

Hydration and Mechanical Properties of High Content Nano-Coated Cements with Nano-Silica, Clay and Calcium Carbonate

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Abstract

Nano-modified cements have gained significant interest due to their ability to enhance fresh and hardened properties and it is suggested that for a given nanomaterial, matrix or application type, there exists an optimum content where further dosing of nanomaterials could cause agglomeration, deterring performance. In this work, we introduce a novel nano-coating dry dispersion method and compare it against conventional sonication in aqueous form to evaluate their effect on hydration and mechanical properties for mixtures prepared with nanoclay, nanosilica or calcium carbonate nanoparticles at 4 wt.%. The results show that mechanical performance is sensitive to the dispersion method, driven by changes to early hydration kinetics. The degree of influence of the dispersion method on hydration kinetics was also found to be dependent on the nanomaterial type, where sonication in water was more mechanically favorable for silica and calcium carbonate nanoparticles and dry dispersion was more favorable for nanoclay.

Key words

Nanomaterials, nanoclays, silica nanoparticles, calcium carbonate nanoparticles, dispersion

1. Introduction and motivation

Concrete construction is undergoing a paradigm shift with the introduction of additive manufacturing and advances in admixture technologies. The increased demand for sustainable, rapid and optimized structures have created high demand for a wide variety of tailored cement properties, which is becoming more accessible with the aid of machine learning. This in turn has cultivated significant interest in incorporating and reinforcing cements with nanomaterials due to their superior properties. In fact, Metaxa et al. (2021) showed that the number of publications on cement composites modified with nanomaterials have increased by five times from the 2000s to 2010s [1]. The contents of nanomaterials vary greatly based on their type, application, w/b ratio, use supplementary cementitious materials and dispersion technique, but recently the contents reported in literature have been increasing dramatically: 3, 5, 6, 10, and 12 wt.% or 15% by volume [2–11]. It is generally accepted that achieving uniform dispersion is critical to maximizing efficiency and performance, and many have reported an optimum content where any further dosing of nanomaterials deteriorates the observed benefits [5,6,12,13]. Because of their high surface area compared to cement ($>60 \text{ m}^2/\text{g}$ compared to $1 \text{ m}^2/\text{g}$ [14]), the surface area of nanomaterials can easily exceed that of cement at high dosages and in turn clustering or agglomeration of nanomaterials is more likely to occur. Few inquiries have been made to explore whether some level of clustering or agglomeration could be beneficial to increasing performance. However, Danoglidis et al. (2019) found that the entanglement of carbon nanotubes can amplify energy storage capacity of mortars [15]. In addition, Kong et al. (2012) showed that larger silica nanoparticles in the form of larger agglomerates led to greater acceleration effects on cement hydration [16]. We have also shown that at high contents (3-4%wt.) nanoclay interactions, i.e. in the form of small agglomerates, can be more beneficial rheologically than their interaction with

cement [17]. Therefore, and because of the potential health hazard [18] and high cost [14] of nanomaterials, it is essential to investigate the role of dispersion of nanomaterials at high contents: whether some level of agglomeration can be beneficial or if changing the dispersion method can offer further enhancement when performance deteriorates due to agglomeration.

Nanomaterials can improve mechanical performance by strengthening the interfacial transition zone (ITZ), which is often the weakest part in concrete [19], likely due to their high nucleation potential, increased portlandite consumption or improved microstructural density [6,10,20–22]. However, more recent studies suggest that nanoparticles, specifically spherical or cubic 0D nanomaterials, may not have direct seeding effects [16,23–25]. Asserting such effects remains challenging due to limitations in quantitative analysis to distinguish and classify early hydration products and nanomaterials, as they share similar size and chemical compositions [13]. Nonetheless, the main nanomaterials of interest for cement applications are carbon nanomaterials (especially carbon nanotubes (CNTs)) occupying ~58% of nano-reinforced cements literature followed by silica nanoparticles (SNP) at ~34% and nanotitania at ~7% [1]. SNP have been found to densify the microstructure [5,20,21,26], and increase compressive strength [5,10,17,20,21,26,27], and tensile or flexural strength [5,10,27]. Additionally, nanoclays (NC) have also been gaining significant interest in tailoring cement rheology for 3D concrete printing and self-compacting concrete (SCC) due to the exceptional increase in static yield stress [28,29]. The contents of NC used in literature have also been increasing, reaching 2, 2.5, 3, and 6 wt.% [30–33]. Calcium carbon nanoparticles (CCNP) have also been of increasing interest for improving the compressive strength of UHPC, in particular, which has been linked to C-S-H nucleation and improved ITZ [4,7,34,35]. Because of the aforementioned effects and similarities between NC,

SNP and CCNP, we focus on studying the state of dispersion of these three nanomaterials in this work.

2. Background

Nanomaterials are often dispersed through chemical, physical or combined methods. Physical dispersion focuses on transferring mechanical energy in the form of shearing, sonication or ball milling while chemical methods rely on using surfactants, covalent functionalization, admixtures or growing nanomaterials on the host's particle surfaces [1,13,14,20,36–40]. However, in any method where nanomaterials are dispersed indirectly through the mixing water or admixtures, nanomaterials oftentimes do not remain dispersed uniformly in the cement composite [14,25,41]. Additionally, because cement is still in an agglomerated state [42], uniform dispersion of nanomaterials in solution cannot guarantee uniform composite dispersion. On the other hand, mechanical powder mixing does not break agglomerates down [43]. Growing nanomaterials on cement requires the use of temperatures between 550°C to 950°C, which critically impact the chemical structure of cement [36]. While traditional sonication can disperse nanomaterials uniformly, there is still a need for new powder dispersion methods that can disperse both cement and nanomaterials simultaneously while maintaining the cement's chemistry.

Such method has been suggested by Zhan et al. (2003) where they dispersed CNTs onto alumina nanocomposites as a coating by pulsed sonication in alcohol ethers, which showed improvements in fracture toughness by 12 times compared to conventional techniques [44]. This method was later adopted by Makar et al. (2005) to disperse 2 wt.% single-wall CNTs onto the surface of cement, which initially showed poor mixability [45] but was later refined by Makar and Chan (2009) to enable characterization of the growth of cement hydration products on single wall

CNTs [46]. Rocha et al. (20019), and Hogancamp and Grasley (2017) successfully replicated this method of coating cements with multi-walled CNTs [47] and carbon nanofibers [2]. We then further modified this approach under the name dry dispersion (dd) and successfully coated cement with up to 4 wt.% NCs, which led to greater effectiveness of NCs in increasing static yield stress over magnetic stirring or powder mixing [17]. In this work, we further explore the feasibility of this method to disperse 4 wt.% NC, SNP and CCNP, and examine their impact on early hydration kinetics via scanning electron microscopy (SEM), isothermal calorimetry and quantitative x-ray diffraction (QXRD) and the corresponding effects on the mechanical performance of mortars up to 28 days. The effect of dry dispersed NC, SNP, and CCNP are compared against those that are dispersed via conventional sonication in solution.

3. Materials and methods

3.1 Materials

Ordinary Portland cement type I/II was used with w/b ratio maintained at 0.46 and 3:1 sand to cement ratio to prepare mortars. The chemical composition of the OPC used is shown in Table 1. All nanomaterials are supplied in powder form and dispersed via sonication in water or dry dispersion onto the cement surface, as detailed in the following section. The SNP are 15-20 nm spherical nanoparticles with purity >99.5% acquired from US-Research Nanomaterials Inc. and CCNP are 15-40nm cubic nanoparticles with purity >97.5% acquired from SkySpring Nanomaterials Inc. The NC used are palygorskite nanorods at >97% purity with a 30 nm outer diameter and 1.5 μ m average length supplied by Active Minerals. All three nanomaterials are pristine with no surface modification or functionalization and are used at 4 wt.% replacement weight of cement.

Table 1: Chemical composition of cement.

Content (%)						
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Loss on ignition
19.27	4.68	3.51	63	3.21	2.72	2.09

3.2 Mixing and dispersion

3.2.1 Dry dispersion

The process of dry dispersion described by [2,45–47] was modified by the author and first published for NC in [17]. In this process, nanomaterial powders are added into an ethanol solution with >99.9% purity in a stainless-steel flask that is placed inside an ice bath to prevent excessive evaporation of the ethanol due to heat generated during sonication. When the solution temperature is at 5°C, magnetic stirring at 360 rpm and continuous sonication at 100 J/sec are initiated. Once 10 kJ/g of nanomaterials is reached, nanomaterials are considered well dispersed as such energy is twice as that reported for successful dispersion in water [48] and the cement is gradually added into the solution. When all the cement is added, sonication is switched to pulse at 2 sec intervals (2 on/ 2 off) until 15 kJ/g of nanomaterials is achieved. During this process, cement agglomerates are broken down when sonication is transmitted, and nanomaterials adsorb onto the surface of cement when sonication is paused. Throughout sonication, the solution is kept in an ice bath where it maintains a temperature under 20°C, which helps avoid excessive evaporation of the suspension liquid to ensure the nanomaterial to ethanol ratio is maintained. After sonication, the solution is transferred into a distillation apparatus to recover the ethanol. The solution is magnetically stirred at 560 rpm and heated using an oil bath with silicon oil where the oil temperature reaches a maximum of 220 °C. The distillation process is concluded within 1 hour, at which point the dry nanomaterial-cement cake is removed and placed onto an aluminum sheet and placed in a drying oven at 105 °C for 24-72 hrs to ensure complete removal of ethanol and to prevent hydration with

air moisture. Then the cake of cement and nanomaterials is broken back down to a powder using a mortar and pestle and stored in air-tight bags until use.

3.2.2 Sonicated solutions

To produce nanomaterial solutions, a probe sonication was used at the same energy used in dry dispersion of 15 kJ/g. Because no dispersants or functionalization are used, such suspensions are prone to instability soon after sonication energy is removed. Thus, all sonicated solutions were used within 1-minute of preparation. To ensure the solution temperature remained at room temperature of $24 \pm 2^\circ\text{C}$, an ice bath was used during sonication to maintain the temperature below 20°C . The ice bath was removed once 15 kJ/g was achieved and sonication continued briefly until the solution temperature reached $\sim 24^\circ\text{C}$.

3.2.3 Mixture design

To investigate the effects of the dry dispersion process on cement chemistry, cement without nanomaterials were processed using the same processes as the nano modified cements and is referred to as Neatdd, whereas cement that is not processed is referred to as Neat. The hydration kinetics of Neat and Neatdd were investigated for up to 24 hrs to measure differences associated with the dry dispersion process. Mixtures prepared with nanomaterials are named after the nanomaterials used, SNP, NC or CCNP, and are suffixed by their dispersion method where “dd” indicates when nanomaterials are dispersed onto cement via dry dispersion and “son” indicates that nanomaterials are dispersed in mixing water.

3.3 Hydration arrest

Solvent exchange was used to arrest cement paste hydration using isopropyl alcohol (grade >99.7%) at 33.3:1 alcohol to cement ratio at 15 min, 60 min, 6 hrs and 24 hrs. 40g of cement were first mixed via hand mixer and time from water addition was used as hydration time. At 15 and 60

mins, before set, 2-3g of paste were transferred to separate cups where isopropyl alcohol was added and mixed for 2 mins to allow for solvent exchange. At 6 and 24 hrs, after set, an automatic pulverizer ball mill was used to crush the hardened paste into powder before it was mixed with isopropanol. The mixture was then filtered under vacuum pressure and a glass microfiber filtering paper with 1 μm pore size. After filtration, powders were kept under vacuum inside a desiccator chamber.

3.4 SEM

A Zeiss Sigma VP Scanning electron microscope (SEM) was used to collect scans of the nanomaterial powders, unhydrated nano-coated cement and hydrated samples. Scans were collected at a resolution of 12 $\text{\AA}$ at 2-10 kV. 1 nm gold palladium (Au-Pd) coating was used prior to scanning via a 108 Manual Sputter Coater. For hydrated samples, the dry powders were removed from vacuum and loaded into the SEM within 30-60 minutes.

3.5 Isothermal calorimetry

The heat of hydration of cement pastes were recorded using isothermal calorimetry TAM Air III at 25°C. 20g of cement were mixed with water or nanomaterial suspension and 5g pastes were loaded into a glass ambulette, which was then placed in the calorimeter within 5 minutes of hydration. To ensure accuracy, three samples were tested for each method where dd cement were sampled from three different batches and sonicated samples were prepared from at least two different batches of sonicated solutions. Because of the instrument limitation, the first 45 minutes of data recording are disturbed by the process of loading the ambulettes and thus excluded from analysis. Instead, XRD was used to probe the hydration reaction at this age.

3.6 XRD

Quantitative X-ray diffraction (QXRD) was carried out using a Malvern Panalytical XPert³ powder diffractometer according to the Rietveld method. Scans were executed at a step size (2 θ) of 0.0130° starting at 5.0116° and ending at 69.9856° to total a 58.3950 s scan step time. Dry powders were pulverized by an automatic pulverizer ball mill and then packed onto a circular sample holder and exposed to Cu-K α radiation with a generator at 40 V and 40 mA. For every 6-8 test runs, a corundum sample was run to correct the instrument intensity extracting k-factor. Phase assemblage was analyzed using HighScore Plus 4.0 with phase assembly obtained from the ICSD database using the following: C3S #94742 [49], C2S #81096 [50], C3A-mono #100221 [51], C3A-ortho #1880 [52], C4AF #2841[53], Portlandite #202229 [54], Ettringite #155395 [55], Calcite #73446 [56], Periclase #9863 [57], Gypsum #409581 [58], Bassanite #380286 [59], Monocarbonate #59327 [60], and Palygorskite #159934 [61]. SNP are amorphous and cannot be detected using XRD while NC and CCNP are crystalline and are detected under Palygorskite and Calcite phases, respectively. Because of the overlap between C₂S and C₃S peaks, distinguishing the amounts of these two phases using this method is inadequate and thus they are treated as one phase under the name silicates. Arrested hydration cement samples were tested within 3 hours after being removed from vacuum. Due to the sensitivity of this method, differences or measurements under 1% are considered insignificant. Additionally, because the interest of this study is within the first 24 hours, the results of calcite, monocarbonate, periclase, and palygorskite are grouped together as “other”.

3.7 Mechanical performance

In addition to microstructural investigation, the mechanical performance of cement mortars incorporating nano-coated cements versus sonicated nanomaterials (dd vs son) were examined through the compressive strength of 50 mm cubes and split tensile strength of 100 x 50 mm

cylinders at 1, 3, 7 and 28 days. 15 specimens were made from a single batch and cast into their respective molds in 2 layers for cubes and 3 layers for cylinders, where each layer is tamped 25 times and vibrated using a vibration table. Cast specimens were covered for the first 24 hours after casting and 3 specimens are tested at 24-26 hours from casting for 1 day strength results. The other specimens were cured in water and removed 4-6 hours prior to testing then dried on meshed trays at 40-60 °C. Care was taken to ensure that 3-day test specimens were conducted at 70-76 hrs from casting. Compression tests were run according to ASTM C109/C109M-02 [62] with a load rate of 1500 N/s, while split tensile strength tests were conducted with reference to ASTM C496/C496M-19 [63] with a load rate of 192.75 N/s and 3 mm plywood strips 25 mm in thickness and 150 mm in length.

4. Results and discussion

4.1 Mechanical Properties

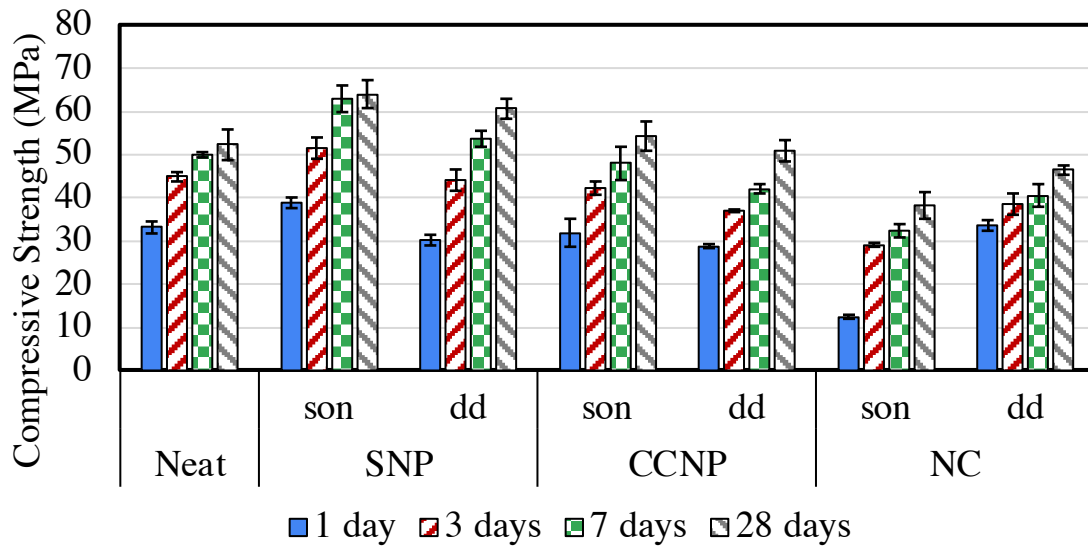


Figure 1: Compressive strength results of cement mortars with 4 wt.% nanomaterials.

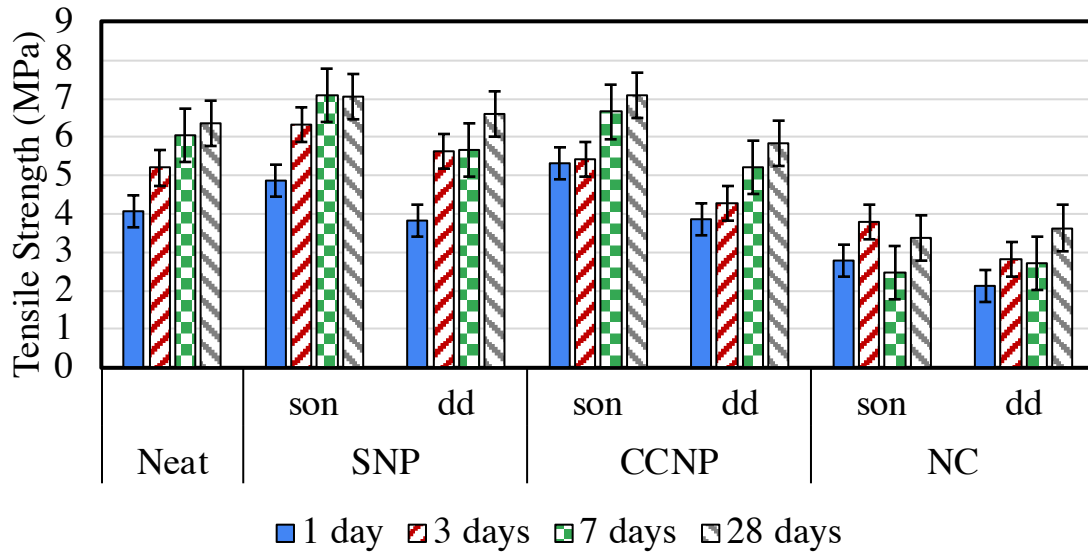


Figure 2: Splitting tensile strength results of cement mortars with 4 wt.% nanomaterials.

The compressive and split tensile strengths were evaluated for cement mortars prepared via sonication and dry dispersion and the results are shown in Figure 1 and Figure 2, respectively. SNP mortars showed similar or higher compressive and tensile strength compared to Neat at most testing ages. Those improvements are in agreement with literature [5,6,8,10,17,20,21,26,27] where they have been attributed to increased microstructural density within the ITZ caused by greater CH conversion into C-S-H [5,20,21,26]. SNP mortars prepared with dry dispersion showed lower early age strength compared to sonication but comparable 28 day strengths, indicating delayed strength rate development. These differences signify the role of the dispersion method on mechanical strength and strength development rate, which in turn can influence the optimal dosage for mechanical strength gain. For example, Rong et al. (2015) investigated up to 5 wt.% SNP via sonication and showed an optimum increase of compressive and flexural strengths at 3 wt.%, where further addition decreased strength due to agglomeration [5]. On the other hand, Li et al. (2004) used up to 10 wt.% SNP and showed an enhancement of compressive and flexural strengths

at both 7 and 28 days but nanoparticles were dispersed through high-speed stirring and the aid of a dispersant [8].

CCNP modified mortars showed similar differences with respect to the effects of dispersion method on strength rate development as SNP mortars. However, CCNP modified mortars showed lower compressive strength at the early ages of 1, 3 and 7 days but similar 28 day strength when compared to Neat. On the other hand, the tensile strength decreased for dry dispersion mortars at all ages whereas sonication maintained similar strength at 3 and 7 days but higher at 1 and 28 days compared to Neat. A similar decrease in strength was reported by Makar et al. (2012) which was attributed to increased production of ettringite and monosulfate [64]. On the other hand, Li et al. (2015) reported an increase in compressive and flexural strengths at 4 wt.% CCNP in UHPC containing superplasticizer at 28 days, which was attributed to nucleation effects [3]. Camiletti et al. (2013) also observed higher compressive strength with the addition of CCNP to UHPC but only at a curing temperature of 10 °C, where increasing curing temperature to 20 °C resulted in loss of strength compared to the reference for CCNP contents between 2.5 – 15% by volume, which was attributed to dilution effects and CCNP agglomeration [7]. Therefore, the literature suggests that such discrepancy of the effects of CCNP on strength are likely attributed to cement phase decomposition, w/b ratio, superplasticizer content, and curing temperatures. The results suggest that in addition to the previous, the dispersion method also contributes to differences in strength and strength development rate.

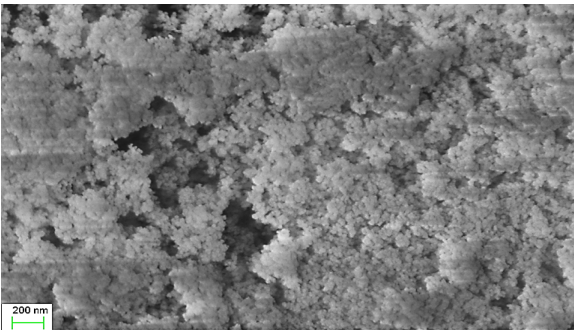
NC modified mortars showed a decrease in compressive and tensile strength at all ages compared to Neat, with the exception of 1-day compressive strength of dry dispersion mortars, in agreement

with the findings of Dejaeghere et al. (2019) [65]. Unlike SNP and CCNP, mortars prepared with dry dispersion showed greater compressive strength compared to sonication at all ages where the tensile strength of NC-modified mortars was greater for sonication at 1 and 3 days but statistically similar at 7 and 28 days. The loss in strength could be caused by poor consolidation of the stiff mortar since NC increases static yield stress dramatically [17,66] and the decrease in available water caused by the high-water adsorption of NC [67]. This is further supported by the consistent decrease in tensile strength irrespective of the dispersion method ranging between 30-60% compared to Neat, which is likely caused by larger sized pores resulting from poor consolidation. It was proposed that the addition of SNP with NC up to 3 wt.% each can significantly improve the compressive strength of cement mortars [68] which was similarly deduced for CCNP [3]. Nevertheless, the results highlight the impact of dispersion method on mechanical properties and their development rate. To further probe those differences, microstructural characterization of the effect of dispersion method on the hydration kinetics of all nano modified cement were carried out and discussed in the following section.

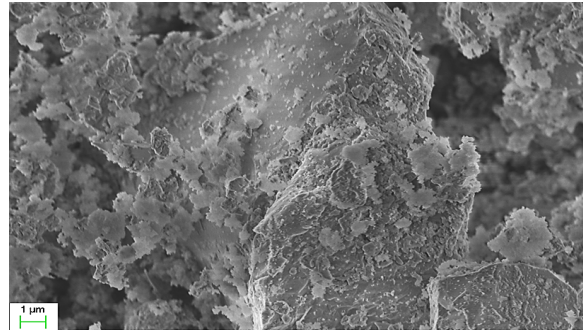
4.2 SEM

SEM images of the nanomaterials in their as-received powder form and dry dispersed on cement are shown in Figure 3. Because of their aspect ratio, it is easier to identify the presence of NC needles on the surface of cement as observed in Figure 3 (d). On the other hand, because of their limited size, individual particles of SNP and CCNP on the surface of cement cannot be confirmed via SEM imaging. However, comparing Figure 3 (b) and (f), clusters of small particles appear on the surface of cement that are not visible in (d). Furthermore, the clusters in (b) are made up of round particles whereas those in (f) are angular, which follow the morphologies of their respective

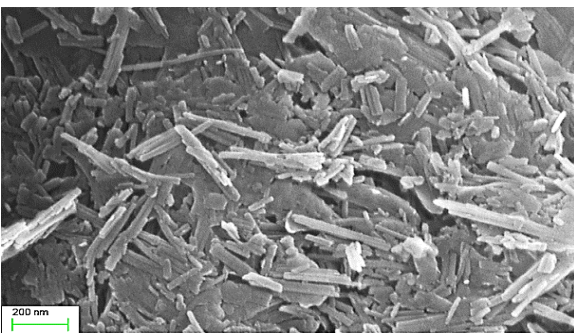
280 nanomaterial powder images and are likely clusters of SNP or CCNP, respectively. Furthermore,
281 while a good number of NC needles are observed individually on the surface of cement, multiple
282 clusters can also be observed in (d). However, all nanomaterial clusters observed in the dry
283 dispersed cement are of significantly smaller size and lower densities compared to their
284 agglomerated state in powders. Similar observations in hardened cement paste were made by
285 Sargam and Wang (2021), as they showed that SNP was more agglomerated in the hardened
286 cement matrix than in the mixing water solutions but with smaller mean size [13]. The images
287 suggest that dry dispersion at the studied 4 wt.% dosage produce both individual and clusters of
288 nanomaterials on the surface of cement.



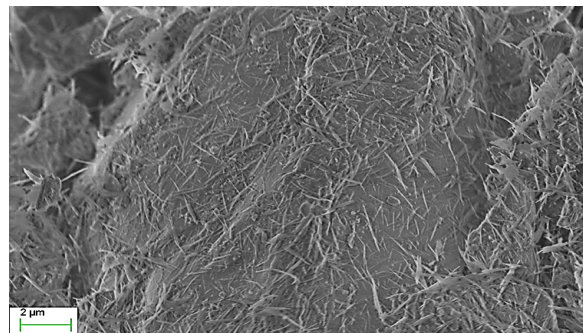
a. SNP particles



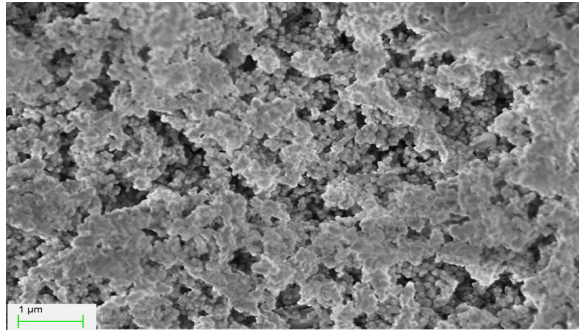
b. SNP coated cement



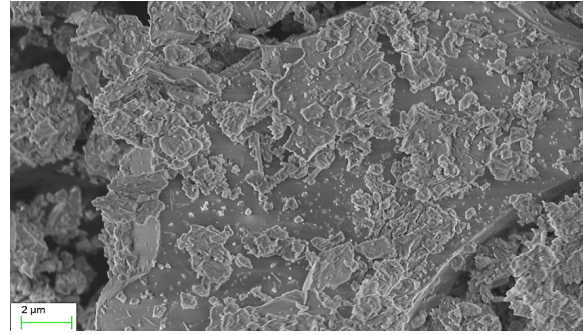
c. NC needles



d. NC coated cement



e. CCNP particles

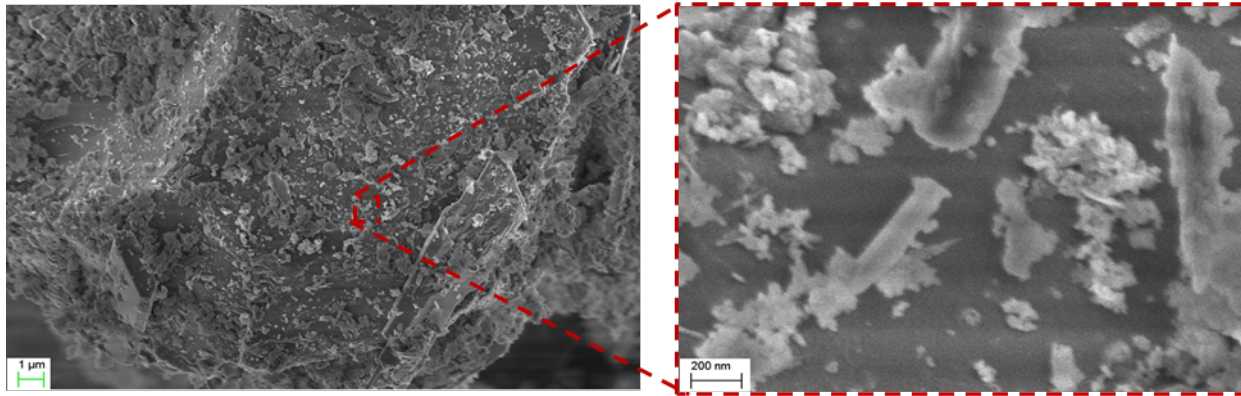


f. CCNP coated cement

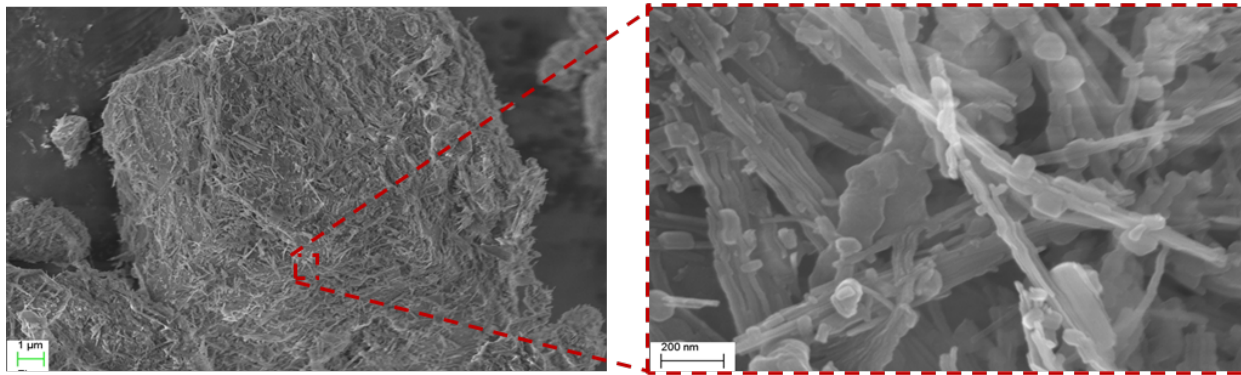
Figure 3: SEM images of dry nanomaterials powders and unhydrated cements coated with nanomaterials at 4 wt.% content via dry dispersion at 5,000x magnification.

Hydration of nano modified cement paste was arrested at 60 minutes and SEM images were collected to visually inspect the interactions between dry dispersed nanomaterials and hydration products, as shown in Figure 4. First, all SEM images maintain similar appearance to that of unhydrated nano-coated cements, shown in Figure 3, with similar particle geometries (especially clear for NC needles) remaining on the surface of cement, indicating that at least some nanomaterials remained adsorbed onto the surface of cement after water-cement contact. Second, and upon closer inspection, new nano-sized particles are observed on the surface of NC needles in Figure 4 (b) that were not present in Figure 3 (d) and are therefore assumed to be new hydration products. Similar new nano-sized particles are also observed in Figure 4 (a) and (c) on the surface of cement grains. Because of the overlap in chemical structure, physical shape and size between the nanomaterials investigated and hydration products, typical SEM and EDS analysis are not sufficient in distinguishing the two at this hydration age [13]. However, similar morphologies were reported by Quyang et al. (2017) with the growth of cement hydration products on the surface of micronized silica and limestone [69]. SNP and NC are rich in the partially ionized SiO^- group which along with calcite in CCNP offer high affinity for ionic adsorption of Ca^{2+} ions resulting in

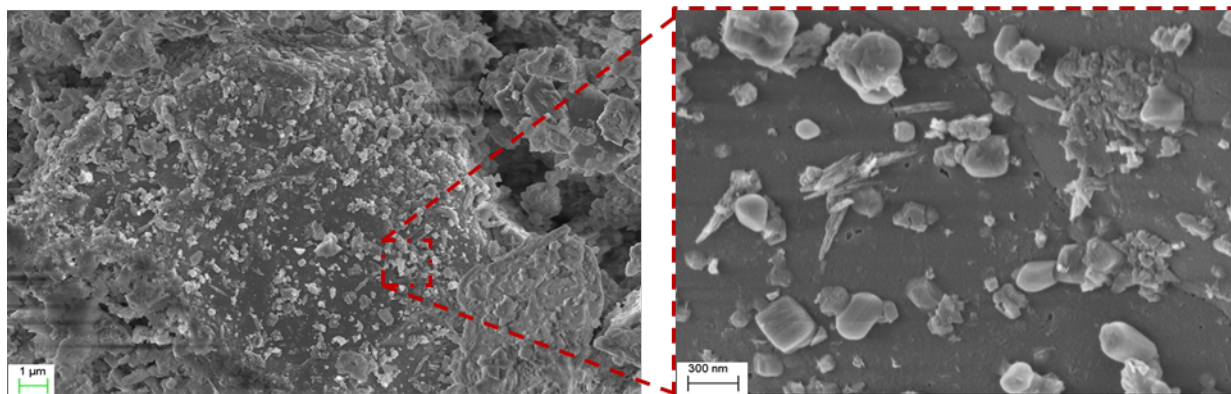
306 the precipitation of calcium hydroxide or C-S-H [69]. Therefore, all three nanomaterials are likely
307 to act as points of attraction for C-S-H nucleation on cement grain surfaces. [9]. This hypothesis
308 can explain the increase in microstructural density of the ITZ surrounding cement grains observed
309 with SNP and CCNP [5,20,21,25,26]. Nonetheless, the results discussed here provide only a
310 hypothesis in need of further investigation and highlight the great need for new methodologies to
311 confirm or quantify the nucleation potential of nanoparticles in cement in early hydration times.



a. SNP cement at 5,000x and 72,000x magnification



b. NC cement at 5,000x and 53,000x magnification

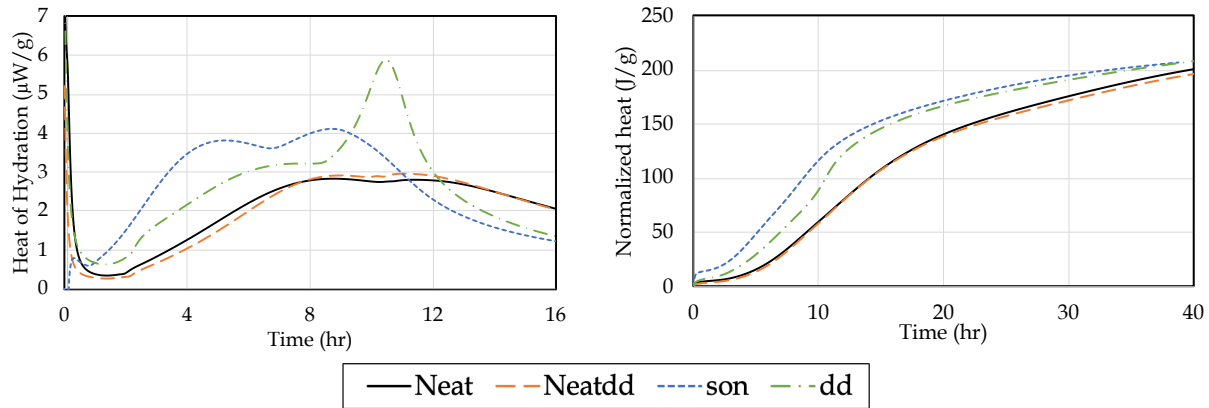


c. CCNP cement at 5,000x and 36,000x magnification

Figure 4: SEM images of dry dispersed cement with nanomaterials at 60 minutes arrested hydration times.

4.3 Calorimetry and QXRD of SNP-modified cement pastes

The heat of hydration for SNP modified cement paste was recorded via isothermal calorimetry for dry dispersion and sonication alongside their reference mixes and results are shown in Figure 5. Little difference is observed between Neat and Neatdd but, in comparison, both SNP pastes exhibit greater acceleration in heat of hydration, where sonication shows the fastest acceleration. Additionally, both sonication and dry dispersed mixes show an increase in heat of hydration that is maintained up to 40 hours. Similar acceleration and increase in total heat of hydration were reported by Sun et al. (2017) [22] and Rong et al. (2015) [5]. More notably, critical differences between sonication and dry dispersed mixes appear at the acceleration phase: sonication mixes show an acceleration in heat of hydration by 2 hours whereas dry dispersion mixes show lower silicates hydration peak followed by significant uptake in the aluminates hydration peak. Those differences are further probed with the aid of QXRD.



(a) Normalized heat of hydration (b) Normalized total heat of hydration

Figure 5: Calorimetry results of SNP modified cement pastes

QXRD scans were collected for SNP modified cement pastes and their respective reference and the results are shown in Table 2. SNP modified mixes show lower silicate content than that of the reference due to dilution effects, i.e. replacing 4 wt.% of cement with SNP. In addition, the results confirm greater silicate consumption of SNP-modified pastes compared to their respective reference mixes at 0.25 and 1 hrs in agreement with the acceleration observed in calorimetry. Furthermore, sonication pastes showed greater silicates consumption at 0.25, 1 and 6 hrs of hydration compared to dry dispersion, which was the likely cause for the greater acceleration observed in calorimetry. Wu et al. (1984) and Thomas et al. (2009) reported similar acceleration of SNP modified cement and attributed it to early C₃S hydration – SNP reacted with CH to provide new nucleation sites for C-S-H, leading to less C-S-H growth on the surface of cement, which in turn increased C₃S consumption [70,71]. On the other hand, a significant delay in ettringite formation and gypsum consumption is found in dry dispersed pastes compared to sonication up to 6 hrs followed by a significant increase at 24 hrs. This sudden jump agrees with the increase in heat of hydration observed in calorimetry at the peak associated with aluminates consumption. Hou et al. (2020) and Zheng et al. (2021) showed that colloidal SNP adsorb on the surface of C₃A, essentially retarding its consumption for up to 10 hours, which in turn retards gypsum consumption

and results in an overall acceleration of C_3S and the formation of a greater amount of C-S-H [72,73]. However, because in dry dispersed pastes SNP are adsorbed on the surface of cement prior to hydration, it's likely that SNP adsorption on C_3A had a more suppressive effect on early ettringite formation, including early dissolution, whereas such effects may be weaker or have not taken place in sonication mixes. In addition, the partially ionized SiO^- on the surface of SNP offers high affinity for SO_4^{2-} and Ca^{2+} as reported by Ouyang et al. (2017) and Nachbaur et al. (1998) [69,74] which is one of the main drivers of the nucleation potential of SNP. Because it's likely that greater amounts of SNP were adsorbed on C_3A surface in dry dispersion, less SNP were available for SO_4^{2-} and Ca^{2+} adsorption resulting in greater ionic concentration which in turn slows down gypsum dissolution in agreement with gypsum readings at 6 hrs. As a result, dry dispersed SNP pastes had greater silicates acceleration than the references but lower than sonication. The hydration of silicates (just after 6 hrs) causes the formation of large amounts of C-S-H which in turn depleted SO_4^{2-} through adsorption [75]. Because this reaction is controlled by the solubility of gypsum [75] the high content of gypsum in dd requires longer time to deplete and stabilize the aluminate reaction causing the excessive ettringite formation.

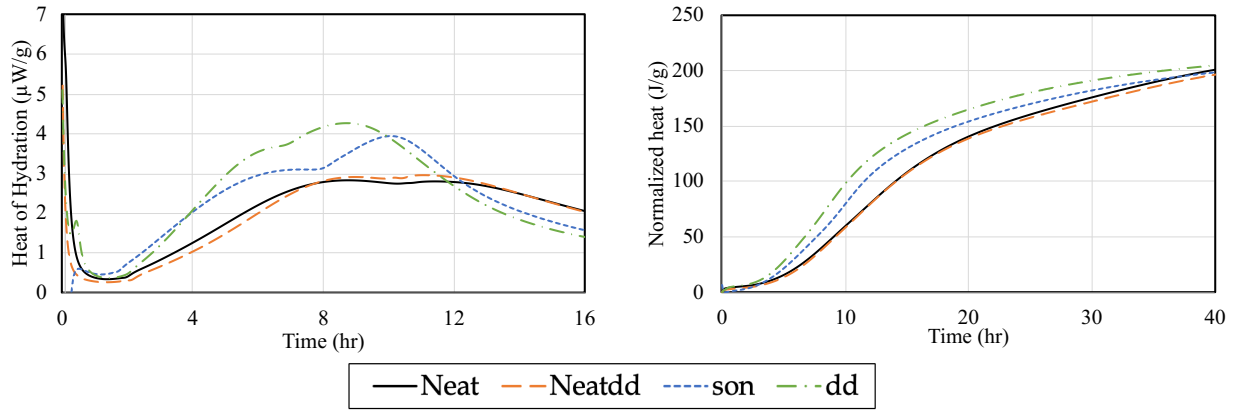
Table 2: SNP modified cement content via qualitative XRD at different arrested hydration times.

Time (hrs)	Content (%)									
	Mix	Silicates (C2S & C3S)	C3A	C4AF	Gypsum	Bassanite	Ettringite	Portlandite	Amorphous	Other
0.25	Neat	63.9	9.2	5.0	3.3	1.85	2.7	1.1	7.8	5.15
	Neatdd	64	8.9	4.8	3.5	1.25	2.7	0.9	7	6.95

	son	58.7	8.7	4.2	3.5	0.9	3.8	0.4	11.8	8
	dd	60.4	9	4.4	5.05	0.3	2.4	0.3	12.9	5.25
1	Neat	61.2	8.7	4.5	3.3	1	3.8	1.1	8.1	8.3
	Neatdd	61.8	9	4.8	3.4	1.1	3.8	0.8	8	7.3
	son	58.4	8.7	4.7	2.6	0.6	4.1	0.4	15.5	5
	dd	59.7	8.9	4.5	4.25	0.2	2.3	0.6	14.1	5.45
6	Neat	59	8.3	5.1	2.4	0.1	5.5	0.7	11.3	7.6
	Neatdd	55.5	8.2	4.4	2.5	1.2	5.4	1.4	15.3	6.1
	son	54.4	8.3	4.8	2.4	0.3	6.5	0.8	16.1	6.4
	dd	56.1	9.05	4.8	4.2	0.3	3.5	0.4	16.5	5.15
24	Neat	41.1	7.3	5	0.3	0	7.6	3.5	28.1	7.1
	Neatdd	44.6	7.3	4	0	0	8.5	3.4	28.6	3.6
	son	43.6	7.1	4.5	0.9	0	6.5	2.2	30.1	5.1
	dd	40.9	6.7	4.5	1	0	8.9	2.8	30.1	5.1

4.4 Calorimetry and QXRD of NC-modified cement pastes

The heat of hydration of NC modified cements was recorded and is shown in Figure 6. The results show relatively little difference in the duration of the induction period when compared to reference mixes but greater heat of hydration with the addition of NC, which is in agreement with literature [30,32,76]. Although the increase in heat of hydration alone does not indicate a nucleation effect of NC [16], our SEM images in Figure 4 (b) are in support of such potential, at least for the case of dry dispersion, which is also supported by other authors in solution dispersion [30,77,78]. The dry dispersed pastes additionally showed greater heat of hydration in the acceleration period where both hydration peaks appeared 1 hr earlier than the sonication mix.



(a) Normalized heat of hydration (b) Normalized total heat of hydration

Figure 6: Calorimetry results of NC modified cement pastes

To further explore the effects of NC on cement hydration, QXRD scans were collected for all NC modified pastes and the results are shown in Table 3. Insignificant differences in NC modified cement decompositions are found at 0.25 and 1 hrs compared to each other. However, greater silicate and aluminate consumption are observed in NC mixes compared to their respective reference at all hydration times with greater ettringite precipitation in sonication starting from 6 hrs. The greater silicate consumption in both NC mixes didn't yield a similar increase in portlandite but did yield an increase in the amorphous phase, which likely indicates greater C-S-H precipitation and growth. This in turns supports the nucleation potential of NC discussed earlier which likely follows the same mechanism of SNP due to their negative surface charge [79,80] originating from the ionization of hydroxyl groups or breakage of M-O-M bonds (M=Si, Mg or Al) [80]. In addition, greater amount of ettringite is observed in the NC sonication mix prepared compared to dry dispersion or Neat mixes. While the mechanism for such increase is unclear, for both NC and SNP the higher ettringite content at 24 hours corresponded to lower mechanical performance at early age up to 7 days when comparing the two dispersion methods within the respective nanomaterial.

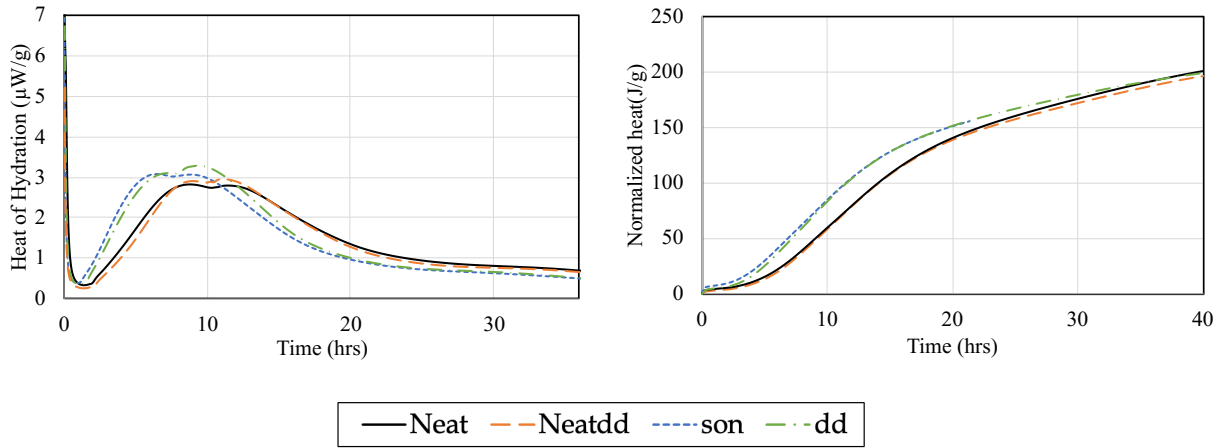
Table 3: NC modified cement content via qualitative XRD at different arrested hydration times.

Time (hrs)	Content (%)									
	Mix	Silicates (C2S & C3S)	C3A	C4AF	Gypsum	Bassanite	Ettringite	Portlandite	Amorphous	Other
0.25	Neat	63.9	9.2	5.0	3.3	1.85	2.7	1.1	7.8	5.15
	Neatdd	64	8.9	4.8	3.5	1.25	2.7	0.9	7	6.95
	son	59.7	7.6	4.1	1.2	3.2	3.8	0.4	16	4
	dd	58.7	7.9	4.5	2.5	0.2	3.1	0.1	14.5	8.5
1	Neat	61.2	8.7	4.5	3.3	1	3.8	1.1	8.1	8.3
	Neatdd	61.8	9	4.8	3.4	1.1	3.8	0.8	8	7.3
	Son	56.8	7.7	4.2	2.4	1.4	4.1	0.3	17.1	6
	dd	56.5	7.7	4.3	2.3	0.6	4.3	0.1	17.6	6.6
6	Neat	59	8.3	5.1	2.4	0.1	5.5	0.7	11.3	7.6
	Neatdd	55.5	8.2	4.4	2.5	1.2	5.4	1.4	15.3	6.1
	son	50.1	7	4.2	1.4	1.4	7.2	1	19.6	8.1
	dd	49.4	6.6	4.3	0.7	2.1	5.9	0.8	20.4	9.8
24	Neat	41.1	7.3	5	0.3	0	7.6	3.5	28.1	7.1
	Neatdd	44.6	7.3	4	0	0	8.5	3.4	28.6	3.6
	son	33.7	5.3	3.5	0.5	0.1	10.8	4.3	35	6.8
	dd	35.9	6	4.3	0.3	0.5	8.9	3	37.9	3.2

4.5 Calorimetry and QXRD of CCNP-modified cement pastes

Similar to SNP and NC modified pastes, the heat of hydration of CCNP modified paste was recorded and the results are presented in Figure 7. The addition of CCNP showed an acceleration and an increase in early heat of hydration in agreement with literature [64,81–84]. Despite the observed acceleration, the total heat of hydration of CCNP modified pastes normalized with the reference mixes by 40 hrs. The acceleration of cement hydration has been suggested to be caused

by the high affinity of Ca^{2+} to adsorb on calcite [69] creating C-S-H nucleation effects [64,82,84] supported by the densification of the ITZ [84]. However, calcite's affinity for Ca^{2+} is almost 7-times higher than that of SO_4^{2-} whereas SNP affinity is similar to both ions [69]. This could explain why little differences are observed in the heat of hydration between both dispersion methods as the pore solution is Ca^{2+} rich independently of the dispersion method.



(a) Normalized heat of hydration

(b) Normalized total heat of hydration

Figure 7: Calorimetry results of CCNP modified cement

Further analysis of CCNP modified cements was performed using QXRD and the results are displayed in Table 4 where CCNP was detected under the calcite phase. The results show greater silicates consumption by CCNP modified cements compared with their reference at all hydration ages, in agreement with acceleration effects observed in calorimetry. In addition, sonication showed significantly higher silicate consumption and portlandite formation than dry dispersion. A delay in bassanite consumption was also observed for CCNP modified cements compared with their references at 0.25 and 1 hrs. Unlike the findings of NC and SNP, little differences are observed in aluminate and gypsum consumption, and consequently ettringite formation, across all ages except for the dry dispersion mix at 24 hrs, which showed a lower amount of ettringite.

Similarly, a lower amount of portlandite is observed for the dry dispersion mix at 24 hrs compared to its reference. These differences may be the cause for the decrease in mechanical performance of the CCNP dry dispersion mix.

Table 4: CCNP modified cement content via qualitative XRD at different arrested hydration times.

Time (hrs)	Content (%)										
	Mix	Silicates (C2S & C3S)	C3A	C4AF	Gypsum	Basanite	Ettringite	Portlandite	Calcite	Amorphous	Other
0.25	Neat	63.9	9.2	5	3.3	1.85	2.7	1.1	1.25	7.8	3.9
	Neatdd	64	8.9	4.8	3.5	1.25	2.7	0.9	1.45	7	5.5
	son	55.9	9.5	3.6	3.2	3.1	3.7	0.3	4.6	12.6	3.5
	dd	55.8	8.9	4.2	3.7	2.5	3.4	0.3	4.5	13.3	3.4
1	Neat	61.2	8.7	4.5	3.3	1	3.8	1.1	1.6	8.1	6.7
	Neatdd	61.8	9	4.8	3.4	1.1	3.8	0.8	1.4	8	5.9
	son	55.4	9.2	4	3.8	2.3	3.6	0.3	4.9	14.1	2.4
	dd	55.5	8.6	3.9	4.3	2.1	3.2	0.1	4.8	14.2	3.3
6	Neat	59	8.3	5.1	2.4	0.1	5.5	0.7	2.3	11.3	5.3
	Neatdd	55.5	8.2	4.4	2.5	1.2	5.4	1.4	1.8	15.3	4.3
	son	52.5	8.3	3.8	2.6	2	5.6	0.1	5.2	15.3	4.6
	dd	53.5	8.1	4.2	2.3	1.4	6	1	4.6	15.8	3.1
24	Neat	41.1	7.3	5	0.3	0	7.6	3.5	2.7	28.1	4.4
	Neatdd	44.6	7.3	4	0	0	8.5	3.4	3	28.6	0.6
	son	33.9	7.1	4.6	0.7	0.1	7.6	3.8	7.3	33.5	1.4
	dd	39	6.6	4.4	0.6	0.6	6.7	2.3	8.6	28.6	2.6

4.6 Discussion

All tested nano modified cement pastes showed greater heat of hydration at early age compared to the reference mixes. Moreover, our results show that nano-coating of unhydrated cement with nanomaterials at 4 wt.% does not inhibit cement hydration and, actually, has the potential to accelerate it. It is important to highlight that all nanomaterials were introduced as partial replacement of cement and the increase in heat of hydration overcame dilution effects. This can be attributed to their nucleation or seeding effects, which in turn increases C-S-H precipitation or the rate of CH conversion into C-S-H, in agreement with literature [3,6,10,20–22,30,64,77,78,82,84]. The SEM images of hydrated pastes suggest the likely growth of hydration products on the NC rods and on the surface of SNP or CCNP coated cement [16], [23]–[25]. Our results suggest that all examined nanomaterials have high nucleation potential for C-S-H precipitation or growth marked by at least SEM images, accelerated hydration, increased total heat of hydration, greater silicate consumption or combination of those phenomena. However, such effects are sensitive to the chemical structure and surface charge as well as the method of dispersion and further work is needed to examine the effect of nanomaterials type (0D vs 1D for example) on seeding/nucleation mechanisms. Similarly, the mechanical performance of all nano modified mixtures showed dispersion method dependent strength development rates and 28-day strength. Therefore, our results confirm the critical role of dispersion method and medium on hydration kinetics and consequently mechanical performance of cement composites. Because the nucleation potential of nanomaterials originates from their high surface charge and their ability to attract ions like SO_4^{2-} and Ca^{2+} to increase C-S-H precipitation [25,69,74], their dispersion medium plays a critical role on enhancing or suppressing such mechanisms. For example, it's likely that SNP adsorption on C_3A was increased using dry dispersion compared to

sonication, which in turn decreased their affinity to Ca^{2+} ions and reduced silicate hydration. Calorimetry results showed that dry dispersed NC modified pastes showed greater acceleration compared to sonication, whereas the opposite was found for SNP modified pastes and no significant differences were observed for CCNP pastes. However, the differences in heat of hydration didn't correlate to mechanical performance where dry dispersed CCNP mortars had lower early age strength compared to sonication while the opposite was true for NC. Collectively, the results reinforce that both the type and properties of nanomaterial and their dispersion method have significant impacts on their effects on microstructure, cement phase decomposition and mechanical performance. For example, despite some visible clustering of NC needles on dry dispersed cement, its mechanical performance exceeded that of mortar prepared via sonication. Therefore, when performance deteriorates due to increasing nanomaterials dosage, a change in dispersion method at higher contents could expand the so called "optimum" nanomaterials dosage range by utilizing agglomerates, changing dispersion medium or time of nanomaterials inclusion with respect to cement hydration.

5. Conclusion

In this study, a new dispersion method – dry dispersion – was introduced and used to coat unhydrated cement grains with NC, SNP and CCNP at 4 wt.% replacement. Cement pastes and mortars modified with each of these nanomaterials were prepared using sonication in water and dry dispersion, and their effects on mechanical performance and hydration kinetics were compared. Mechanical performance included compressive and tensile strength at 1, 3, 7 and 28 days whereas hydration kinetics included isothermal calorimetry and quantitative XRD at 0.25, 1, 6 and 24 hrs. In addition, SEM images of the nanocoated cement pre- and 1 hr post- hydration were collected. Analysis of the results provided the following conclusions:

- The SEM images of unhydrated nanocoated cement show effective coating of the surface of cement, with limited clustering. Any clustering can be attributed to the high dosage, where the surface area of the nanomaterial exceeds that of the cement.
- Although SNP and CCNP modified mortars prepared via sonication and dry dispersion had comparable compressive strengths at 28 days, mortars prepared via sonication showed greater strengths at 1, 3 and 7 days. On the other hand, NC mortars showed greater compressive strength when prepared with dry dispersion compared to sonication at all ages.
- Isothermal calorimetry showed faster acceleration and increase in early heat of hydration for all nano modified mixtures. Sonication showed greater acceleration than dry dispersion for SNP whereas the opposite was observed for NC. Sonication and dry dispersion had comparable effects on CCNP modified pastes.
- QXRD indicated a retardation effect of SNP on ettringite precipitation and aluminate consumption that was more significant for dry dispersion compared to sonication, which agreed with the results of isothermal calorimetry.
- Our collective results support that the type and properties of the nanomaterial and dispersion medium play a critical role on their effect on cement hydration and mechanical performance.

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