The effect of antifreeze additives on concrete performance with and without nano-silica at sub-zero temperature

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Abstract

The addition of antifreeze agents in concrete has been introduced as a practical solution to mitigate the noxious effects of cold weather on concrete. In this study, the effect of two types of economical and commercially available antifreeze additives: calcium nitrate-based (CN) and urea, on the performance of concrete with and without nano-silica cast and cured under a freezing temperature, was evaluated by setting time, strength development, durability performance, and thermogravimetry. The results showed that nano-modified concrete specimens containing CN acquired the highest mechanical and durability properties.

Keywords: Antifreeze additives; Nano-silica; Sub-zero temperature; Concrete

Introduction

The curing conditions (temperature and relative humidity) significantly affect cement hydration reactions, which regulate the development of mechanical, physical, and microstructural properties of concrete. Standard curing conditions for concrete are defined as 20 to 23°C and >95% relative humidity, respectively, as these values are optimal for the hydration process [1]. Accordingly, cold temperatures negatively influence the cement hydration, which theoretically stops at -2.8°C, as the mixing water freezes resulting in 9% volume expansion, and consequently inducing internal cracking [2]. Generally, cold weather concreting without proper precautions leads to delaying setting time and early-age strength gain, and coarse microstructure [3]. For instance, it has been reported that the compressive strength and frost resistance of concrete reduces by up to 40% and 60%, respectively, due to early freezing damage of the cement paste [4]. According to ACI 306R [5] and CSA A23. 1 [6], the weather is considered cold when there is a risk of a temperature drop below 5°C within the protection period of concrete. Hence, ACI 306R [5] recommends that concrete should acquire compressive strengths of 3.5 and 24.5 before being subjected to a single or series of freezing and thawing cycles, respectively. Comparatively, CSA A23.1 [6] states that concrete may resist frost action if it yields a compressive strength of 7 MPa.

To enhance concrete hydration development under cold weather, different techniques such as hot air curing, heating of concrete constituents, enclosures, etc. are recommended, but these methods involve high energy consumption, CO_2 emission, and cost, as well as detrimental effects on the durability of concrete [7-9]. Hence, concrete construction and repair seasons are typically limited in colder regions to three to five months (May to September), leading to socioeconomic losses associated with busy construction periods, backlogged project schedules, and discomfort time to the public. Therefore, there is a constant demand for novel solutions that enable the casting, finishing, and curing of concrete at low temperatures to extend the construction season and alleviate the drawbacks of traditional heating techniques.

Cold weather admixture systems (CWAS) have been investigated because they consist of antifreeze admixtures with or without acceleration effects [10,11]. These systems have the capability of lowering the freezing point of mixing water and, in some cases, accelerating cement hydration, allowing for concrete casting and curing under low temperatures while achieving the target physical and mechanical characteristics [12,13]. It has been reported that antifreeze admixtures such as sodium nitrite, calcium nitrite, sodium nitrate, calcium nitrate, urea, calcium chloride, sodium chloride, potash, and combinations may work as CWAS in concrete [11]. However, some of these chemicals have detrimental effects on the properties of concrete. For instance, the tendency of chloride-based admixtures to provoke accelerated corrosion of steel-reinforced concrete has led to their exclusion from structural concrete [10,14,15]. Additionally, alkali aggregate reactions could be provoked in concrete with the addition of sodium- or potassium-based admixtures [11]. Furthermore, it has been noted that potash results in poor microstructure and inadequate resistance to freezing and thawing cycles [10].

The widespread usage of nanoparticles in concrete is due to their considerable effects on the microstructure, as well as the chemical, physical, mechanical, and durability properties of concrete [16,17]. At normal casting/curing temperatures, their ultrafine nature catalyzes the hydration of cement, resulting in early-strength gain, while their superior pozzolanic and filler effects densify the microstructure of concrete [16-19]. Previous studies at the University of Manitoba showed that hydration and strength development rates were accelerated when nano-silica was added to masonry cement mortars that contained 30% inert filler and were cast and cured at 5°C without the use of any protective measures including heating or CWAS [20,21].

Yasien et al. [20,21] reported that lab-grade calcium nitrate/nitrite solutions could work as efficient CWAS for concrete without and with nano-silica cast/cured at low temperatures down to -5℃, without any adverse effects on the setting time, strength, and durability properties. However, the high cost of these lab reagents might be prohibitive for upscaling and wider application in the concrete industry. Hence, the motive of this study, which aimed at combining commercially available and economical CWAS [calcium nitrate-based (CN)/accelerator, and urea/retarder] with a commercial type of colloidal silica to produce concrete cast and cured at -5℃, without any heating. The fresh, hardened, and durability properties of the produced concrete were evaluated, and the results were corroborated with thermogravimetric analysis. Data from this study may provide practical guidance for producing commercial types of winter concrete at reasonable costs, due to the reduction of the initial materials' cost and elimination of heating protocols during the production and curing stages.

Experimental Program

Materials and mixtures

All mixtures comprised 400 kg/m^3 General Use (GU) portland cement, which complies with CAN/CSA A3001 [22] as the main constituent of the binder at a constant water-to-binder ratio (*w/b*) of 0.32. Also, a nano-silica solution with 50% solid content was used to partially replace cement by weight at a constant dosage of 6%. The mean particle size, specific gravity, and surface area of the used nano-silica are 35 nm, 1.4, and 80 m^2/g, respectively. These proportions achieved balanced performance in terms of fresh, hardened, and durability properties of concrete cast and cured under normal and low temperatures (23 to -5°C) [3,20,23]. The coarse aggregate (CA) was 9.5 mm natural gravel with a specific gravity of 2.65 and 2% absorption, while the fine aggregate (FA) was well-graded river sand with a specific gravity of 2.53, a fineness modulus of 2.9, and 1.5% absorption. A polycarboxylic acid-based water-reducing admixture according to ASTM C494/C494M Type F [24] was added to all mixes to achieve a target consistency/slump of 180±20 mm. Moreover, to achieve a fresh air content of 6%, an air-entraining admixture was utilized following ASTM C260 [25]. All mixtures comprised antifreeze admixtures with/without an accelerating effect: CN (calcium-nitrate-based antifreeze admixture) or urea as cold weather admixture system (CWAS). In this study, the CN and urea were used as 5 and 6% by weight of binding materials (cement + nano-silica), respectively [3,13,26,27]. The physico-chemical properties of CN and urea are listed in Table 1, whilst the proportions of the concrete mixtures tested are listed in Table 2. In the mixture ID, the letters CN, UR, and NS denote calcium nitrate, urea, and nano-silica, respectively.

Table 1: Properties of CN and urea

	CN	**Urea**
Density (g/cm^3)	1.86	0.75
Molecular weight (g/mol)	236.15	60.06
Solubility in water (g/l)	1,470	1080
pH	5	8
Melting point (°C)	105	133

Table 2: Mixtures proportions per cubic meter

Mixture ID.	**Cement (kg)**	**Nano-silica (kg)**	**Water[a] (kg)**	**CN[b] (kg)**	**Urea[b] (kg)**	**CA (kg)**	**FA (kg)**	**Cost CAD[c]**
CN	400	0	128	20	0	1222	658	365
UR	400	0	128	0	24	1233	646	370
CN-NS	376	48	104	20	0	1217	673	412
UR-NS	376	48	104	0	24	1225	662	420

[a] Adjusted amount of water considering the water content of nano-silica (aqueous solution with 50% solid content of SiO_2).

[b] The CN and urea admixtures were in liquid (with about 75% calcium nitrate and adjusted amount of mixing water) and solid forms, respectively.

[C] Canadian Dollar.

Procedures

To mimic cold weather construction, mixing and casting of all mixtures were conducted inside an environmental chamber set at -5ºC, where solid constituents of concrete were stored for 24 h prior to mixing. Furthermore, conditioned water at 5ºC was used in mixing to simulate tap water temperature during winter. According to trial batches and previous studies by the authors [3,20], a particular sequence of mixing was adopted to attain homogenous dispersion of mixtures' constituents. Hence two solutions were prepared; the first one comprised 2/3 of the mixing water containing the nano-silica, air-entraining, and HRWR admixtures, whilst the second solution was the CWAS (CN or urea) diluted in the remaining 1/3 of the mixing water. Both solutions were stirred for one minute to ensure homogeneity. Afterwards, the coarse and fine aggregates were mixed with half of the first solution for one minute, then the cement was added, and mixing continued for another 30 seconds followed by adding the remaining half of the first solution to the pan while mixing for another 30 seconds. Finally, the second solution was added to the pan and then the combined materials were mixed for an additional minute. Concrete mixtures were poured into molds and compacted using a vibrating table at 60 Hz; subsequently, all specimens were covered using economical tarps [3] mm thick layer of closed cell foam sandwiched between two layers of reinforced polyethylene] and kept inside the environmental chamber at -5°C under a 25 km/h fan speed to simulate wind conditions.

Testing

The setting times of the different mixtures were determined inside the environmental chamber at -5°C by measuring the penetration resistance of standard needles into the 150 mm cubes of the mortar portion of each mixture (passing sieve #4 [4.75 mm]), and the initial and final setting times were determined in accordance with ASTM C403/C403M [28]. The early- and later-age compressive strength of all mixtures was assessed by testing triplicate cylindrical specimens (100×200 mm) following ASTM C39/C39M [29] after 7 and 28 days of curing under -5℃.

In addition, the fluid absorption test was conducted to investigate the penetrability of the proposed mixtures at the age of 28 days following the protocol described by Tiznobaik and Bassuoni [30]. Three concrete discs (75×50 mm) for each mix design were prepared and dried at 45°C. The samples were then vacuumed for 6 h at 85 kPa. The fluid absorption values of specimens were calculated to the nearest 0.01 g after 6 h of immersion in 4% calcium chloride solution. Also, prismatic (50×50×285 mm) specimens were prepared for freezing-thawing test according to ASTM C666/C666M [31] at the age of 28 days in water and salt solution (13.6% calcium chloride). This concentration of calcium chloride was selected to provoke the chemical/physical degradation effects of the salt (solution with ice) [32]. All samples were exposed to a total of 300 cycles of freezing-thawing. Each cycle (6 h) consisted of freezing at -18°C±1 for 3 h, thawing for 2 h at 4±1°C, and 15 min to ramp up and down to the target freezing or thawing temperatures. For this test, the ultrasonic pulse velocity (UPV) was determined before and after the freeze-thaw test. This test can be used to find changes, such as deterioration brought on by freezing-thawing cycles. Based on the UPV results the durability factor (DF) was calculated for each mix design.

In addition, thermogravimetric (TG) analysis was performed at the ages of 1, 3, 7, 14, 28, 56, and 90 days at a constant heating rate of 10°C/min on powder samples passing through sieve #200. The percentage drop of an ignited mass of the TG curves at 400–450 °C was multiplied by 4.11 (CH to water molecular masses) to determine the portlandite (calcium hydroxide; CH) contents in the mixtures.

Results

Setting time

Both initial setting (IS) and final setting (FS) times were determined in accordance with ASTM C403 requirements as the mortar portion of each mixture reached penetration resistance of 3.5 and 27.6 MPa, respectively. As shown in Fig- 1, The IS and FS occurred within 2.8 to 6.3 and 5.2 to 10.5 hours, respectively. This highlights the significant impact of the investigated parameters in this study (anti-freeze admixtures type and nano-silica) on the hardening behavior of concrete that was mixed, cast, and cured at -5°C. Generally, the IS and FS of the concrete mixtures tested herein, comply with the period of time needed for concrete placement and finishing operations, indicating the applicability of these mixtures for cold weather construction. The adopted CWAS types and dosages were capable of depressing the freezing point of mixing water and speeding up the kinetics of cementitious materials' reactivity.

Generally, mixtures comprising CN had shorter setting times compared with the counterpart mixtures incorporating urea. The IS and FS of mixture CN were 190 and 320 minutes, respectively, while for the UR mixture, they were 380 and 630 minutes, respectively. This can be attributed to the function of CN, as an antifreeze and accelerator, and consequently it shortened the setting time of concrete at freezing temperatures. The CN contains the same cations as C_3S, catalyzing hydration by acting as nuclei, thus speeding up the process of hydrate crystallization [10,33]. Comparatively, the setting time of concrete was extended with the addition of urea, which is an organic compound that absorbs the heat emitted by cement hydration; and consequently retards hydration kinetics and skeletal rigidity [34].

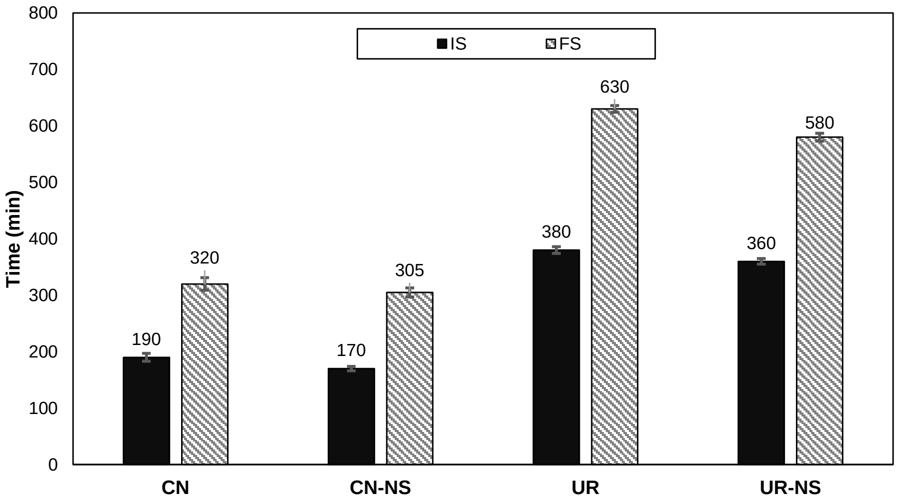


Fig- 1: Initial and final setting times of all mixtures.

The IS and FS were significantly impacted by the nano-silica addition. For instance, the amalgamation of nano-silica in mixture UR to produce mixture UR-NS shortened the IS and FS by 20 and 50 minutes, respectively. This can be linked to the nano-sized particles and high surface area of nano-silica (80,000 m^2/kg) which served as nucleation sites for the hydration products to precipitate on; resulting in faster rates to reach skeletal rigidity, as will be substantiated in the TG section.

Compressive strength

Fig- 2 shows the compressive strengths of all mixtures, which were cast and cured at -5°C without heating. The compressive strength results varied from 31 to 42 MPa and 46 to 59 MPa after 7 and 28 days of curing, respectively. Regardless of the mix design parameters, it is worth noting that all mixtures developed and tested herein achieved the 24 MPa, after 7 days of curing at -5℃ without heating, stipulated in ACI-306R [5] to resist multiple cycles of freezing-thawing. Also, the 28 days strength range of all mixtures complies with the strength requirement of various concrete applications (35 to 45 MPa) [35].

The compressive strength results were in agreement with the hardening trends, in the sense that changing the type of CWAS as well as the incorporation of nano-silica notably affected the strength development of concrete. Hence, concrete mixtures with CN attained higher strength than mixtures comprising urea. For instance, the incorporation of CN as CWAS instead of urea gain an average of 15% increase in the 7 and 28 days compressive strength. This can be attributed to the acceleration nature of calcium nitrate compared with urea, which has a retarding effect as explained in the setting time section; thus, CN-based CWAS was effective at maintaining the hydration development of cement under the adopted low curing temperature (-5℃).

The well-documented positive influence of nano-silica on the strength development of cement-based materials [16–20] was observed in this study. Accordingly, concrete mixtures incorporating nano-silica yielded higher mechanical capacity than that of corresponding mixtures without nano-silica after 7 and 28 days of curing. For instance, the addition of 6% nano-silica by weight of cement to mixture CN to produce mixture CN-NS increased the 7 and 28 days strengths by 20% and 18%, respectively. This can be attributed to multiple mechanisms such as the filler effects, nucleation, pozzolanic, and apparent water reduction effect of nano-silica aggregates on cementitious systems [16-20]; thus, additional calcium silicate hydrate (C-S-H) gel with higher stiffness and consequently denser microstructure characteristics were achieved. Indeed, the coexistence of the adopted CWAS was critical to maintaining the hydration development/pozzolanic development and functionality of nano-silica in cementitious systems.

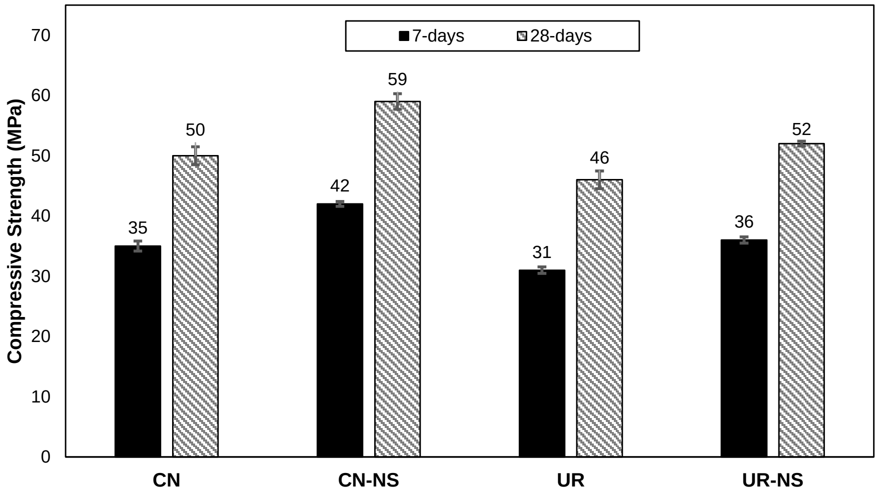


Fig- 2. Compressive strength of all mixtures cast and cured at -5°C.

Durability performance

Fluid absorption (Table 3) and the durability factor (*DF*) of specimens in the freezing-thawing tests in water and a calcium chloride solution $CaCl_2$ solution (Fig- 3) were used to evaluate the durability of the different mixtures. The results of fluid absorption tests were used to evaluate the different concrete mixtures' penetrability. The fluid absorption results varied from 2.05 to 2.65%, while the *DF* ranged from 91 to 101% after 120 cycles of freezing-thawing.

Generally, the type of antifreeze admixture as well as the amalgamation of nano-silica were essential determinants of the mass transport properties. Hence, the use of urea as CWAS resulted in 18% accretion in the fluid absorption , but marginal (4%) reduction in the resistance to frost action of the produced concrete compared with the counterpart mixtures comprising CN. This can be attributed to the capability of CN to accelerate the hydration process of the binder and level of maturity of the hardened paste, as indicated earlier by the setting time and compressive strength trends. Also, it is reported that calcium-based antifreeze admixtures improve the interfacial zone of contact between the cement paste and aggregates; and consequently, reducing the penetrability of concrete, complying with the presented absorption values herein, leading to the shift in the cement paste's pore size towards the zone of micro capillaries and gel pores [13].

Table 3: Fluid absorption of the different mixtures after 28 days of curing under -5℃

Mixture ID	**Absorption (%)**
CN	2.20
CN-NS	2.05
UR	2.65
UR-NS	2.50

The addition of nano-silica had a positive impact on lowering the fluid ingress and enhancing the freezing-thawing resistance of concrete, cast and cured under -5℃. For instance, the absorption values were reduced by an average of 7%, when nano-silica was added to mixtures UR and CN to produce mixtures UR-NS and CN-NS, respectively. While the frost resistance of nano-modified mixtures was marginally (4%) higher than the counterpart mixtures without nano-silica after 120 cycles of freezing-thawing. This alluded to the synergistic influence of nano-silica on the acceleration of the hydration process and development of concrete microstructure through the filler, nucleation, pozzolanic effects as well as reducing the apparent *w/b* [17,19,20], as will be discussed in the TG section. Accordingly, concrete mixtures comprising nano-silica attained denser microstructure and mechanical capacity faster.

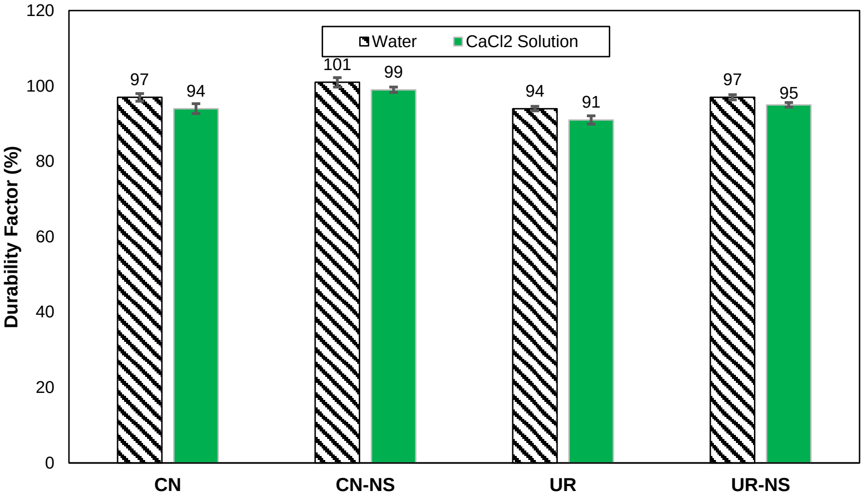
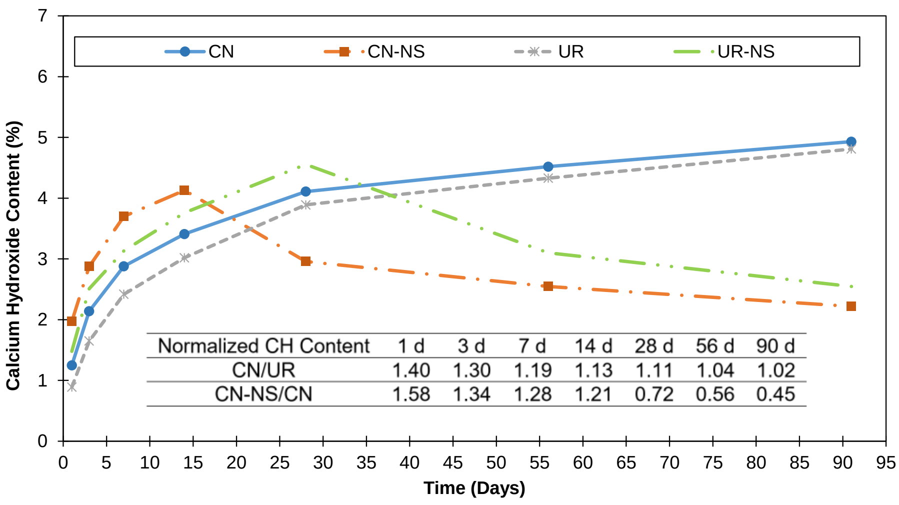


Fig- 3. Durability factors of concrete mixtures after 120 cycles of freezing-thawing in water and $CaCl_2$ solution.

Thermal analysis

TG analysis was performed to monitor the production and consumption of portlandite in the concrete mixtures at various ages (1, 3, 7, 14, 28, 56, and 90 days) of curing at -5℃. The CH results, shown in Fig. 4, agree with the aforementioned bulk results. Hence, at early-age, the addition of CN increased the quantities of CH in the mixtures relative to urea, which explains the considerably quicker hardening rates of CN mixtures than those incorporating urea. For instance, the normalized CH content of mixture CN compared to the counterpart mixtures incorporating urea reached 1.4, 1.3, 1.19, 1.13, and 1.11 after 1, 3, 7, 14, and 28 days of curing. This can be attributed to the substantial acceleration effect of CN on speeding up cement hydration. This corresponded to the shorter setting times, higher mechanical capacity, and better resistance to ingress of fluids of mixtures comprising CN. However, the effect of CWAS type on the longer-term properties of concrete was insignificant, as comparable performance of CN and urea mixtures was observed in terms of freezing-thawing resistance (only 4% difference). This was ascribed to the comparable hydration degree of both mixtures as reflected by the TG results (Fig-4). For instance, changing the CWAS type in mixture CN to produce mixture UR achieved comparable portlandite contents at 56 and 91 days of curing, respectively.

Furthermore, in comparison to counterpart mixtures without nano-silica, nano-modified concrete produced larger CH amounts at an early-ages. For example, at 1, 3, and 7 days, the normalized CH contents of the nano-modified mixture CN-NS in comparison with its corresponding mixture without nano-silica (CN) were 1.58, 1.34, and 1.28, respectively. This is in agreement with the noticeably improved early-age hardening rate and compressive strength of the nano-modified mixtures, which can be linked to the filler as well as the nucleation effects of nano-silica by acting as nuclei sites for the early-age precipitation of hydration products [18-21]. Afterwards, the consumption of the CH up to 90 days of curing was noted in all the nano-modified concrete mixtures after 14 and 28 days, in the case of CN and urea mixtures, respectively, as showed by the sharp decline in the CH contents. This indicated the initiation of a delayed pozzolanic reaction of nano-silica, due to the adopted freezing temperature, which densified the pore structure of concrete by consuming with CH to produce high-stiffness secondary calcium silicate hydrate (C-S-H) gel [16,20,21]. This explains the higher late-age mechanical capacity as well as lower absorption values of concrete mixtures amalgamating nano-silica compared with reference mixtures without nano-silica. This signifies the benefit of incorporating nano-silica particles in concrete for cold weather applications. Indeed, the selection of CWAS was critical to maintain the functionality of nano-silica, although at different delaying rates.



Normalized CH Content	1 d	3 d	7 d	14 d	28 d	56 d	90 d
CN/UR	1.40	1.30	1.19	1.13	1.11	1.04	1.02
CN-NS/CN	1.58	1.34	1.28	1.21	0.72	0.56	0.45

Fig- 4. TG results for CH contents up to 90 days of curing at −5°C.

Conclusions

The following concluding remarks can be extracted from this study:

- Despite the low curing temperature adopted herein, the setting time (5.1 to 10.5 h) and strength (46 to 59 MPa at 28 days) results showed the suitability of the adopted mix design (low *w/b*, adequate binder content, CWAS) implemented herein to achieve an adequate level of maturity of the hardened paste, as supported by the TG analysis.

- Using CN relative to urea as CWAS produced concrete with better performance in terms of hardening rates, strength development up to 28 days, resistance to fluid ingress, and initiation of nano-silica pozzolanic reactivity. However, complying with the TG findings, both mixtures achieved comparable performance of concrete at later-age properties (e.g., resistance to frost damage).

- The performance of concrete produced at -5°C was significantly enhanced by the addition of nano-silica (shorter setting times, increased compressive strength, lower absorption, and enhanced resistance to frost action), especially when combined with CN, which preserved the functionality of nano-silica at the sub-zero temperature. According to the TG analysis, the early-age nucleation, latent pozzolanic, and filler effects of nano-silica significantly improved the hydration development of the concrete mixtures.

- For cold weather concreting down to -5°C, nano-modified concrete mixtures, especially with either commercial grade CN or urea, may present a practical and economic alternative to using conventional heating methods and/or insulation blankets with high thermal resistance. Field trials and cost-benefit analyses compared to conventional construction methods (heating materials, enclosures, insulations) are recommended for future research to further confirm these laboratory findings.

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