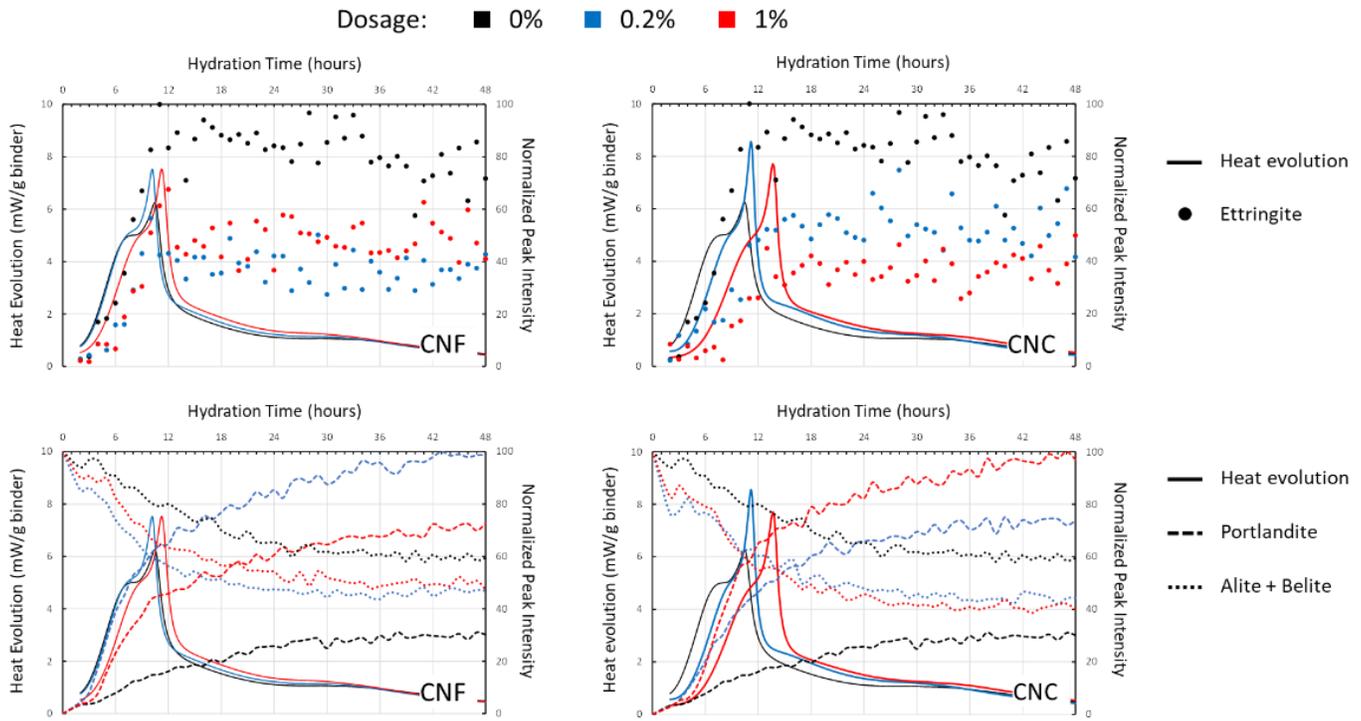


Fig. 3. Amount of ettringite and portlandite formed over the first 48 h of hydration, overlaid on calorimetry data.

Further examination of Fig. 1 reveals that, after 5 days of hydration, the cumulative heat evolved from each sample increased with increasing dosage of nanocellulose material. This can be seen more clearly in Fig. 2, which shows the total heat evolved from each sample over the full 5-day period. This trend indicates that, though the initial hydration reaction appears to be delayed by the addition of nanocellulose materials to cement pastes, the reaction proceeds further overall. A study by Fu et al. suggests a positive correlation between cumulative heat evolution and flexural strength in cement pastes [4], indicating that a potential cause for the structural improvement in nanocellulose-dosed cement pastes could be caused by their effect on heat evolution during hydration.

During the hydration process, several crystal structures are formed as hydration products that bind cement grains together. Two notable crystal structures that typically form in OPCs are ettringite (calcium sulfoaluminate) and portlandite (calcium

hydroxide). Knowing the rate at which these crystal structures form can provide information on hydration kinetics in cement pastes.

Fig. 3 shows the data collected from XRD overlaid on the first 48 h of calorimetry data. From this data, it can be observed that ettringite forms more rapidly in the sample containing no nanocellulose materials, while portlandite forms more slowly in these same samples. To understand why this is relevant, it must be noted that ettringite is an early-stage hydration product, while portlandite is a later-stage hydration product; that is, ettringite primarily forms earlier in the hydration process and portlandite forms later. The higher rate of ettringite formation and slower rate of portlandite formation observed in the sample containing no nanocellulose materials compared to the samples containing CNC and CNF indicates that even though CNC and CNF addition delayed the initial reaction (that is corresponding to C3A hydration to Ettringite), at later stages, the reaction

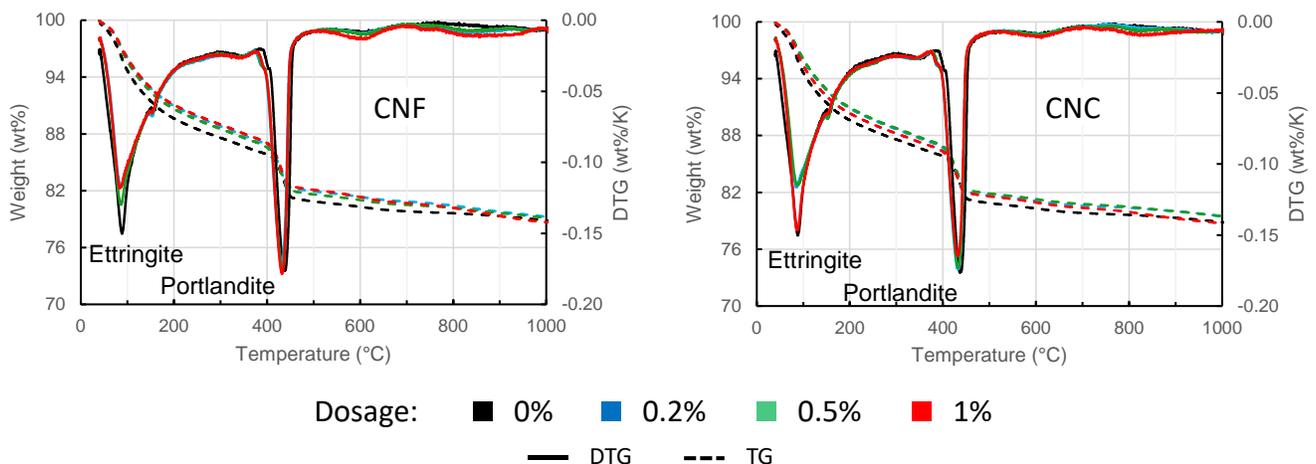


Fig. 4. TGA data with labeled ettringite and portlandite peaks.

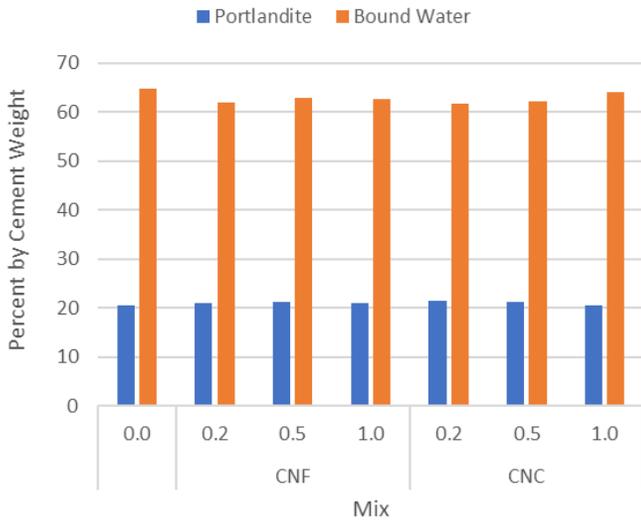


Fig. 5. Quantification of bound water and portlandite from TGA data.

corresponding to portlandite formation is accelerated – that resulted in increased precipitation of portlandite with the addition of CNCs and CNFs. This supports the conclusions drawn from the calorimetry data on the effect of nanocellulose materials on the reaction kinetics.

3.2 Microstructure Composition after 28 Days

As the name suggests, the various hydration products that form during cement hydration contain bound water in their composition. Each of these products has a different characteristic range of temperatures in which it will release water, which provides a method by which to analyze what hydration products are present in a cement paste sample after a certain period of hydration. In TGA, a dried sample of crushed cement powder is heated across some temperature range and the rate of weight loss (due to water release) at each instant is recorded, allowing for identification and potential quantification of hydration products present in the sample.

Fig. 4 depicts the thermogravimetric (TG) data and differential thermogravimetric (DTA) data for each cement paste sample across the range 40-1,000°C after 28 days of hydration. From this data, the amount of portlandite and bound water in each sample was calculated using the tangential method described by Scrivener et al. [3]. This quantification data is represented in Fig. 5. No clear trend was observed between the amount of portlandite and bound water present in the samples after 28 days and the dosage of nanocellulose materials. This suggests that, though there are significant effects of nanocellulose materials on the initial hydration reaction kinetics, nanocellulose materials do not have a significant effect on the composition of the final microstructure of cement pastes.

3.3 CNF Arrangement in Cement Pastes

To gain a qualitative understanding of how CNFs are arranged in cement pastes, SEM images were generated. Fig. 6 depicts SEM images of CNFs located in the crushed 1.0% CNF dosed cement paste sample. These SEM images suggest that: a) CNFs can become embedded in cement paste near the cement

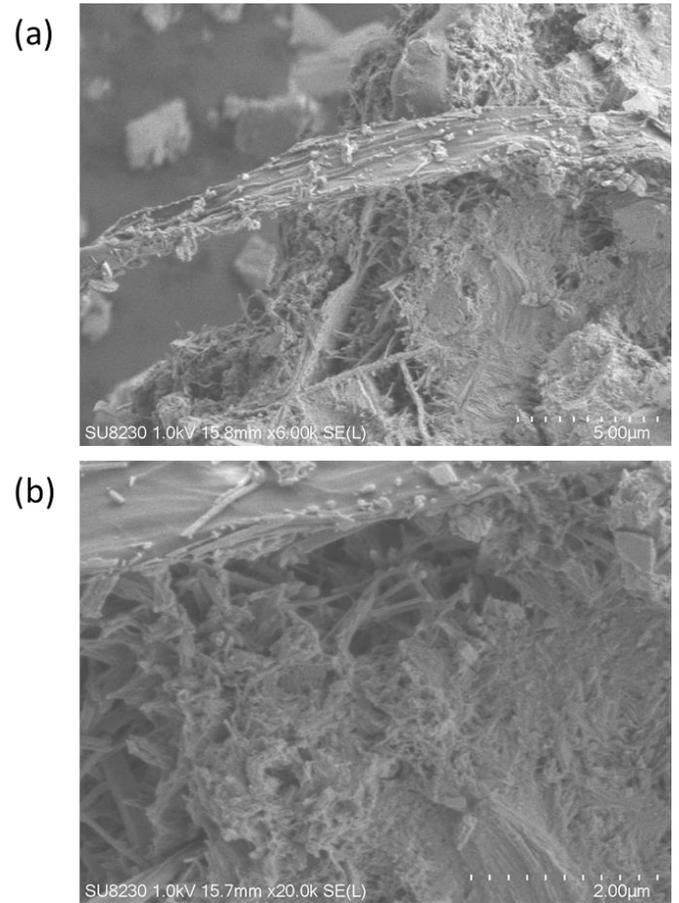


Fig. 6. SEM images depicting a) CNF embedded in cement grain and b) ettringite needles surrounding CNF.

grains and serve as a passageway for free water during hydration (Fig. 6a) and b) ettringite needles seem to form on and around CNFs (Fig. 6b). This increased precipitation of ettringite on the CNF surface could be one of the reasons for increased ettringite crystallization observed in Fig. 3. Because ettringite needles are observed surrounding CNFs, this suggests that removal of CNFs from hydrated cement pastes may also preferentially remove ettringite. This indicates that it is possible that the sieving process used in TGA sample preparation may have removed a significant quantity of ettringite and that the samples used in TGA were not representative of the entire cement paste.

4. Conclusions

This study aims to understand the effects of nanocellulose materials on cement hydration to provide an explanation for the macroscopic structural improvements previously observed from adding these materials to cement pastes. The main conclusions that can be drawn from this work are that addition of nanocellulose materials to cement paste mixes: a) causes a delay in the initial hydration reaction, b) increases the overall extent of hydration, and c) does not significantly influence the composition of the final cement microstructure. Further work can be done to understand how cellulose nanomaterials affect other properties that influence mechanical properties of cement pastes, such as pore structure and chemical shrinkage.

Acknowledgments

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