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Research Article

Cement Hydration Induced Via Al_2O_3 Nanocoating On Carbon Nanofibers

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Abstract

Cement hydration is a process where the raw materials convert to cementitious gel moiety. The rate of conversion is significantly enhanced by the presence of some nanomaterials. Herein, a fluffy-porous Al_2O_3 on carbon nanofibers for inducing cement hydration process was employed. This study mainly utilizes Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) to quantify the degree of hydration. The hydration degree is dictated by measuring Ca+/Si ratio. It was found that Ca+/Si ratio decreases as from Al_2O_3/CNFs to CNFs compared to the plain C0 specimens. It is believed that Al_2O_3 nanolayer offers huge population of active sites such as (OH^-) which was confirmed by zeta-potential analysis. These nucleation sites attract cations facilitating the hydration process. This research is a step forward on understanding the Al_2O_3 nanolayer effect on cement hydration process.

Keywords: Cement hydration; Nanomaterials; Carbon nano fibers; Portland cement

Introduction

Portland cement primarily consists of Calcium Silicate Hydrate (C-S-H), which plays a crucial role in determining the strength characteristics of cement paste [1]. Current trends in nanotechnology have led to extensive research on understanding how nanosized objects additives affect the composition and properties of C-S-H in cementitious materials [2-6]. Chen et al. [2] shown in his study that Multi-Walled Carbon Nanotubes (MWCNTs) enhance the mechanical properties of cement composites by converting low-density C-S-H into high density. In another study, carbon nanofibers were found to increase C-S-H density and promote crystal nucleation [4]. There is compelling evidence that both individual and agglomerated forms of these nanomaterials act as sites for cement hydrates to form and grow. It is evident that once the hydration reaction begins, C-S-H gels tend to form around CNTs, with the layer covering the CNTs becoming progressively thicker over time and a network of C-S-H gel is established [7]. Despite the significant amount of research dedicated to harnessing the effect of carbon nanomaterials on the hydration of cement, others show no effect or even delaying in hydration [8]. The varying results could be due to the quality of dispersion and the chemical affinity of the carbon nanomaterials' surface.

Furthermore, nanoparticles like nano silica SiO_2, nano-TiO_2, and nano-γ-Al_2O_3 have shown to significantly impact hydration products in cement [3-5,9]. Nano silica exhibits a pozzolanic effect like silica fume, resulting in increased hydration product quantities. Many studies [9-11] have suggested that the pozzolanic reaction of nano-SiO_2 leads to the formation of a greater amount of "high-stiffness" C-S-H compared to what is usually produced during the hydration of OPC. This high-stiffness C-S-H is believed to be more durable both mechanically and chemically than low-stiffness C-S-H, and it is theorized that its creation may be responsible for the observed alterations in bulk material properties. Similarly, nano-TiO_2 promotes the growth of high-density C-S-H and calcium hydroxide. However, it does not have pozzolanic effect [5].

To quantify the effect of the nanomaterials on the hydration of cement, different techniques have been applied such us, X-Ray Diffraction (XRD) [12], Or using Derivative thermal analysis–differential Thermogravimetric (TG/DTG) analysis [13], or by the combination of Energy Dispersive X-ray Spectroscopy (EDS) with Scanning Electron Microscopy (SEM) [14] In our previous study [15], we have employed TGA analysis to map the quantity of the C-H conversion to C-S-H which is the key moiety of the hydration indicator. In addition, the XRD analysis was performed to identify the peak intensities of non-hydrate Tricalcium Silicate (C_3S), Dicalcium Silicate (C_2S), and Portlandite (CH) which gave an insight into the hydration process of the cementitious materials with the used additives.

The combination of Energy Dispersive X-ray Spectroscopy (EDS) with the aid of Scanning Electron Microscopy (SEM) is a powerful tool for the chemical characterization of samples, particularly in analysing surface elements and their quantities at various positions. This technique involves directing an electron beam at the sample, causing electrons in different energy levels to be ejected and creating vacancies. The subsequent emission of X-rays as these vacancies are filled provides valuable information about the elemental composition of the sample [14]. The EDS can scan a significant portion of the sample to identify the desired location. Once the location of interest is found, the EDS can produce a spectrum that reveals the percentage composition of each element present in that specific area. By scanning locations, EDS can give a sense on how the nanomaterials are distributed, how much, and where the hydration products (such as CH, C-S-H, C-A-H, C-A-S-H) are located [16]. Based on our previous research results [15], CNFs-0.25% and Al_2O_3/CNFs-0.125% showed the best compressive strength. Here in this work, we used EDS analysis to confirm the effects of Al_2O_3/CNF on cement mortars compared to bare carbon nanofibers and plain samples. The high surface hydrophilicity of Al_2O_3/CNFs-0.125% dictates the high surface activity toward Ca and Si cations adsorption as confirmed by zeta potential analysis.

Materials and Methods

The preparation of mortar mixtures at different ratios of coated and bare CNFs is described as follows. Ordinary Portland Cement (OPC type I) classified within the ASTM C150 standard type I was used in combination with commercially available sand to make the mortar mix. Carbon Nanofibers (CNFs) were purchased from pyrograph nanomaterials Inc (USA). Transmission Electron Microscopy (TEM) of CNF taken by Jeol-1400 (Thermo Fisher) as in Figure (1a & 1b). Figure (1c & 1d) shows the TEM image of the Al_2O_3/CNFs. Trimethylaluminum (TMA-1.0M) as a precursor was obtained from Sigma-Aldrich. A water-reducing admixture (Master Glenium-7500) was obtained from BASF. The Al_2O_3 nanocoating was done using CLD [17] . All the samples preparation was fully described in our previous published work [15].

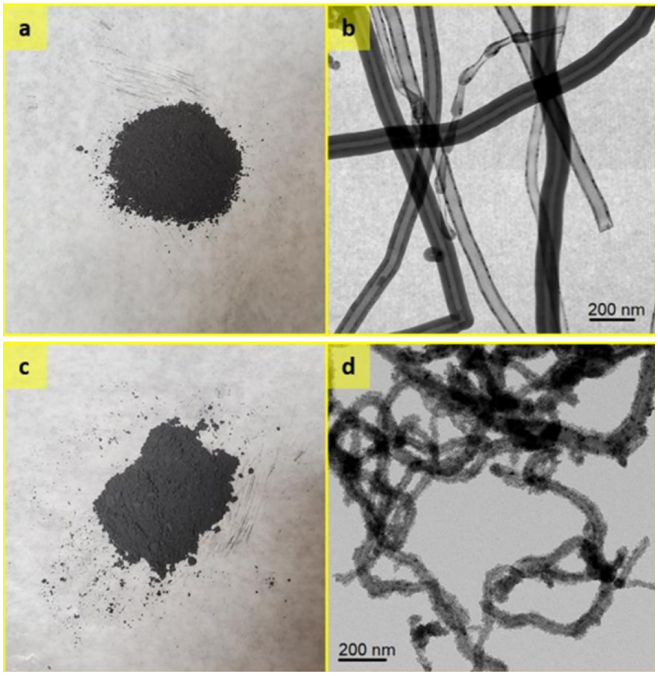

Figure 1: (a) CNFs in powder form, (b) TEM image at 200nm scale, (c) Al_2O_3/CNFs in powder form, and (d) TEM image at 200nm scale.

Characterization techniques

Microscopy: Scanning electron microscopy SEM is a surface imaging technique that can capture nanometer resolution of topographical features. Secondary Electron (SE) imaging was used to study the microstructure of cement mortar specimens for the CNFs-0.25 and Al_2O_3/CNFs0.125 samples due to its feasibility with fracture surfaces. The SEM specimens were prepared by using the cracked residue from the cubic specimens that underwent a compressive test at 28 days of age, without any additional treatment. Scanning Electron Microscopy (SEM) FEI Quanta 600 FEG SEM scope was used to investigate the cement internal structure.

Energy dispersive X-ray spectroscopy (EDS): EDS has been used to determine the main compositions of the Portland cement reinforced by different nanomaterials qualitatively [14]. The EDS has also the ability to scan a descent area of the sample to spot the location of interest. After finding the location of interest, EDS can generate a spectrum 27 which can provide the percentage of each element in the selected location [14]. By scanning multiple locations, EDS can give a sense on how the nanomaterials are distributed, how much, and where the hydration products (such as CH, C-S-H, C-A-H, C-A-S-H) are located [18]. In this research, the samples were prepared by taking a small amount of the material in a disc-like mold after 28 days of age see Figure 2. The disc samples were characterized by FEI Quanta 600 FEG SEM scope.

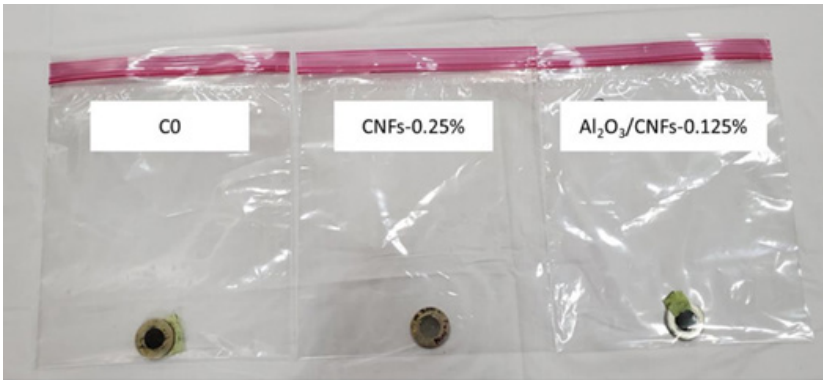

Figure 2: Preparation of the samples for EDS analysis inside a washer disc.

Zeta potential analysis: The Zeta potential of the samples was recorded at room temperature employing a Z Malvern/ Zettaliter Nano-ZS. A 2mg of either CNFs or Al_2O_3/CNFs was dispersed in DI-water before the analysis.

Results and Discussion

Microscopic analysis

Numerous studies have confirmed the effectiveness of Carbon Nano Fibers (CNFs) in bridging the microcracks through visualizing microstructure analysis [19,20]. This research investigates the morphology and microstructure characteristics of Al_2O_3/CNFs and composites to assess their ability to bridge microcracks in comparison with control sample C0. The results, as depicted in Figure 3, demonstrate that the control sample exhibits microcracks, whereas the presence of Al_2O_3/CNFs in the mortar composites effectively bridges narrow microcracks. This effect is significant as it restricts the development of internal microcracks in the mortar matrix, ultimately leading to improved mechanical properties. This is attributed to the high aspect ratio of the coated CNFs, which physically enables the bridging property.

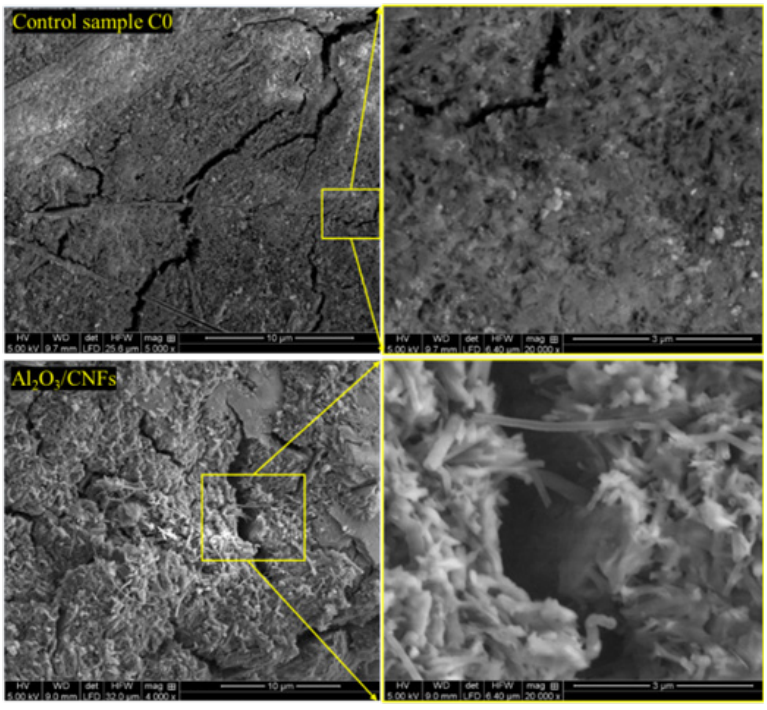

Figure 3: Micro cracks in Control sample (C0) and Al_2O_3/CNFs-mortar composites.

Energy-dispersive X-ray spectroscopy

The EDS spectrum analysis for the reference sample C0, CNFs-0.25% and Al_2O_3/CNFs-0.125% is shown in Figure 4. The ratio of calcium to silicon Ca/Si is used as a metric to determine the consumption of calcium converted to silicate hydrated moiety. The amount of Si or Al relative to Ca was determined to decide at what extent the hydration reaction progressed [21,22]. The Al_2O_3/CNFs-0.125% has shown 3.59 ratio of Ca/Si, however, CNFs-0.25 and C0 have shown a ratio of 4.02, and 10.97, respectively and as shown in Table 1. The higher the ratio the less production of hydration gel products. Therefore, the presence of Al_2O_3 induces the formation of the hydration products in the form of calcium-silicate hydrate.

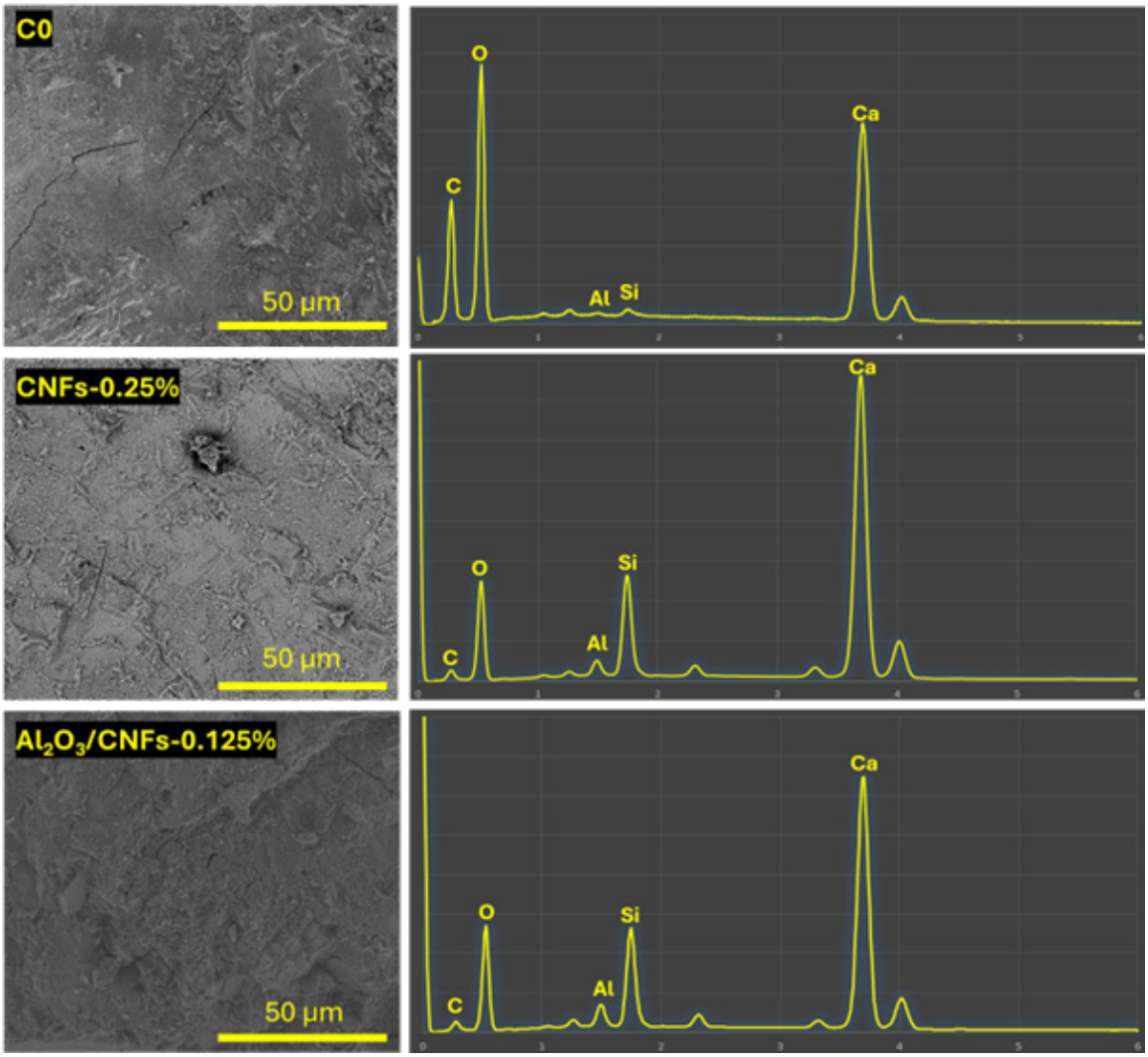

Figure 4: EDS spectrum and elements mass percent for C0, CNFs-0.25% and Al_2O_3/CNFs-0.125% composites.

Additionally, the EDS technique (Figure 4 & Table 1) can be utilized to verify the presence and determine the quantity of Carbon Nanotubes (CNFs) in the two composites (CNFs-0.25% and Al_2O_3/CNFs-0.125%). The carbon content detected in the 0.25 wt.% CNFs composite was 2.20 wt.% and in the Al_2O_3/CNFs-0.125% composite was 1.80 wt.%. This is attributed to the higher concentration of the CNFs in the first composite. Although the carbon content is typically used as an indicator for the presence of CNFs in the matrix, we observed a higher carbon level (6.98 wt.%) in the control sample due to carbonation, leading to the formation of calcium carbonate ($CaCO_3$). Carbonation occurs when CO_2 in the atmosphere reacts with Calcium Hydroxide (CH) in concrete to form $CaCO_3$. The high porosity of the control sample increases exposure to carbonation, while low porosity is essential for limiting CO_2 transport into the cementitious matrix through diffusion [23]. This is observed in matrices with pure and coated CNFs. In addition, oxygen, aluminium, silica, and calcium made up 45.2 wt.%, 1.20 wt.%, 9.40 wt.% and 37.80 wt.% respectively in the CNFs-0.25% composite, representing the general composition of Portland cement hydration products. The composition amounts for the Al_2O_3/CNFs-0.125% composite was 45.80 wt.%, 1.70 wt.%, 9.90 wt.% and 35.6 wt.% for oxygen, aluminium, silica, and calcium respectively. The composites reinforced with coated CNFs show higher Al content, as evidenced by the element mapping in Figure 5. Figure (5a-5d), (5e-5h) display SEM mapping of a 0.125 wt.% Al_2O_3/CNFs mix and a 0.25 wt.% CNFs mix, illustrating various elements such as carbon, calcium, silicon, and aluminium. The images reveal that carbon, the primary component of carbon nanofibers in both mixes, dispersed

among the hydration products of Portland cement when bare and coated CNFs were incorporated into the Portland cement pastes, as depicted in Figure 5. Figure (5e & 5f) clearly illustrates the filler effect of the bare CNFs within the hydration products, while Figures (a-d) show the growth of hydration products on the coated CNFs. The addition of coated CNFs results in a denser microstructure, likely due to the active layer of γ-Al_2O_3 covering the CNFs, leading to a higher density of C-S-H components. These findings align with our previous study where TGA and XRD results also support [15].

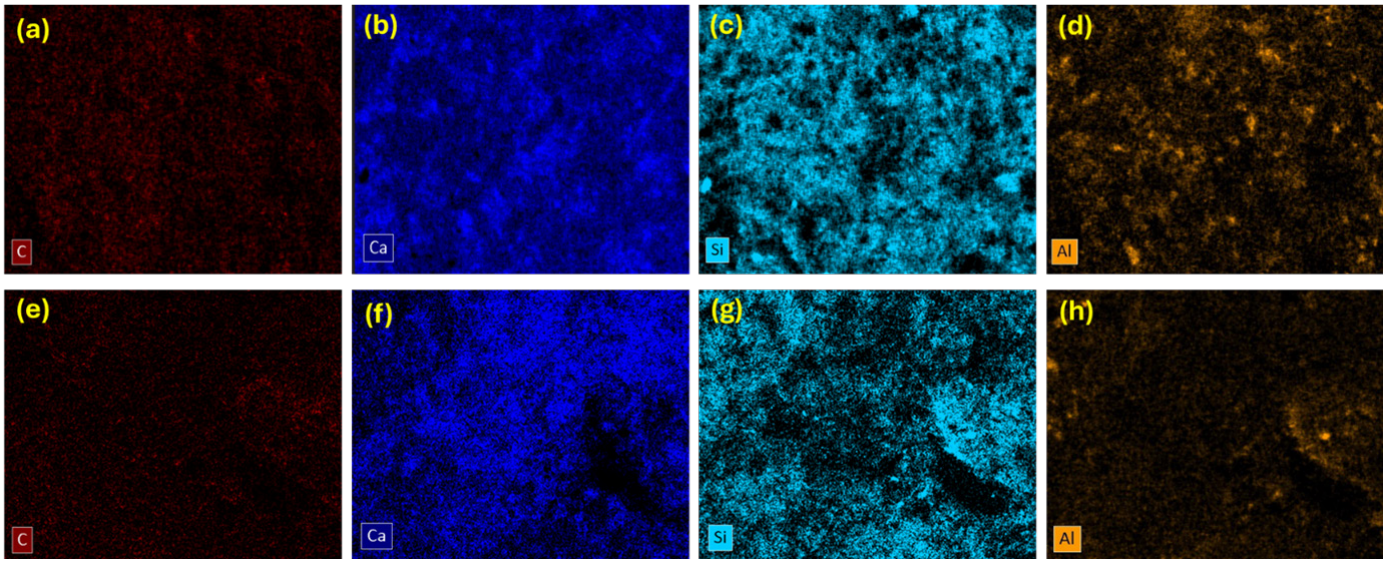

Figure 5: SEM mapping of (a-d) Al_2O_3/CNFs-0.125% and (e-h) CNFs-0.25% mix at age 28 days; showing carbon, calcium, silicon, and aluminum.

Table 1: Element analysis of EDS from Figure 4.

Mixes	Weight %					Ca/Si ratio
	C	O	Al	Si	Ca	
Control C0	6.98	44.80	0.74	3.87	41.70	3.59
CNFs-0.25%	2.20	45.20	1.20	9.40	37.80	4.02
Al_2O_3/CNFs-0.125%	1.80	45.80	1.70	9.90	35.60	10.97

Proposed surface activity

As shown in Figure 6, the presence of the Al_2O_3 layer, filled with functional groups or defects on its surface, attracts calcium cations and silicate cations, crucial components in the formation of C-S-H gel. Functional groups like hydroxyl (-OH) provide sites for ions to adsorb and react, leading to nucleation and growth of C-S-H gel. Moreover, this layer offers a high surface area for interaction with water molecules, enhancing water dispersion and distribution in the cement matrix. This improved water dispersion promotes hydration reactions by ensuring water availability throughout the cement matrix for reaction with cement particles, as demonstrated in our previous work [15]. Zeta potential is a powerful tool that assesses the surface group's identity [24]. Figure 7 shows zeta potential of both bare CNFs and Al_2O_3/CNFs. Figure 7(a) shows the surface of bare CNFs is mostly protonated as the point of zero charge (pzc) locates at 5.3 whereas the pzc of Al_2O_3/CNFs locates at ~8. Having surface PH around 8 means the surface is mostly deprotonated offering high OH sites.

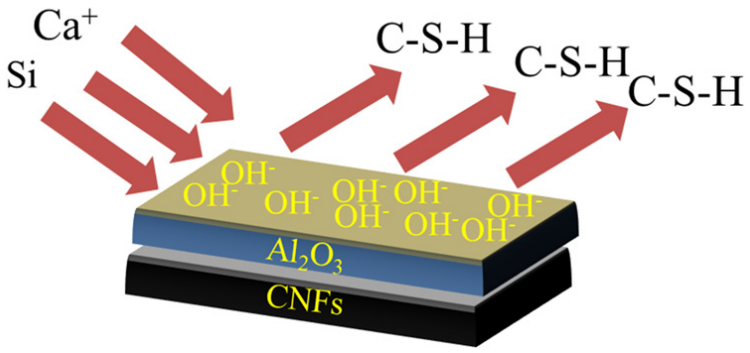

Figure 6: Schematic diagram of the seeding effect of the Al_2O_3/CNFs.

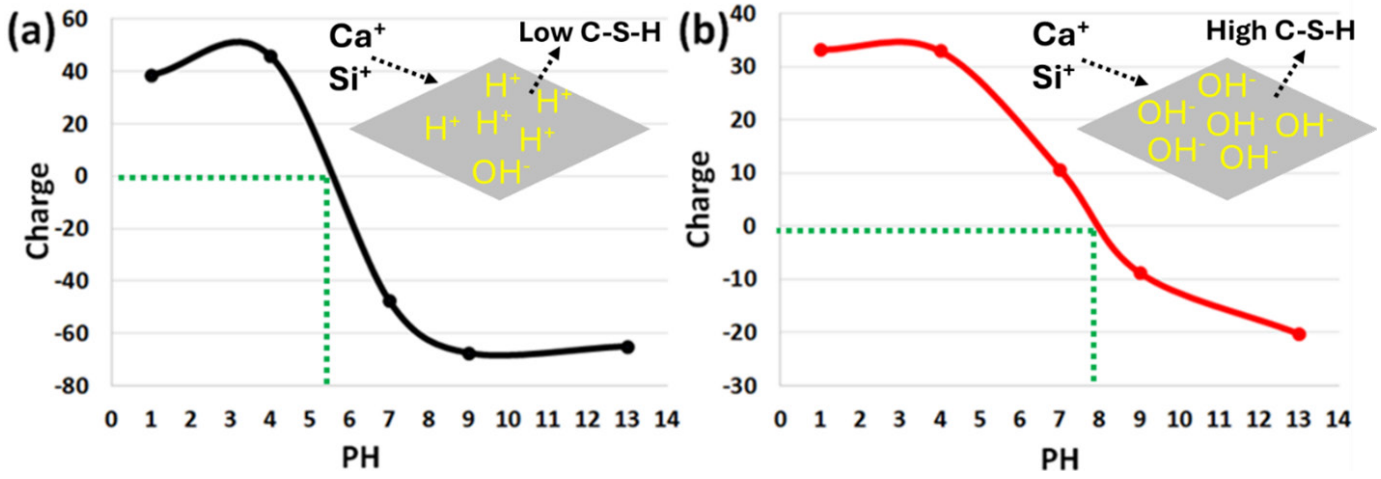

Figure 7: Zeta Potential (a) CNFs, (b) Al_2O_3 /CNFs.

Conclusion

The impact of Al_2O_3-coated CNFs on cement hydration was investigated using EDS characterization. The research findings highlight the significant effectiveness of Al_2O_3/CNFs, in bridging microcracks within mortar composites. The study's visual microstructure analysis reveals that the presence of Al_2O_3/CNFs restricts the development of internal microcracks, enhancing mechanical properties as it was shown previously. The EDS spectrum analysis revealed varying Ca/Si ratios for the reference sample C0, CNFs-0.25%, and Al_2O_3/CNFs -0.125%. A lower Ca/Si ratio in Al_2O_3/CNFs -0.125% indicates enhanced formation of calcium-silicate hydrate products. The EDS technique also confirmed the presence and quantity of carbon nanofibers in the composites, with higher CNFs concentration in CNFs-0.25%. The composition of hydration products in both composites resembled that of Portland cement. Additionally, composites reinforced with coated CNFs exhibited higher Al content, as demonstrated by element mapping. The presence of an Al_2O_3 layer with functional groups or defects on its surface plays a crucial role in attracting calcium and silicate cations, essential for the formation of C-S-H gel in cement. Functional groups like hydroxyl (-OH) as confirmed by Zeta potential facilitate ion adsorption and reaction, promoting nucleation and growth of C-S-H gel. Additionally, this layer's high surface area enhances water dispersion and distribution in the cement matrix, improving hydration reactions by ensuring water availability throughout.

References

1. Allen AJ, Thomas JJ, Jennings HM (2007) Composition and density of nanoscale calcium-silicate-hydrate in cement. Nat Mater 6(4): 311-316.
2. Chen J, Akono AT (2020) Influence of multi-walled carbon nanotubes on the hydration products of ordinary Portland cement paste. Cem Concr Res 137: 106197.
3. Akono AT (2020) Effect of nano-TiO_2 on C-S-H phase distribution within Portland cement paste. J Mater Sci 55(25): 11106-11119.
4. Akono AT (2020) Nanostructure and fracture behavior of carbon nanofiber-reinforced cement using nanoscale depth-sensing methods. Materials 13(17): 3837.
5. Reches Y, Thomson K, Helbing M, Kosson DS, Sanchez F (2018) Agglomeration and reactivity of nanoparticles of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, and clays in cement pastes and effects on compressive strength at ambient and elevated temperatures. Constr Build Mater 167: 860-873.
6. Yang Z, Gao Y, Mu S, Chang H, Sun W, et al. (2019) Improving the chloride binding capacity of cement paste by adding nano-Al_2O_3. Constr Build Mater 195: 415-422.
7. Makar JM, Chan GW (2009) Growth of cement hydration products on single-walled carbon nanotubes. The American Ceramic Society 92(6): 1303-1310.
8. Tafesse M, Kim HK (2019) The role of carbon nanotube on hydration kinetics and shrinkage of cement composite. Compos B Eng 169: 55-64.
9. Singh LP, Goel A, Bhattacharyya SK, Sharma U, Mishra G (2015) Hydration studies of cementitious material using silica nanoparticles. Journal of Advanced Concrete Technology 13(7): 345-354.
10. Monasterio M, Gaitero JJ, Erkizia E, Guerrero Bustos AM, Miccio LA, et al. (2015) Effect of addition of silica- and amine functionalized silica-nanoparticles on the microstructure of calcium silicate hydrate (C-S-H) gel. J Colloid Interface Sci 450: 109-118.
11. Gaitero JJ, Zhu W, Campillo I (2009) Multi-scale study of calcium leaching in cement pastes with silica nanoparticles. Nanotechnology in Construction 3: 193-198.
12. Singh LP, Goel A, Bhattacharyya SK, Mishra G (2016) Quantification of hydration products in cementitious materials incorporating silica nanoparticles. Frontiers of Structural and Civil Engineering 10(2): 162-167.
13. Sun J, Xu K, Shi C, Ma J, Li W, et al. (2017) Influence of core/shell TiO_2@ SiO_2 nanoparticles on cement hydration. Constr Build Mater 156: 114-122.
14. Nochaiya T, Chaipanich A (2011) Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials. Appl Surf Sci 257(6): 1941-1945.
15. Al Qader H, Jasim AM, Salim H, Xing Y, Stalla D (2022) Enhanced mechanical and durability properties of cement mortar by using alumina nanocoating on carbon nanofibers. Materials 15(8): 2768.
16. Nguyen HA, Chang TP, Shih JY, Chen CT (2019) Influence of low calcium fly ash on compressive strength and hydration product of low energy super sulfated cement paste. Cem Concr Compos 99: 40-48.
17. Jasim AM, He X, White TA, Xing Y (2020) Nano-layer deposition of metal oxides via a condensed water film. Commun Mater 1(1):

18. Nguyen HA, Chang TP, Shih JY, Chen CT (2019) Influence of low calcium fly ash on compressive strength and hydration product of low energy super sulfated cement paste. Cem Concr Compos 99: 40-48.

19. Fehervari A, Neil MacLeod AJ, Garcez EO, Aldridge L, Gates WP, et al. (2020) On the mechanisms for improved strengths of carbon nanofiber-enriched mortars. Cem Concr Res 136: 106178.

20. Afzal MT, Khushnood RA (2021) Influence of carbon nano fibers (CNF) on the performance of high strength concrete exposed to elevated temperatures. Constr Build Mater 268: 121108.

21. Sharma S, Kothiyal NC (2016) Comparative effects of pristine and ball-milled graphene oxide on physico-chemical characteristics of cement mortar nanocomposites. Constr Build Mater 115: 256-268.

22. da Silva Andrade D, da Silva Rêgo JH, Morais PC, de Mendonça Lopes AN, Rojas MF (2019) Investigation of C-S-H in ternary cement pastes containing nanosilica and highly-reactive supplementary cementitious materials (SCMs): Microstructure and strength. Constr Build Mater 198: 445-455.

23. https://www.sintef.no/globalassets/upload/byggforsk/publikasjoner/prosjektrapport-395.pdf

24. Sim K, Lee J, Lee H, Youn HJ (2015) Flocculation behavior of cellulose nanofibrils under different salt conditions and its impact on network strength and dewatering ability. Cellulose 22(6): 3689-3700.