

MICROSTRUCTURAL INVESTIGATION OF NANOCELLULOSE ADDITION ON THE PERFORMANCE OF CEMENTITIOUS MATERIALS CURED IN AGGRESSIVE ENVIRONMENTS

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Abstract

During the last years, incorporation of nano-constituents into cement-based construction materials has been increasingly spreading thanks to their unique physicochemical properties which enable both nano- and micro-mechanical improvement of cementitious composites. It has been well established that besides increasing concretes strength, refinement of pore size occurs causing a significant reduction in total porosity values and improvement in specimens durability. The present work aims at the analysis and performance evaluation of nanocellulose (NC) enriched Ultra High Durable Concretes (UHDC) exposed to aggressive environmental conditions (i.e. chemical attack - XA environmental exposure class). To this purpose, two reference UHDC materials containing crystalline admixtures and steel fibers were compared with mixes holding also cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) into their structures. In all cases, NC loading remained constant and equal to 0.15% (by %wt of cement amount). The excellent reinforcing capabilities of NCs are demonstrated by the enhanced fracture resistance properties of the cementitious matrix. Additionally, microstructural analysis results of as derived specimens suggest that the use of NCs can lead to the development of materials with advanced textural and morphological characteristics and therefore widen their application prospects to aggressive environmental conditions.

Keywords: Nanoadditives, Nanocellulose (CNFs, CNCs) Ultra-High Durable Concretes

1. INTRODUCTION

Cement based materials are generally characterized as quasi-brittle due to their low tensile strength and fracture toughness. At the material level, typical reinforcement may be accomplished through the incorporation of dispersed fibers into the matrix. In that way, crack formation and propagation are being delayed to a great extent resulting into improved mechanical performance

[1,2]. The ultimate goal of this research is to modify the properties of concretes at the nanoscale and develop nano-engineered materials with improved macroscopic properties.

It has been reported that integration of cellulosic fibers into cementitious composites (C-FCCs) impart an adequate bonding capacity to the matrix resulting in substantial improvements in toughness, ductility, flexural strength and impact resistance [3]. Indeed, cellulose is characterized by superior mechanical properties (tensile strength up to 700MPa), low density and an internal curing ability due to the high water retention capacity. Moreover, cellulose is considered as non-toxic, renewable, cost effective and abundant compared to other fibers (e.g. asbestos, polyvinyl-alcohol PVOH, polypropylene) satisfying the need for the development of novel, biodegradable and non-petroleum materials with low environmental impact. However, several drawbacks arose in the performance of C-FCCs, which mainly lay on fibers mineralization, low durability and low biopolymer loading dictated from poor dispersion issues and the formation of inhomogeneous regions in more cellulose concentrated materials [3,4].

A likely feasible alternative for enhancing cellulose reinforcement capacity without increasing its loading in cementitious mix-designs is to utilize biopolymer at the nanometer scale. Incorporation of nanocellulose (NCs) has opened a new field for nanosized reinforcement within cementitious composites and the development of materials with improved performance [5,6]. Several reasons can be attributed to NCs reinforcement activity. Their high specific surface area and chemical reactivity derived from the high population of hydroxylic and carboxylic surface groups, significantly promotes interactions between materials components (e.g. PVOH fibers, SiO₂ etc.) also favoring the formation of an extensive NCs-matrix network [7]. The latter, improves bonding strength and act as stress boundary uniformly distributing stress in a bridge-like pattern and inhibiting fiber pull out phenomena [8]. More than that, during cement hydration the small sized NCs tend to interlock with each other and accumulate along with the precipitated hydration products into structure defects contributing to the reduction of porosity and micro-cracking activity. NCs hydrophilic nature also play an important role during cement hydration process. Acting as nuclei, NCs promote the formation of hydration products (especially CSH), whereas the already formed NCs-matrix network operates as water reservoir that gradually releases water to the matrix in dry environment. In this way, the matrix is able to undergo continuous hydration with partially replenished porosity and low micro-crack formation.

Summarizing, there is a significant potential for NCs (CNFs or CNCs) in improving the properties of cementitious composites. In this study, that was performed under the scope of H2020 ReSHEALience project, the effect was investigated of NCs on the macro- to micro- to nano-scale mechanical properties of cementitious composites. The main objective is the development of Ultra High Durability Concretes (UHDC) with improved strength, toughness and durability performance in aggressive environmental conditions (chemical attack exposure-XA). To this goal, specimens containing crystalline admixtures, steel fibers and cellulose nanocrystals (CNCs) or cellulose nanofibrils (CNFs) were produced. Incorporation of different NC species into cementitious mixtures will offer a side-by-side performance comparison between CNCs and CNFs leading to a better understanding of particle morphology impact on composite properties.

2. MATERIALS & METHODS

In an attempt to evaluate the microstructural characteristics and mechanical properties of nanocellulose enriched concretes exposed in XA environmental conditions, three different High-Performance Fiber Reinforced Cementitious Composites (HPFRCCs) were cast (Table 1). Among them, HPFRCCs mixture containing CEM I and slag as binder, sand, crystalline admixtures and steel fibers was used as reference material (labeled as XA-CA). The adopted mixing procedure and the employed dosages of constituents were formulated in order to guarantee self-compacting properties. Following the same experimental protocol two additional mixtures were produced containing also cellulose nanocrystals (XA-CA-CNC) and cellulose nanofibrils (XA-CA-CNF). Nanocellulose polymers used were derived from softwood biomass using AVAP® biorefinery technology and were supplied as 10%wt aqueous suspension. Prior to their addition to cement, both NC additives were further dispersed in water down to 1.5%wt in order to achieve a final NC loading equal to 0.15%wt (by %wt of cement) at concretes. Slag, crystalline admixtures and cellulose nanoadditions have been added in the mixes to improve the mechanical and durability performance of the concretes when are exposed to chemical attack targeting to the new concept of “Ultra-High Durable Concrete (UHDC)”. The water to cement ratio in the mix was set at 0.33. Following mixing, the mixtures were casted in appropriate molds to produce prismatic 40x40x160 mm beam specimens, for flexural and compressive strength testing. After demolding (one day after casting) the specimens were cured in moist (20°C, 95% RH) and geothermal water conditions until testing. The geothermal water used for specimen immersion, originates from the cooling basins of a geothermal plant owned by Enel Green Power (Tuscany, Italy). Chemical analysis results indicate the presence of both sulfate (SO_4^{2-}) and chloride (Cl^-) ions at of 2678ppm and 441 ppm, respectively.

Table 1 : mix-composition of investigated UHDCs

Constituents	XA-CA	XA-CA+CNC	XA-CA+CNF
CEM I 52.5R	600	600	600
Slag	500	500	500
Water	200	200	200
Steel fibers ($l_f = 20$ mm; $d_f = 0.22$ mm)	120	120	120
Sand 0-2mm	982	982	982
Superplasticizer	33	33	33
Crystalline admixtures (CA)	4.8	4.8	4.8
Cellulose nanocrystals (CNC)	-	0.15*	-
Cellulose nanofibrils (CNF)	-	-	0.15*

*by % wt cement

Morphological investigation of materials was conducted with a Jeol JSM 7401F Field Emission Scanning Electron Microscope equipped with Gentle Beam mode and EDAX analyser. The applied acceleration voltage was 2 kV and samples were mounted on metallic (brass) substrates using a double coated carbon conductive tape. Prior to their observation, nanocellulose polymers and the fracture surface of the specimens were sputter coated at a 20nm thick layer of gold-palladium

(Au/Pd). Specimens were tested at For X-ray diffraction measurements, NC samples were prepared on microscope glass slides and allowed to dry in a silica designator for 72h. The corresponding patterns were acquired using a Rigaku rotating anode X-ray generator (operating at 50kV, 100mA, nickel filtered CuK α 1 radiation) and a R-Axis IV imaging plate. Thermogravimetric analysis was performed on a SETARAM SETSYS Evolution 18 Analyser, at a heating rate of 10 °C/min, in an alumina crucible using dried air as the carrier gas.

The mechanical performance of as prepared specimens was evaluated by flexural toughness (3-point bending) and compressive strength tests. Flexural tests were performed according to EN 1015-11:1999 on prismatic specimens (40x40x160mm). To this purpose, a 7 mm deep notch was cut at mid-span of the specimens. Three-point bending tests were performed in displacement control by measuring the Crack Mouth Opening Displacement (CMOD) at the tip of the notch. Then, once each specimen was completely tested in flexure and broken in two halves, compressive strength tests were performed also according to EN 1015-11. Tests were performed after 28, 56 and 84 days curing the specimens in both a climate room (T = 20°C and 95%) and in the geothermal water as above.

3. RESULTS AND DISCUSSION

3.1 Physicochemical and Morphological characterization of NC additives

3.1.1. Fourier-transform infrared spectroscopy (FT-IR)

Fourier Transform Infrared spectroscopy (FT-IR) provided a quantitative estimation of the presence of hydroxyl, sulphate and carboxylic groups attached on nanocellulose polymeric chains, as well as the existence of residual lignin amount. Recorded FT-IR spectrums of the examined NC samples along with a summary of transmittance signals associated with the corresponding bond vibrations are illustrated in **Errore. L'origine riferimento non è stata trovata.** and Table 2, respectively.

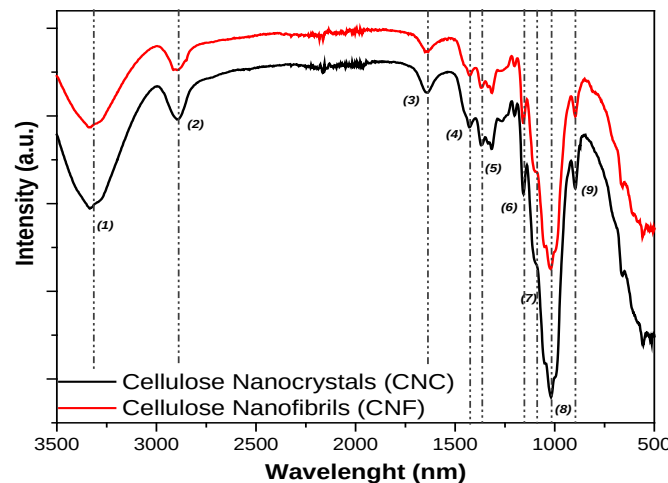


Figure 1: FT-IR spectrums of NC fibrils (CNF) & crystals (CNC).

As seen, all samples exhibit similar FTIR spectrums with analogous stretching-bending bond vibrations and signal intensities, displaying all characteristic α -cellulose peaks. These data are constituent with analogues results for NCs found in the literature (Figure 1, Table 2). The intense band noted at $\sim 1025\text{cm}^{-1}$ (Label 8) is related to the glycosidic $^4\text{C}_1$ ring conformation deformation and β -glycosidic linkages between glucopyranose rings in cellulose. On the other hand, the band located at $\sim 1430\text{cm}^{-1}$ (Label 4) is associated with the amount of crystalline structure within cellulose, while the band at $\sim 895\text{cm}^{-1}$ (Label 8) is generally assigned to the amorphous regions of cellulose. Characteristic bands attributed to lignin functional groups ($\sim 3570\text{cm}^{-1}$, $\sim 1715\text{-}1675\text{cm}^{-1}$, $\sim 1602\text{-}1502\text{cm}^{-1}$), carboxylic ($\sim 1729\text{cm}^{-1}$) or sulphate ($\sim 1376\text{cm}^{-1}$) compounds could not be distinguished in the spectrums, signifying the absence of these groups in NC polymers.

Table 2: Infrared band assignments for NC materials.

Wavenumber (nm)	Characteristic bands
(1) - 3320	OH stretching
(2) - 2890	Aliphatic C-H stretching
(3) - 1630	OH bending (absorbed water)
(4) - 1430	C-H symmetric bending (CH_2)
(5) - 1370	C-H & C-O pyranose ring bending
(6) - 1160	C-O-C stretching
(7) - 1100	Out of phase bending
(8) - 1025	C-C, C-OH, C-H pyranose ring & side groups
(9) - 895	C-O-C, C-C-O, C-C-H deformation & stretching

3.1.2. X-Ray Diffraction analysis (XRD)

Both nanocellulose polymers exhibit a single broad peak at low angle region centered between 15° and 15.5° , accompanied with a higher order Bragg reflection located at 22.5° assigned to crystallographic planes (110) and (200), respectively (Figure 2). These polymorphs correspond to cellulose I structure, which consider as the polymorph of cellulose with the highest mechanical integrity [9]. A low intensity peak can also be observed at $2\theta=34^\circ$, which corresponds to (004) cellulose plane, whereas (110) diffraction peak is convoluted under the broad peak at 15° .

Crystallinity index (CI) of NC samples was estimated from the empirical Segal equation using the height ratio between the intensity of crystalline peak and total intensity after baseline subtraction. CI equal to 94% was obtained in the case of CNC sample, whereas its value decreased to 85% regarding CNF signifying also the presence of a higher amorphous cellulose fraction.

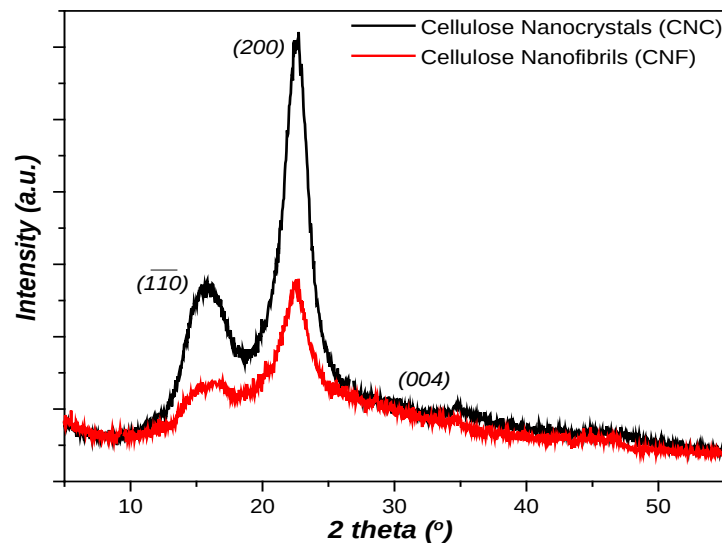


Figure 2: X-ray diffraction patterns of NC fibrils (CNF) & crystals (CNC).

3.1.3 Thermal Stability

Thermogravimetric weight changes were recorded in order to evaluate the onset and crystal decomposition temperatures of NC samples. The respective TGA/DTG profiles along with DSC curves are presented in Figure 3. As seen, all samples exhibit analogous TGA degradation patterns demonstrating an initial weight loss at around 70°C related to the desorption of physically absorbed water and volatile compounds. Likewise, the major steep weight loss displayed in the range 245–350°C can be assigned to onset and maximum rate of crystal decomposition, accompanied with the complete removal of the organic content at higher temperatures. In addition, the TGA curve of CNC sample is slightly shifted towards higher temperatures, signifying a moderately delayed onset of decomposition temperature due to the higher CI, as obtained from XRD analysis. These results are further validated from dTG curves, in which crystal decomposition at 325±5°C is also assigned. Differential scanning Calorimetry (DSC) was also performed in order to elucidate the onset of melting and crystallization temperature (Figure 3). Similar patterns appear also in this case, demonstrating a sharp and well defined exothermic peak located at 325±5°C indexed to crystal decomposition phenomena, in accordance to TGA/DTG results. In the area of endothermic activity, peaks of different intensity are illustrated at low temperature values, which could be regarded as an indication of different bounded water amounts.

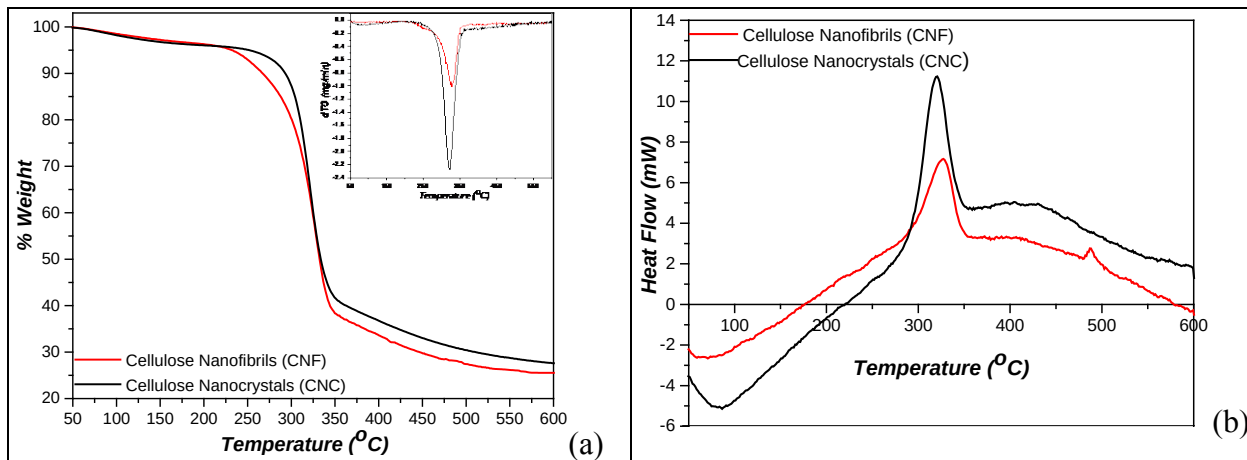


Figure 3: Thermogravimetric analysis (a) & Differential Scanning Calorimetry curves (b) of NC fibrils (CNF) and crystals (CNC)¹.

¹ TGA/DSC experimental conditions: Ar, Flow=50ml/min, $T_{\max}$ =600°C, T_{rate} =5°C/min, isotherm=40°C/ 20min.

3.2. Thermal, Morphological & Mechanical characterization of NC UHDCs

3.2.1. Thermo-gravimetric analysis

TGA/DTGA analyses of samples extracted from UHDC specimens cured under both aforementioned conditions showed, for all the investigated mixes, absolutely similar trends, highlighting delayed hydration (CSH peak) and carbonation (CaCO_3 peak) as the main reactions responsible of healing (Figure 4).

It can be interestingly observed, in the curves of the samples reinforced with both cellulose nanofibrils and nano-crystals, the presence of a small peak in correspondence of the decomposition temperature of the same nano-cellulose, observed as above. This can be called as a confirmation for good dispersion, given the randomness of sampling material for TGA analysis, of the nano-constituent and hence of the effectiveness of the employed mixing procedure as well as of the actions on the mechanical performance of the composite, as further elucidated. Higher intensity of peaks in correspondence of CSH decomposition also confirms the effects of NC as seed for hydration of cement, as hypothesized.

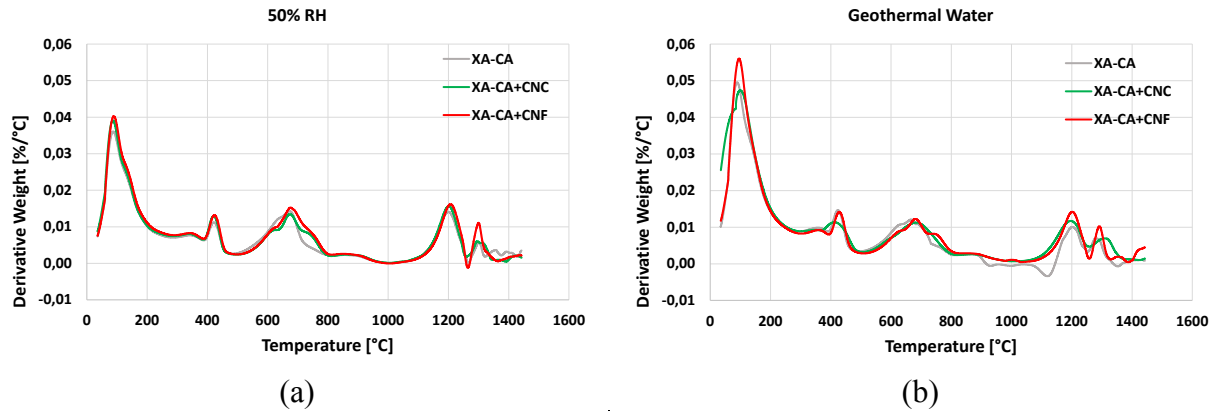


Figure 4: DTGA curves of samples extracted in the vicinity of cracks healed in different regimes: a) 50%RH and b) geothermal water.

3.2.2. Mechanical characterization: Compressive & Flexural strength tests

Table 3 summarizes the average values of six (compression strength) and three (flexural strength) tests on nominally identical specimens cured under moist room and geothermal water (GW).

According to the results, the presence of NCs positively affects the performance of specimens in both curing environments, with those exposed to GW treatment demonstrating better results. One possible reason could evolve interactions between NCs and defects existing on the matrix at the very onset of their formation. Specifically, after curing in GW, XA-CA-CNF and XA-CA-CNC samples exhibit 43% and 29% increase in flexural strength values respectively at 28 days and 27% for XA-CA-CNC at later ages (84 days). On the other hand, materials efficiency cured under moist environment is much lower as flexural strength values range between 8% and 16% increase at 28d and 56d, with the percentage raising up to 27% only in the case of CNF at the later age (84d). Based on these results, it could be hypothesized that the beneficial role of NC presence into cementitious mixtures under XA conditions is actually a synergetic effect of NCs particle size and crystalline structure. In particular, the small size of nano-cellulose (CNC: 4-5nm width & ~300nm length, CNF: 5-200nm width & 500nm to several μm length, as from SEM measurements) allow their accumulation into matrix defects that originally are filled with water contributing to the refinement of micro-porosity. Beyond that, the hydrophilic nature of NCs and their tendency to interact with cementitious constituents facilitate hydration reactions and the formation of insoluble products (C-S-H) that also fill the pore network leading to further pore refinement [6, 8, 10,11]. The latter, as also indicated from MIP measurements [12], demonstrate reduction of pore size values when NC is also present in the matrix. Considering both porosity of specimens and XRD analysis results that highlight the presence of a higher amorphous fraction in CNF structures it could be suggested that the enhanced efficiency of XA-CA-CNF samples, especially in earlier stages, is due to the higher diffusivity of water molecules through the amorphous regions of the nano-consituent. In that way, hydration of cement particles is facilitated increasing the number of hydration loci and the population of inorganic hydration products.

On contrary to what stated for flexural strength efficiency, compressive strength tests demonstrate that increasing in the performance in both curing environments is negligible. A

maximum of 10-12% at the age of 28 and 56 days is revealed for mixes cured in RH which turns to zero at later cement ages. Similar trend is followed from the materials cured under GW conditions.

Table 3: Influence of curing exposure on compressive/flexural strength values

Mix	Curing	Compressive strength [MPa]			Flexural strength [MPa]		
		28 d	56 d	84 d	28 d	56 d	84 d
XA-CA	Moist room	127,0 (1.0)	142,9 (12.2)	166,3 (1.5)	24,4 (15.4)	28,9 (17.1)	29,0 (41.3)
XA-CA+CNC		147,6 (1.0)	157,0 (12.5)	170,5 (2.6)	27,3 (9.1)	31,4 (15.6)	30,4 (6.5)
XA-CA+CNF		137,7 (1.4)	145,0 (13.3)	152,3 (7.6)	29,1 (25.2)	32,5 (27.0)	40,0 (12.5)
XA-CA	Immersion in geothermal water	140,4 (11.1)	152,8 (4.1)	161,4 (3.6)	26,1 (6.5)	26,2 (5.4)	27,5 (17.8)
XA-CA+CNC		137,3 (15.6)	147,0 (11.6)	169,2 (2.0)	33,7 (17.2)	34,9 (17.4)	32,2 (14.7)
XA-CA+CNF		152,8 (4.1)	158,7 (5.9)	164,5 (1.0)	33,6 (8.9)	32,2 (13.5)	30,3 (5.2)

* CoV (%) in brackets

3.2.3. Morphological characterization: SEM/BS/EDAX analysis

Morphological characteristics NC-enriched specimens and reference materials were investigated through SEM measurements. Preliminary results of the samples treated under geothermal water conditions are illustrated in Figure & 6.

All materials demonstrate the typical morphology of cementitious composites. At low magnifications, regions of different morphologies could not be distinguished, whereas small cracks and pore openings prevail in the surface of reference sample. On contrary, at higher magnifications different morphologies can be distinguished attributed to the presence of hydration products (mainly C-S-H and CaOH to a lesser extent) (Figure 6). SEM micrographs of NC loaded samples reveal that hydration products exist in a much higher degree, justifying the improved strength properties and the enhanced hydration rhythm. The beneficial role of CNF presence into cementitious mixture with respect to facilitation of hydration reactions and increase of microstructure consistency ("bridging effect") is well evident in the micrograph of Figure Figure D. In this case, nano-fibrillated cellulosic components appear to act as nuclei for hydration reactions and as bridge binding inorganic constituents covered with hydration products.

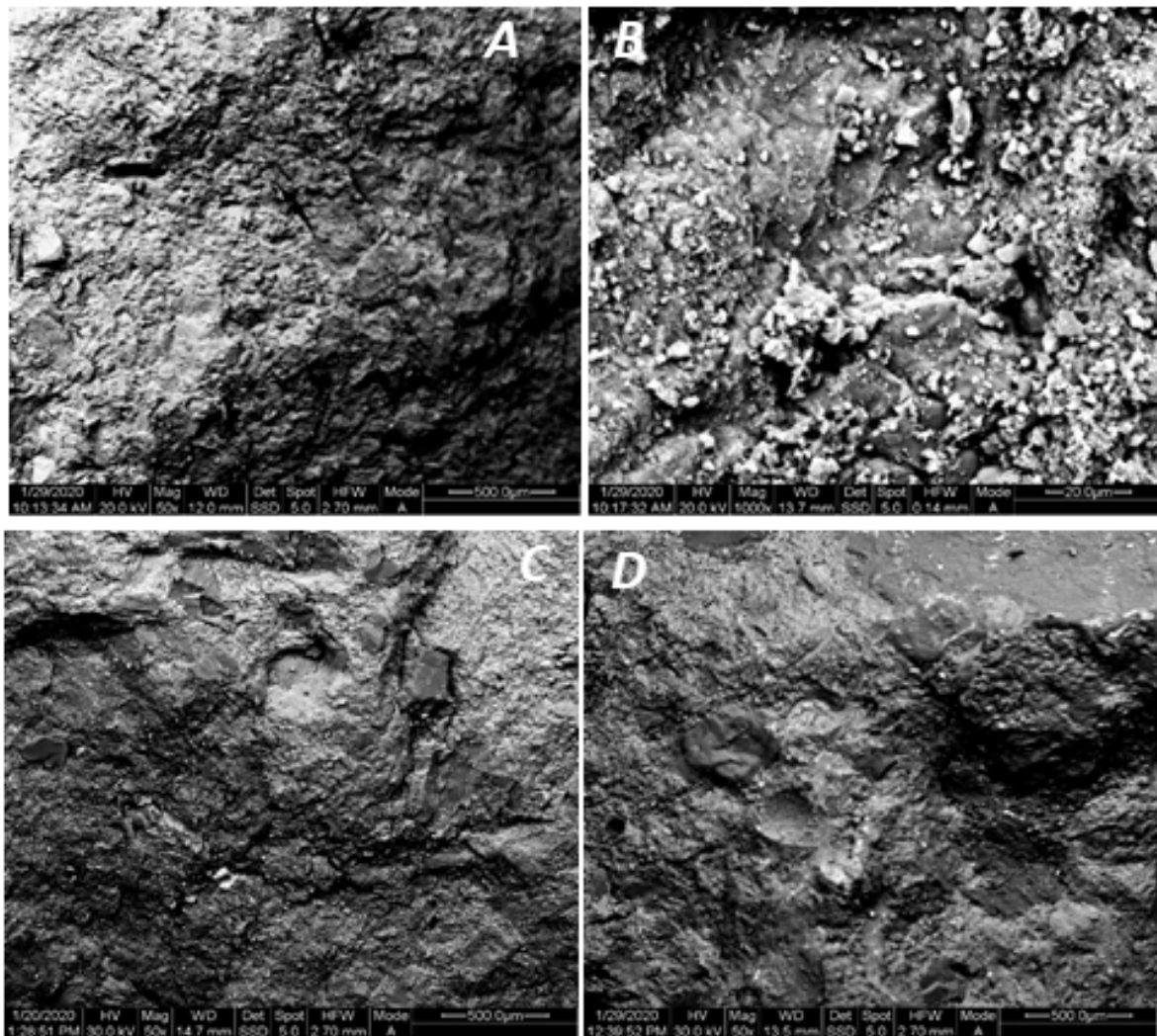


Figure 5: BS-SEM micrographs at low magnifications of specimens treated under GW (A, B) Reference (C) XA-CA-CNC & (D) XA-CA-CNF.

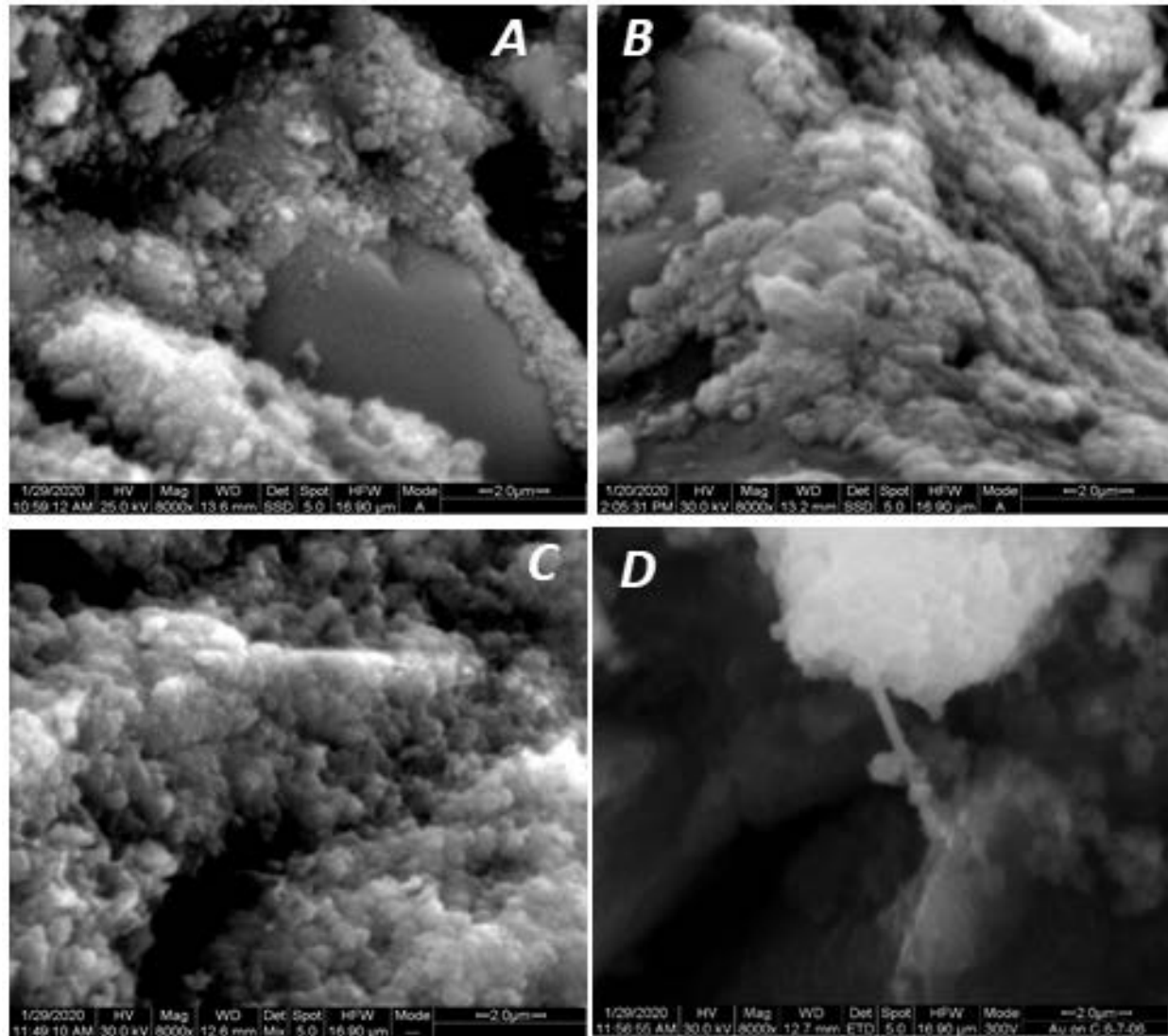


Figure 6: BS-SEM micrographs at high magnifications of specimens treated under GW (A,B) Reference, (C) XA-CA-CNC & (D) XA-CA-CNF.

4. CONCLUSIONS

The effect of Nanocellulose (NCs) on the nanostructure, as well as the macro-scale mechanical properties of UHDCs containing nanocellulose and cured under aggressive XA environmental conditions has been investigated. Flexural strength test results indicate that fracture properties of NC-cement matrix have been enhanced when materials are cured in GW conditions. In particular, an increase up to 43% has been achieved using CNFs and 29% when CNCs are added in the mixture at a constant 0.15%wt loading. Characterization analysis results suggest that CNs can strongly modify and reinforce cement paste matrix at the nanoscale by increasing the amount of high stiffness hydration products and decreasing the porosity. It has been hypothesized that

incorporation of CNFs is more effective also due to the higher amorphous fraction that facilitates the diffusion of water molecules and hydration reactions. Further characterization tests such as XRD, N₂ adsorption/desorption porosimetry and H₂O diffusion measurements will be performed in order to clarify CNs reinforcement mechanisms.

5. ACKNOWLEDGEMENTS

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UHDC characterization tests were held at the facilities of Civil & Environmental engineering Department of Politecnico di Milano. CNs characterization tests were performed at the Laboratory of Materials & Membranes for Environmental Separations (INN) at NCSR "Demokritos", Athens.

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