COLD WEATHER CONCRETE: INNOVATIVE MIXTURES DESIGNS AND PROTECTION METHODS

by

Ahmed Mohammed Yasien Soliman

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ABSTRACT

In cold regions, concrete practitioners face challenges to achieve target performance criteria of concrete produced under low temperatures. There is still dearth of knowledge on how to alleviate the heating requirements for cold weather concreting. Nano-silica has the potential to produce concrete mixtures with dense microstructure and improved hardened properties under cold temperatures. This thesis applied the response surface method to assess the effect of multiple parameters on 40 concrete mixtures cast and cured under freezing temperatures down to \(-5\)°C. In addition, a comprehensive study was conducted to further understand the behavior of these mixtures and suitability for repair applications under cold temperatures. Also, this thesis explored the efficacy of using a hybrid protection system (insulation blankets + Phase change material (PCM) mat) on hydration development, mechanical properties and bonding behavior with steel of nano-modified concrete cured under lower freezing temperatures (-10 and -20°C), without heating, using experimental and numerical studies.

The results suggested that the incorporation of at least 2% nano-silica with single or blended binders (maximum of 15% fly ash), especially with low w/b and calcium nitrate-nitrite (CNAI), achieved satisfactory performance when cured under freezing temperatures down to -5°C. This was substantiated by the complementary investigation which proved the applicability of nano-modified concrete, especially with a higher nano-silica dosage (4%) without and with fly ash (15%), for repair applications. Hence, it achieved satisfactory performance and compatibility with parent concrete.

Furthermore, the experimental and numerical results showed that nano-modified concrete comprising CNAI, without or with fly ash (20%) and protected using the hybrid system achieved adequate hydration development, mechanical properties and bonding
with steel re-bars due to the nucleation, pozzolanic and filler effects of nano-silica. Moreover, the developed thermal analysis and mechanical models showed an adequate generalization capability to predict concrete-steel interfacial temperature evolution, as well as bond strength with less than 10% error between predicted and experimental results.

The synoptic outcomes of this thesis suggest that nano-modified concrete mixtures and hybrid protection system may provide an integrated strategy for alleviating heating requirements and improving the quality of concrete for various cold weather concreting applications down to -20°C.
CO-AUTHORSHIP

This thesis has been prepared in accordance with the regulation of integrated-article format stipulated by the Faculty of Graduate Studies at the University of Manitoba. Substantial parts of this thesis were either published in or submitted for publication to peer-reviewed technical journals and international conferences as shown below:

Journal Papers


Conference Proceedings


Others

Dedication

Every challenging journey requires self-efforts as well as guidance from people we love and care for

This work is dedicated to:

My Mom, Dad, Sister and My Fiancée

My family that has a great effect on my life,

All my love to you for your care and support to achieve such success and honor.

Along with my hard working and respected supervisor

Prof. Mohamed Bassuoni
Acknowledgements

First and above all, I have to thank Almighty Allah who bestowed upon me guidance and benevolence to complete this work.

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CHAPTER 1: INTRODUCTION

1.1 Overview

Concrete gains its strength and design performance by a chemical reaction between water and cement to form gel that hardens and binds aggregates together (Mehta and Monteiro 2014; Neville 2011). This hydration process depends mainly on the temperature and relative humidity (RH) conditions. The favorable temperature and relative humidity for the hydration process are 20 to 23°C and >95%, respectively (Mehta and Monteiro 2014; Neville 2011), which are referred to as standard curing conditions of concrete. Therefore, the performance of concrete may be adversely affected by exposure to cold weather during construction and curing periods (Karagöl et al. 2015; Neville 2011; Mehta and Monteiro 2014). When concrete temperature is low (e.g. 5°C), the hydration process slows down significantly, and it completely stops when the temperature reaches -2.8°C with approximately 95% of the mixing water turning into ice (Karagöl et al. 2015; Ratinov et al. 1996; Korhonen et al. 1992). This hinders strength development of concrete due to limited production of calcium silicate hydrate (C-S-H) gel, leading for example to the loss of 40%, 70% and 60% of concrete compressive and bond strengths as well as freeze-thaw resistance (Rixom and Mailvaganam 2002).

In addition, frozen water in concrete expands and induces hydraulic and osmotic pressures due to the movement of water among smaller and bigger pores (Prado et al. 1998; Powers et al. 1953; Picket 1953). These pressures are considerably higher than concrete typical tensile strength (3-8 MPa), consequently the produced concrete suffer from micro-and macro-cracks, porous microstructure and lower final strength resulting in rapid deterioration, especially if it is kept under freezing or freezing-thawing conditions.
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after casting without reaching adequate strength particularly at early-age (Cai et al. 1998; Prado et al. 1998; Pigeon et al. 1991).  Albeit concrete can continue the hydration process when it is allowed to thaw (Korhonen 1999), the resulting concrete will be porous and heterogeneous (Kohronen 2002; Rixom and Mailvaganam 2002) due to the coexistence of large voids of the melting ice which were not blocked with the hydration products despite the continual hydration (Çullu and Arslan 2013). Subsequently, the target mechanical and physical properties of concrete will not be achieved, and the concrete will fail target its service life performance and purpose.

According to ACI 306R (2016): Guide to Cold Weather Concreting, and CSA A23.1 (2019): Concrete Materials and Methods of Concrete Construction, cold weather is defined as when air temperature has fallen or expected to fall below 4 or 5ºC, respectively during the protection period required for concrete to achieve mechanical and physical properties that can resist the effect of being exposed to such harsh conditions. According to the aforementioned definitions of cold weather, different countries such as Canada, United States, Russia and Scandinavian countries suffer from a significant reduction in operational periods (Husem and Gozutok 2005; Korhonen et al. 1997). For instance, air temperature in most Canadian provinces remains well below zero from October to March resulting in delays of vital infrastructural projects and maintenance operations, busy summer seasons with construction activities, and disruption to the comfort of the public with considerable socioeconomic losses.

The aforementioned documents give multiple provisions, including mixing, placement and curing temperatures during cold weather applications, to prevent freezing of concrete at early ages, maintain adequate strength development and reduce the potential for thermal cracking. These include heating of concrete constituents including
water and aggregates between 40°C and 60°C, metallic embedments and forms as well as using enclosures with industrial heaters to provide voluminous construction sites with normal environmental conditions for placement and curing operations (above 10°C). While these practices can make concrete continue hydration and develop the required strength, they will incur considerably additional costs due to the high expenditures associated with energy consumption, required materials/skilled labour and CO₂ emissions during construction. For instance, in United States, the estimated cost to thermally protect concrete during construction from freezing has been recently estimated at one billion dollars per year (Barna et al. 2011).

1.2 Need for Research

The incorporation of cold weather admixture systems (CWAS), antifreeze without/with accelerating admixtures, in concrete has been introduced as practical and economically efficient solution to mitigate the negative effects of cold weather on concrete (Ratinov et al. 1996; Korhonen 1990). Antifreeze admixtures depress the freezing point of mixing water while accelerators speed up the kinetics of cement hydration; thus, concrete can achieve adequate physical and mechanical properties when cured under low temperatures (eg. Polat 2016; Karagöl et al. 2013; Ratinov et al. 1996; Korhonen 1990). Antifreeze admixtures such as sodium nitrite, calcium nitrite, calcium nitrate, urea, calcium chloride, sodium chloride, potash and combinations have been reported to be efficient CWAS by allowing concrete to reach degree of hydration comparable to normally cured concrete (21±1°C) (Korhonen 1990).

Although several studies (e.g. Karagöl et al. 2015; Demirboğa et al. 2014; Karagöl et al. 2013) investigated the effect of using these admixtures on preparing concrete at low temperatures down to -20°C, they only focused on the workability and compressive
strength of concrete without much attention to durability properties (e.g. development of microstructure, penetrability). For instance, sodium-based CWAS may provoke alkali aggregate reaction (Ratinov et al. 1996; Korhonen 1990) while Chloride-based admixtures may initiate corrosion of steel reinforcement (Ratinov et al. 1996; Korhonen 1990) and cause decomposition and expansion of hardened paste by forming calcium oxychloride (Peterson et al. 2013). In addition, potash was found to negatively affect concrete microstructure and resistance to freezing-thawing cycles (Ratinov et al. 1996; Korhonen 1990), whilst urea was reported to act as a retarder (Ratinov et al. 1996; Korhonen 1990). Comparatively, calcium nitrate, calcium nitrite and combinations were reported to be efficient in terms of accelerating the kinetics of cement hydration, however it was reported to produce concrete vulnerable to excessive shrinkage cracking (Korhonen et al. 1997). Hence, the effect of CWAS on the durability of concrete is uncertain, and the microstructure of such concrete needs to be improved.

Recently, nanomaterials have become one of the most important research areas in different disciplines including construction materials. They have attracted the interest of scientists due to the benefits of using particles in nanometer scale at modifying the functionality of many construction materials including concrete. For example, due to their ultrafine nature, nano-silica can enhance the mechanical and durability properties of concrete (eg. Ghazy et al. 2016; Haruehansapong et al. 2014; Said et al. 2012). It can speed-up the kinetics of cement hydration (Hou et al. 2013; Senff et al. 2009), efficiently refine the pore structure of concrete, densify the interfacial transition zone (ITZ) between aggregates and cement paste and reduce the amount of freezable water in the matrix (Ghazy et al. 2016; Korpa et al. 2008). However, only a few studies, which were pioneered by the Cementitious Materials Research Group at the University of Manitoba,
have been introduced to investigate the effect of using nano-silica on concrete/mortar mixed, placed and cured under low temperatures (5°C) (Kazempour et al. 2017; Kazempour et al. 2014). Moreover, the possible mechanism of interactions between nano-silica and CWAS and their effects on concrete cast and cured under freezing temperatures remain largely unexplored.

The effects of varying key mixture design parameters such as cement type, water-to-binder ratio (w/b), nano-silica, fly ash dosages and CWAS on the fresh, hardened and durability properties of concrete cast and cured under freezing/low temperatures have not been well-documented in the technical literature. Moreover, neither ACI 306R (2016) nor CSA A23.1/A23.2 (2019) provide specific guidance on the proper cement content, w/b and cement type suitable for different low temperature scenarios in the field [e.g. late fall, early spring periods and low freezing temperatures (e.g. -20°C)]. At the present time, optimization of cold weather concrete mixtures has become necessary with the variety of construction materials and admixtures available in North America. Optimization studies based on rigorous statistical analysis are particularly suitable to understand the relationships and interactions among key mixture design parameters of concrete and their consequent effects on placement, strength, dimensional stability and durability aspects. Unfortunately, there is dearth of information in this area, which warrants focused research studies to identify optimum concrete mixtures for specified cold weather scenarios and civil infrastructure applications such as repair.

Phase change materials (PCMs) are a combination of sensible-and-latent thermal energy storage materials, which can store and emit energy in the form of heat based on its solidifying and melting temperatures (Aguayo et al. 2016). The applications of PCMs in building sectors have attracted scientists’ interest in the past two decades (Baetens et al.}
Incorporating PCMs in concrete is a new cost-effective technique, which has the capability of boosting concrete thermal energy storage capacity to limit the rise and drop in temperatures (Cao et al. 2017; Farnam et al. 2015). It may mitigate the risk of thermal cracking (Kim et al. 2015) and improve the resistance to freezing-thawing by delaying ice formation (Meshgin and Xi 2012). However, PCM can impart negative effects on concrete (e.g., reduction of strength/elastic modulus (Farnam et al. 2015), higher porosity (Aguayo et al. 2016) and drying shrinkage (Meshgin and Xi 2012), which may limit their use to non-structural applications (Cao et al. 2017; Memon et al. 2015). Despite the potential of PCM to control ice formation through its heat fusion, thus aiding the continuity of cement hydration under cold weather, the applicability of using PCMs pouches as external curing mats, to alleviate the negative effects of incorporating them in the cementitious matrix, to protect newly poured concrete under freezing conditions (e.g. -10 and -20°C), without the need for enclosures or traditional heating techniques, is still unexplored.

The excessive loss of heat from concrete element outer surfaces and edges under cold weather generates a temperature gradient relative to the core, resulting in excessive shrinkage and tensile cracks, if the concrete element is restrained, especially with the presence of high dosages of CWAS (Korhonen et al. 1997). Both ACI 306R (2016) and CSA A23.2 (2019) stipulate stringent limitations on concrete temperature gradients and the ambient temperature to avoid thermal cracking. Finite-element models can predict the internal temperature of concrete elements at any location under different environmental conditions. These predictions aid to identify the heat evolution with time and critical temperature locations such as concrete-cold metallic embedments interfaces, which indicates the formation of ice lensing (Prado et al. 1998) leading to bond failure.
However, the temperature profiles in concrete, especially incorporating speciality materials such as nano-silica and CWAS, cast and cured under cold weather with respect to time has not been investigated yet.

The performance of reinforced concrete is significantly affected by the concrete-steel bond strength, which defines it is overall design criteria and ductility limitations (MacGregor et al. 1997). The hydration development within concrete-steel ITZ is the main key to bond strength development. In cold weather applications, the bonding between concrete and steel maybe inferior, due to the development of inadequately hydrated interfacial zone (Schroeder and Wood 1996), leading to reduction in the different structural elements capacity and rapid failure. Using finite-element software to model concrete-steel force-slip relationship proved to be efficient to simulate cracking pattern and to define deformation and stiffness of structures (Murcia-Delso and Benson-Shing 2015). However, there is dearth of information on bond strength of concrete cast and cured under cold weather, with steel and the potential of numerically predicating concrete-steel bond strength based on the hydration development and heat of hydration produced within the concrete-steel ITZ.

1.3 Objectives of Research

To respond to the aforementioned research needs, the fundamental theme of this research program is to investigate new mixtures and protection methods to advance the current practices of cold weather concreting. The specific objectives of this doctoral research are to:

- Identify optimum key mixture design parameters for cold weather concrete such as $w/b$, nano-silica dosages, contents of fly ash and type of CWAS.
• Study the interaction of CWAS with nano-silica to develop innovative concrete mixtures suitable for multiple low temperature (down to -5°C) scenarios to extend the construction and repair periods for civil infrastructure in cold regions.

• Investigate the performance of concrete incorporating different types of cements, CWAS, nano-silica and fly ash protected using insulation blankets without and PCM mats under freezing temperatures down to -20°C.

• Develop a model to predict the effect of changing different parameters such as curing temperature, mix design and protection method on concrete internal heat evolution and temperature gradient.

• Investigate the correlations between concrete, which is cast and cured under -10 and -20°C, hydration development, mechanical properties and heat produced at concrete-steel interface, which can be used to predict concrete-steel bond strength through modeling.

1.4 Scope of Research

To achieve the aforementioned objectives, the scope of the work involves laboratory work, and modeling as described below:

• Studying the interaction of different types and dosages of CWAS (calcium nitrite and nitrate) with various percentages of nano-silica and fly ash on concretes, cast and cured at freezing (-5°C) or cyclic freezing/low temperatures (-5/5°C), with various w/b in terms of placement, strength and durability using a response surface method (RSM) approach. Optimization analysis was conducted based on the experimental results of placement (setting time), strength (compressive
strength), durability (freezing-thawing resistance and absorption) tests as well as cost.

- Evaluating the optimum nano-modified and nano-modified fly ash concrete mixtures for repair applications of concrete pavements and bridge decks at cyclic freezing/low temperatures (-5/5°C). Setting time, internal temperature evolution, compressive and tensile strengths, modulus of elasticity, absorption, pull-off strength, shrinkage and surface scaling tests as well as microstructural analysis were conducted to evaluate the performance of these repair mixtures in terms of hardening rate, mechanical and physical properties as well as compatibility with parent concrete.

- Investigating the effect of using different types of cement [General Use (GU) and High Early Strength (HE)], nano-silica, fly ash on the performance of concrete poured under freezing temperatures (-10 and -20°C) using conventional (insulation blankets) and hybrid systems (Insulation blankets + PCM mat). The performance was studied based on fresh, hardened and durability properties of concrete. The tests included setting time, internal temperature, compressive strength, absorption, freezing and thawing resistance as well as microstructural analysis.

- Developing finite element models to study the effect of changing the mix design parameters (nano-silica and fly ash), curing temperature (-10 and -20°C) as well as protection methods (conventional and hybrid system) on concrete heat evolution and concrete-steel bond strength development. In addition, a correlation between heat generated at concrete-steel interface, hydration development and mechanical properties of concrete was developed based on the experimental work.
1.5 Original Contributions

The current Ph.D. thesis introduces an integrated approach for cold weather concreting based on the next generation of concrete engineered with nanomaterials and thermally efficient curing method, and provide systematic knowledge on such a protocol including mixture designs, and fitness for purpose in multiple applications. The outcomes of this work will contribute to the scientific and engineering communities as follows:

- Providing a large pool of data on a novel approach amalgamating nano-modified concrete and CWAS for cold weather applications, based on key mixture design parameters ($w/b$, fly ash and nano-silica dosages as well as type of CWAS) and its influence on concrete performance.

- Modeling the performance of cold weather concrete statistically in terms of fresh, hardened and durability properties to provide an assistive design tool for selecting optimum concrete mixtures suitable for different applications.

- Offering a strategic solution for improving productivity rates during late fall and early spring through the production of high-performance nano-modified concrete suitable for various construction and repair/restoration applications.

- Demonstrating the influence of using a hybrid protection technique (insulation blanket + PCM mat) on the overall performance of nano-modified concrete, cured under low freezing temperatures down to -20°C, and its effect on concrete-steel interfacial transitional zone (ITZ), to emphasize the applicability of cold weather nano-modified concrete for structural applications.

- Modeling the behavior of nano-modified concrete, protected using conventional/hybrid techniques and cured under -10 and -20°C, to numerically predict and correlate between concrete temperature stratification and the quality
of the concrete-steel interface in terms of hydration development and bond strength.

- Contributing practical outcomes suitable for updating construction codes and specifications for concrete such as ACI 306R (2016) and CSA A23.1 (2019) with a measurable impact on the technical community. Optimized cold weather nano-modified concrete with CWAS protected using the hybrid strategy, which do not involve voluminous enclosures and continual heating, will enable prolonging construction seasons for most of the year. This will lead to less congested work schedules and discomfort time to the public in summer, which will effectively contribute to the continual development of sustainable infrastructure in cold regions such as Canada by decreasing project budgets, save on energy consumption and reduce adverse environmental impact.

1.6 Structure of the Thesis

This thesis consists of eight chapters as described below:

- Chapter 1 provides a brief description for the main problem statement and contributions of the proposed research.
- Chapter 2 provides a comprehensive literature review on different aspects of cold weather concreting approaches, CWAS, innovative materials, and comparison between codes and various curing methods.
- Chapter 3 and 4 present the results and discussion of the statistical models and optimization analysis to identify concrete mixtures to be used for cold weather applications such as repair activities for two different curing scenarios [constant freezing temperature -5°C and cyclic freezing/low temperatures (-5/5°C)].
Chapter 5 presents the results and discussion of the performance of different nano-modified and nano-modified fly ash concrete mixtures for repair applications of concrete pavements at mild low temperatures (down to -5°C).

Chapter 6 presents the results and discussion of using different types of cement, nano-silica, fly ash and protection methods (conventional and hybrid systems using PCM mats) on the performance of concrete poured under low freezing temperatures (-10 to -20°C).

Chapter 7 focuses on developing analytical models to predict the effect of changing the mix design parameters, curing temperature as well protection methods on concrete heat evolution and concrete-steel bond strength development and the correlation between heat generated at concrete-steel interface, hydration development and mechanical properties of concrete.

Chapter 8 contains a summary of the major findings and significant conclusions of this thesis as well as recommendations for future research.
CHAPTER 2: LITERATURE REVIEW

Cold weather concreting is one of the most challenging problems that face concrete practitioners in North America. According to ACI 306R (2016) and CSA A23.1/A23.2 (2019), cold weather is when air temperature has fallen or expected to fall below 4 or 5°C during the protection period required for concrete to achieve mechanical and physical properties that can resist the effect of being exposed to such harsh conditions. The hydration reaction between cement and water, which is responsible for concrete mechanical, physical and microstructural properties, depends mainly on temperature and humidity conditions. It has been postulated that the hydration process theoretically ceases at -2.8°C and (Ratinov and Rozenberg 1996; Korhonen et al. 1992), due to freezing of mixing water and consequently the placed concrete will suffer from durability issues and early deterioration. Furthermore, freezable water inside capillary pores expands by 9% when it turns into ice, resulting in hydraulic and osmotic stresses (Polat 2016) within immature cement paste, leading the loss of 40%, 70% and 60% of concrete compressive and bond strengths as well as freeze-thaw resistance (Karagöl et al. 2015; Rixom and Mailvaganam 2002; Cai and Liu 1998; Pigeon et al. 1991). Consequently, concrete elements will fail target its service life performance and purpose if not protected and cured at appropriate temperatures (> 10°C). Till date, cold weather still poses various challenges to concrete practitioners in cold regions in terms of placement, curing, protection and achieving target performance criteria.

Air temperature in most Canadian provinces remains well below zero from October to March, resulting in delays of vital infrastructural projects and maintenance operations, busy summer seasons with construction activities, and disruption to the comfort of the public with considerable socioeconomic losses. ACI 306R (2016) and
CSA A23.1/A23.2 (2019) different options to deal with cold weather concreting by preventing freezing of concrete at early ages, maintaining adequate strength development and reducing the potential for thermal cracking. These include heating of concrete ingredients like water and aggregates, using enclosures and providing the construction site with normal environmental conditions for concreting, using additional amount of cement or high early strength (HE) cement (Type III) and the use of protective insulations. These mentioned practices can offer the concrete the environment to continue hydration and develop the required strength. However, they will incur extra time and costs due to the consumption of huge amounts of energy in addition to the required high-skilled labor to deal with enclosures construction. Therefore, there has been need to investigate and discover other approaches to overcome the challenges of placing concrete under low temperatures. This literature review introduces code provisions in North America, the up-to-date knowledge on cold weather concreting, mixtures components, new inventions and methods of concrete curing under low temperatures.

2.1 Construction Practices and Codes Provisions in North America

Concrete practitioners in North America typically follow ACI and/or CSA documents. When placing concrete under cold weather and against cold surfaces, they are often directed to Guide to Cold Weather Concreting (ACI 306R 2016), Standard Specification for Cold Weather Concreting (ACI 306.1 1990), Specifications for Structural Concrete (ACI 301 2016) and Concrete materials and methods of concrete construction (CSA A23.1 2019). The main objective of these standards and guides is to prevent the early concrete damage due to freezing of mixing water. However, there are contradictions and discrepancies in cold weather concreting strategies and definitions mentioned in these documents. For instance, both ACI 306R (2016) and CSA A23.1 (2019) define the cold
weather as when the air temperature is expected to fall below 4°C and 5°C, respectively during the protection period of concrete. While ACI 301 (2016) and ACI 306.1 (1990) define the cold weather as when more than three successive days the average daily temperature drops below 4°C and if a temperature of 10°C or higher occur for more than half of any day, the period shall no longer considered as cold weather.

2.1.1 Materials

Both ACI 301 (2016) and CSA A23.1 (2019) do not put explicit constrains on cold weather concreting materials. However, CSA A23.1 (2019) stipulates target strength values within a specific period of time and maximum water-to-cement ratio (w/c) based on the exposure class of the structure. On the other hand, ACI 306R (2016) recommends to use HE cement, high cement content (without specifying a minimum cement content) and accelerators to speed up concrete setting time and achieve the compressive strength required to resist freezing and thawing cycles within a reasonable time span. In addition, low w/c mixtures with lower slump values are recommended to prevent excessive water bleeding, which can amplify the consequences of freezing-thawing cycles. It is also mentioned that cold weather admixture systems (CWAS) complying with ASTM C1622/C1622M (2016), antifreeze and/accelerating admixtures, can mitigate the effect of low temperatures on concrete placement and strength development by depressing the freezing point of mixing water down to -5°C; however, no specific recommendations on constituent materials are given below this temperature.

2.1.2 Construction Precautions and Protection/Curing Methods

2.1.2.1 Mixing and Transportation

Regarding the limitations on mixing temperatures, ACI 306R (2016) is the only document which addresses this aspect based on the concrete element thickness.
-300 mm to more than 1800 mm] and air temperature [above -1°C to below -18°C). The minimum concrete temperature as mixed ranges from 7 to 21°C, while the maximum temperature ranges from 16 to 30°C. An efficient way to reach the target mixing temperatures of concrete is by heating mixing water and aggregates. Heating mixing water and aggregates to 60 and 40°C, respectively can produce concrete with the recommended mixing temperature (ACI 306R 2016). Comparatively, it is stated that heating mixing water and aggregates above 80 and 65°C, respectively can result in flash setting of concrete (ACI 306R 2016). It is worth noting that, using heated materials may cause cement conglomerates, rapid setting of concrete and negative effects on the air entrainment admixtures performance resulting in marked reduction in concrete resistance to freezing-thawing (ACI 306R 2016). It is also very important to consider the temperature loss of the concrete during delivery and handling. ACI 306R (2016) provides useful equations to estimate concrete internal temperature as well as heat loss during the transportation process based on cement, water and aggregates properties.

2.1.2.2 Placement

All the aforementioned documents (code/specifications/guide) have limitations on the minimum and maximum placement temperatures. This is defined as the internal temperature of freshly mixed concrete in either the transporting equipment or the forms after discharge provided that the measuring sensor has a clear concrete cover of 75 mm in all directions (ASTM C1064/C1064M 2017), based on the thickness of the concrete element regardless of the adiabatic conditions. However, there are differences among ACI and CSA documents stipulations. For example, the minimum and maximum placement temperatures for a concrete element with a thickness of 300 mm based on ACI documents (ACI 306R 2016; ACI 301 2016; ACI 306.1 1990) are 13°C and 24°C,
respectively. Whereas these temperatures in CSA A23.1 (2019) are 10 and 32°C, respectively for the same concrete element thickness. The upper limits of placement temperatures are set to avoid high rates of heat loss, due to larger differential temperature between concrete and air temperature, significant reduction in setting times, increased slump loss rate and excessive plastic shrinkage cracks (ACI 306R 2016). In addition, higher placement temperatures require more water content to alleviate the evaporation of mixing water due to concrete high internal heat, which contradicts the ACI 306R (2016) recommendations for reduction of w/c in cold weather concrete.

All the mentioned documents are concerned about the placement temperatures and their maintenance. Thus, these documents recommend to do conditioning procedures and preparation before casting. For this purpose, it is stated that any surfaces, bases, and subgrades that will receive concrete should be free of ice or snow. Also, it is recommended to maintain the temperature of any surface in contact with concrete at 0°C to the temperature of the placed concrete to avoid inconsistent setting, plastic shrinkage cracking and rapid moisture loss. In addition, the use of calcium chloride as de-icing salt on surfaces is not permitted to avoid durability issues such as corrosion of steel reinforcement and oxychloride formation. Moreover, ACI 301 (2016) stipulates that any surface that will be in contact with concrete shall be heated to at least 1.7°C. While according to ACI 306.1 (1990), it is required to heat massive metallic embedments above freezing temperature, but it does not provide any information or definition for the term “massive embedments”. Recently, ACI 306R (2016) recommends not to heat any embedments including bars or rebar unless the air temperature is below -12°C. Embedments with cross-sectional area of 2580 mm² should be heated to above 0°C. Reinforcing bars smaller than No. 57 are not considered massive embedments. These
numbers were based on an experimental study conducted by Kozikowski et al. (2014a). Furthermore, it is stated that concrete embedments can be heated to temperature not to cause any thermal shock or ice formation in the concrete-embedments interface depending on the placed concrete temperature or any other external source such as hot air. Moreover, ACI 306R- (2016) recommends to heat concrete slab subgrade to be above freezing temperature (0°C). Then, it is recommended to place insulation directly after the subgrade is re-compacted to protect it from dropping below 0°C. The differential temperature between concrete and soil-on-ground is recommended to be less than 11°C.

2.1.2.3 Curing and Protection

For protection and curing methods, all ACI and CSA documents recommend heating to protect freshly placed concrete from freezing, and maintain an internal temperature of at least 5 to 10°C. Thus, temporary heated enclosures are constructed to adjust surrounding/air temperature to normal conditions (i.e. 10 to 20°C) to ensure continuity of hydration reactions in cement paste. Indirect and hydronic heaters are recommended to force the exhaust gases outside the enclosure to prevent carbonation of the fresh concrete. Heating concrete internally, complying with concrete internal temperature requirements, through embedded heat transfer tubing systems is also mentioned in ACI 306R (2016). However, such heating practices consume additional energy and resources. They require more labor and coverage materials to construct the enclosures and maintain them, in addition to the negative environmental impact due to CO₂ emissions.

The use of insulation blankets/covers is also mentioned in both ACI and CSA documents. ACI 306R (2016) provides different insulation grades (based on the R-Value: capacity of an insulating material to resist heat flow; higher numbers designate greater efficiency) to protect freshly poured concrete under cold weather considering ambient
temperature, concrete thickness, cement content, target concrete surface temperature as well as concrete location in terms of being in contact with ground or not.

Regarding the protection period, ACI 306.1 (1990) stipulates minimum protection period of three days, and it can be reduced to two days by using HE cement, extra 60 kg/m$^3$ of cement, or accelerating admixtures. ACI 301- (2016) stipulates a curing period of 7 days unless otherwise specified. In ACI 306R (2016), the protection period and forms removal depend mainly on concrete elements exposure and loading condition as well as the target strength during and after the protection period. CSA A23.1 (2019) provides three different methods of curing according to the exposure class of the structure and inclusion of supplementary cementing materials. In these three methods of curing, a minimum internal temperature of concrete (10°C) must be maintained during the required curing period.

2.1.2.4 Post Curing

Another difference between ACI documents (ACI 306R 2016; ACI 301 2016; ACI 306.1 1990) and CSA code (CSA A23.1 2019) is the concrete temperature gradient after the protection period which can lead to thermal stresses and cracking. According to ACI documents, the differential temperature depends only on concrete element thickness, while according to CSA code, it additionally depends on the length/thickness of the element to its height ratio. For example, according to ACI documents, a 300 mm concrete element surface temperature drop should not exceed 28°C after one day of the end of the protection period, while according to CSA the surface-ambient difference in temperature is limited between 29°C and 12°C if the length-to-height ratio is in between 0 to 20. Note that ‘0’ refers to very high and narrow structural elements such as columns.
Moreover, ACI 306R (2016) recommends that fresh concrete should not be exposed to single or multiple freezing and thawing cycles till it gains a compressive strength of at least 3.5 and 24.5 MPa, respectively. These reported values define the required concrete protection period under winter conditions to develop the required strength for safe removal of forms. Most well-proportioned concrete mixtures can reach 3.5 MPa after two days of curing, which is a benchmark for adequate cement hydration at early-age (Kozikowski et al. (2014b). The freezing of mixing water prior to reaching 3.5 MPa strength can lead to concrete durability issues as well as deficient development in hardened properties resulting in rapid deterioration. Comparatively, CSA A23.1 (2016) states that concrete can resist frost damage once it reaches 7 MPa compressive, which is twice the value in ACI 306R (2016); however, no distinction is made between single and multiple cycles in this CSA document. Table 2.1 summarizes the discrepancies among the above-mentioned documents.
Table 2.1: Comparison between North American codes/specifications/guidelines with respect to cold weather concreting

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Definition of cold weather</strong></td>
<td>5°C</td>
<td>4°C for three successive days</td>
<td>4°C for three successive days</td>
<td>4°C</td>
<td>--</td>
</tr>
<tr>
<td><strong>Materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Low w/c</td>
</tr>
<tr>
<td></td>
<td>Limitations on the w/c and min. strength based on the exposure class.</td>
<td>Limitations on the w/c and min. strength based on the exposure class.</td>
<td>--</td>
<td>High cement content</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Type III cement Accelerator</td>
</tr>
<tr>
<td><strong>Mixing temperatures</strong></td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Depends on element thickness</td>
<td>Supplier</td>
</tr>
<tr>
<td></td>
<td>Snow and ice shall be removed- no Calcium Chloride as de-icing salt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Preparation of forms/surfaces</strong></td>
<td>Nothing to affect min. placement temperature</td>
<td>Heat surfaces to at least 1.7°C</td>
<td>Massive embeddings shall be heated</td>
<td>Formwork or embedsments with area above 2580 mm² to be heated to at least 0°C. Otherwise all embeddings should be heated if the temperature is below -12°C.</td>
<td>Contractor</td>
</tr>
<tr>
<td><strong>Min. concrete placement temp.</strong></td>
<td>Depends on Element thickness</td>
<td>Depends on Element thickness</td>
<td>Depends on Element thickness</td>
<td>Depends on Element thickness</td>
<td>Supplier</td>
</tr>
<tr>
<td><strong>Max. concrete placement temp.</strong></td>
<td>Depends on Element thickness</td>
<td>Min temp + 11°C</td>
<td>Min temp + 11°C</td>
<td>Min temp +11°C</td>
<td>Supplier</td>
</tr>
</tbody>
</table>

*These responsibilities comply with CSA A23.1 (2019) stipulations. Please refer to the document for further details.
Table 2.1 Cont’d: Comparison between North American codes/specifications/guidelines with respect to cold weather concreting

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Protection methods</td>
<td>Enclosures with heating, insulation or coverings</td>
<td>Enclosures with heating, coverings</td>
<td>Enclosures with heating</td>
<td>Enclosures with heating, internal heating, insulation or coverings</td>
<td>Contractor</td>
</tr>
<tr>
<td>Protection period</td>
<td>Depends on the exposure class</td>
<td>7 days unless otherwise specified</td>
<td>3 days and it can be reduced to 2 days</td>
<td>Depends on the service conditions of the structure and target strength</td>
<td>Contractor</td>
</tr>
<tr>
<td>Differential temperature</td>
<td>Depends on element thickness and length to height ratio</td>
<td>Depends on element thickness</td>
<td>Depends on element thickness</td>
<td>Depends on element thickness</td>
<td>Contractor</td>
</tr>
<tr>
<td>Resistance to frost Action</td>
<td>7 MPa</td>
<td>--</td>
<td>--</td>
<td>3.5 MPa for one cycle, and 24.5 MPa for multiple cycles</td>
<td>Contractor</td>
</tr>
</tbody>
</table>

*These responsibilities comply with CSA A23.1 (2019) stipulations. Please refer to the document for further details.

2.2 Cold Weather Admixture System (CWAS)

There has been a motivation to discover alternative or additional solutions to traditional curing and site conditioning procedures such as using enclosures because of the aforementioned limitations like energy consumption and carbon dioxide emissions. The estimated cost to thermally protect concrete during construction from freezing was $800 million in 1991 and nowadays it reached $1 billion per year (Barna et al. 2011). In addition, enclosures are impractical in some construction works including lengthy horizontal construction such as pavements. Moreover, the discomfort of workers
operating under these conditions and their needs to finish the work as fast as possible make accelerating concrete setting time urgent. Therefore, finding another approach for cold weather concreting such as using new materials and admixtures in concrete mixtures to overcome such severe conditions is very challenging for scientist, ready-mix concrete suppliers and contractors.

Using chemical admixtures such as antifreeze admixtures and accelerators can depress the freezing point of mixing water and accelerate the hydration process of cement (Kozikowski et al. 2014b). Thus, these antifreeze admixtures allow concrete to be placed and cured at below-freezing temperatures without weakening and deterioration of concrete through ice formation, thus it offers a new approach to cast concrete in cold weather without the need for enclosures nor artificial heating. CWAS has the potential to save more than 50% of the cost required to place normal concrete under low temperatures (Korhonen et al. 1997) which makes CWAS an energy-efficient alternative solution. However, when using new chemical admixtures all the concerns will go toward its cost and effect on concrete fresh and hardened properties (Korhonen et al. 1997). For example, in the early 1950’s, calcium chloride and sodium chloride were the introduced materials to prevent freezing of mixing water under cold weather, but using this type of admixtures led to corrosion problems (Ratinov and Rozenberg 1996). However, using these types of admixtures proved to produce concrete with adequate strength development rate (Mironov et al. 1976). Afterwards, different studies (Demirboğa et al. 2014; Cullu and Arslan 2013; Karagöl et al. 2013) have been introduced to investigate the effect of using different non-chloride based admixtures such as potash, calcium nitrite, calcium nitrate, sodium nitrate, urea, and combination between them on concrete produced under low and freezing temperatures. Table 2.2 shows approximate eutectic
temperatures, which is the intersection temperature between liquidus and solidus curves in any material’s phase diagram, of most common antifreeze admixtures and their concentration in solution.

Table 2.2: Eutectic temperatures of exemplar anti-freeze admixtures. (Nmai 1998; Korhonen 1990)

<table>
<thead>
<tr>
<th>Percentage in Solution (%)</th>
<th>Eutectic Temperature (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia (NH₄OH)</td>
<td>61</td>
</tr>
<tr>
<td>Calcium chloride (CaCl₂)</td>
<td>30</td>
</tr>
<tr>
<td>Potassium carbonate (K₂CO₃)</td>
<td>40</td>
</tr>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>23</td>
</tr>
<tr>
<td>Sodium nitrite (NaNO₂)</td>
<td>28</td>
</tr>
<tr>
<td>Calcium nitrite (Ca(NO₃)₂)</td>
<td>34</td>
</tr>
<tr>
<td>Calcium nitrate (Ca(NO₃)₂)</td>
<td>35</td>
</tr>
<tr>
<td>Sodium sulphate (Na₂SO₄)</td>
<td>13</td>
</tr>
<tr>
<td>Urea (CH₄N₂O)</td>
<td>31</td>
</tr>
<tr>
<td>Calcium-Nitrate-Nitrate</td>
<td>35</td>
</tr>
<tr>
<td>Calcium-Chloride-Nitrite-Nitrate</td>
<td>30</td>
</tr>
</tbody>
</table>

2.2.1 Effect of CWAS on Concrete Fresh Properties

2.2.1.1 Workability

Workability of concrete is considered the key factor that will determine the effort required to keep concrete homogenous during mixing, placing, compaction and finishing. In order to produce high quality concrete, it is better for fresh concrete to have suitable consistency for the application (Tattersall 2003). Otherwise, insufficient workability may cause compressive strength reductions and durability issues. It was reported that concrete will lose 2 cm of its slump for every 11℃ decrease in its temperature (Tattersall 2003). ACI 306R (2016) recommends low slump values in cold weather concreting to reduce the possibility of water bleeding on concrete surface. Excess water bleeding will weaken the strength and frost resistance of the surface leading to durability issues like surface scaling.
Chapter 2: Literature Review

(ACI 306R 2016; Korhonen et al. 1990). Therefore, to accept CWAS into practice, the modified mixtures must give almost the same performance as normal concrete (Barna et al. 2011).

Karagöl et al. (2013) reported that using 6% by wt. of cement calcium nitrate increased concrete slump from 40 to 60 mm. This conclusion was attributed to the behavior of calcium nitrate as a plasticizer; thus, it increased the workability of concrete. Moreover, it was revealed that increasing calcium nitrate dosage from 4 to 8% by wt. of cement slightly increased concrete slump whether the concrete was air entrained or not (Franke et al. 2014). In addition, Karagol et al. (2015) reported that using 9% calcium nitrate, 9% urea and combination of 4.5% urea + 4.5% calcium nitrate by weight of cement as antifreeze admixtures increased the workability of concrete from 40 mm to 60, 120 and 220 mm at room temperature, respectively. Furthermore, Arslan et al. (2011) concluded that concrete workability increases when increasing different antifreeze admixtures dosages (polyhydroxy amine, calcium nitrate and 30% calcium nitrate+5% hydroxy ethoxy amine). For example, when increasing the percentage of calcium nitrate from 0.5% to 1, 1.5 and 2% wt. of cement, concrete workability increased from 70 to 80, 95 and 100 mm, respectively. Moreover, in the same study, the Ve-Be results decreased from 12 to 10, 5 and 4 sn when using the same percentages of calcium nitrate, respectively. Wang et al. (2012) reported that using 4 and 5 % of antifreeze admixtures (BM) had no effect on concrete workability. However, the base of this antifreeze was not mentioned in the study but the composition of it was mentioned as follows : lowering freezing point component (2.5%) + air entraining component (0.1%) + oxidant component (0.7%) + preventing condensation and carbonization component (0.3%) + increased ph value component (0.4%). It is worth noting that all of the above-mentioned
studies focused on the effect of using antifreeze admixtures on concrete workability under normal temperatures neglecting the real practice of mixing and placing concrete under low temperatures.

2.2.1.2 Setting time and heat of hydration

Reducing the setting time of concrete leads to reduction of the protection period and minimizing the possibility of mixing water freezing. At freezing temperatures, concrete sets at slower rate which adversely affects the construction schedule and increase time and manpower to finish the job. Tatersall (2003) reported an approximate 30% to 35% increase in setting time for every 6°C decrease in ambient temperature. ACI 306R (2016) recommends in cold weather concreting to use extra cement, rapid setting cement or accelerating admixtures to reduce the setting time of the concrete to shorten the protection period. The use of antifreeze admixtures can depress the freezing point of mixing water and prevent ice formation, thus concrete hydration may continue leading to faster hardening and setting time of concrete, and consequently faster strength gain.

Korhonen and Orchino (2001) reported that using 2% by wt. of cement calcium chloride could shorten the initial and final setting times of concrete from 192 and 270 min to 162 and 264 min, respectively at 19°C. Moreover, Wang et al. (2012) stated that using 4 and 5 % by wt. of cement antifreeze admixtures (BM) decreased the initial setting times from 413 to 336 and 315 min, respectively, while the final setting times were reduced from 585 to 503 and 482 min, respectively. Furthermore, Ratinov and Rozenberg (1996) demonstrated that increasing the percentage of (calcium+sodium chloride) from 10 to 15% reduced the initial and final setting times of cement mortar from 105 to 10 min and from 135 to 22 min, respectively. In addition, Cheeseman and Asavapisit (1999) proved that increasing chloride content in concrete can lead to high early heat of
hydration and cracking due to the acceleration effect. Furthermore, the same acceleration effect and high early heat of hydration were reported by using potash (K₂CO₃) as an antifreeze admixture (Nmai 1998; Ratinov and Rozenberg 1996). On the other side, urea was proved to work as a retarder due to it is reaction with water which absorbs heat, leading to slower rates in cement hydration (Demirboğa et al. 2014; Mwaluwinga et al. 1997). It is worth noting that, the aforementioned studies monitored concrete setting times under room temperature, neglecting the influence of the real cold weather conditions (low temperatures and wind).

2.2.1.3 Air content

Regardless concrete mix design parameters, high air content, typically 4-8% by volume of concrete, is essential to enhance concrete resistance to freezing and thawing cycles. Entrained air voids can partially relief the hydraulic and osmotic pressures associated with freezing and thawing cycles. It was reported that the optimum percentage of air voids for concrete mixtures exposed to freezing and thawing cycles is (6%±1) (Barna et al. 2011). Franke et al. (2014) reported that using 4 and 8 % of calcium nitrate as antifreeze admixtures has no effect on neither the capillary pores nor the air-entrained voids of fresh concrete at 20℃. While, Arslan et al. (2011) concluded that concrete air content increased by the increase of the dosage of the antifreeze admixture at room temperature. ACI 306R (2016) stated that air entraining admixtures lose their effectiveness due to the contact with hot mixing water which makes heating mixture ingredients such as aggregate and water to high temperatures harmful to concrete resistance to freezing and thawing and promote the need to use CWAS.

Based on the aforementioned studies, it can be deduced that the effects of using antifreeze admixtures on concrete fresh properties such as setting times are uncertain.
Therefore, concrete fresh properties should be investigated considering the effect of low temperatures on mixing and placing concrete incorporating CWAS.

2.2.2 Effect of CWAS on Concrete Mechanical Properties

2.2.2.1 Compressive Strength

According to ACI 306R (2016), concrete should reach 3.5, 24.5 MPa before being exposed to one single or multiple cycles of freezing and thawing, respectively. Therefore, the effect of using CWAS on concrete rate of gaining both early and final design strengths is very important under low temperatures. However, it was reported that not only the strength gain of concrete containing CWAS continue after 28 days as normal concrete but also antifreeze admixtures like calcium nitrate and calcium nitrite help concrete to gain strength faster due to their acceleration effect (Korhonen 1990).

Many studies have been introduced until 1985 to investigate the effect of using different admixtures on compressive strength of cold weather concrete. Then, antifreeze admixtures were mentioned in an International Union of Testing and Research Laboratories for Materials and Structures (RILEM) publication in the field of cold weather concreting (Kukko abd Koskinen 1988). In this publication, a table of seven antifreeze admixtures was presented with their low-temperature strengths as percentage of control samples strength cured under normal conditions for 28 days (Table 2.3). However, RILEM did not give any mixture proportions, mixing procedures or curing method and stated that this table was only a guide and recommended to cast trial mixes containing antifreeze admixture in the laboratory before preforming any field application.

In 1990, Korhonen (1990) presented the different percentages of antifreeze admixtures, even admixtures which were not referenced by RILEM, that had been used up to 1990 and their effect on strength in comparison to control samples that had been cured under
normal conditions for 28 days. Table 2.4 shows the most common antifreeze admixtures used up to date and their effect on concrete strength.

Table 2.3: RILEM mentioned antifreeze admixtures.

<table>
<thead>
<tr>
<th>Admixture Composition</th>
<th>Mean Temperature</th>
<th>*Strength % (days)</th>
<th>7</th>
<th>14</th>
<th>28</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% NaNO₂</td>
<td>-5</td>
<td></td>
<td>30</td>
<td>50</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td>75% Ca(NO₃)₂ + 25% CH₄N₂O</td>
<td>-10</td>
<td></td>
<td>20</td>
<td>35</td>
<td>55</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>-15</td>
<td></td>
<td>10</td>
<td>25</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>100% NaCl</td>
<td>-5</td>
<td></td>
<td>35</td>
<td>65</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>70% NaCl+30% CaCl₂</td>
<td>-10</td>
<td></td>
<td>25</td>
<td>35</td>
<td>45</td>
<td>70</td>
</tr>
<tr>
<td>40% NaCl+60% CaCl₂</td>
<td>-15</td>
<td></td>
<td>15</td>
<td>25</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>50% NaNO₂+50% CaCl₂</td>
<td>-5</td>
<td></td>
<td>40</td>
<td>60</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>-10</td>
<td></td>
<td>25</td>
<td>40</td>
<td>50</td>
<td>80</td>
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<td>20</td>
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<tr>
<td></td>
<td>-20</td>
<td></td>
<td>15</td>
<td>30</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>100% K₂CO₃</td>
<td>-5</td>
<td></td>
<td>50</td>
<td>65</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>-10</td>
<td></td>
<td>30</td>
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<td>90</td>
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<td>-25</td>
<td></td>
<td>20</td>
<td>30</td>
<td>50</td>
<td>60</td>
</tr>
</tbody>
</table>

*Relative to control samples cured at room temperature for 28 days.

Karagöl et al. (2013) reported an increase in compressive strength from 7.92, 7.81, 6.97 and 6.55 to 35.93, 18.23, 16.1 and 15.53 MPa after 7 days of curing at -5, -10, -15 and -20°C respectively using 6% by mass of cement calcium nitrate. In addition, it was reported that even when the concrete specimens were cured in water for additional 7, 14 and 28 days, calcium nitrate samples always gave higher strength than plain concrete samples under the same curing conditions. Moreover, in the same study (Karagöl et al. 2013), the same initial curing period was increased from 7 days to be 14 and 28 days and the compressive strength was investigated before and after being exposed to water curing for another 7, 14 and 28 days. It worth noting that the calcium nitrate samples always gave the best performance in terms of strength. Moreover, Karagol et al. (2015) reported that concrete containing 9% calcium nitrate cured at -5°C could reach the same compressive strength as normal concrete cured under normal
conditions. However, there was a significant reduction of strength at -10, -15 and -20°C and concrete could not gain strength at acceptable rate. In addition, Arslan et al. (2011) reported that increasing the calcium nitrate percentage from 0.5 to 2% by wt. of cement increases concrete compressive strength from 16.12, 15.09, 14.95, 14.82 and 14.75 MPa to 18.29, 15.63, 15.52, 15.47 and 15.25 MPa at 0, -5, -10, -15 and -20°C, respectively.

Moreover, urea was reported to be adequate antifreeze admixture under low temperatures down to -5°C, hence Demirboga et al. (2014) investigated the effect of using 6% urea by wt. of cement on concrete samples compressive strength cured at -5, -10, -15 and -20°C for 7 and 14 days. In addition, the effect of extending the curing period for additional 7, 14 and 28 days in lime saturated water at 23±1.7°C on samples compressive strength was investigated. Generally, it was stated that using urea gave higher strength than control samples under all curing conditions and temperatures. Furthermore, Bennett et al. (1994) reported that compressive strength of concrete incorporating 10% urea by wt. of cement with 0.45 w/c and cured at 20, -5, -10, -20°C were 91, 88, 42, 0% of 28 days compressive strength of normally cured mixtures at 20°C, respectively. Korhonen (1999) presented another study to investigate the effect of using 3, 6 and 9% urea on concrete compressive strength. The 28 day compressive strengths of concrete containing 3, 6, 9% urea were 94.1, 98 and 92.2% at 20°C, 30, 38.6 and 60.8% at -5 °C and 13, 14.6 and 18.7% -10°C of 28 day compressive strength of control samples cured at 20°C, respectively. Furthermore, Korhonen and Orchino (1999) experimentally studied the effect of combining 4.5% urea and 1.5 % P20 (ready additive) on the compressive strength of concrete cured at different temperatures. The compressive strengths at 20, -5, -10°C were 28.1, 13.3 and 3.8 MPa at 7 days, 34.9, 22.2 and 9.3 MPa at 14 days and 37.6, 27.1 and 12.9 MPa at 28 days, respectively. It is worth noting that
the properties and the base of the ready additive P20 were not mentioned or defined. In addition, Wang et al. (2012) reported that using 4 and 5% of new type antifreeze (BM) produced concrete with compressive strength comparable to concrete cured under normal conditions of temperature and moisture.

From Tables 2.3 and 2.4, it can be seen that using antifreeze admixtures could maintain cement hydration and strength gain under low temperatures. The compressive strength may reach 100% of normal cured concrete within 90 days of curing under -5°C. Moreover, Korhonen (2002) reported that, based on quantitative X-ray analysis, percentages of the hydrated cement paste with w/c of 0.25 reached (44, 43, 17%) using 2% of NaNO$_2$ and (41, 46, 37%) using 10% of K$_2$CO$_3$ by cement weight under 0, -10, -20 ºC, respectively. While the control mix hydration percentages were 39, 20, 1% at the same temperatures, respectively. Therefore, it can be concluded that antifreeze admixtures not only depress the freezing point of water but also accelerate the hydration process and strength gain of concrete. However, it is stated that concrete produced using CWAS suffered from durability issues.

For instance, antifreeze admixtures with high alkalinity such as sodium-based CWAS may provoke alkali aggregate reaction (Ratinov and Rozenberg 1996; Korhonen, 1990) while Chloride-based admixtures may initiate corrosion of steel reinforcement (Ratinov and Rozenberg 1996; Korhonen, 1990) and cause decomposition and expansion of hardened paste by forming calcium oxychloride (Peterson et al. 2013). In addition, potash was found to negatively affect concrete microstructure and resistance to freezing-thawing cycles (Ratinov and Rozenberg 1996; Korhonen, 1990), while urea was reported to act as a retarder (Ratinov and Rozenberg 1996; Korhonen, 1990). Comparatively, calcium nitrate, calcium nitrite and combinations were reported to be more efficient in
terms of accelerating the kinetics of cement hydration, and thus the development in concrete strength (Nmai, 1998; Ratinov and Rozenberg 1996; Korhonen, 1990). However, it was reported that the microstructure of concrete containing 6% calcium nitrate were adversely affected after being exposed to only 28 freezing-thawing cycles resulting in significant reduction in compressive strength and increase in water absorption (Polat 2016). Moreover, concrete incorporating high dosages (more than 6%) of calcium nitrate and/or calcium nitrite was reported to be vulnerable to shrinkage cracking (Korhonen et al. 1997).
Table 2.4: The most common antifreeze admixtures up to 2018.

<table>
<thead>
<tr>
<th>Admixture</th>
<th>Percentage by Weight of Cement</th>
<th>Temperature (°C)</th>
<th>*Strength (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7</td>
<td>-15</td>
<td>50</td>
<td>(Arslan et al. 2011; Kukko and Koshinen 1988; Mironov 1977; Mironov et al. 1976; Darrington 1967; Blenkinsop 1963; Rapp 1935)</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.7</td>
<td>-5</td>
<td>80</td>
<td>(Arslan et al. 2011; Kukko and Koshinen 1988; Mironov et al. 1976; Darrington 1967)</td>
</tr>
<tr>
<td>NaNO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6</td>
<td>-5</td>
<td>70</td>
<td>(Kivekäs et al. 1985; Mironov et al. 1976)</td>
</tr>
<tr>
<td>NaCl+CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7.7</td>
<td>-20</td>
<td>85</td>
<td>(Mironov 1977; Goncharova and Ivanov 1975)</td>
</tr>
<tr>
<td>NaNO&lt;sub&gt;2&lt;/sub&gt;+CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9</td>
<td>-20</td>
<td>42</td>
<td>(Kukko and Koshinen 1988; Kivekäs et al. 1985; Goncharova and Ivanov 1975)</td>
</tr>
<tr>
<td>Ca(NO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; + CO(NH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9.5</td>
<td>-5</td>
<td>80</td>
<td>(Karagöl et al. 2015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10</td>
<td>55</td>
<td>(Karagöl et al. 2015; Kukko and Koshinen 1988; Goluboy et al. 1974)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-15</td>
<td>35</td>
<td>(Kukko and Koshinen 1988; Goncharova and Ivanov 1975; Goluboy et al. 1974)</td>
</tr>
<tr>
<td>Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; + CO(NH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>8.8</td>
<td>-10</td>
<td>34</td>
<td>(Kivekäs et al. 1985; Goncharova and Ivanov 1975; Goluboy et al. 1974)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-20</td>
<td>29</td>
<td>(Kivekäs et al. 1985; Goncharova and Ivanov 1975; Goluboy et al. 1974)</td>
</tr>
<tr>
<td>Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>6.5</td>
<td>-10</td>
<td>56</td>
<td>(Kivekäs et al. 1985; Goncharova and Ivanov 1975; Goluboy et al. 1974)</td>
</tr>
<tr>
<td>Ca(NO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;/NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; + CaCl&lt;sub&gt;2&lt;/sub&gt; +CO(NH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9</td>
<td>-20</td>
<td>61</td>
<td>(Goncharova and Ivanov 1975; Goluboy et al. 1974)</td>
</tr>
<tr>
<td>Ca(NO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;/NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; + CaCl&lt;sub&gt;2&lt;/sub&gt; +CO(NH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>11.5</td>
<td>-20</td>
<td>40</td>
<td>(Goncharova and Ivanov 1975; Goluboy et al. 1974)</td>
</tr>
</tbody>
</table>

*Relative to control samples cured at room temperature for 28 days.
Table 2.4 Cont’d: The most common antifreeze admixtures up to 2018.

<table>
<thead>
<tr>
<th>Admixture</th>
<th>Percentage by Weight of Cement</th>
<th>Temperature (℃)</th>
<th>*Strength (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(NH$_2$)$_2$</td>
<td>6</td>
<td>-5, -10</td>
<td>32, 14</td>
<td>(Demirboğa et al. 2014)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>-5, -10</td>
<td>56, 20</td>
<td>(Karagöl et al. 2015)</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>6</td>
<td>-5, -10</td>
<td>65, 21</td>
<td>(Karagöl et al. 2013)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>-5, -10</td>
<td>67, 11</td>
<td>(Karagöl et al. 2015)</td>
</tr>
</tbody>
</table>

*Relative to control samples cured at room temperature for 28 days.
2.2.2.2 Tensile Strength

Despite the importance of the tensile strength of concrete with respect to freezing and thawing resistance, few studies were published on this concrete property for concrete placed under low temperatures. It was stated that the tensile strength of concrete with different antifreeze admixtures was almost the same as reference concrete (Ratinov and Rozenberg 1996; Korhonen, 1990; Goncharova and Ivanov 1975). However, it was reported that using potash (K₂CO₃) as antifreeze admixture led to considerable decrease in tensile strength of concrete under low temperatures (Ratinov and Rozenberg 1996; Korhonen, 1990; Grapp et al. 1975). Cullu et al. (2013) investigated the effect of using 1% of calcium nitrate (KN) at 0, -5, -10, -15, -20 °C on concrete tensile strength. Moreover, polyhydroxy amine (PHA) and combination of calcium nitrate and hydroxyethylaminemixture (HEA) were also used as alternatives antifreeze admixtures calcium nitrate. Concrete samples were exposed to the aforementioned temperatures for 2 days before being cured for another 26 days at normal conditions of moisture and temperature until the 28 days. Generally, the tensile strength of concrete decreased with the reduction in the curing temperature, it reached 4.61, 3.58, 3.50, 3.48 and 3.44 MPa using KN, 5.25, 4, 3.81, 3.73 and 3.66 using HEA and 4.91, 3.92, 3.73, 3.61 and 3.57 using PHA at 0, -5, -10, -20°C, respectively.

2.2.2.3 Bond Strength

Bond strength of concrete can be significantly affected by frost damage. It was stated that concrete may lose 70% of its bond strength due to early frost (Rixom and Mailvaganam 2002). Schroeder and Wood (1996) investigated the effect of using calcium nitrite and sodium nitrite at dosages of 2% and 6% of the total cement mass, respectively on concrete (cement content of 370 kg/m³ and w/c of 0.48) bond strength with 20 mm steel
bars. After casting the specimens, using hot water (54°C) and room temperature steel bars, they were cured at -5 and -10°C for 28 days. The bond strengths of the different specimens after 15 days of curing were less than 1 MPa and increased to reach 6 MPa after 28 days.

2.2.3 Effect of CWAS on Concrete Durability

2.2.3.1 Freeze and thaw resistance

Using antifreeze admixtures can improve the freezing-thawing resistance of concrete by increasing the rate of strength gain at early age. Franke et al. (2014) investigated the effect of using 4 and 8% of calcium nitrate only, air entraining admixture (AE) only and combination between them on concrete resistance of freezing-thawing cycles. It was concluded that using AE is very important to produce concrete with high resistance to freezing and thawing, but it will affect negatively on concrete compressive strength. However, it was stated that calcium nitrate could help improving concrete compressive strength to overcome the reduction in strength due to the use of air entraining admixture. Furthermore, it was reported that calcium nitrate could help in the distribution of air voids and increasing the number of micro voids in favor of less macro voids. In addition, Mason and Schroeder (1996) reported that concrete containing different types of antifreeze admixtures could resist freezing and thawing cycles better than plain concrete cured under the same conditions. However, Polat (2016) reported that concrete mixtures, cured at -10/10°C regime, produced using 6% by wt. of cement urea and calcium nitrate as antifreeze admixtures, suffered from an average decrease of 33% in compressive strength and increase of 25% in water absorption after 28 cycles of freezing and thawing. Furthermore, mixture incorporating potash proved to have coarse paste structure and

Therefore, it can be concluded that choosing the proper antifreeze admixture and its dosage to be applied in CWAS is critical. It depends on many factors such as cement type and content, \( w/c \), mixture ingredients and ambient temperature. These admixtures could affect the durability of concrete, and accordingly its service life. CWAS uses combination of chemical admixtures like antifreeze admixtures to depress the freezing point of mixing water and enhance the rate of strength gain in early age to resist frost actions (Korhonen et al. 1997; Korhonen and Brook 1996). In addition, by using admixtures that contain the same ions as in the cement, they significantly accelerate the hydration process by increasing \( C_3S \) and \( \beta C_2S \) solubility (Ratinov and Rozenberg 1996). Electrolytes in contact with \( C_3S \) and \( C_2S \) change ionic strength and density of the pore solution (Ratinov and Rozenberg 1996). Therefore, cement paste surface area will increase leading to improvement in the contact zone between the paste and the aggregates (Ratinov and Rozenberg 1996). However, using some antifreeze admixtures may lead to increasing the temperature during concrete placement which may adversely affect the late age strength of concrete by provoking micro-cracks in microstructure of produced concrete (Ortiz et al. 2005). In addition, chloride or sodium based antifreeze admixtures may lead to durability issues such as corrosion and alkali aggregate reaction, respectively (Polat 2016; Karagöl et al. 2015; Karagöl et al. 2013; Nmai 1998; Ratinov and Rozenberg 1996; Korhonen, 1990). In addition, multiple studies reported the heterogeneous microstructure of concrete as well as strength loss of concrete containing Potash (Karagöl et al. 2015; Demirboğa et al. 2013; Korhonen 1999). Although multiple studies have been introduced to evaluate the performance of cold weather concrete incorporating
different antifreeze and accelerating admixtures with different dosages (up to 9%) at low temperatures (-5, -10, -15 and -20 °C), their long-term effects on concrete durability properties remain unknown (Powers and Helmuth 1953).

2.3 Nano-Materials in Cold Weather Construction

Recently, nano-materials have become one of the most efficacious research areas that encompasses different disciplines including civil engineering and construction materials. They have attracted the interest of scientists due to the new benefits of using particles in nanometer scale. They have the potential to re-engineer many existing products that function at unprecedented levels. Due to their ultrafine nature, they can enhance mechanical properties of concrete (Abd.El.Aleem et al. 2014; Haruehansapong et al. 2014). Furthermore, they can speed-up the kinetics of cement hydration, efficiently refine the pore structure of concrete, densify the interfacial transition zone between aggregates and cement paste and replace cement to reduce the emission of CO₂ (Kazempour et al. 2017; Gonzalez et al. 2016; Li et al. 2004). Among these materials, nano-silica proved to be one of the most important pozzolanic materials that has been significantly used in in the field of concrete research.

However, little number of studies have been done to investigate the effect of using these nano-materials on concrete under cold temperatures (Kazempour et al. 2017; Gonzalez et al. 2016; Behfania and Salemi 2013; Xu et al. 2012). In addition, these studies focused on the performance of concrete incorporating nano-materials under freezing condition after being cured at normal temperatures for 28 days overlooking the practical procedures in the field and the effect of cold weather on concrete placement and curing. Gonzalez et al. (2016) investigated the effect of using 1 and 2 % of nano-silica as partial replacement of cement with different w/c of 0.3 and 0.45 on concrete performance
after 324 freezing-thawing cycles. The presence of nano-silica in the concrete generated a denser and less permeable concrete consequently it reduced the deterioration of concrete due to the repetitive freezing-thawing cycles even in the presence of deicers. Moreover, Behfarnia and Salemi (2013) reported the effect of using up to 7% of nano-silica, 3% of nano-alumina as a partial replacement of cement on concrete mechanical properties and frost resistance after 300 cycles of freezing and thawing. It was concluded that using nano materials in concrete led to better results than normal plain concrete in terms of frost resistance and mechanical properties. It is worth noting that concrete incorporating nano-silica achieved higher strength values due to its high pozzolanic activity specially 5%. In addition, Xu et al. (2012) studied the effect of using 0.5, 1 and 2% of nano-CaCO₃ with 7% of fly ash, 10% of slag by wt. of cement and 1.5% of calcium nitrate by mass of cementitious materials on the compressive strength of high strength concrete cured in both standard temperature (21±1°C) and low temperature (6.5±1°C). It was concluded that nano-CaCO₃ affected negatively on the performance of concrete cured at low temperatures. Moreover, Kazempour et al. (2014) reported that nano silica could mitigate the performance issues such as delay of setting time and strength development of mortar cast and cured at low temperatures. hence the effect of using (2, 4 and 6% by mass of masonry cement) nano silica and nano alumina in masonry mortar mixtures, which were cast and cured at 5±1°C, on mortar fresh and hardened properties were investigated. It was reported that both 6% NA or 6% NS can mitigate the negative effects of low curing temperature on the different mixtures due to the acceleration of the kinetics of hydration and strength development especially nano-silica. Despite the focused research on using nano-particles in concrete, their ability to improve the performance of concrete incorporating CWAS under freezing temperatures (e.g. -5 to -20°C) to overcome the
technical limitations of cold weather concreting is largely unexplored and should be investigated.

2.4 Curing Methods

2.4.1 Innovative Curing Techniques

According to the authentic literature, concrete should not be placed under (4~5°C) without special precautions, hence both high performance and normal concretes cured at 10°C proved to lose 19% and 30% of their 28 day compressive strength respectively (Husem and Gozutok 2005; Korhonen and Orchino 1999). However, Korhonen and Orchino (1999) proved experimentally that concrete cured at low temperatures but well protected, could gain strength after 28 days higher than normal cured concrete reaching 10 and 15% gain in strength when applying 5 and 10°C curing temperatures, respectively. Nevertheless, in the same study it was reported that below zero temperatures, there was a great loss in strength and the properties of concrete were negatively affected.

Therefore, it has been essential to direct the research to develop specific techniques and methods to protect and cure concrete placed in cold weather. Won et al. (2016) fabricated an insulated gang form through integrating a rigid urethane board into ordinary gang form (Fig. 2.1). Concrete was then placed and cured in a chamber with a temperature varying between -5°C to -15°C. The form showed efficient temperature retention which improved the development of initial concrete strength. Choi et al. (2017) developed a heating sheet which exploited the exothermic reaction between quicklime and water, which was used to provide concrete with heat to accelerate the hydration process when the air temperature was -10°C as shown in Fig. 2.2. It was concluded that the 3 days compressive strength of mortar was close to 3.5 MPa which is required to
prevent frost damage (ACI 306R 2016), and it was three times higher than the compressive strength of mortar cured without such sheets.

Electric heating technologies, e.g. contact heating, electrode heating and induction heating (Krylov 1998), might be utilized as thermal treatment methods to accelerate the
hardening of concrete in winter. Electric contact heating method depends on supplying the heat from a heater to the surface of the concrete by radiation or conduction (Krylov 1998). While electrode-heating method depends on concrete resistivity by bringing it into electric circuit after being placed and heats up like any resistor when electric current passes through it (Krylov 1998). Induction heating method depends on generating electromagnetic field around a conductor by electric current passing through it. This electromagnetic field will induce Eddy currents and heat the concrete through heated steel reinforcement, steel formwork or embedded steel (Krylov 1998). For instance, McIntosh (1949) investigated the effect of heating newly poured concrete placed at refrigeration on its compressive strength by passing alternating electric current, provided by constant voltage, through it. It was concluded that concrete cast in such environment could reach compressive strength of 20 MPa after 24 h by applying this electrical method. However, it was reported that this method of curing has some difficulties like determining concrete resistance with time, hence concrete resistance was significantly affected by temperature rise due to heat emission from the hydration process and the continual improvement in the microstructure due to the continuous hydration.

2.4.2 Phase Changing Materials (PCMs)

PCMs are a combination of sensible-and-latent thermal energy storage materials which can store energy and emit it in the form of heat based on its solidifying and melting temperatures (Aguayo et al. 2016). Using phase change materials (PCMs) in concrete to store and release thermal energy is a new technique to limit the rise and drop in temperature. PCMs proved to have the potential to mitigate the risk of thermal cracking and increase concrete freezing and thawing resistance (Šavija and Shlangen 2016). There are several ways to produce concrete with PCMs like direct incorporation and micro
encapsulation which can be added directly during the mixing process of concrete (Liu et al. 2017; Aguayo et al. 2016; Shi et al 2014; Fernandes et al. 2014). Another way to apply PCMs in concrete is macro encapsulation through the saturation of lightweight aggregates pores (Farnam et al. 2015), nano-silica (Li et al. 2015), and carbon nanotubes (Dorigato et al. 2017) with liquid PCMs. PCMs can be classified as organic and inorganic. The Organic PCMs, Paraffin or non paraffin (Kalnæs and Jelle 2015), are preferable to be used with concrete because of their non corrosive nature and applicability (melting and solidifying temperatures range) (Kalnæs and Jelle 2015). While the inorganic PCMs are mainly metallic or salt hydrates. Metallic PCMs require extreme temperatures for crystallization and melting that are not within the in-service temperatures of concrete (Kalnæs and Jelle 2015). Whereas, the salt hydrates PCMs may react with cement hydration products causing deterioration in addition to their instability leading to thermal properties change after being exposed to freeze-thaw cycles due to the continual release/gain of water (Kalnæs and Jelle 2015; Ling and Poon 2013; Shi et al. 2011).

Although PCMs have a significant effect on mitigating concrete thermal cracks, there is a contradiction on its effect on concrete mechanical performance. For example, Yang et al. (2016) investigated the effect of using liquid phase-change material on the mechanical properties of concrete including elastic modulus and compressive strength. Moreover, the effect of solid and liquid phases on these mechanical properties was also investigated. It worth noting that, the base of this PCM was not provided but it was mentioned that its supporting structure was hydrophilic silica. The results revealed that increasing the percentage of PCMs led to a significant reduction in strength and elastic modulus. Moreover, concrete drying shrinkage increased with the increase in the PCMs content. The same behavior was noticed in different studies (Memon et al. 2015;
Eddhahak-Ouni et al. (2014). So, Yan et al. (2016) concluded that PCM concrete is not suitable for structural elements. However, Aguayo et al. (2016) investigated the effect of using two different paraffin based PCMs (PCM-E and PCM-M). The median particle size (d50) of PCM-E was 7 while for the PCM-M it was 10 mm. The two different PCMs were incorporated in concrete at different dosages of 5, 10, 15 and 20% as a partial replacement of the fine aggregates and their effect on mortar compressive and flexural strengths was investigated. It was concluded that using PCM-M significantly reduced the mortar mechanical properties especially with higher content of PCM. The 28 day compressive strength of the mortar reduced from 48 to 30 MPa after using 30% PCM-M. However, using PCM-E, especially 5 and 10%, enhanced the mortar mechanical properties. Hence the 28 day compressive strength of the mortar increased from 48 to 60 MPa with the use of 30% of PCM-M.

Despite the potential of PCM to control ice formation through heat fusion, thus aiding the continuity of cement hydration under cold weather by acting as an external curing agent, this strategy has not been explored yet.

2.5 Statistical Analysis and Design of Experiments

Optimization models for concrete mixtures based on statistical analysis have become much needed due to the existence of different admixtures, supplementary cementitious materials (SCMs), and curing methods which can affect the performance of concrete. Design of Experiments is a statistical method adopted to setup a matrix of experimental runs to evaluate the effect of different factors rather than one factor in addition to the interaction between these factors on certain responses which can ameliorate the understanding regarding specific conditions (Montgomery 2017; Ghezal and Khayat 2002). Various types of models were used for the optimization of concrete
mixtures such as factorial design, fractional factorial design and response surface method (RSM) (e.g. Akalin et al. 2010; Sonebi 2004; Soudki et al. 2001). These models depend mainly on fundamental statistical concepts such as regression analysis and analysis of variance (ANOVA) (Montgomery 2017). Among these different models, factorial design is the most common due to its applicability on any experimental setup. However, it has different drawbacks as the need for huge number of runs when a lot of factors are involved especially at three levels. Thus, this method maybe cost ineffective and time consumer. In addition, it is not necessary to perform all the required runs by the full factorial design to reach a model with high confidence and reliability (Montgomery 2017). Therefore, other modeling methods like response surface method are preferable when it comes to statistical analysis and optimization process considering high number of factors (3 or higher).

Response surface method (RSM) is a collection of statistical and mathematical techniques to develop and optimize process by analysing the effect of factors and their interaction on the response of interest. The main objective of RSM is to determine factors’ optimum conditions to reach a target response (Montgomery 2017). Central composite design (CCD) and face-centered composite design (FCCD) are the most used RSM design techniques which have been applied in different concrete studies (e.g. Al-alaily and Hassan 2016; Kang et al. 2010; Bayramov et al. 2004). The experimental sequence of both CCD and FCCD can be divided into three parts: full two level factorial part, two axial points for each factor part, and central point part (Montgomery 2017). As shown in Fig. 2.4 the difference between CCD and FCCD is the location of the axial points. For FCCD, the location of the axial points lay on the boundary of the design space while for CCD, they are located outside the design space at a constant distance.
Damle (2009) conducted a study to optimize the proportions of three different commercial admixture formulations (IPANEX, Rheobuild 1000, Na Silicate) for cold weather concreting. For this purpose, different factors were considered in the proposed statistical analysis model (RSM), varying the dosage of each admixture in addition to the temperature. The formulations were tested in terms of mortar physical and mechanical properties based on vicat setting time and compressive strength. The results of the experimental runs were analyzed and a characteristic behavior pattern was introduced over the range of the chosen admixture dosages. This pattern was used to predict the optimized dosage of the admixtures in each formulation based on a desirability function to reach a specific response value or option (maximum or minimum). It was concluded that changing any of the used admixtures dosage had a significant effect on the studied responses, especially the IPANEX which is a water tightening agent.

Moreover, Arslan et al. (2011) studied the effect of using three different antifreeze admixtures (calcium nitrate, combination of 30% calcium nitrate + 5% hydroxy ethoxy amin, and finally polyhydroxy amine) at different dosages (0.5%, 1%,...
1.5%, 2%) on concrete compressive strength after being cured for 48 h at different temperatures (0, -5, -10, -15 and -20°C). The results obtained from this study were evaluated based on three factor variance analysis technique with repeated measures in addition to nonlinear regression analysis to determine the effect of the studied factors (type of antifreeze, admixture ratio and temperature) on concrete compressive strength. It was concluded that all the chosen factors and their interactions were statistically significant (P-value <0.05). Moreover, the model’s equations, which were obtained through the nonlinear regression analysis, were introduced to correlate between the studied factors and concrete compressive strength.

Despite the importance of statistical analysis models to better understand and optimize different parameters such as CWAS type, nano-silica dosage and w/b, which may have a marked effect on concrete, cast and cured under cold weather, there is lack of information in this area.

2.6 Modeling of Concrete Internal Heat Evolution and Bond Strength

Fundamentally, the heat exchange between two objects, which is governed by the energy conservation and Fourier’s laws (Bergman et al. 2011, Mills 1999), occurs through one or combinations of three main mechanisms: conduction, convection and radiation. By definition, conduction is the energy transfer between different objects through direct contact, while convection is the transfer of energy through the movement of fluids, whereas the radiation is the energy transfer by electromagnetic emission such as light (Bergman et al. 2011; Mills 1999).

The excessive loss of heat on concrete element outer surfaces and edges under cold weather generates a temperature gradient in relation to the core, resulting in excessive shrinkage and tensile cracks, if the concrete element is constrained, resulting in
structural damage, especially with the presence of high dosages of CWAS (Korhonen 1990). As mentioned in section 2.1 Both ACI 306R (2016) and CSA A23.2 (2019) stipulate stringent limitations on concrete internal temperature gradient and the ambient temperature to avoid thermal shocks. Finite-element software can predict the internal temperature of concrete elements at any location under different environment conditions based on energy conservation and Fourier’s laws.

These predictions aid to identify the heat evolution with time and critical temperature locations such as concrete-cold metallic embedments interface, which indicates the formation of ice lens leading to bond failure. Many studies have presented the behavior of concrete, especially mass concrete (e.g. Yang et al. 2012; Wu and Luna 2001). However, the temperature profile development of concrete, particularly incorporating speciality materials such as nano-silica and CWAS, cast and cured under cold weather with respect to time is still uncertain. Furthermore, the influence of using innovative protection techniques such as PCMs to consistently maintain concrete internal heat gradient under cold temperatures needs to be numerically investigated.

Using finite-element software to model concrete-steel force-slip relationship proved to be efficient to simulate cracking pattern and to define deformation and stiffness of structures (Murcia-Delso and Benson Shing 2015). Multiple studies modeled the force-slip relationship of concrete cast and cured under normal temperatures (e.g. Murcia-Delso and Benson Shing 2015; Lundgren and Gylltoft 2000). In these models, the interaction between concrete and re-bars is defined by the bond stress-slip relation in the longitudinal bar direction. Indeed, the definition of this constitutive relation relies on experimental results, which requires time and effort. Swift et al. (1992) presented a finite-element model to capture the depth of ice lenses between concrete, under cold weather down to -
Chapter 2: Literature Review

60°C, and different sizes of steel bars under different conditions (heated and unheated) as well as the time required to melt the ice layers based on multiple concrete initial temperatures and thermal properties. In addition, Kozikowski et al. (2014a) presented an experimental program to predict concrete (initial temperature of 13°C) and different sizes of steel (initial temperature of -21°C) equilibrium temperatures, which were in close range with the predicted results of Swift et al. (1992). However, modeling the bond strength of concrete, cast and cured under cold weather, and steel re-bars as well as its correlation with the numerically developed heat at the concrete-steel interface is uncertain and needs further investigations.

2.7 Closure

Research on cold weather concreting has become active since more than 80 years because of the continual need to extend the construction period in cold regions. This literature review presented the current research progress and efforts on the topic of cold weather admixture systems and concreting using advanced materials and techniques in addition to the code provisions for casting concrete at low temperatures in North America. There is a general consensus that the hydration process of cement will significantly decrease at 5°C and stop at the freezing point of water. The mixing water will turn into ice and expand producing high tensile stresses on concrete, leading to cracking and deterioration. While, cold weather admixture systems (CWAS) have the potential to resolve the challenges of casting concrete in cold weather by depressing the freezing point of mixing water, accelerating the hydration rate of cement and enhancing the rate of strength gain in early age to resist freezing. However, some CWAS may lead to obvious losses in late age strength, freeze-thaw resistance, and excessive shrinkage. In addition, they may produce heterogeneous microstructure, and thus impair the
penetrability of concrete. Thus, various authorities (e.g. transportation agencies) have limited or no use of such systems, because of their adverse effects, and require construction of concrete elements in warmer periods. For example, surface works specifications in Manitoba mandate that construction of concrete pavements, curbs, sidewalks, etc. is between May 15 and September 30 neglecting the possibility of concrete placement under cold weather (CW3310 2015). Using nano-materials generally proved to be beneficial for concrete mechanical and physical properties. They can mitigate delay of setting time, enhance mechanical properties of concrete, refine the pore structure and densify the cementitious matrix. In addition, applying innovative curing techniques such as PCMs mat can enhance concrete microstructure and strength development through phase transition by releasing heat under freezing temperature that can help in delaying any ice formation, without the need to heat up the whole construction site which can reduce cost, time and energy for cold weather concreting. Despite the possible success of the CWAS, nano-materials and PCMs mats as curing agents to alleviate the obstacles of cold weather concreting, limited research has been done in this area. In addition, the long-term effects of using CWAS on nano-modified concrete durability should be further investigated. Furthermore, numerical simulation of concrete internal temperature under different conditions (curing temperatures, protection methods and mix design) as well as bond strength with steel bars has not been performed yet. Thus, further research should be done to better understand the effect of using these materials and their combination in addition to advanced methods of protection on the properties and durability of concrete produced under cold weather.
CHAPTER 3: NANO-MODIFIED CONCRETE AT A FREEZING TEMPERATURE: EXPERIMENTAL AND STATISTICAL MODELING

3.1 Introduction

Cement hydration reactions, which control the development in concrete mechanical, physical and microstructural properties, depend on the curing conditions such as temperature and relative humidity (Neville 2011). Temperatures of 10 to 20°C and R.H. above 90% are favorable for cement hydration (Karagöl et al. 2015; Neville 2011). Drop in temperature and loss of moisture lead to slower hydration development associated with delayed hardening and strength gain (Karagöl et al. 2015; Prado et al. 1998; Powers and Helmuth 1953). When the temperature drops below -2.8°C, the hydration reactions completely cease due to freezing of mixing water (Karagöl et al. 2015; Ratinov and Rozenberg 1996; Korhonen et al. 1992), which also induces osmotic and hydraulic pressures within immaturely developed paste, resulting in cracking and irreversible damage of concrete (Karagöl et al. 2015; Prado et al. 1998; Powers and Helmuth 1953). Therefore, ACI 306R (2016): Guide to Cold Weather Concreting, recommends that concrete should not be exposed to one or multiple cycles of freezing-thawing till reaching adequate strength of 3.5 and 24.5 MPa, respectively.

According to ACI 306R (2016), cold weather holds when the environment temperature has fallen or expected to fall below 4°C during the protection period of concrete. Other codes and guides such as CSA A23.1 (2014): Concrete Materials and Methods of Concrete Construction, and CS164 (2016): Guidance on the Practical Aspects of Concreting, set this limit at 5°C. The aforementioned documents provide stringent
recommendations for cold weather concreting such as limits on concrete mixing/placement/curing temperatures (minimum of 10°C), protection methods (insulation, voluminously heated enclosures), and associated period to ensure adequate development in concrete properties. In addition, heating concrete constituents (water, aggregates), is typically required. However, these techniques are costly, energy intensive and pollutive (Barna et al. 2011; Korhonen et al. 1997), especially with long-term protection, due to the required skilled labor, consumption of energy and CO₂ emissions (Korhonen et al. 1997). For example, the annual cost estimation of expenditures on these heating practices in U.S. is around one billion dollars to cast concrete during cold weather (Barna et al. 2011; Korhonen et al. 1997). Thus, in cold regions, concreting activities is commonly limited to warmer seasons (from May to September), resulting in busy construction summer seasons and socio-economic losses. Hence, there is continual need to seek innovative and energy-efficient options that allow concrete to be mixed, cast and cured under freezing temperatures.

The incorporation of cold weather admixture systems (CWAS), antifreeze without/with accelerating admixtures, in concrete has been introduced as practical and economical efficient solution to mitigate the noxious effects of cold weather on concrete (Ratinov and Rozenberg 1996; Korhonen 1990). Antifreeze admixtures depress the freezing point of mixing water while accelerators speed up the kinetics of cement hydration; thus, concrete can achieve adequate physical and mechanical properties when cured under low temperatures (eg. Polat 2016; Karagöl et al. 2013; Ratinov and Rozenberg 1996; Korhonen 1990). Antifreeze admixtures such as sodium nitrite, calcium nitrite, calcium nitrate, urea, calcium chloride, sodium chloride, potash and combinations have been reported to be efficient CWAS by allowing concrete to reach degree of
Chapter 3: Statistical Modeling of Concrete Mixtures Cured Under -5°C

hydration comparable to normally cured concrete (21±1°C) (Korhonen 1990). However, sodium-based CWAS may provoke alkali aggregate reaction (Ratinov and Rozenberg 1996; Korhonen 1990) while Chloride-based admixtures may initiate corrosion of steel reinforcement (Ratinov and Rozenberg 1996; Korhonen 1990) and cause decomposition and expansion of hardened paste by forming calcium oxychloride (Peterson et al. 2013). In addition, potash was found to negatively affect concrete microstructure and resistance to freezing-thawing cycles (Ratinov and Rozenberg 1996; Korhonen 1990), while urea was reported to act as a retarder (Ratinov and Rozenberg 1996; Korhonen 1990).

Comparatively, calcium nitrate, calcium nitrite and combinations were reported to be efficient in terms of accelerating the kinetics of cement hydration, and thus the development in concrete strength (Nmai 1998; Ratinov and Rozenberg 1996; Korhonen 1990). However, it was reported that the microstructure of concrete containing 6% calcium nitrate were adversely affected after being exposed to only 28 freezing-thawing cycles resulting in significant reduction in compressive strength and increase in water absorption (Polat 2016). Moreover, concrete incorporating high dosages (more than 6%) of calcium nitrate and/or calcium nitrite was reported to be vulnerable to shrinkage cracking (Korhonen et al. 1997). Hence, the effect of CWAS on the durability of concrete is uncertain, and the microstructure of such concrete needs to be improved.

The positive effects of nanoparticles on concrete hardened and durability properties as well as microstructural characteristics have been reported in many studies (eg. Ghazy et al. 2016; Haruehansapong et al. 2014; Said et al. 2012). They can accelerate the kinetics of hydration (Hou et al. 2013; Senff et al. 2009), evolution of microstructure and refine the pore structure (Ghazy et al. 2016; Korpa et al. 2008) of cement-based materials. However, most previous studies focused on the effect of
nanoparticles on concrete cast and cured under normal temperatures (20 to 30°C) (eg. Ghazy et al. 2016; Haruehansapong et al. 2014; Hou et al. 2013; Said et al. 2012; Senff et al. 2009; Korpa et al. 2008), without considering the potential of these materials to produce durable concrete cast and cured under freezing temperatures. In a previous studies, the addition of nano-silica in masonry cement mortars comprising 30% inert filler, which were cast and cured under 5°C without any protection method, enhanced its hydration and strength development rates (Kazempour et al. 2017; Kazempour et al. 2014).

3.2 Research Significance

There is constant need to minimize the consumption of energy associated with casting and curing concrete under cold weather; in addition, the performance of concrete comprising nano-silica cast and cured under freezing temperatures and its interaction with CWAS is unknown. Therefore, in this study, statistical modeling was implemented to a wide range of concrete mixtures cast and cured at -5°C. The models considered the influence of different parameters (w/b, dosages of fly ash and nano-silica, and type of CWAS) on concrete fresh, hardened and durability properties to capture the optimum mixture design parameters, which affect the performance of concrete placed and cured under the freezing temperature, and the interaction among them. In addition, multi objective optimization was performed to identify cold weather concrete mixtures suitable for different scenarios to extend the construction season in late fall and early spring without the need for conventional heating practices. This study should contribute fundamental understanding on the performance of nano-modified concrete cast and cured in cold weather, thus evaluating its suitability for such severe conditions.
3.3 Methodology

3.3.1 Statistical Model

The Response Surface Method (RSM) based on face-centred composite design (FCCD) was used to evaluate the effect of each mixture design variable on the performance of concrete. The theory behind this method is that the response space can be accurately predicted by considering additional points to the factorial set of the model. Four factors, which were expected to affect the performance of concrete in cold weather, were considered in the developed models: (A) \( w/b \), (B) fly ash content, (C) nano-silica dosage, and (D) type of CWAS. The influence of each factor was evaluated at two different levels with coded values of -1 and +1. Furthermore, one central point and eight axial points were chosen to run the model and investigate the quadratic effect of each variable, if any. The central point was repeated four times to obtain robust predictions and attain a high level of confidence to improve the reliability and estimate the experimental error of the models (Montgomery 2017). Subsequently, 28 mixtures were cast to run the model \( 2^4 = 16 \) mixtures for the factorial part, \( 2*4 = 8 \) mixtures for the axial part, and the central mixture, which was repeated 4 times).

The model is valid for concrete mixtures with specific proportions and a casting/curing temperature of -5°C. The total binder (single or blended) content was kept constant at 400 kg/m\(^3\). Each factor was assessed at three different levels, to study the quadratic effect of each variable, and coded as maximum (+1), central (0) and minimum (-1). The \( w/b \) ranged between 0.32 to 0.4, while fly ash and nano-silica dosages varied between 0-25\% and 0-4\% by mass of binder, respectively. Furthermore, two types of admixtures, calcium nitrate (CNA) and calcium nitrite, were used at different CNA/CNI ratios (1:0 to 1:1) to produce different CWAS as shown in Table 3.1. The selected ranges
for w/b, fly ash and nano-silica as well as CWAS were chosen based on the published literature (Ghazy et al. 2016; Ratinov and Rozenberg 1996; Korhonen 1990), to cover a wide range of concrete mixture proportions that was cast and cured under normal temperatures. The independent responses (fresh, hardened and durability properties) of the models are setting times (initial and final), compressive strength (7 and 28 days), and resistance to freezing-thawing cycles as well as cost.

### Table 3.1: Coded and absolute values of the factors

<table>
<thead>
<tr>
<th>Variable</th>
<th>Level</th>
<th>Level</th>
<th>0</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) w/b</td>
<td>0.32</td>
<td>0.36</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>(B) Fly ash, kg/m³</td>
<td>0</td>
<td>50</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>(C): Nano-silica, kg/m³</td>
<td>0</td>
<td>8</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>(D) CWAS CNA/CNI</td>
<td>1:1</td>
<td>2:1</td>
<td>1:0</td>
<td></td>
</tr>
</tbody>
</table>

*The components of CWAS for levels -1, 0 and +1 were 50% CNA + 50% CNI, 67% CNA + 33% CNI and 100% CNA by mass, respectively.*

### 3.4 Experimental Program

#### 3.4.1 Materials and mixtures

General use (GU) portland cement and Class F fly ash, which meet the stipulations of the CAN/CSA-A3001 (2018) standard, were used as the main binder components. In addition, a commercial nano-silica sol (50% solid content of SiO₂ dispersed in an aqueous solution) was incorporated in some mixtures as partial replacement of the binder. The chemical and physical properties of these materials are presented in Table 3.2. Locally available well-graded river sand with fineness modulus of 2.9 and natural gravel with maximum size of 9.5 mm were used in this study. The absorption and specific gravity were 1.5% and 2.53, respectively, for sand, and 2% and 2.65, for gravel, respectively. The particle size distribution of the used fine and coarse aggregates is shown in Fig. A.1. A high-range water reducing admixture (HRWRA) based on polycarboxylic acid complying with ASTM C494 (2019), Type F was used to achieve a
target consistency of 175±25 mm. In addition, an air entraining admixture, complying with ASTM C260 (2016), was used to achieve fresh air content of 6±1%.

Table 3.2: Chemical composition and physical properties of cement, fly ash and nano-silica

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>GU Cement</th>
<th>Fly Ash</th>
<th>Nano-silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (%)</td>
<td>19.8</td>
<td>56.0</td>
<td>99.17</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>5</td>
<td>23.1</td>
<td>0.38</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>2.4</td>
<td>3.6</td>
<td>0.02</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>63.2</td>
<td>10.8</td>
<td>--</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>3.3</td>
<td>1.1</td>
<td>0.21</td>
</tr>
<tr>
<td>SO₃ (%)</td>
<td>3</td>
<td>0.2</td>
<td>--</td>
</tr>
<tr>
<td>Na₂Oeq (%)</td>
<td>0.6</td>
<td>3.1</td>
<td>0.20</td>
</tr>
</tbody>
</table>

| Physical properties  |          |         |             |
| Mean particle size, µm | 13.15    | 16.56   | 35 x 10⁻³   |
| Fineness, m²/kg       | 390⁺     | 290⁺    | 80,000⁺     |

*Blaine fineness.
†Fineness was determined by titration with sodium hydroxide.

Calcium nitrate (CNA) and combination of calcium nitrate and calcium nitrite (CNI) were used as anti-freeze admixtures, at constant dosage of 15% by mass of mixing water. This concentration was conservatively selected according to the phase diagrams for these admixtures (Fig. 3.1) to depress the freezing point of water down to the target casting and curing temperature (-5°C). These admixtures have proven to achieve efficient performance as anti-freeze and accelerating admixtures (Ratinov and Rozenberg 1996; Korhonen 1990). The chemical properties of the CNI and CNA are given in Table 3.3. The anti-freeze admixtures phase diagrams were obtained by visually assessing the liquid-solid transition/temperature of different dosages, considering the water content of each admixture. The different dosages were dissolved in one liter of distilled water and...
kept inside an environmental chamber, which was set at wide range of freezing temperatures for 24 hours each.

Figure 3.1: Phase diagrams of: (a) calcium nitrate (CNA), and (b) calcium nitrate-nitrite (CNAI).

Table 3.3: Chemical properties of CNA and CNI

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CNA</th>
<th>CNI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/ml</td>
<td>1.86</td>
<td>2.26</td>
</tr>
<tr>
<td>Sulfate, %</td>
<td>0.01 max.</td>
<td>--</td>
</tr>
<tr>
<td>Chloride, %</td>
<td>0.01 max.</td>
<td>--</td>
</tr>
<tr>
<td>Molecular weight, g/mol</td>
<td>236.15</td>
<td>132.09</td>
</tr>
<tr>
<td>Solubility in water, g/l (0°C)</td>
<td>1470</td>
<td>Freely soluble in water</td>
</tr>
<tr>
<td>pH</td>
<td>5.0 to 9.0</td>
<td>8 to 12</td>
</tr>
</tbody>
</table>

28 mixtures (Table 3.4) were cast and cured at -5°C to investigate the effect of each factor on the responses. Each mixture ID starts with a number denoting the w/b (0.32, 0.36 and 0.4) followed by letter ‘F’ with number indicating fly ash percentage (12.5 or 25%), subsequent letter ‘N’ with a number designating the nano-silica dosage (2 and 4%), and finally letters indicating the type of CWAS: A for CNA, AI for CNAI while AAI for CNAAI. For instance, mixture 0.32-F25-N4-AI refers to concrete mixture with w/b of 0.32 and incorporating 25% fly ash with 4% nano-silica, and CNAI.
Table 3.4: Mixtures proportions per cubic meter

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Mixture Code</th>
<th>Actual values</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water* (kg)</td>
<td>Fly Ash (kg)</td>
<td>Nano-silica (kg)</td>
<td>CWAS CNA**+CNI kg</td>
<td>Cement (kg)</td>
</tr>
<tr>
<td>0.4-A</td>
<td>1,-1,-1,1</td>
<td>160</td>
<td>0</td>
<td>0</td>
<td>34+0</td>
<td>400</td>
</tr>
<tr>
<td>0.32-A</td>
<td>-1,-1,-1,1</td>
<td>128</td>
<td>0</td>
<td>0</td>
<td>28+0</td>
<td>400</td>
</tr>
<tr>
<td>0.4-AI</td>
<td>1,-1,-1,-1</td>
<td>132</td>
<td>0</td>
<td>0</td>
<td>17+40</td>
<td>400</td>
</tr>
<tr>
<td>0.32-AI</td>
<td>-1,-1,-1,-1</td>
<td>106</td>
<td>0</td>
<td>0</td>
<td>14+32</td>
<td>400</td>
</tr>
<tr>
<td>0.4-F25-A</td>
<td>1,-1,-1,1</td>
<td>160</td>
<td>100</td>
<td>0</td>
<td>34+0</td>
<td>300</td>
</tr>
<tr>
<td>0.32-F25-A</td>
<td>-1,-1,-1,1</td>
<td>128</td>
<td>100</td>
<td>0</td>
<td>28+0</td>
<td>300</td>
</tr>
<tr>
<td>0.4-F25-AI</td>
<td>1,-1,-1,-1</td>
<td>132</td>
<td>100</td>
<td>0</td>
<td>17+40</td>
<td>300</td>
</tr>
<tr>
<td>0.32-F25-AI</td>
<td>-1,-1,-1,-1</td>
<td>106</td>
<td>100</td>
<td>0</td>
<td>14+32</td>
<td>300</td>
</tr>
<tr>
<td>0.4-N4-A</td>
<td>1,-1,-1,1</td>
<td>144</td>
<td>0</td>
<td>32</td>
<td>34+0</td>
<td>384</td>
</tr>
<tr>
<td>0.32-N4-A</td>
<td>-1,-1,-1,1</td>
<td>112</td>
<td>0</td>
<td>32</td>
<td>28+0</td>
<td>384</td>
</tr>
<tr>
<td>0.4-N4-AI</td>
<td>1,-1,-1,-1</td>
<td>116</td>
<td>0</td>
<td>32</td>
<td>17+40</td>
<td>384</td>
</tr>
<tr>
<td>0.32-N4-AI</td>
<td>-1,-1,-1,-1</td>
<td>90</td>
<td>0</td>
<td>32</td>
<td>14+32</td>
<td>384</td>
</tr>
<tr>
<td>0.4-F25-N4-A</td>
<td>1,1,1,1</td>
<td>144</td>
<td>100</td>
<td>32</td>
<td>34+0</td>
<td>284</td>
</tr>
<tr>
<td>0.32-F25-N4-A</td>
<td>-1,1,1,1</td>
<td>112</td>
<td>100</td>
<td>32</td>
<td>28+0</td>
<td>284</td>
</tr>
<tr>
<td>0.4-F25-N4-AI</td>
<td>1,1,1,1</td>
<td>116</td>
<td>100</td>
<td>32</td>
<td>17+40</td>
<td>284</td>
</tr>
<tr>
<td>0.32-F25-N4-AI</td>
<td>-1,1,1,1</td>
<td>90</td>
<td>100</td>
<td>32</td>
<td>14+32</td>
<td>284</td>
</tr>
</tbody>
</table>

*The amount of water was adjusted considering the water content of nano-silica (aqueous solution with 50% solid content of SiO$_2$) and the CNI (aqueous solution with 30% solid content).
**The CNA admixture was in solid form with 70% active ingredient.
†Canadian dollar, Isoreponse curves are shown in Fig. A.2.
### Table 3.4 Cont’d: Mixtures proportions per cubic meter

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Mixture Code</th>
<th>Actual values</th>
<th>Cement (kg)</th>
<th>Fine/Coarse Aggregate (kg)</th>
<th>Cost CAD†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water* (kg)</td>
<td>Fly Ash (kg)</td>
<td>Nano-silica (kg)</td>
<td>CWAS CNA**+CNI kg</td>
<td></td>
</tr>
<tr>
<td>0.4-F12.5-N2-AAI</td>
<td>1,0,0,0</td>
<td>133</td>
<td>50</td>
<td>16</td>
<td>23+27</td>
</tr>
<tr>
<td>0.32-F12.5-N2-AAI</td>
<td>-1,0,0,0</td>
<td>105</td>
<td>50</td>
<td>16</td>
<td>18+21</td>
</tr>
<tr>
<td>0.36-F25-N2-AAI</td>
<td>0,1,0,0</td>
<td>119</td>
<td>100</td>
<td>16</td>
<td>21+24</td>
</tr>
<tr>
<td>0.36-N2-AAI</td>
<td>0,-1,0,0</td>
<td>119</td>
<td>0</td>
<td>16</td>
<td>21+24</td>
</tr>
<tr>
<td>0.36-F12.5-N4-AAI</td>
<td>0,0,1,0</td>
<td>111</td>
<td>50</td>
<td>32</td>
<td>21+24</td>
</tr>
<tr>
<td>0.36-F12.5-AAI</td>
<td>0,0,-1,0</td>
<td>127</td>
<td>50</td>
<td>0</td>
<td>21+24</td>
</tr>
<tr>
<td>0.36-F12.5-N2-A</td>
<td>0,0,0,1</td>
<td>136</td>
<td>50</td>
<td>16</td>
<td>31+0</td>
</tr>
<tr>
<td>0.36-F12.5-N2-AI</td>
<td>0,0,0,-1</td>
<td>111</td>
<td>50</td>
<td>16</td>
<td>16+36</td>
</tr>
<tr>
<td>0.36-F12.5-N2-AAI††</td>
<td>0,0,0,0</td>
<td>119</td>
<td>50</td>
<td>16</td>
<td>21+24</td>
</tr>
</tbody>
</table>

*The amount of water was adjusted considering the water content of nano-silica (aqueous solution with 50% solid content of SiO$_2$) and the CNI (aqueous solution with 30% solid content).

**The CNA admixture was in solid form with 70% active ingredient.

†Canadian dollar.

††The central mixture was repeated four times.
3.4.2 Procedures

Mixing, casting and curing procedures were implemented in a controlled environmental chamber (See Fig. A.3), where solid constituents of concrete were stored for 24 h prior to mixing, to simulate field conditions at the worst average freezing threshold (-5±1°C) in late fall and early spring in many geographic regions in North America and Europe such as Manitoba, Canada. Conditioned cold mixing water (5±1°C) was used to mimic realistic winter tap water condition.

To reach homogenous dispersion of components, specific sequence of mixing was followed based on trial batches, using a stationary drill mixer. The nano-silica and the liquid form admixtures (air-entraining admixture, HRWRA) were added to two third of the mixing water (solution A) while the other admixtures (CNA and CNI) were added to the remaining amount of the mixing water (solution B). The solutions were stirred vigorously for 45 s; afterwards, approximately, half of solution A was added to the aggregates and mixed together for 30 s. The main binder components (cement and fly ash) were added to the aggregates and mixed together for another 30 s. Thereafter, the remaining amount of solution A was added to mixture and mixing continued for 30 s. Finally, solution B was added to the mixer pan and mixing continued for 2 min. After pouring concrete in moulds, a vibrating table (60 Hz) was used until air bubbles stopped appearing on the specimens’ surface. Moreover, to represent a worst case curing scenario, the specimens were kept exposed to the curing temperature of -5±1°C and RH of 50±5 % in the environmental chamber without any method of protection and subjected to a circulating air flow at an average speed of 25 km/h. After 24 h, the specimens were demoulded and kept in the environmental chamber at the aforementioned conditions until testing.
3.4.3 Testing

The initial (IST) and final setting times (FST) were determined by measuring the penetration resistance of mortar fraction of each mixture (portion passing sieve #4 [4.75 mm]), using standard needles according to ASTM C403 (2016). The setting time specimens were mixed and placed in a container at the casting and curing temperature [-5±1°C] during the test. In addition, the compressive strength of triplicate concrete cylinders (100×200 mm) were determined according to ASTM C39 (2020) at 7 and 28 days. After 28 days, the resistance of the different mixtures to freezing-thawing cycles were assessed based on the durability factor (DF) of triplicate prisms (50×50×285) mm according to ASTM C666 (2015), Procedure A, which was calculated based on the dynamic modulus of elasticity according to ASTM C215 (2019).

In addition, mercury intrusion porosimetry (MIP) test was conducted on concrete samples to assess the characteristics of pore structure after 28 days of curing at -5±1°C. Large chunks (8–12 mm) were extracted from concrete cores, visually inspected and all large aggregate particles were removed from the samples. Afterwards, 20 smaller chunks with the size of 4–7 mm were chosen for the MIP test. These small chunks were oven dried at a 45°C until reaching a constant mass. This drying method was adopted to avoid decomposition of the hydration products or development of shrinkage micro-cracks within the samples. The surface tension and contact angle of mercury were taken as 485 dynes/cm and 130°, respectively (Tiznobaik and Bassuoni 2018; Shi and Winslow 1985). In addition, thermal and microscopy studies were conducted to corroborate the trends acquired from the bulk tests. Thermogravimetry (TG) at a constant heating rate of 10°C/min was done on powder samples which were extracted from the concrete specimens. The portlandite content (CH) was calculated by determining the percentage
drop of an ignited mass of the TG curves at a temperature range of 400 to 450°C and multiplying it by 4.11 (ratio of the molecular mass of CH to that of water). Backscattered scanning electron microscopy (BSEM) with elemental dispersive X-ray (EDX) analysis were applied on polished thin sections from different mixtures. Slices were cut out from specimens, which were then dried and impregnated by a low-viscosity epoxy resin under vacuum pressure and polished by successive diamond surface-grinding to a thickness of 30 to 50 μm. Thereafter, these sections were carbon coated to enhance the conductivity for the BSEM analysis.

3.5 Results

3.5.1 Derived Statistical Models

Statistical analysis was done for the results of fresh (initial [IST] and final [FST] setting times), hardened (7 [f’c 7d] and 28 days [f’c 28d] compressive strength) and durability (durability factor [DF] to freezing-thawing cycles) properties of concrete, which are summarized in Table 3.5. The general model for each response can be expressed by:

\[ y = \beta_0 + \Sigma \beta_i X_i + \Sigma \beta_{ij} X_i X_j + \Sigma \beta_{ii} X_i^2 + \epsilon \]  
(Eq. 3.1)

where, \( y \) is the response, \( X_i \) is the independent variable, \( \beta_0 \) is model intercept (constant), while \( \beta_i \) (i= 1, 2, 3, 4), \( \beta_{ij} \) (i= 1, 2, 3, 4; j= 2, 3, 4; i > j) and \( \beta_{ii} \) (i = 1, 2, 3,4) represent the linear, interaction, and quadratic regression coefficients of each factor, respectively, whereas \( \epsilon \) is the model random error for uncontrolled factors.

The models’ coefficients were determined using non-linear regression analysis (polynomial function) based on the input parameters to map all responses. The developed equations were derived based on the significant variables and their interaction, which were determined based on the analysis of variance (ANOVA). A factor was considered
significant if its probability is less than 0.05, i.e. there is less than 5% chance (or 95% confidence limit) that a tested response exceeds the value of the specified coefficient. Factors with \( P \)-values >0.05 indicate that they have insignificant effect on the measured response; thus, they were discarded from the equations. Consequently, the selection of model’s order (linear, quadratic, etc.) was based on the aforementioned criteria to reach the highest possible \( R^2 \) (coefficient of determination) value. The \( R^2 \) values of all derived models were more than 0.94 relative to the experimental results, indicating that the factors varied systematically with experimentation (Montgomery 2017).

The models’ results as well as the relative significance of variables according to ANOVA are listed in Table 3.6. The best fit responses, using Design-Expert version 11 (2018) as a statistical software (see Fig A.4), are given in Eqs. (3.2-3.6).

\[
\text{Log}_{10}(\text{IST})[\text{min}] = 2.02 + 0.11 \times \text{w/b} + 0.15 \times \text{FA} - 0.06 \times \text{NS} + 0.24 \times \text{A} \quad \text{(Eq. 3.2)}
\]

\[
\text{Log}_{10}(\text{FST})[\text{min}] = 2.69 + 0.13 \times \text{w/b} + 0.10 \times \text{FA} - 0.06 \times \text{NS} + 0.12 \times \text{A} + 0.03 \times \text{FA} \times \text{A} + 0.024 \times \text{w/b} \times \text{NS} \quad \text{(Eq. 3.3)}
\]

\[
\text{f}_c\text{7d [MPa]} = 12.92 - 3.01 \times \text{w/b} - 3.01 \times \text{FA} + 2.8 \times \text{NS} - 2.61 \times \text{A} + 0.65 \times \text{w/b} \times \text{FA} + 0.63 \times \text{FA} \times \text{A} \quad \text{(Eq. 3.4)}
\]

\[
\text{f}_c\text{28d [MPa]} = 23.80 - 5.80 \times \text{w/b} - 5.36 \times \text{FA} + 3.33 \times \text{NS} - 2.69 \times \text{A} + 1.22 \times \text{w/b} \times \text{FA} - 2.92 \times \text{NS}^2 - 1.77 \times \text{A}^2 \quad \text{(Eq. 3.5)}
\]

\[
\text{DF [\%]} = 95.93 - 15.44 \times \text{w/b} + 21.61 \times \text{NS} + 16.81 \times \text{w/b} \times \text{NS} - 25.39 \times \text{NS}^2 \quad \text{(Eq. 3.6)}
\]

Where, \( w/b, \text{FA}, \text{NS} \) and \( \text{A} \) represent water-to-binder ratio, fly ash, nano-silica and CWAS (CNA:CNI) coded values, respectively.
In addition, four graphs were plotted for each response, as examples to map the relation and interaction between the different variables and responses. For all graphs, the abscissa and ordinate represent fly ash (0 to 25%) and nano-silica (0 to 4%) contents, respectively, with two levels of w/b (0.4 and 0.32) and types of CWAS (CNA and CNAI), representing the extreme limits of these models.
### Table 3.6: Derived coefficients for the models and their significance based on ANOVA

<table>
<thead>
<tr>
<th>Multiplied by</th>
<th>( \log_{10}(\text{IST}) )</th>
<th>( \log_{10}(\text{FST}) )</th>
<th>( f_c',7d )</th>
<th>( f_c',28d )</th>
<th>( DF )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>2.02</td>
<td>2.69</td>
<td>12.92</td>
<td>23.80</td>
<td>95.93</td>
</tr>
<tr>
<td>( w/b )</td>
<td>0.11</td>
<td>0.13</td>
<td>-3.01</td>
<td>-5.80</td>
<td>-15.44</td>
</tr>
<tr>
<td>FA</td>
<td>0.15</td>
<td>0.1</td>
<td>-3.01</td>
<td>-5.36</td>
<td>-4.00</td>
</tr>
<tr>
<td>NS</td>
<td>-0.06</td>
<td>-0.06</td>
<td>2.80</td>
<td>3.33</td>
<td>21.61</td>
</tr>
<tr>
<td>A</td>
<td>0.24</td>
<td>0.12</td>
<td>-2.61</td>
<td>-2.69</td>
<td>-3.28</td>
</tr>
<tr>
<td>( w/b )*FA</td>
<td>0.016</td>
<td>-0.013</td>
<td>0.65</td>
<td>1.22</td>
<td>-2.00</td>
</tr>
<tr>
<td>( w/b )*NS</td>
<td>0.012</td>
<td>0.024</td>
<td>-0.50</td>
<td>0.06</td>
<td>16.81</td>
</tr>
<tr>
<td>( w/b )*A</td>
<td>0.017</td>
<td>-0.005</td>
<td>0.09</td>
<td>-0.33</td>
<td>-0.56</td>
</tr>
<tr>
<td>FA*NS</td>
<td>-0.01</td>
<td>0.004</td>
<td>-0.54</td>
<td>-0.16</td>
<td>3.00</td>
</tr>
<tr>
<td>FA*A</td>
<td>0.03</td>
<td>0.033</td>
<td>0.63</td>
<td>0.46</td>
<td>-1.12</td>
</tr>
<tr>
<td>NS*A</td>
<td>-0.015</td>
<td>-0.02</td>
<td>-0.28</td>
<td>-0.38</td>
<td>2.81</td>
</tr>
<tr>
<td>( w/b )^2</td>
<td>0.013</td>
<td>-0.035</td>
<td>0.52</td>
<td>1.53</td>
<td>6.11</td>
</tr>
<tr>
<td>FA^2</td>
<td>-0.05</td>
<td>0.038</td>
<td>0.075</td>
<td>-0.42</td>
<td>-1.39</td>
</tr>
<tr>
<td>NS^2</td>
<td>-0.009</td>
<td>0.03</td>
<td>-1.23</td>
<td>-2.92</td>
<td>-25.39</td>
</tr>
<tr>
<td>A^2</td>
<td>0.06</td>
<td>0.01</td>
<td>-1.38</td>
<td>-1.77</td>
<td>3.61</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.94</td>
<td>0.98</td>
<td>0.98</td>
<td>0.99</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Note: bold factors and interactions are significant.

#### 3.5.2 Setting Time

According to ASTM C403 (2016) stipulations, both IST and FST were determined when the penetration resistance of the mixtures reached 3.5 and 27.6 MPa, respectively. The IST and FST of all mixtures varied between 0.5 to 8.9 h and 3.7 to 22.9 h, respectively (Table 3.5). The statistical models presented by Eqs. 3.2 and 3.3 indicated that the hardening behavior of concrete, which was mixed and cured at -5°C, was significantly influenced by all the factors investigated in this study. The type of CWAS had a dominant effect on the IST response compared with both the fly ash content and \( w/b \) (coefficients of 0.24, 0.15 and 0.11, respectively). The \( w/b \) had slightly higher coefficient (0.13) than that of the type of CWAS (0.12) and fly ash (0.1) in the case of FST. Nano-silica had a significant effect (-0.06) on both IST and FST (Table 3.6), but to a lesser extent relative to the other factors.
The isoresponse curves shown in Figs. 3.2 (a-d) and 3.3 (a-d) map the trends obtained from the setting time models. Increasing the w/b led to prolonging both IST and FST of concrete [Figs. 3.2(c) and 3.3(c) vs. 3.2(a) and 3.3(a)]. For example, increasing the w/b of mixture 0.32-F25-N4-A from 0.32 to 0.4 to produce mixture 0.4-F25-N4-A extended both IST and FST by 4.8 and 10.1 h, respectively. This could be ascribed to increasing the water content in concrete, which led to increasing the rate of bleeding and hence forming a weaker layer, i.e. lower penetration resistance to standard needles, within the top part of concrete mixtures with higher w/b. In addition, the incorporation of fly ash extended the setting times compared to corresponding concrete without fly ash, as shown in Figs. 3.2 (a-d) and 3.3 (a-d). For instance, mixture 0.32-F25-A had 1.8 and 7.2 h longer IST and FST, respectively than that of mixtures 0.32-A. The effect of fly ash, especially at higher dosages (25%), on retarding both setting times of concrete cast at normal temperatures is well-documented (Wesche 2014; Neville 2011), and it was replicated at the freezing temperature adopted in this study. This is attributed to replacement of cement with less reactive supplementary cementitious material (SCM) of much lower lime content, resulting in slowing down the kinetics of hydration and consequently the hardening rate of concrete.

The effect of nano-silica on the IST of concrete was inconspicuous. This could be ascribed to the coexistence of CWAS, especially CNI, which partially masked the nucleation effect of nano-silica at very early ages, as depicted in Figs. 3.2 (a-d). For instance, the IST of mixtures 0.4-N4-AI and 0.32-N4-AI were only 5 min shorter than that of corresponding mixtures without nano-silica (0.4-AI and 0.32-AI). On the other hand, the FST was markedly affected by the incorporation of nano-silica, as depicted in Figs. 3.3 (a-d). For example, the FST of mixtures 0.4-N4-A and 0.32-N4-A were 2.5 and
3.5 h shorter than that of corresponding mixtures without nano-silica (0.4-A and 0.32-A, respectively).

Figure 3.2: Exemplar IST isoresponse plots (min): (a) 0.4 w/b with CNA, (b) 0.4 w/b CNAI, (c) 0.32 w/b with CNA, and (d) 0.32 w/b with CNAI.

In addition, the presence of nano-silica in fly ash mixtures shortened their setting times. For instance, mixtures 0.4-F25-N4-A and 0.32-F25-N4 A had 3.3 and 6 h shorter FST, respectively compared with mixtures 0.4-F25-A and 0.32-F25-A. Previous studies (Ghazy et al. 2016; Senff et al. 2009) showed that nano-silica accelerates the formation of

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calcium hydroxide and the hydration process of cementitious systems cured at normal temperatures. This can be attributed to the nucleation effect of nano-silica by providing ultrafine sites for precipitation of hydration products at early-age, thus speeding up the dissolution of calcium silicate phases (Ghazy et al. 2016; Senff et al. 2009). At this freezing temperature, this process was still maintained due to the consistence of CWAS, which increased the production of calcium hydroxide and subsequently promoted the pozzloanic activity in the matrix, as will be shown in the thermal analysis section.

The type of CWAS significantly affected the IST and FST of concrete. Increasing the CNI dosage in the CWAS shortened the setting times markedly [e.g. Fig. 3.3(d) vs. Fig. 3.3(c)]. For instance, mixture 0.4-N4-AI had 1.1 and 2.3 h shorter IST and FST, respectively compared to that of mixture 0.4-N4-A. This can be ascribed to the substitution of up to 50% of the CNA portion in the CWAS with a stronger and more effective accelerator (CNI) (Ratinov and Rozenberg 1996). It is worth noting that, regardless of the type of CWAS, the FST of nano-modified and nano-modified fly ash concrete mixtures, which were cast and cured at -5°C, with w/b of 0.32 varied between 3.7 to 9.5 h (Table 3.5). This is comparable to the typical hardening times (4 to 8 h) for concrete cast and cured under normal temperatures (Neville 2011). This highlighted the synergistic effects of CWAS and nano-silica in accelerating the hydration and hardening processes, which mitigated the effect of freezing temperature on concrete without the need for protection.
Compressive Strength

As shown in Table 3.5, the (100×200 mm) concrete cylinders compressive strength at 7 and 28 days of all mixtures, which were cast and cured at -5°C, varied between 2.3 to 18.2 MPa and 5 to 39 MPa, respectively. The corresponding statistical models presented by Eqs. 3.4 and 3.5 and the isoresponse curves [Figs. 3.4(a-d) and 3.5(a-d)] showed that
strength at both ages were significantly influenced by the factors selected in this study. For the 7 days strength, the \( w/b \) and fly ash dosage had dominant effects with similar regression coefficients of 3.01 followed by the nano-silica dosage (2.80) and type of CWAS (2.61). The same trend was replicated for the 28 days strength; also, the interactions between the different factors in Eqs. 3.4 and 3.5 were statistically significant, as shown in Table 3.6.

Figure 3.4: Exemplar 7 days strength isoresponse charts (MPa): (a) 0.4 \( w/b \) with CNA, (b) 0.4 \( w/b \) CNAI, (c) 0.32 \( w/b \) with CNA, and (d) 0.32 \( w/b \) with CNAI.
Concrete mixtures with higher w/b yielded lower strength than that of corresponding mixtures with lower w/b, [e.g. Figs. 3.4(a) and 3.5(a) vs. 3.4(c) and 3.5(c)]. This can be ascribed to the well-documented effect of w/b on reducing the mechanical properties of concrete (Neville 2011), as higher water content in concrete produces more and larger capillary pores, as well be shown in the MIP and SEM sections. Likewise, increasing the fly ash dosage negatively affected the strength development of concrete, as shown in Figs. 3.4(a-d) and 3.5(a-d). For instance, incorporating 25% of fly ash in mixture 0.4-AI to produce mixture 0.4-F25-AI reduced the 7 and 28 day strengths by 38 and 47%, respectively. Slowly reactive pozzolans like fly ash in concrete cast and cured under cold weather is not recommended by ACI 306R (2016) to provide for adequate development of strength, required to resist severe environmental effects such freezing and thawing cycles. According to ACI 306R (2016), air-entrained concrete should not be exposed to one and multiple cycles of freezing and thawing till reaching compressive strength of 3 and 24.5 MPa respectively. Comparatively, both CSA A-23.1 (2019) and CS164 (2016) stipulate a strength threshold of 7 and 5 MPa, respectively for concrete to mitigate frost damage. The presence of large dosages of CWAS (more than 6% by mass of cement) was reported to lead to severe shrinkage cracking due to the high acceleration effect of such admixtures (Korhonen et al. 1997). Hence, the presence of fly ash, especially with the coexistence of highly reactive material such as nano-silica, is important to mitigate/balance the high shrinkage expected for these mixtures. Also, inclusion of fly ash in concrete is needed to achieve long-term durability (Ghazy et al. 2016; Neville 2011).
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Increasing the dosage of nano-silica in the binder notably improved the strength development of concrete, cast and cured at -5°C, as depicted in Figs. 3.4(a-d) and 3.5(a-d). The improvement in compressive strength of cement-based materials, cast and cured under normal (21 to 23°C) (eg. Ghazy et al. 2016; Haruehansapong et al. 2014; Said et al. 2012) and low (+5°C) (Kazempour et al. 2017; Kazempour et al. 2014) temperatures, incorporating nano-silica has been previously reported. In this study, nano-modified...
concrete mixtures yielded higher strength values at 7 and 28 days than that of corresponding mixtures without nano-silica. For instance, incorporating nano-silica in mixture 0.4-A to develop mixture 0.4-N4-A improved the 7 and 28 days strengths by 78 and 54%, respectively. Furthermore, the incorporation of nano-silica significantly enhanced the strength development of fly ash mixtures. For example, the 7 and 28 days strength of mixture 0.4-F25-A increased by 143% and 112%, respectively with the incorporation of 4% nano-silica to produce mixture 0.4-F25-N4-A. It is worth noting that the strength requirements, 20 to 40 MPa, of normal concrete for many infrastructural applications such as concrete sidewalks, pavements, bridges, buildings, etc. (MacGregor et al. 1997) comply with the strength range of both nano-modified and nano-modified fly ash concrete mixtures with w/b of 0.32, which varied between 20 to 39 MPa as shown in Table 3.5. The performance of nano-silica mixtures can be ascribed to the actions of nano-silica such as the nucleation, pozzolanic and filler effects and water reduction in the cementitious matrix, leading to accelerated hydration reactions, production of additional calcium silicate hydrate (C-S-H) (Ghazy et al. 2016; Said et al. 2012; Senff et al. 2009), and thus denser microstructure and durable concrete, as will be shown in the subsequent sections.

Increasing the CNI content in the CWAS enhanced the strength development of concrete cured under the freezing temperature [e.g. Fig. 3.5(d) vs. Fig. 3.5(c)]. For instance, incorporating CNI in mixture 0.4-A to produce mixture 0.4-AI increased the 7 and 28 days strength by 96 and 58%, respectively. This can be attributed to the better acceleration nature of CNI relative to CNA (Ratinov and Rozenberg 1996), which was efficient at maintaining the functionality of binder components, especially nano-silica;
therefore, it maintained continual strength development of concrete cast and cured at -5°C up to 28 days.

3.5.4 Resistance to Freezing-Thawing Cycles

The durability factor \( (DF) \) was determined to assess the resistance of the concrete mixtures to repetitive freezing-thawing cycles. It is worth noting that an air entraining admixture was added to the different concrete mixtures to achieve air content of \( 6\pm1\% \) as per ACI 306R (2016) and CSA A23.1 (2019) recommendations. Air entrainment produces a network of closely spaced air bubbles (10 to 100 µm) in the hardened cement paste to accommodate the hydraulic/osmotic pressures in concrete, which are associated with the freezing-thawing cycles (Neville 2011; Powers and Helmuth 1953). From Eq. 3.6 and Figs. 3.6(a-d), it was noted that the nano-silica dosage and \( w/b \), in order of significance, had a dominant effect on the \( DF \) with regression coefficients of 21.61 and 14.44, respectively. The type of CWAS did not significantly affect the \( DF \) values; however, incorporating CNAI instead of CNA in concrete slightly enhanced its durability performance [e.g. Fig. 3.6(c) vs. 3.6(d)].

Excluding the nano-modified mixtures, increasing the water and fly ash contents in mixtures adversely affected their resistance to freezing-thawing cycles [Figs. 3.6(a) and 3.6(b) vs Figs. 3.6(c) and 3.6(d)]. For instance, increasing the \( w/b \) of mixtures 0.32-F25-A and 0.32-A from 0.32 to 0.4 to produce mixtures 0.4-F25-A and 0.4-A reduced the \( DF \) from 80% and 95% to 9% and 27%, respectively. Mixture 0.4-F25-AI had a very low \( DF \) of 21% after only 140 cycles compared with mixture 0.4-AI which had \( DF \) of 43% after 220 cycles. This can be attributed to the ease of saturation, at the same air content, of mixtures with higher water and fly ash contents, due to the formation of a coarse pore structure as will be discussed in the MIP and SEM sections. Furthermore, the presence of
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relatively higher initial water content (w/b of 0.4) increased the amount of freezable water in the mixtures, and consequently vulnerability to pressures generated within the cementitious matrix. This was aggravated by the lower strength values (5 to 9.8 MPa) of concrete mixtures with the higher fly ash content, as discussed in the previous section. Thus, concrete mixtures with high water and fly ash contents, cast and cured at -5°C, had inadequate development of microstructure and strength at 28 days, which made them vulnerable to severe damage when exposed to multiple freezing-thawing cycles.

Regardless of the w/b or fly ash content, the presence of nano-silica remarkably enhanced the resistance of concrete to freezing-thawing cycles, relative to corresponding specimens without nano-silica. From Figs. 3.6(a-d), it can be noted that incorporating about 2% nano-silica or higher can attain DF of 85% or higher irrespective of the other variables. For instance, incorporating 4% nano-silica in mixture 0.4-F25-A to produce mixture 0.4-F25-N4-A increased the DF from 9% to 96%. Despite the recommendation of ACI 306R (2016) to not expose concrete to one or multiple cycles of freezing and thawing till achieving compressive strength of at least 3.5 and 24.5 MPa, respectively, all the mixtures incorporating nano-silica (even with high w/b and fly ash contents) achieved DF above 84% (mixture 0.36-F25-N2-AAI) after 300 cycles, irrespective of the strength grade. For instance mixture 0.4-F25-N4-A which had 28 day strength of 10.6 MPa, achieved a DF of 96%. This can be attributed to the pozzolanic and filler effects of nano-silica on refining the pore structure of concrete, even with curing at a freezing temperature, as will be substantiated in the subsequent sections. This improvement in microstructural resulted in reducing the penetrability and saturation of cement paste in concrete, as indicated by the high DF values of nano-modified concrete specimens.
Figure 3.6: Exemplar durability factor isoresponse charts: (a) 0.4CNA, (b) 0.4CNAI, (c) 0.32CNA, and (d) 0.32CNAI.

3.5.5 Numerical Optimization

The derived models can be used to identify concrete mixtures, cast and cured at a freezing temperature, suitable for different applications through numerical optimization. Exemplar optimization scenarios were conducted herein for a combination of factors at multiple levels, in a manner such that the outcome would satisfy the desired requirements
for the target applications. Each response/property was assigned different goals: none, maximum, minimum, target, or within a specific range. Subsequently, each goal was given a weight on a scale from one to five reflecting the degree of importance with one being least important and five being most important. Once the goals were specified, they were all combined into a desirability function, reflecting the best compromise solution satisfying all target goals through multi objective optimization. Using a statistical software (Design-Expert version 11 2018), the highest desirability function was obtained starting with 100 random points and moving forward to the steepest slope to a maximum value. Two or more maxima could be obtained due to the curvature of the response surfaces and their combinations. The desirability function ranges from zero to one, with one being the ideal solution and zero indicating that one or more responses fall outside the target boundaries.

Two scenarios were developed, representing non-structural and structural applications based on the City of Winnipeg (COW) portland cement concrete pavement works specifications, CW3310 (2015). For non-structural applications (Scenario I) such as curbs and sidewalks, the COW specifications (CW3310 2015) stipulate only a target compressive strength of 30 MPa after 28 days. While for structural applications (Scenario II) such as reinforced concrete pavements, the criteria aim to achieve balance between strength (32 MPa) and durability (resistance to infiltration of fluids). Moreover, a third scenario (III) was attempted in which all responses were set to give their extreme potential in terms of minimized setting and cost and maximized strength and durability with equal importance factors of 5. The third scenario might represent repair applications which require fast hardening rates with high early- and late-age strengths and improved durability performance at a minimal cost. The target criteria for the three scenarios
adopted and their corresponding results are listed in Table 3.7. The obtained results showed a desirability of 0.72, 0.66 and 0.75 for Scenarios I, II and III, respectively as shown in Fig. 3.7(a-c).

Table 3.7: Selected criteria, goals, weights and results of the numerical optimization

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Goal</th>
<th>Weight</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w/b</td>
<td>Within range from 0.32 to 0.4</td>
<td>-</td>
<td>0.32</td>
</tr>
<tr>
<td>Fly ash</td>
<td>Within range from 0 to 25%</td>
<td>-</td>
<td>9.8%</td>
</tr>
<tr>
<td>Nano-silica</td>
<td>Within range from 0 to 4%</td>
<td>-</td>
<td>0.8%</td>
</tr>
<tr>
<td>CNA:CNI</td>
<td>Within range</td>
<td>-</td>
<td>1.63:1</td>
</tr>
<tr>
<td>Initial setting time</td>
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<td>-</td>
<td>78 min</td>
</tr>
<tr>
<td>Final setting time</td>
<td>Within range 240-480 min</td>
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<td>335 min</td>
</tr>
<tr>
<td>$f'_c$ 7d</td>
<td>None</td>
<td>-</td>
<td>15.74 MPa</td>
</tr>
<tr>
<td>$f'_c$ 28d</td>
<td>Within range 30 to 32 MPa</td>
<td>-</td>
<td>30 MPa</td>
</tr>
<tr>
<td>Durability factor</td>
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<td>107.7%</td>
</tr>
<tr>
<td>Cost</td>
<td>Minimize</td>
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<td>CAD $369</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w/b</td>
<td>Within range from 0.32 to 0.4</td>
<td>-</td>
<td>0.32</td>
</tr>
<tr>
<td>Fly ash</td>
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<td>11.2%</td>
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</tr>
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<td>1.38:1</td>
</tr>
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<td>Initial setting time</td>
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<td>-</td>
<td>68 min</td>
</tr>
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<td>Final setting time</td>
<td>Within range 240-480 min</td>
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<td>292 min</td>
</tr>
<tr>
<td>$f'_c$ 7d</td>
<td>None</td>
<td>-</td>
<td>17.5 MPa</td>
</tr>
<tr>
<td>$f'_c$ 28d</td>
<td>Within range from 32 to 35 MPa</td>
<td>-</td>
<td>32 MPa</td>
</tr>
<tr>
<td>Durability factor</td>
<td>Maximize</td>
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<td>109.8%</td>
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<tr>
<td>Cost</td>
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<td>4</td>
<td>CAD $383.3</td>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w/b</td>
<td>Within range from 0.32 to 0.4</td>
<td>-</td>
<td>0.32</td>
</tr>
<tr>
<td>Fly Ash</td>
<td>Within range from 0 to 25%</td>
<td>-</td>
<td>0%</td>
</tr>
<tr>
<td>Nano-silica</td>
<td>Within range from 0 to 4%</td>
<td>-</td>
<td>2.3%</td>
</tr>
<tr>
<td>CNA:CNI</td>
<td>Within range</td>
<td>-</td>
<td>1.25:1</td>
</tr>
<tr>
<td>Initial setting time</td>
<td>Minimize</td>
<td>5</td>
<td>62 min</td>
</tr>
<tr>
<td>Final setting time</td>
<td>Minimize</td>
<td>5</td>
<td>292 min</td>
</tr>
<tr>
<td>$f'_c$ 7d</td>
<td>Maximize</td>
<td>5</td>
<td>19.8 MPa</td>
</tr>
<tr>
<td>$f'_c$ 28d</td>
<td>Maximize</td>
<td>5</td>
<td>36.9 MPa</td>
</tr>
<tr>
<td>Durability factor</td>
<td>Maximize</td>
<td>5</td>
<td>107.7%</td>
</tr>
<tr>
<td>Cost</td>
<td>Minimize</td>
<td>5</td>
<td>CAD $402</td>
</tr>
</tbody>
</table>

Note: CAD refers to Canadian dollar.
Chapter 3: Statistical Modeling of Concrete Mixtures Cured Under -5°C

The contour plots in Fig. 3.7 graphically show the desirability functions of the different scenarios obtained from the optimization process for the criteria listed in Table 3.7. For Scenarios I and II, within the range of the axes shown in Figs. 3.7, the contour plots indicated that the desirability function increased with increasing the fly ash dosage and dilution of the nano-silica content. The highest desirability function for Scenario I was achieved with 0.32 w/b, 9.8% fly ash, 0.8% nano-silica, and ratio of CNA to CNI of 1.63:1. The highest desirability function for Scenario II was obtained with 0.32 w/b, 11.2% fly ash, 1.85% nano-silica, and ratio of CNA to CNI of 1.38:1. The suggested mixtures should achieve 30-32 MPa compressive strength at 28 days and DF of more than 100%, if they were cast and cured at a freezing temperature of -5°C. This does not conform to the CW3310 (2015) specifications, which restrict the use of fly ash between October 1 and May 15 (which represent the cold weather period in Winnipeg, Manitoba, Canada). For Scenario III, the isoresponse curves showed that mixture with 0.32 w/b, 0% fly ash, 2.3% nano-silica, and ratio of CNA to CNI of 1.25:1 can reach the desired goals of this scenario. The optimum mixture showed lower setting times, and marginally higher compressive strength and DF compared with that of the other scenarios.

Figure 3.7: Contour plots of the desirability function at 0.32 w/b for: (a) Scenario I (CNA:CNI = 1.63:1), (b) Scenario II (CNA:CNI = 1.38:1), (c) and Scenario III (CNA:CNI = 1.25:1).
The optimization exercises showed that the incorporation of nano-silica with a low water content was key to achieve the desired responses for the different scenarios. Also, it allowed for the incorporation of some (10 to 13%) fly ash in concrete cast and cured at a freezing temperature (except for Scenario III targeting repair work), which contributed to reducing the overall all cost of mixtures, while meeting the desired goals for different applications. It is worth noting that the isoresponses of the desirability function may change if different criteria are selected in the optimization process.

3.6 Discussion

3.6.1 Mercury Intrusion Porosimetry (MIP)

To characterize the pore structure of concrete mixtures and interpret the results of bulk tests, mixtures representing the factorial part of the model, were selected for the MIP test. Table 3.8 shows the MIP results obtained from these mixtures after curing at -5°C for 28 days. The MIP trends conformed to the aforementioned hardened properties and proved the remarkable effect of the variables studied on concrete microstructure. The presence of higher water content in concrete resulted in coarse microstructure as indicated by increasing specimens’ porosity, threshold pore diameter and proportion of macro-pores. For instance, mixture 0.4-A had 42% and 143% increase in porosity and threshold pore diameter as well as 55% lower proportion of micro-pores compared to mixture 0.32-A. The coarser microstructure associated with higher water content negatively affected specimens’ strength; thus, the susceptibility to fluid penetration and saturation. Subsequently, it aggravated the deterioration of concrete when exposed to freezing-thawing cycles.
Similarly, incorporating fly ash in concrete, cast and cured at a sub-zero temperature, adversely affected the pore structure after 28 days. For example, the incorporation of 25% fly ash in mixture 0.32-A to produce mixture 0.32-F25-A increased both concrete porosity and threshold pore diameter by 24% and 14%, respectively; correspondingly, the proportion of micro-pores was decreased by 28%. This can be attributed to the replacement of cement with slowly reactive material, with much less lime content than that of cement. The pozzolanic reactivity of fly ash was particularly impaired due to the freezing temperature, as will be substantiated in the TG section. Fly ash concrete specimens, without nano-silica, suffered from coarse microstructure, especially at high dosages (25%) of fly ash. Therefore, these specimens yielded the lowest strength and inferior resistance to freezing-thawing cycles.

The incorporation of nano-silica in concrete, regardless of the w/b, fly ash dosage or CWAS type, significantly improved the pore structure of concrete cast and cured at -5°C.
5°C. For example, the addition of 4% nano-silica in mixture 0.4-A to produce mixture 0.4-N4-A decreased the 28 days porosity and threshold pore diameter by 13% and 65%, respectively, and increased the proportion of micro-pores by 57%. In addition, the incorporation of nano-silica in fly ash concrete imparted a positive effect on its microstructure features. For instance, compared with mixture 0.4-F25-AI, mixture 0.4-F25-N4-AI had 8% and 58% reduction in porosity and threshold pore diameter, respectively and 369% increase in proportion of micro-pores. These trends verified the functionality of nano-silica, in the presence of CWAS, to densify the microstructure of concrete, cast and cured under sub-zero temperature, resulting in relatively higher strength. Also, the refined pore structure of concrete links to the superior resistance of nano-modified concrete specimens, with or without fly ash, to freezing-thawing cycles likely due to discounting the susceptibility to saturation, irrespective of the strength grade of concrete.

Increasing the dosage of CNI in the CWAS significantly affected the microstructural development of concrete. For instance, incorporating CNAI in concrete to produce mixture 0.4-N4-AI reduced concrete porosity and threshold pore diameter by 12% and 17%, respectively and increased the proportion of micro-pores by 76% compared with that of mixture 0.4-N4-A incorporating CNA only. Calcium nitrate and nitrite based CWAS, which contain the same cations as C₃S and β-C₂S in cement, have the capability of accelerating the hydration kinetics of cement through a nucleation effect resulting in concrete microstructure improvement, especially at early-age (Ratinov and Rozenberg 1996). The stronger accelerating nature of CNI compared to CNA may be ascribed to the relatively higher proportion of calcium ions, by molecular mass, in CNI (30%) compared to CNA (24%). These calcium ions help at reaching critical saturation of
the pore solution in concrete at early-age; thus, faster production of CH, which is essential for nano-silica to start its pozzolanic reaction. Therefore, the presence of CNI in CWAS resulted in more development in microstructure of concrete cast and cured at a freezing temperature, especially with the presence of nano-silica, which explains the faster setting times and improved performance of mixtures comprising CNI. The hydration development and microstructure of mixtures comprising CNAI were further studied in the succeeding sections.

3.6.2 Thermal Analysis

The portlandite (CH) contents in the hardened paste was quantified by TG, which was performed for concrete mixtures representing the factorial part of the model with CNAI, after 4 and 12 h and 1, 3, 7, 14, 28, 56 and 120 days of curing at -5°C as shown in Figs. 3.8 and 3.9. The production of CH content up to 12 h conformed to the hardening rates of the different mixtures; the mixtures with w/b of 0.32 had higher contents of CH compared with that of corresponding mixtures with w/b of 0.4. This was ascribed to the earlier hydration development due to reaching critical saturation levels of Ca²⁺ and OH⁻ ions in the pore solution of the mixtures with lower water content (Neville 2011), and thus faster production of hydration products resulting in accelerating skeletal rigidity of concrete. In addition, the incorporation of fly ash in concrete mixtures produced lower contents of CH at early-age (Fig. 3.8). This can be attributed to the dilution of cement with a slowly reactive pozzolan, especially under cold weather, even with the coexistence of an efficient CWAS (CNAI). Thus, mixtures incorporating higher contents of water and/or fly ash showed retarded setting times and slow strength development at early-age.
Figure 3.8: Early-age thermogravimetry results for the portlandite contents up to 7 days of curing at -5°C.

Comparatively, nano-modified mixtures comprised higher CH contents in the hardened paste at early-age. For instance, as shown in Fig. 3.9, the normalized CH contents in nano-modified mixtures relative to the corresponding mixtures without nano-silica varied between 1.15 to 1.65 and 1.22 to 1.32 after 1 and 3 days of curing at -5°C, respectively which links to the improved mechanical properties of these mixtures at early-age. This emphasized the role of CWAS used herein to maintain the functionality of nano-silica at a freezing temperature; agglomerates of nano-silica provided additional surfaces for the hydration products to precipitate on (Ghazy et al. 2016; Said et al. 2012; Senff et al. 2009), resulting in further accelerating the kinetics of hydration reactions, hardening rates, and microstructural development at early-age.
Chapter 3: Statistical Modeling of Concrete Mixtures Cured Under -5°C

Figure 3.9: Late-age thermogravimetry results for the portlandite contents up to 120 days of curing at -5°C.

At later ages, the CH contents in mixtures without nano-silica and fly ash (0.4-AI and 0.32-AI) steadily increased up to 120 days of curing at the adopted curing temperature (Fig. 3.9) due to the hydration of cement. After 56 days of curing at -5°C, the fly ash concrete mixtures 0.4-F25-AI and 0.32-F25-AI showed a steady plateau for CH contents, implying some consumption of CH by the late pozzolanic reactivity of fly ash, which was insufficient with respect to the amount of CH produced by the hydration of un-hydrated cement grains. This was substantiated by the absence of a downward trend of CH contents due efficient pozzolanic activity of fly ash, which typically commences after 28 days under normal curing temperatures (Ghazy et al. 2016; Wesche 2014; Neville 2011). Thereby, these mixtures had insufficient degree of microstructural development, which explains their low strength and inferior resistance to freezing-thawing cycles.
Comparatively, after 14 days of curing at -5°C, the nano-modified mixtures showed notable consumption of CH up to 120 days as the normalized ratios of these mixtures to the corresponding mixtures without nano-silica decreased significantly. For instance, the normalized CH contents in mixture 0.32-N4-AI relative to mixture 0.32-AI were 0.85 and 0.48 at 28 and 120 days, respectively. This trend can be attributed to a delayed pozzolanic effect of nano-silica, due to the freezing temperature of curing, by reacting with CH to produce additional C-S-H gel. This delay in pozzolanic effect was previously reported to reach up 28 days in nano-modified masonry mortar that was cured at +5°C without CWAS (Kazempour et al. 2017; Kazempour et al. 2014). At normal curing temperatures, the pozzolanic activity of nano-silica starts after 3.5 h when cured at 23±2°C (Madani et al. 2012). Correspondingly, the nano-modified fly ash concrete mixtures (0.32-F25-N4-AI and 0.4-F25-N4-AI) showed higher consumption rates of CH up to 120 days relative to their reference mixtures (0.32-F25-AI and 0.4-F25-AI) [Fig. 3.9]. This alluded to the ability of nano-silica to catalyze the indolent reactivity of fly ash at a freezing temperature. Accordingly, the presence of CWAS was essential to maintain the functionally of nano-silica in terms of its nucleation, filler and pozzolanic effects which led to enhancing and densifying the microstructure of concrete, which was reflected by the high resistance to freezing-thawing cycles, irrespective of the strength grade.

3.6.3 Scanning Electron Microscopy

Thin sections of exemplar mixtures from the factorial component with CNAI were selected to perform BSEM after 28 days of curing at -5°C to corroborate the findings of the previous tests. Moreover, the average calcium-to-silicate ratio (C/S) within the interfacial transition zone (ITZ) was assessed by EDX which was performed at several
points in each mixture. The C/S of secondary/pozzolanic and conventional C-S-H was reported to be approximately 1.1 and 1.7, respectively (Detwiler et al. 1996). As shown in Fig. 3.10, the microstructural features of the different mixtures were dissimilar, which indicated the significant effect of the factors studied on concrete cast and cured at a freezing temperature. Complying with the previously discussed trends, increasing the w/b from 0.32 to 0.4 produced concrete with coarser and heterogenous microstructure, as depicted in Figs. 3.10(a-b) vs. 3.10(c-d). This can be attributed to the effect of high water content on increasing the capillary pores and continuity of pore structure. In addition, fly ash concrete mixtures showed coarse microstructure containing interconnected micro-cracks in the ITZ; the C/S of mixture 0.32-AI [Fig. 3.10 (c)] increased from 1.6 to 1.8 with the addition of 25% fly ash to produce mixture 0.32-F25-AI [Fig. 3.10 (e)]. This indicated insufficient degree of hydration, which was reflected by the low strength and DF of mixtures with high w/b and fly ash content.

The inclusion of nano-silica in concrete cast and cured at a freezing temperature produced more homogenous microstructure, regardless of the w/b or type of binder. For example, the incorporation of 4 % nano-silica in mixture 0.32-AI to produce mixture 0.32-N4-AI reduced the C/S from 1.6 to be 1.1 as shown in Fig. 3.10 (c and d) which highlights the influence of nano-silica’s pozzolanic effect, even at -5°C, on densifying the microstructure of concrete by producing secondary C-S-H gel. The actions of nano-silica agglomerates in concrete can be attributed to the nucleation, pozzolanic and filler effects as well as reducing the apparent w/b due to the absorption of water into their ultra-high nano porosity (Ghazy et al. 2016; Haruehansapong et al. 2014; Said et al. 2012; Senff et al. 2009)
Figure 3.10: BSEM micrographs for thin sections from mixtures: (a) 0.4-AI (avg. $C/S = 1.8$), (b) 0.4-N4-AI (avg. $C/S = 1.1$), (c) 0.32-AI (avg. $C/S = 1.6$), (d) 0.32-N4-AI (avg. $C/S = 1.1$), (e) 0.32-F25-AI (avg. $C/S = 1.8$), and (f) 0.32-F25-N4-AI (avg. $C/S = 1.4$).

Note: The $C/S$ values were calculated at 20 \( \mu \text{m} \) from the aggregates surfaces.

Accordingly, the addition of nano-silica to fly ash mixtures markedly improved the densification of the ITZ and refinement of the pore structure, [Fig. 3.10 (f vs. e)]; the average $C/S$ in mixtures 0.32-F25-N4-AI and 0.32-F25-AI was 1.4 and 1.8, respectively. These trends correlate to the improved performance of nano-modified and nano-modified fly ash concrete mixtures, that were cast and cured at -5°C, in terms of strength,
resistance to freezing-thawing cycles, pore structure refinement and hydration development. Therefore, the incorporation of nano-silica in concrete, at low w/b, along with the presence of CWAS (especially CNI), may present a viable option for cold weather construction applications. Such mixtures did neither need heating nor protection at -5°C, while achieving mutual balance of early-age and durability properties.
CHAPTER 4: PROPERTIES OF NANO-SILICA-MODIFIED CONCRETE CAST AND CURED UNDER CYCLIC FREEZING/LOW TEMPERATURES

In Chapter 3, the response surface method, a statistical modeling approach, was adopted to investigate the effect of different parameters; \(w/b\), fly ash, nano-silica and CWAS type, on performance of concrete, cast and cured under constant freezing temperature -5°C. However, based on the temperature data extracted from the City of Winnipeg weather, in late fall (October and November) and early spring (March and April), the temperature yielded approximately 67% and 33% of the occurrences of -5°C and 5°C, respectively. Consequently, concrete mixtures, cast under the aforementioned conditions, are exposed to daily freezing-thawing cycles which may cause earlier deterioration. Hence, the current chapter presents evaluation of concrete mixtures, cast and cured under cyclic freezing/low temperatures (-5/5°C), performance in terms of fresh, hardened, durability as well as microstructure characteristics based on the response surface method statistical approach.

4.1 Introduction

Temperature is a key factor affecting the hydration of cement paste in concrete. As the temperature drops, the hydration process proceeds at a slower rate and completely stops when the temperature drops below 0°C with approximately 95% of the mixing water turning into ice (Karagöl et al. 2015; Ratinov and Rozenberg 1996; Korhonen et al. 1992), resulting in a heterogonous matrix with coarse microstructure. Moreover, when mixing water turns into ice, it experiences a volume expansion of about 9% inducing hydraulic and osmotic pressures on the walls of concrete pores causing micro-cracks and
rapid deterioration (Karagöl et al. 2015; Prado et al. 1998; Powers and Helmuth 1953). The optimum temperature and relative humidity for hydration of cement are 10 to 22°C and more than 85%, respectively (Karagöl et al. 2015). Under freezing conditions, concrete may lose approximately one-half or more of its design strength when compared with concrete cast and cured under normal temperatures (Korhonen et al. 1992).

Cold weather, according to ACI 306R (2016): Guide to Cold Weather Concreting, and CSA A23.1 (2019): Concrete Materials and Methods of Concrete Construction, is defined as when the air temperature has fallen to or below 4°C and 5°C during concrete protection period, respectively. Therefore, both documents strongly advocate not to place concrete under cold weather conditions without extra precautions during the curing period of concrete to achieve desired physical and mechanical properties, allowing concrete to resist harsh conditions such as freezing-thawing cycles. During cold weather, ACI 306R (2016) and CSA A23.1 (2019) recommend conventional techniques such as heating concrete ingredients (water and aggregate), or installing heated enclosures to avert water from freezing and provide adequate curing conditions for concrete. These practices come at high costs and adverse environmental impacts (Barna et al. 2011). Thus, in cold regions, construction and maintenance season of concrete infrastructure is typically limited to three to five months (usually within May to September) leading to overwhelmingly busy construction periods, backlogged repair schedules and significant socioeconomic losses. Therefore, there is continual need for new and innovative options that permit concrete to be cast, finished, and cured at low temperatures. Consequently, the construction season may be extended within late fall (October to November) and early spring (March to April) periods without the shortcomings of conventional heating practices.
One option that has been introduced to mitigate the negative effects of low temperatures on concrete is cold weather admixture systems (CWAS). The incorporation of CWAS into concrete has two main functions: depressing the freezing point of the mixing water (antifreeze), and accelerating the rate of cement hydration and solidification (acceleration). Therefore, concrete can achieve adequate hardening and strength development rates (Polat 2016; Karagöl et al. 2013). CWAS including calcium chloride, sodium chloride, potash, calcium nitrite, calcium nitrate, sodium nitrate, urea, and their combinations have been reported as effective accelerators and anti-freeze admixtures (Korhonen et al. 1997; Ratinov and Rozenberg 1996). However, chloride-based admixtures have been excluded due to their ability to initiate rapid corrosion problems in steel reinforced concrete (Ratinov and Rozenberg 1996). In addition, sodium-based admixtures have provoked alkali aggregate reactivity (AAR) issues (Ratinov and Rozenberg 1996). Urea was found to retard the setting of concrete; thus, it has adverse effects on the early-age properties (Mwaluwinga et al. 1997). Furthermore, potash was reported to produce defective microstructure and inferior resistance to freezing and thawing cycles (Nmai 1998; Korhonen et al. 1997; Korhonen 1990). Comparatively, calcium nitrite and calcium nitrate were found to be effective in terms of enhancing the early-age properties of concrete by promoting superior strength gain and improving the hydration rates (Nmai 1998; Ratinov and Rozenberg 1996; Korhonen 1990). They increase the strength gain rate and ultimate strength of concrete cured at -5°C to comparable levels of normally cured concrete within 90 days (Karagöl et al. 2015; Korhonen 1990). However, incorporating large amounts of more than 6% of CWAS (calcium nitrite and calcium nitrate) by mass of cement was reported to cause severe shrinkage cracking of concrete (Korhonen; 1997). Moreover, the compressive strength
and water absorption of concrete incorporating 6% calcium nitrate were negatively affected after being exposed to only 28 freezing and thawing cycles (Polat 2016), implicating coarse microstructure. Thus, while the use of CWAS may achieve satisfactory results in terms of hardening and strength rates, their effects on microstructure and durability of concrete are still uncertain.

The emerging innovations in nanotechnology have attracted much attention in the field of concrete research due to the considerable enhancement in concrete physical and mechanical properties by the incorporation of nanoparticles, which have high surface area and vigorous reactivity, to binders (Ghazy et al. 2016; Haruehansapong et al. 2014). Numerous studies (Ghazy et al. 2016; Haruehansapong et al. 2014; Said et al. 2012) have investigated the inclusion of nanoparticles such as nano-silica in cement-based systems mixed and cured under normal temperatures up to 30°C. The findings from these studies showed that nanoparticles contributed positively to concrete properties by speeding up the kinetics of cement hydration and refining the pore structure of hydrated cement paste, leading to producing durable concrete capable of enduring harsh exposures (Ghazy et al. 2016; Haruehansapong et al. 2014; Said et al. 2012).

A recent study at the University of Manitoba (Kazempour et al. 2017; Kazempour et al. 2014) reported the ability of nano-silica to enhance the performance of masonry cement mortars (comprising 30% inert component), which were cast and cured at 5°C without any method of protection. However, there is still dearth of information on nano-silica reactivity under sub-zero temperatures and its interaction with CWAS and other types of cements (e.g. ordinary cement, blended cements containing fly ash) to produce concrete mixtures at lower (e.g. freezing) temperatures. Therefore, in this study combinations of fly ash, nano-silica and CWAS were used to prepare concretes that were
Chapter 4: Statistical Modeling of Concrete Mixtures Cured Under 5/-5°C

mixed, cast and cured under cyclic freezing/low temperatures (-5 and 5°C) representing the temperature range of late fall and early spring in cold regions including North America and Europe. The study followed the design of experiments (DOEs) modeling approach to test 15 concrete mixtures based on the response surface method (RSM). The fresh, hardened and microstructural properties of these mixtures were assessed.

4.2 Methodology

4.2.1 Statistical Models

The Response Surface Method (RSM) based on face-centred composite design (FCCD) was used to evaluate the effect of each mixture design variable on the performance of concrete (refer to Section 3.3.1). The three parameters investigated were fly ash and nano-silica dosages, as well as the type of the antifreeze admixture. The w/b of the different mixtures were kept constant at 0.32 based on its advantageous effect on the properties of concrete, cast and cured under -5°C (refer to Chapter 3). Each factor was evaluated at three different levels and coded as follows; maximum (+1), minimum (-1), and central (0). This model is valid for mixtures with water-to-binder ratio (w/b) of 0.32 mixed, cast, and cured under cyclic freezing/low temperatures and made with fly ash contents of 0 to 25%, nano-silica contents of 0 to 4% and a combination of calcium nitrite (CNI) and calcium nitrate (CNA) admixtures as shown in Table 4.1. Independent responses were used to run the models, these modeled responses were initial (IST) and final (FST) setting times, 3 and 28 days compressive strengths, and absorption of fluids to represent the fresh, hardened and durability properties, respectively.
### Table 4.1: Coded and absolute values of investigated parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coding Values</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>-1</td>
</tr>
<tr>
<td>Fly ash content, kg/m³</td>
<td>0</td>
</tr>
<tr>
<td>Nano-silica content, kg/m³</td>
<td>0</td>
</tr>
<tr>
<td>Antifreeze ratio (CNA:CNI)</td>
<td>1:0</td>
</tr>
</tbody>
</table>

Note: The components of antifreeze for levels -1, 0 and +1 were 100% CNA, 67% CNA + 33% CNI and 50% CNA + 50% CNI by mass, respectively.

### 4.3 Experimental Program

#### 4.3.1 Materials and Mixtures

The materials used in this chapter were similar to that used in Chapter 3 (refer to Section 3.4.1). SEM images of GU cement and fly ash are shown in Fig. 4.1. While Fig. 4.2 presents a TEM image of the used nano-silica.

![Figure 4.1: SEM image of : (a) GU cement and (b) fly ash.](image)

![Figure 4.2: TEM image of nano-silica particles.](image)
Chapter 4: Statistical Modeling of Concrete Mixtures Cured Under 5/-5°C

Fifteen concrete mixtures were prepared to investigate the three parameters adopted (Table 4.2), which were expected to have significant effects on the properties of concrete: fly ash content, nano-silica dosage, and type of anti-freeze admixture. Each mixture ID starts with a number that stands for the percentage of the subsequent letter and then the type of antifreeze admixture. The letters in the mixture ID are defined as follows: general use cement (GU), fly ash (F), nano-silica (N), level -1 of antifreeze (A), level 0 (AAI) and level 1 (AI).

Table 4.2: Proportions of mixtures per cubic meter

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Coding Notation</th>
<th>Fly Ash (kg)</th>
<th>Nano-Silica (kg)</th>
<th>CNA\textsuperscript{a}+CNI (kg)</th>
<th>Cement (kg)</th>
<th>Water\textsuperscript{b} (kg)</th>
<th>Fine/Coarse Aggregate (kg)</th>
</tr>
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<tbody>
<tr>
<td>F25-N4-AI</td>
<td>1, 1, 1</td>
<td>100</td>
<td>32</td>
<td>14+32</td>
<td>284</td>
<td>90</td>
<td>608/1130</td>
</tr>
<tr>
<td>F25-N4-A</td>
<td>1, 1, -1</td>
<td>100</td>
<td>32</td>
<td>27+0</td>
<td>284</td>
<td>112</td>
<td>603/1120</td>
</tr>
<tr>
<td>N4-AI</td>
<td>-1, 1, 1</td>
<td>0</td>
<td>32</td>
<td>14+32</td>
<td>384</td>
<td>90</td>
<td>621/1152</td>
</tr>
<tr>
<td>N4-A</td>
<td>-1, 1, -1</td>
<td>0</td>
<td>32</td>
<td>27+0</td>
<td>384</td>
<td>112</td>
<td>616/1143</td>
</tr>
<tr>
<td>F25-AI</td>
<td>1, -1, 1</td>
<td>100</td>
<td>0</td>
<td>14+32</td>
<td>300</td>
<td>106</td>
<td>610/1132</td>
</tr>
<tr>
<td>F25-A</td>
<td>1, -1, -1</td>
<td>100</td>
<td>0</td>
<td>27+0</td>
<td>300</td>
<td>128</td>
<td>6051123</td>
</tr>
<tr>
<td>GU-AI</td>
<td>-1, -1, 1</td>
<td>0</td>
<td>0</td>
<td>14+32</td>
<td>400</td>
<td>106</td>
<td>622/1156</td>
</tr>
<tr>
<td>GU-A</td>
<td>-1, -1, -1</td>
<td>0</td>
<td>0</td>
<td>27+0</td>
<td>400</td>
<td>128</td>
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</tr>
<tr>
<td>F12.5-AAI</td>
<td>0, -1, 0</td>
<td>50</td>
<td>0</td>
<td>18+21</td>
<td>350</td>
<td>113</td>
<td>614/1141</td>
</tr>
<tr>
<td>F12.5-N4-AAI</td>
<td>0, 1, 0</td>
<td>50</td>
<td>32</td>
<td>18+21</td>
<td>334</td>
<td>97</td>
<td>613/1138</td>
</tr>
<tr>
<td>F25-N2-AAI</td>
<td>1, 0, 0</td>
<td>100</td>
<td>16</td>
<td>18+21</td>
<td>292</td>
<td>100</td>
<td>607/1128</td>
</tr>
<tr>
<td>N2-AAI</td>
<td>-1, 0, 0</td>
<td>0</td>
<td>16</td>
<td>18+21</td>
<td>392</td>
<td>105</td>
<td>620/1151</td>
</tr>
<tr>
<td>12.5F-2N-AI</td>
<td>0, 0, 1</td>
<td>50</td>
<td>16</td>
<td>14+32</td>
<td>342</td>
<td>98</td>
<td>615/1142</td>
</tr>
<tr>
<td>12.5F-2N-A</td>
<td>0, 0, -1</td>
<td>50</td>
<td>16</td>
<td>27+0</td>
<td>342</td>
<td>120</td>
<td>610/1133</td>
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<tr>
<td>12.5F-2N-AAI</td>
<td>0, 0, 0</td>
<td>50</td>
<td>16</td>
<td>18+21</td>
<td>342</td>
<td>105</td>
<td>613/1139</td>
</tr>
</tbody>
</table>

Note: \textsuperscript{a}The CNA admixture was in a solid form with 70% active ingredient.\textsuperscript{b}Adjusted amount of water considering the water content of nano-silica (aqueous solution with 50% solid content of SiO\textsubscript{2}) and the CNI (aqueous solution with 30% solid content).

4.3.2 Procedures

The mixing and casting operations were done at temperature of -5±1°C, and the curing was done under cyclic freezing/low temperatures until testing. These cycles were designed based on the temperature data extracted from the city of Winnipeg weather data.
for the last 10 years (Fig. 4.3). The data represents weather in late fall (October and November) and early spring (March and April), where approximately 67% of the occurrences yielded an average of -5°C and 33% reached an average of 5°C. Thus, an environmentally controlled chamber was utilized to mimic these cycles. The temperature of the chamber was calibrated before casting at -5±1°C for 16 hours, 0.5 hour for ramping up to +5±1°C for 7 hours and then 0.5 hour for ramping down to -5±1°C. To ensure homogeneous air temperature throughout the controlled area and to simulate wind effect, the chamber was equipped with a fan that circulated the air at an average speed of 25 km/h. The sequence of mixing was similar to Chapter 3 (Section 3.4.2). All specimens were demolded after 24 h of casting and covered with polyethylene sheets for 3 days. Then, they were left uncovered in the environmental chamber under the cyclic temperatures until testing.

Figure 4.3: Temperature history of Winnipeg (Manitoba) for the past 10 years in (a) early spring and (b) late fall

4.3.3 Testing

The IST and FST were characterized based on the penetration resistance of the mortar part of each mixtures according to ASTM C403 (2016). Mortar specimens were cast in molds with lateral dimension of 150 mm and height of 150 mm. Both IST and FST were measured inside the environmental chamber, at -5°C, using standard penetration needles.
In addition, triplicates 100×200 mm concrete cylinders were tested for compressive strength according to ASTM C39 (2020) at early (3 days) and later (28 days) ages. The fluid absorption of concrete was evaluated based on a test protocol developed by Tiznobik and Bassuoni (2018) on concrete discs (75×50 mm). After 28 days of curing in the environmental chamber at the stated cyclic temperatures, three concrete discs were placed in an oven at 50±2˚C and 40% RH until reaching a constant mass. They were then put in a sealed desiccator under vacuum pressure (~85 kPa) for 6 hours. Subsequently, each specimen was freely immersed in 4% calcium chloride (CaCl$_2$) solution for up to 360 min, and the amounts of absorption were recorded after 1, 5, 10, 20, 40, 80, 160 and 360 min to the nearest 0.01 g. Furthermore, mercury intrusion porosimetry (MIP) was conducted on concrete samples to examine the characteristics of their pore structure after 28 days of curing under the cyclic freezing/low temperatures. In addition, thermal analysis and microscopy studies were conducted to corroborate the trends acquired from the bulk tests. Same procedures as per Chapter 3 (Section 3.4.3) were followed to prepare concrete samples for the MIP, TG and BSEM analysis.

4.4 Results

4.4.1 Derived Statistical Models

The experimental results of five responses that represent fresh (IST and FST), hardened (compressive strength at 3 and 28 days), and durability (fluid absorption) properties are summarized in Table 4.3. Statistical models were derived to evaluate the three independent variables (fly ash, nano-silica, antifreeze admixture) at three levels (high, medium and low). The general model is expressed by Eq. 3.1 (refer to Section 3.5.1).
Models’ coefficients were determined using non-linear regression analysis with an assumption that the data are normally distributed. Moreover, Analysis of Variance (ANOVA) was used to test the different factors and their interactions to identify insignificant variables and secondary interactions, which were subsequently eliminated from the derived modeling equations. The probability value (P-value), which determines the statistical significance of each term in the models was limited to 5%; thus, there is less than 5% chance (or 95% confidence limit) that a tested response exceeds the value of the specified coefficient. Large P-values (>0.05) is an indication that the term is insignificant, and thus it did not have an effect on the measured response.

Table 4.3: Average results from the bulk tests

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Model Code</th>
<th>IST (min)</th>
<th>FST (min)</th>
<th>(f'_c) 3d (MPa)</th>
<th>(f'_c) 28d (MPa)</th>
<th>Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F25-N4-AI</td>
<td>1, 1, 1</td>
<td>60 (2.4)</td>
<td>335 (6.2)</td>
<td>16.0 (1.1)</td>
<td>33.3 (0.3)</td>
<td>2.9% (0.2%)</td>
</tr>
<tr>
<td>F25-N4-A</td>
<td>1, 1, -1</td>
<td>145 (2.4)</td>
<td>570 (2.4)</td>
<td>14.8 (0.7)</td>
<td>34.8 (0.9)</td>
<td>3.2% (0.1%)</td>
</tr>
<tr>
<td>N4-AI</td>
<td>-1, 1, 1</td>
<td>30 (0)</td>
<td>220 (4.1)</td>
<td>24.4 (1.8)</td>
<td>50.2 (0.9)</td>
<td>2.0% (0.06%)</td>
</tr>
<tr>
<td>N4-A</td>
<td>-1, 1, -1</td>
<td>100 (4.1)</td>
<td>290 (4.1)</td>
<td>21.2 (0.9)</td>
<td>49.9 (1.0)</td>
<td>2.4% (0.1%)</td>
</tr>
<tr>
<td>F25-AI</td>
<td>1, -1, 1</td>
<td>80 (2.4)</td>
<td>430 (6.2)</td>
<td>13.0 (1.0)</td>
<td>24.1 (1.7)</td>
<td>3.2% (0.05%)</td>
</tr>
<tr>
<td>F25-A</td>
<td>1, -1, -1</td>
<td>240 (4.1)</td>
<td>930 (2.4)</td>
<td>11.7 (0.1)</td>
<td>25.2 (0.7)</td>
<td>3.8% (0.1%)</td>
</tr>
<tr>
<td>GU-AI</td>
<td>-1, -1, 1</td>
<td>35 (0)</td>
<td>275 (4.1)</td>
<td>19.9 (0.6)</td>
<td>42.4 (1)</td>
<td>2.3% (0.02%)</td>
</tr>
<tr>
<td>GU-A</td>
<td>-1, -1, -1</td>
<td>130 (2.4)</td>
<td>500 (2.4)</td>
<td>17.1 (0.9)</td>
<td>39.9 (0.9)</td>
<td>3.2% (0.01%)</td>
</tr>
<tr>
<td>F12.5-AAI</td>
<td>0, -1, 0</td>
<td>110 (4.1)</td>
<td>500 (6.2)</td>
<td>14.8 (1.1)</td>
<td>34.9 (1.1)</td>
<td>2.7% (0.08%)</td>
</tr>
<tr>
<td>F12.5-N4-AAI</td>
<td>0, 1, 0</td>
<td>65 (0)</td>
<td>375 (6.2)</td>
<td>22.6 (0.5)</td>
<td>41.6 (1.3)</td>
<td>2.5% (0.06%)</td>
</tr>
<tr>
<td>F25-N2-AAI</td>
<td>1, 0, 0</td>
<td>90 (4.1)</td>
<td>460 (2.4)</td>
<td>17.5 (0.3)</td>
<td>33.8 (0.7)</td>
<td>2.8% (0.2%)</td>
</tr>
<tr>
<td>N2-AAI</td>
<td>-1, 0, 0</td>
<td>65 (2.4)</td>
<td>315 (4.1)</td>
<td>26.9 (0.7)</td>
<td>48.4 (1.6)</td>
<td>2.2% (0.2%)</td>
</tr>
<tr>
<td>12.5F-2N-AI</td>
<td>0, 0, 1</td>
<td>65 (2.4)</td>
<td>310 (4.1)</td>
<td>22.8 (1.9)</td>
<td>41.3 (1.4)</td>
<td>2.5% (0.2%)</td>
</tr>
<tr>
<td>12.5F-2N-A</td>
<td>0, 0, -1</td>
<td>125 (4.1)</td>
<td>615 (6.2)</td>
<td>19.3 (1.3)</td>
<td>37.7 (1.1)</td>
<td>2.7% (0.08%)</td>
</tr>
<tr>
<td>12.5F-2N-AAI</td>
<td>0, 0, 0</td>
<td>85 (2.4)</td>
<td>415 (4.1)</td>
<td>21.4 (1.0)</td>
<td>41.9 (1.0)</td>
<td>2.6% (0.04%)</td>
</tr>
</tbody>
</table>

Note: Numbers in brackets represent the standard deviation

\(f'_c\) 3d refers to 3 days compressive strength

\(f'_c\) 28d refers to 28 days compressive strength

The coefficients of determination \((R^2)\) of all the derived statistical models were \(\geq 94\%\) with the experimental results, and the statistical software (Design-Expert 11 2018)
validated the assumption that the residual terms are normally distributed. This indicates a high confidence level in the models. The results of the models as well as their correlation coefficients and the relative significance of variables according to ANOVA are listed in Table 4.4. The best fit responses of the models for IST, FST, 3 and 28 days compressive strengths and absorption are given in Eqs. (4.1-4.5).

\[
\log_{10}[\text{IST}(\text{min})] = 0.12 \times FA - 0.08 \times NS - 0.22 \times A + 1.92 \quad \text{(Eq. 4.1)}
\]

\[
\log_{10}[\text{FST}(\text{min})] = 0.11 \times F - 0.08 \times N - 0.12 \times A + 0.03 \times NA + 2.61 \quad \text{(Eq. 4.1)}
\]

\[
\frac{1}{(f'_{c3d})} \text{(MPa)} = 0.01 \times FA - 0.008 \times NS - 0.004 \times A + 0.01 \times NS^2 + 0.05 \quad \text{(Eq. 4.3)}
\]

\[
f'_{c28d} \text{(MPa)} = -7.96 \times FA + 4.33 \times NS - 2.54 \times N^2 + 40.99 \quad \text{(Eq. 4.4)}
\]

\[
\text{Absorption (\%)} = 0.38 \times FA - 0.22 \times NS - 0.23 \times A + 2.54 \quad \text{(Eq. 4.5)}
\]

where, \(FA\), \(NS\) and \(A\) represent fly ash, nano-silica and antifreeze (CNA:CNI), respectively. These equations are in terms of coded factors and can be used to make predictions for a response at given levels of each factor. Each coefficient indicates an expected change in a response per unit change in the factor value. Coded equations are useful for identifying the relative impact of the factors by comparing factors coefficients. The validity of the models is bounded by the high level factor (+1) and the low level factor (-1).
Table 4.4: Derived coefficients for the models and their significance based on ANOVA

<table>
<thead>
<tr>
<th>Multiplied by</th>
<th>Log(IST)</th>
<th>Log(FST)</th>
<th>$1/f'_{c,3d}$</th>
<th>$f'_{c,28d}$</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>1.92</td>
<td>2.61</td>
<td>0.046</td>
<td>40.99</td>
<td>0.38</td>
</tr>
<tr>
<td>FA</td>
<td>0.12</td>
<td>0.11</td>
<td>0.012</td>
<td>-7.96</td>
<td>-0.22</td>
</tr>
<tr>
<td>NS</td>
<td>-0.08</td>
<td>-0.08</td>
<td>-0.008</td>
<td>4.33</td>
<td>-0.23</td>
</tr>
<tr>
<td>A</td>
<td>-0.22</td>
<td>-0.12</td>
<td>-0.004</td>
<td>0.39</td>
<td>0.02</td>
</tr>
<tr>
<td>FA*NS</td>
<td>-</td>
<td>0.002</td>
<td>-0.001</td>
<td>0.12</td>
<td>0.07</td>
</tr>
<tr>
<td>NS*A</td>
<td>-</td>
<td>0.03</td>
<td>0.001</td>
<td>-0.33</td>
<td>0.05</td>
</tr>
<tr>
<td>FA*A</td>
<td>-</td>
<td>-0.02</td>
<td>0.000</td>
<td>-0.67</td>
<td>0.03</td>
</tr>
<tr>
<td>FA$^2$</td>
<td>-</td>
<td>-</td>
<td>0.002</td>
<td>0.29</td>
<td>0.16</td>
</tr>
<tr>
<td>NS$^2$</td>
<td>-</td>
<td>-</td>
<td>0.011</td>
<td>-2.54</td>
<td>0.16</td>
</tr>
<tr>
<td>A$^2$</td>
<td>-</td>
<td>-</td>
<td>0.003</td>
<td>-1.31</td>
<td>2.54</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.94</td>
<td>0.97</td>
<td>0.98</td>
<td>0.97</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Note: Bold factors and interactions are significant ($P\text{-Value} < 0.05$)

4.4.2 Setting Times

The experimental results of IST and FST widely varied between 30 to 240 min and 220 to 930 min, respectively. Thus, the hardening process of all mixtures took place during the first freezing time interval at $-5^\circ\text{C}$. The corresponding statistical models presented by Eqs. 4.1 and 4.2 indicated that the IST and FST were significantly influenced by the fly ash content and antifreeze admixtures. The antifreeze admixture had a dominant effect on the IST relative to the fly ash content (-0.22 vs. 0.12). However, the effect of the antifreeze admixtures and fly ash content was comparable in the case of FST. The nano-silica content had a significant effect on the IST and FST models, but its coefficients were less than that of the fly ash content and antifreeze admixtures.

The isoresponse curves, generated from the derived models in Figs. 4.4 and 4.5, graphically show these trends. For instance Figs. 4.4 and 4.5 show that the IST and FST were extended with increasing the fly ash dosage, whereas they were shortened with increasing the nano-silica dosage, irrespective of the type of antifreeze admixture. Also, at any fixed fly ash and nano-silica contents, the IST and FST were markedly shortened.
with the use of a mixed CWAS such as CNAI, as depicted by Figs. 4.4(b) and 4.5(b) in comparison to Figs. 4.4(a) and 4.5(a). This can be ascribed to the incorporation of CNI, which acts as a stronger accelerator compared to CNA (Ratinov and Rozenberg 1996), thus speeding the setting process of concrete under the freezing temperature.

Figure 4.4: Isoresponse curves of IST (min): (a) CNA, (b) CNAAI, and (c) CNAI.

The effect of high dosages of fly ash in delaying the setting time of concrete cast and cured at normal temperatures is well-documented in the literature (Wesche 2014; Neville 2011). In this study, increasing the fly ash content up to 25% markedly prolonged the setting time under the freezing temperature, even with the incorporation of CWAS, especially in the case of CNA alone. For example, incorporating 25% fly ash in mixture GU-A to produce mixture F25-A resulted in 85% and 86% increase of IST and FST, respectively. This can be attributed to the dilution of cement with less reactive SCM, resulting in slowing down the kinetics of the hydration and hardening processes. While the incorporation of fly ash in concrete is not recommended for cold weather applications (ACI 306R 2016; CW3310 2015), it is needed to produce concrete with improved long-term performance/durability. Thus, such early-age technical limitations should be mitigated.
Nano-silica decreased the setting time of nano-modified and nano-modified fly ash mixtures. For the GU mixtures (single binders), the decrease for the nano-modified mixtures ranged between 5 to 30 min and 55 to 210 min for IST and FST, respectively. Compared to the fly ash mixtures (blended binders), the nano-modified fly ash mixtures showed more pronounced reductions in the IST and FST, which ranged between 20 to 95 min and 95 to 360 min, respectively. This alluded to synergistic effects of nano-silica and fly ash on accelerating the reactivity of produced mixture, as will be discussed in the TG section. For instance, adding 4% nano-silica to mixture F25-A to produce mixture F25-N-A resulted in decreasing the IST and FST by 40% and 39%, respectively. Indeed, the setting times of all nano-modified and nano-modified fly ash mixtures were further shortened with the incorporation of mixed CWAS (e.g. CNAI), suggesting efficient placement and finishing operations in cold weather within a reasonable time frame (4 to 8 h). Previous studies (Ghazy et al. 2016; Haruehansapong et al. 2014; Senff et al. 2009) reported the ability of nano-silica to accelerate the hydration process of cementitious binders at early-age under normal temperatures. In this study, complying with Chapter 3 findings, the functionality of nano-silica was still maintained under the freezing

Figure 4.5: Isoresponse curves of FST (min): (a) CNA, (b) CNAI, and (c) CNAI.
temperature. The high surface area of nano-silica (80,000 m$^2$/g) might act as nucleation sites for the hydration products to precipitate, which led to faster dissolution of calcium silicate phases ($C_3S$ and $C_2S$) and in turn increasing the production of calcium hydroxide (CH). These trends are highlighted in the thermal analysis section.

4.4.3 Compressive Strength

The experimental results of compressive strengths at 3 and 28 days varied from 11.7 to 26.9 MPa and 24.1 to 50.2 MPa, respectively. Generally, mixtures with blended binders incorporating high dosages of fly ash (25%) showed lower compressive strength, while nano-modified mixtures showed higher compressive strengths. These trends were depicted by the contour plots shown in Figs. 4.6 and 4.7. Eq. 4.3 indicates that the 3 day compressive strength was affected by the fly ash content, nano-silica content and antifreeze admixtures ratio. The fly ash content had the most significant effect (0.012) on the 3 days compressive strength when compared to nano-silica and antifreeze admixtures which had coefficients of -0.008 and -0.004, respectively. Similarly, the 28 days compressive strength was significantly influenced by the fly ash content followed by nano-silica content (-7.96 vs. 4.33) as shown by Eq. 4.4. However, in contrast to the 3 day compressive strength, the effect of the antifreeze admixtures was insignificant on the 28 compressive strength (Table 4.4). This indicates that the type of antifreeze was important in accelerating the hardening process (setting time) and strength development of concrete at early-age. Subsequently, the development of strength of concrete curing under the cyclic freezing/low temperatures up to 28 days was governed by the reactivity of fly ash and nano-silica, irrespective of the type of antifreeze admixtures.
Increasing the fly ash content up to 25% resulted in decreasing the compressive strength at a constant nano-silica dosage. For instance, incorporating 25% fly ash in mixture GU-A to produce mixture F25-A led to 32% (11.7 MPa) and 37% (25.2 MPa) reduction of compressive strength at 3 and 28 days, respectively. The incorporation of high dosages of fly ash in cold weather concrete mixtures is not recommended by ACI 306R (2016). Slowly reactive SCMs such as fly ash and slag delay the strength development of concrete at early-age; thus, they may prevent concrete from developing adequate resistance to cold weather conditions such as freezing and thawing, especially at early-age. However, the addition of high dosages of CWAS (more than 6% by mass of cement) led to severe shrinkage cracking due to the high acceleration effect of these admixtures (Korhonen et al. 1997). Therefore, the incorporation of fly ash, especially with the coexistence of vigorously reactive materials such as nano-silica, is needed to balance the expected high shrinkage of these mixtures. In addition, the inclusion of fly ash in concrete is reported to be a key factor to achieve long-term durability (Wesche 2014; Neville 2011). At 28 days, all the mixtures tested in this study achieved compressive strength higher than 24.5 MPa, which is required by ACI 306R (2016) for concrete to resist multiple cycles of freezing and thawing, even with the replacement of
Chapter 4: Statistical Modeling of Concrete Mixtures Cured Under 5/-5°C

GU cement with 25% fly ash. It seems that the developed mixture designs herein with low w/b of 0.32, binder content of 400 kg/m³ and incorporation of 15% antifreeze admixtures were efficient at maintaining adequate levels of hydration and strength development under these freezing/low temperature curing conditions.

Figure 4.7: Isoresponse curves of 28-days compressive strength (MPa): (a) CAN, (b) CNAAI, and (c) CNAI

Generally, the incorporation of nano-silica to produce nano-modified concrete mixtures without or with fly ash significantly improved strength values. For the GU mixtures (single binders), the increase for nano-modified mixtures was approximately 4.5 and 9 MPa at 3 days and 28 days compressive strength, respectively. Nano-modified mixtures with GU cement showed the highest compressive strength. For instance, mixture N4-AI had 24.4 and 50.2 MPa compressive strength at 3 and 28 days, respectively. Compared to the fly ash mixtures (blended binders), the nano-modified fly ash mixtures showed increase in the 3 and 28 days compressive strengths, which was approximately 3 and 9.5 MPa, respectively. For instance, adding 4% nano-silica to mixture F25-AI to produce mixture F25-N4-AI resulted in increasing the 3 and 28 days compressive strengths by 27% (16 MPa) and 38% (33.3 MPa), respectively. This role was captured in
Eqs. 4.3 and 4.4 by the appearance of two terms for the nano-silica content (non-squared and squared).

The effect of nano-silica on enhancing the compressive strength of concrete at normal temperatures has been reported in previous studies (Ghazy et al. 2016; Haruehansapong et al. 2014). It was reported that nano-silica has various effects on hardened properties of concrete through enhancing hydration reactions, pozzolanic and filler effects and reducing the apparent w/b in cementitious systems by absorbing water into its ultrafine surface (Ghazy et al. 2016; Haruehansapong et al. 2014; Senff et al. 2009). Complying with the fresh properties behavior of nano-modified mixtures, the results herein indicated that nano-silica maintained its functionality under the freezing/low temperatures with the coexistence of antifreeze systems. Nano-silica led to fast rate of strength gain, high degree of hydration and dense matrix as will be discussed in the MIP, thermal and microscopy sections. It is worth noting that the compressive strength values (30 to 50 MPa) of nano-modified concrete mixtures, cast and cured under cyclic freezing/low temperatures, qualify them for various infrastructural applications, including concrete pavements and bridges (CW3310 2015; MacGregor et al. 1997).

4.4.4 Fluid Absorption
Penetrability of the different concrete mixtures was assessed based on a fluid absorption test results after 28 days of curing under the adopted curing regime. The results ranged from 2.0 to 3.8% (Table 4.3). The derived model, represented by Eq. 4.5, indicates that the fly ash and nano-silica contents as well as antifreeze admixtures are all significant factors controlling the mass transport properties. The fly ash content had a predominant effect on absorption with a coefficient of 0.38, followed by nano-silica content and antifreeze admixtures which had comparable coefficients of 0.22 and -0.23.
Complying with the compressive strength results, the absorption of concrete yielded marked accretion (up to 3.8%) with increasing the fly ash dosage, when holding other variables constant. This trend is depicted in the isoresponse curves in Fig. 4.8. For instance, incorporating 25% fly ash in mixture GU-AI to produce mixture F25-AI led to increasing the fluid absorption by 28% (3.2%). As previously discussed, this can be ascribed to the dilution of cement with a slower reactivity SCM which deaccelerated the kinetics of the hydration processes, subsequently less degree of hydration was reached at the time of testing, especially under the curing regime adopted. Thus, the microstructure produced comprised higher proportion of accessible capillary pores, as will be discussed in the subsequent section, which facilitated fluid penetration.

Figure 4.8: Isoresponse curves of fluid absorption: (a) CAN, (b) CNAAI, and (c) CNAI

Contrary to the effect of fly ash, the increase of nano-silica and CNI dosages had a positive effect on reducing the amount of fluid absorbed by concrete. For the nano-modified mixtures (single binders), the fluid absorption ranged from 2.0 to 2.4%, whereas the nano-modified fly ash mixtures (blended binders) had absorption values which ranged from 2.5 to 3.2%. For instance, the incorporation of 4% nano-silica in mixtures GU-A and F25-A to produce mixtures N4-A and F25-N4-A resulted in decreasing the absorption by 25% and 16%, respectively.
The synergistic effect of nano-silica and fly ash on the development of concrete microstructure, which was cast and cured at normal temperatures has been reported in the literature (Ghazy et al. 2016). In this study, the effect of nano-silica on improving the resistance of concrete to infiltration of fluids was still maintained under the cold curing regime (-5 and 5°C). This can be attributed to the previously discussed physical and chemical actions of nano-silica, which significantly densified the microstructure of concrete. In addition, further reduction of absorption was achieved with the inclusion of mixed CWAS. Figs. 4.8 (a)-(c) indicate adding CNAAI and CNAI to concrete led to lower absorption in comparison to CNA. This can be attributed to the incorporation of CNI that sped up the hydration process of concrete, as shown earlier by the setting times trends and substantiated later in the microstructural analysis sections.

4.4.5 Numerical Optimization

A criteria similar to the third scenario in Section 3.5.5 was selected to optimize a concrete mixtures suitable for repair applications under the 5/-5°C curing regime adopted herein as shown in Table 4.5 (more scenarios are shown in Table B.1 and Fig. B.1). The obtained results showed a desirability of 0.92 as shown in Fig. 4.9. The optimization exercise showed that the incorporation of nano-silica with CNAI as CWAS achieved the desired responses in terms of fast hardening rates, high early- and late-age strengths and high resistance to fluid ingress. Subsequently, nano-modified concrete incorporating CNAI as CWAS may present a viable option for repair applications under cold temperatures down to -5°C.
4.5 Discussion

4.5.1 Mercury Intrusion Porosimetry (MIP)

After 28 days, the MIP test was performed on specimens extracted from eight mixtures (the factorial component of the model), which were selected to capture the effect of the variables tested on the concrete pore structure and corroborate the trends obtained from the bulk tests. The MIP results are listed in Table 4.6.

Generally, the MIP trends complied with that of the macro-scale tests. The use of mixed antifreeze admixtures improved the microstructural features of concrete. For instance, mixture GU-AI had 9% and 50% lower porosity and threshold pore diameter,
respectively as well as 16% higher proportions of micro-pores compared to that of mixture GU-A. The increase in the CNI (strong accelerator) dosage in the CNAI system led to improving the degree of hydration of the cement paste under this cold curing regime, and consequently enhanced the pore structure of the different concrete mixtures. This explains the relatively lower fluid absorption values of mixtures incorporating CNAI [Fig. 4.8(c)], relative to corresponding mixtures comprising CNA and CNAAI [Figs. 4.8(a)-(b)].

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Apparent Total Porosity (%)</th>
<th>Threshold Pore Diameter (μm)</th>
<th>Proportion of Micro-pores [&lt;0.1 μm] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU-A</td>
<td>15.6</td>
<td>0.5</td>
<td>51</td>
</tr>
<tr>
<td>F25-A</td>
<td>18.6</td>
<td>0.80</td>
<td>45</td>
</tr>
<tr>
<td>N4-A</td>
<td>14.8</td>
<td>0.16</td>
<td>61</td>
</tr>
<tr>
<td>F25-N4-A</td>
<td>16.1</td>
<td>0.35</td>
<td>50</td>
</tr>
<tr>
<td>GU-AI</td>
<td>14.2</td>
<td>0.25</td>
<td>59</td>
</tr>
<tr>
<td>F25-AI</td>
<td>17.9</td>
<td>0.75</td>
<td>48</td>
</tr>
<tr>
<td>N4-AI</td>
<td>12.1</td>
<td>0.07</td>
<td>68</td>
</tr>
<tr>
<td>F25-N4-AI</td>
<td>15.4</td>
<td>0.25</td>
<td>55</td>
</tr>
</tbody>
</table>

Generally, mixtures incorporating fly ash showed higher porosity and threshold pore diameter as well as lower proportions of micro-pores. For instance, mixture F25-AI showed 26% and 200% higher total porosity and threshold pore diameter, respectively as well as 19% increase in the proportion of macro-pores compared with mixture GU-AI. The coarser pore structure of mixtures incorporating fly ash explains the reduction in strength and increase in fluid absorption of concrete. Accordingly, mixtures F25-AI and F25-A, comprising 25% fly ash, had the highest porosity, lowest compressive strength (at 3 and 28 days) and highest absorption among all mixtures.
Chapter 4: Statistical Modeling of Concrete Mixtures Cured Under 5/-5°C

The MIP results of nano-modified and nano-modified fly ash mixtures substantiated the positive effects of nano-silica on densifying the pore structure of concrete mixtures cast and cured under freezing/low temperature cycles. For instance, incorporating 4% nano-silica in mixture GU-AI to produce mixture N4-AI decreased the porosity and threshold pore diameter by 15% and 72%, respectively as well as increasing the proportion of micro-pores by 15%. Similarly, addition of nano-silica refined the coarse microstructure of fly ash mixtures. For example, adding 4% nano-silica to mixture F25-AI to produce mixture F25-N4-AI resulted in decreasing the porosity by 14% and threshold pore diameter by 67%; correspondingly, the proportion of micro-pores increased by 15%. These trends implicated the increased resistance to saturation of nano-modified mixtures due to their refined pore structure, which corresponds to their relatively lower absorption and improved compressive strength.

4.5.2 Thermal Analysis

The portlandite production and consumption in eight concrete mixtures (factorial component), which were cured under the adopted curing regime, were determined using TG at different ages: 12 h and 1, 3, 7, 14, 28, 56 and 120 days (Figs. 4.10 and 4.11). As depicted in Fig. 4.10, the CH content in the factorial mixtures at very early-age (12 hr), complied with the setting time results. Generally, the mixtures with high dosages of fly ash (F25-A and F25-AI) produced the smallest amounts of CH due to the dilution of cement component and slow reactivity of fly ash at early-age (Wesche 2014; Neville 2011), which led to decelerating the hydration and hardening rates of these mixtures, especially at this freezing temperature (-5°C) during the first 16 h.

Comparatively, the incorporation of nano-silica in concrete led to producing higher CH contents at early-age compared with counterpart mixtures without nano-silica.
For instance, at 1 and 3 days, the normalized CH contents of the nano-silica mixtures relative to their corresponding mixtures without nano-silica ranged from 1.9 to 2.1 and 1.17 to 1.27, respectively, which conformed to the noticeable improvement in early-age hardening rate and compressive strength of the nano-modified mixtures (Table 4.3). This substantiated the role of nano-silica in accelerating the kinetics of hydration reactions with the coexistence of CWAS, under freezing/low temperatures, through its nucleation effect by creating additional nucleation sites for the precipitation of hydration products at early-age (Ghazy et al. 2016; Senff et al. 2009). Complying with the setting time results, the incorporation of CNAI produced higher amounts of CH in the mixtures compared to CNA which explains the relatively faster hardening and reactivity rates of CNAI mixtures compared with corresponding mixtures incorporating CNA. This can be ascribed to the relatively stronger accelerating effect of CNI on speeding up hydration of cement.

![Graph showing Thermogravimetry results for the portlandite contents at early-age up to 7 days.](image-url)
At later ages (Fig. 4.11), the previously described trends continued in the case of mixtures without nano-silica up to 120 days under the adopted curing regime. Conforming to the strength results, the CH contents in these mixtures steadily increased at different rates depending on the type of binder and CWAS. After 56 days, a slight reduction in CH content was observed in the fly ash mixtures without nano-silica which alluded to very slow and delayed pozzolanic reactivity because of the freezing/low temperatures; typically, concrete comprising fly ash show the commencement of pozzolanic reactivity after 28 days at normal curing temperatures (Wesche 2014; Neville 2011).

Figure 4.11: Thermogravimetry results for the portlandite contents up to 120 days.

Comparatively, after 7 days, all the nano-modified concrete mixtures showed consumption of the CH contents up to 120 days, which was indicated by the significant decrease in the normalized CH contents (Fig. 4.11). For example, the average normalized CH contents in mixture 4NCNA relative to mixture GUCNA at 28 and 120 days were 0.63 and 0.41, respectively. These trends can be attributed to the pozzolanic effect of

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nano-silica by reacting with CH to produce secondary C-S-H gel, which was reported to have high stiffness (Ghazy et al. 2016; Senff et al. 2009), and thus densifying the pore structure of concrete. This explains the superior performance of nano-modified concrete mixtures in terms of higher strength and lower absorption capacity. The latent behavior of nano-silica, which was proved in Chapter 3, was reported in the previous study at the University of Manitoba, which showed that the pozzolanic effect of nano-silica commenced after 28 days in masonry mortar that were cast and cured at +5°C, but without CWAS (Kazempour et al. 2017; Kazempour et al. 2014). Under normal conditions, nano-silica starts its pozzolanic activity in cementitious systems within 1 to 3 days depending on the other binder components (Ghazy et al. 2016; Hou et al. 2013).

As discussed earlier in the setting time section, the incorporation of CNAI in concrete catalyzed the hydration reactions and led to higher amounts of CH in the matrix compared to CNA. It nucleated the early precipitation of CH, which in turn led to better/earlier development in the microstructure, especially with the coexistence of nano-silica which requires CH to start its pozzolanic reactivity. Together with the filler effect of nano-silica, this led to densifying the pore structure and reducing the absorption of CNAI concrete mixtures compared to that of corresponding CNA mixtures. Thus, the combination of CNAI and nano-silica may present a viable option for low temperature construction, as it produces concrete with mutual balance of early-age and durability properties.

4.5.3 Scanning Electron Microscopy

Based on the superior performance of CNAI compared to CNA, BSEM on thin sections prepared from four CNAI mixtures (half of the factorial part) was performed to augment the findings drawn from the previous tests, with respect to fly ash and nano-silica. In
addition, EDX analysis was performed on several points within the interfacial transitional zone (ITZ) between hardened paste and aggregates to calculate the calcium-to-silicate ratio ($C/S$) of calcium silicate hydrate (C-S-H). It was reported that the $C/S$ of secondary/pozzolanic and conventional C-S-H are approximately 1.1 and 1.7, respectively (Detwiller et al. 1996).

Generally, there was dissimilarity between the microstructure of the different CNAI mixtures as shown in Figs. 4.12 (a)-(d), depending on the inclusion of fly ash nano-silica, or both. Generally, antifreeze admixtures such as calcium nitrite, that contain similar cations as $\beta$-C$_2$S and C$_3$S in cement, may accelerate the hydration process due to the nucleation action of these ions leading to intensification of the hydrate precipitation processes and improvement in concrete microstructure and strength at the very early-age (Ratinov and Rozenberg 1996). However, the replacement of cement with either fly ash or nano-silica or both significantly affected the morphology of concrete microstructure. For instance, mixture GU-AI had an intermediate microstructure in the ITZ, where the $C/S$ varied between 1.65 and 2.1 with an average of 1.9 [Fig. 4.12 (a)]. The incorporation of 25% fly ash to produce mixture F25-AI produced coarser microstructure comprising interconnected micro-cracks in the ITZ, where the $C/S$ varied from 1.8 up to 2.4 with an average of 2.1 [Fig. 4.12 (b)]. These features indicate less degree of hydration conforming the previously described trends of strength, absorption and pore structure of mixtures containing fly ash, without nano-silica.

Comparatively, the incorporation of nano-silica in mixture GU-AI to develop mixture N4-AI produced the most homogenous matrix and refined microstructure with the lowest $C/S$ in the ITZ of 1.1 [Fig. 4.12 (c)], which indicated efficient pozzolanic activity and densification of ITZ by deposition of secondary C-S-H. In addition, when
comparing the fly ash mixtures F25-AI, to the nano-modified fly ash mixture F25-N4-AI, noticeable improvement was achieved in the degree of hydration and refinement in the ITZ and hydrated paste due to the synergistic effects of nano-silica and fly ash [Fig. 4.12 (d)]; correspondingly, the average $C/S$ in the nano-modified fly ash mixture was around 1.4. Again, this substantiates the superior performance of nano-modified mixtures with the coexistence of antifreeze admixtures, and highlights the promising potential of these mixtures for construction applications at freezing/low temperatures.

Figure 4.12: BSEM micrographs for thin sections from mixtures: (a) GU-AI, (b) F25-AI, (c) N4-AI, (d) F25-N4-AI.

It is worth noting that nano-silica agglomeration is a normal phenomenon and it does not necessarily combat its functionality unless the agglomeration is excessive, resulting in sub-micron clusters formation. The latter case will produce a coarse matrix with inferior mechanical and durability properties. Previous studies attributed the accelerated
hydration of C\textsubscript{3}S to the higher conversion rate of the protective hydrate layer formed close to the C\textsubscript{3}S surface to a less permeable form due to the abundance of silicate ions (Stein and Stevels 1964) from nano-silica aggregates. These agglomerates can reach up to few hundred nm in the pore solution, which can be attributed to high pH (Depasse 1999) or bridging of silica particles by calcium ions (Zerrouk et al. 1990) and reduction of calcium ions through fast pozzolanic activity (within a few hours) (Madani et al. 2012; Korpa et al. 2008). This led to shortening the setting time of nano-modified concrete, which was observed in the current study even at -5°C, owing to the coexistence of CWAS. These nano-silica aggregates effectively contributed to the strength and microstructure development of the mixtures through high pozzolanic activity (Hou et al. 2013), filler effect, (Oertel et al. 2013; Kong et al. 2012) and water absorption (Kong et al. 2012). These trends were previously substantiated by the MIP and TG analyses. If agglomeration of nano-silica was excessive, all the fresh, hardened, and durability properties of nano-modified concrete would have been inferior, with coarse microstructure. Indeed, this was not the case herein, which supports the efficient dispersion of the nano-silica sol used in this study.
CHAPTER 5: NANO-MODIFIED CONCRETE AS A REPAIR MATERIAL IN COLD WEATHER

In Chapters 3 and 4, the response surface method, a statistical modeling approach, was applied on 40 mixtures to assess and optimize the effect of different parameters and their interactions on concrete mixtures, cast and cured at mild freezing temperatures down to -5°C. The current chapter is concerned with further understanding the behavior of the optimized mixtures and their suitability for different cold weather applications such as repair to extend the construction/repair season in cold regions to late fall and early spring.

5.1 Introduction

Efficient repair concrete should typically exhibit rapid setting, high-early strength, and adequate compatibility with substrate/existing concrete. However, when concrete temperature drops to -2.8°C, the hydration development of cementitious binder ceases due to freezing of mixing water (Karagöl et al. 2015; Ratinov and Rozenberg 1996; Korhonen et al. 1992). Consequently, the hardening and strength gain rates of concrete are adversely affected (Ratinov and Rozenberg 1996; Korhonen et al. 1992), which makes concreting, and repair applications, in particular, challenging under cold weather. In addition, the associated hydraulic and osmotic pressures within inadequately hydrated paste due to ice formation (Pardo et al. 1998; Powers and Helmuth 1953), result in early damage of concrete and failure of the repair layer relative to substrate concrete (Korhonen et al. 1992). Therefore, ACI 306R (2016) and CSA A23.1 (2019) set a limit of 4 and 5°C, respectively as the ambient temperature benchmarks to apply cold weather concreting practices to ensure continual hydration of the binder.
Chapter 5: Nano-modified Concrete as a Repair Material in Cold Weather

These aforementioned documents provide rigorous stipulations for cold weather concreting, including target concrete temperature during mixing, placement and curing, which can be achieved by heating concrete constituents (water and aggregates), protection methods (heated enclosures and insulations) and required protection period to achieve the desired concrete properties. However, these practices are associated with high costs and pollution intensity due to increased energy consumption/CO$_2$ emissions and additional required materials/skilled labor (Barna et al. 2011; Korhonen et al. 1997). It is estimated that the expenditures on these practices in the U.S. are around one billion dollars annually to cast concrete in cold weather (Barna et al. 2011). Thus, in cold regions, construction and repair activities are commonly postponed to warmer periods (typically from May to September), leading to overpoweringly busy construction periods, backlogged repair schedules, and significant socioeconomic losses. Thus, there is a constant need to develop innovative and energy-efficient strategies that can alleviate impacts of low temperatures on concrete to extend the construction/repair periods in cold regions.

Since the last decade, nano-silica has been the subject of extensive investigation in concrete research due to its effects at enhancing hydration, microstructural, and hardened characteristics of concrete (Ghazy et al. 2016; Belkowitz et al. 2015; Madani et al. 2012). However, most of these studies were done under normal casting/curing temperatures (20 to 30°C), and the effects of nano-silica on properties of concrete prepared under low temperatures remain largely unexplored. In Chapters 3 and 4, experimental work and statistical modelling were performed to explore numerous combinations of water-to-binder ratios ($w/b$), nano-silica, and cold weather admixture systems (CWAS; antifreeze/accelerating admixtures) to cast/cure concrete under low
Chapter 5: Nano-modified Concrete as a Repair Material in Cold Weather

Temperatures down to -5°C. It was found that combinations of low w/b (0.32), nano-silica (2 to 4%), and combined calcium nitrate-nitrite solutions (CWAS) showed promising trends in terms of acceptable hardening rates (less than 11 h) and strength (more than 25 MPa at 28 days) and resistance to 300 freezing-thawing cycles in fresh water.

However, concrete mixtures incorporating CWAS may be susceptible to intense micro-cracking due to shrinkage stresses and thermal gradients (Korhonen 1997), which may lead to rapid deterioration and durability problems in the field, for example under severe exposures involving de-icing salts and frost action (e.g. pavements, bridges). Therefore, comprehensive studies are still needed to further understand the behavior of these nano-modified mixtures, cast and cured at cold temperatures, to examine their suitability for different applications. In particular, for partial depth repair, the compatibility of these mixtures with existing concrete substrate has not been tested, which makes their performance uncertain in this application. Ghazy et al. (2016) highlighted the beneficial effects of combining fly ash and nano-silica to produce high-performance nano-modified concrete for partial depth repair applications, cast and cured under normal temperatures. However, ACI 3.6R (2016) and CSA A23.1 (2019) documents do not recommend the use of slowly reactive supplementary cementitious material (SCMs) such as fly and slag in cold weather concrete. Indeed, incorporating fly ash in nano-modified concrete produced under low temperatures is quite challenging, but it is worth investigating to produce repair concrete with balanced early-age and long-term performance.
Chapter 5: Nano-modified Concrete as a Repair Material in Cold Weather

5.2 Research Significance

Repair is essential to maintain serviceability of concrete infrastructure. Developing repair concrete for cold weather conditions remains a challenging area, which warrants focused research. Thus, this study aimed at investigating the applicability of different nano-modified mixtures (without and with fly ash) comprising CWAS, as repair concrete cast and cured under freezing/low temperatures. The mixtures were tested in an integrated manner exploring fresh, hardened and durability properties, as well as compatibility with substrate concrete. Nano-modified concretes with balanced performance and minimum protection may present an attractive option for repair applications in cold regions during late fall and early spring.

5.3 Experimental Procedure

5.3.1 Materials and Mixtures

The materials used in this chapter were similar to that used in Chapters 3 and 4 (refer to Sections 3.4.1 and 4.3.1).

As listed in Table 5.1, seven mixtures, incorporating CNAI as CWAS, were cast and cured at the cyclic freezing low temperatures regime (5/-5°C). In the mixture ID, the letters GU, F, N denote GU cement, fly ash and nano-silica respectively, while the numbers indicate the dosages of SCMs used. For instance, mixture F25N2 refers to concrete mixture incorporating 25% fly ash with 2% nano-silica.

5.3.2 Procedures

The procedures followed in this chapter were similar to that used in Chapter 4 (refer to Section 4.3.2).
### Table 5.1: Mixtures proportions and cost per cubic meter

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Cement (kg)</th>
<th>Fly Ash (kg)</th>
<th>Nano-silica (kg)</th>
<th>Water* (kg)</th>
<th>CWAS CNA**+CNI* (kg)</th>
<th>Fine/Coarse Aggregate (kg)</th>
<th>Cost (US $)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU</td>
<td>400</td>
<td>0</td>
<td>0</td>
<td>106</td>
<td>14+32</td>
<td>622/1156</td>
<td>284</td>
</tr>
<tr>
<td>N2</td>
<td>400</td>
<td>0</td>
<td>16</td>
<td>98</td>
<td>14+32</td>
<td>621/1153</td>
<td>301</td>
</tr>
<tr>
<td>N4</td>
<td>384</td>
<td>0</td>
<td>32</td>
<td>90</td>
<td>14+32</td>
<td>621/1153</td>
<td>310</td>
</tr>
<tr>
<td>F15N2</td>
<td>332</td>
<td>60</td>
<td>16</td>
<td>98</td>
<td>14+32</td>
<td>614/1140</td>
<td>282</td>
</tr>
<tr>
<td>F15N4</td>
<td>324</td>
<td>60</td>
<td>32</td>
<td>90</td>
<td>14+32</td>
<td>613/1139</td>
<td>293</td>
</tr>
<tr>
<td>F25N2</td>
<td>292</td>
<td>100</td>
<td>16</td>
<td>98</td>
<td>14+32</td>
<td>609/1130</td>
<td>273</td>
</tr>
<tr>
<td>F25N4</td>
<td>284</td>
<td>100</td>
<td>32</td>
<td>90</td>
<td>14+32</td>
<td>608/1129</td>
<td>281</td>
</tr>
</tbody>
</table>

*The amount of water was adjusted considering the water content of nano-silica (aqueous solution with 50% solid content of SiO$_2$) and the CNI (aqueous solution with 30% solid content).

**The CNA was in solid form with 70% active ingredient.

5.3.3 Testing

The initial (IST) and final setting times (FST) were determined according to ASTM C403 (2016) inside the environmental chamber set to the curing regime described earlier on 150 mm cubes of the mortar part of each mixture. In addition, thermocouples were embedded within the top 40 mm of each cubic specimen to monitor the internal temperature change of concrete up to 40 h.

Triplicate cylinders (100×200 mm) were tested, as per ASTM C39 (2020), to determine the compressive strength development of the concrete mixtures at 1, 3, 7, 14, 28, 56 and 91 days of curing under cyclic freezing/low temperatures. In addition, splitting tensile strength and modulus of elasticity of the different mixtures were tested as per ASTM C496 (2017) and ASTM C469 (2014), respectively on triplicate cylinders (100×200 mm) after 1, 7, 28 and 91 days of curing. Moreover, fluid absorption of concrete was assessed on triplicate concrete discs (75×50 mm) based on a test protocol introduced by Tiznobaik and Bassuoni (2018). In addition, the resistance of triplicate concrete slabs (250×250×100 mm) to salt-frost scaling was evaluated as per ASTM C672
Chapter 5: Nano-modified Concrete as a Repair Material in Cold Weather

The resistance to surface scaling of concrete was assessed qualitatively by visual examination and quantitatively by weighing the scaled mass of specimens’ surfaces.

To evaluate the compatibility between substrate/parent concrete and the nano-modified (repair) concrete developed in this study, restrained shrinkage and pull-off tests were performed. Duplicate concrete slabs (250×250×130 mm) for both tests were cast as the parent concrete (400 kg/m³ GU cement with 15% fly ash replacement at w/b of 0.4, which is a typical mix design of concrete pavement in Manitoba (CW3310 2015). The slabs were then kept inside the curing room (21°C and >95% RH) for 7 days, followed by storage in laboratory conditions for 450 days, to eliminate residual shrinkage strain. The surface of each slabs was wire brushed and cleaned (Fig. C.1), acting as the substrate concrete. After dampening the roughened surface, the repair layer (70 mm) was poured on top of the parent concrete at -5°C using the mixtures listed in Table 5.1. To determine the restrained shrinkage of the repair mixtures, four demec points were attached to the surface of the repair mixtures after 1 hr of casting (Fig. C.2). The shrinkage of the repair mixtures was measured under the freezing/low temperature curing regime for 28 days. The specimens were then moved to a hot/dry exposure of 40±1°C and 35±5% RH and the cumulative shrinkage of the repair layer was monitored up to 154 days. After 28 days of curing, the pull-off test slabs were partially cored to evaluate the bond between the parent concrete and repair layer as per CSA A23.2-6B (2019). Furthermore, the pull-off strength of the repaired lab assembly was determined after 50 freezing-thawing cycles, followed by 50 wetting-drying cycles. This customized exposure was selected to mimic alternating climatic conditions of successive winter and summer seasons. ASTM C672 (2012) regime was followed for the freezing-thawing stage, while the wetting-drying cycles consisted of 21±1°C and 95% RH for 16 h followed by 8h at 40±1°C and 35±5% RH.
The bulk tests were corroborated by thermal and microstructural studies (TG and MIP), following the procedures mentioned in Chapter 3 (Section 3.4.3).

5.4 Experimental Results and Discussion

5.4.1 Setting Time and Internal Heat Evolution

The hardening behaviour of the mixtures was evaluated by the setting times as shown in Fig. 5.1. The IST and FST results varied between 60 to 145 min and 330 to 635 min, respectively. These ranges provide ample time for placement, compaction and finishing, which typically require at least 45 min, even at normal temperatures (Ghazy et al. 2016). The nano-modified mixtures hardening time was shortened due to the incorporation of ultrafine nano-silica compared to the reference mixture GU. For instance, adding 4% nano-silica to GU mixture to produce mixture N4 resulted in shortening the IST and FST by 20% and 23%, respectively. Conversely, the mixtures incorporating fly ash showed significant increase in both setting times compared to that of other mixtures, especially at higher dosages of fly ash (25%). The longest hardening rate was observed for the F25N2 mixture with IST and FST of 145 and 635 minutes, respectively. The effect of higher dosages of fly ash on prolonging the setting time of concrete under normal temperatures is well-documented (Wesche 2014; Neville 2011). Class F fly ash has slow pozzolanic reactivity due to the low lime content compared to portland cement; thus, the rate of skeletal rigidity at early-age was delayed due to the dilution of cement with fly ash, especially under the cold regime adopted.
The retarding effect of fly ash on the setting time of concrete was partially offset by incremental addition of nano-silica. For example, increasing the dosage of nano-silica to 4% to produce mixture F15N4 resulted in shortening the IST and FST by 14% and 10%, respectively relative to that of mixture F15N2. This effect on setting times of concrete without and with fly ash can be attributed to the very high specific surface area (80,000 m²/kg) of nano-silica which accelerated the hydration kinetics through the nucleation effect by providing additional sites for the hydration products to precipitate on at very early-age (Belkowitz et al. 2015; Madani et al. 2012). The incorporation of CNAI, which acts as anti-freeze and accelerating admixture, kept the functionality of nano-silica under the cold temperature regime implemented herein, which conforms to the results of Chapters 3 and 4. Overall the FST of the nano-modified mixture, except for F25N2, was within the typical range (6 to 8 h) of concrete cast under normal temperatures, suggesting
the practicality of these nano-modified mixtures in the field, under similar freezing/low temperature conditions.

The internal temperature of each mixture was continuously monitored up to 40 h (freezing, low temperature, and freezing curing intervals) (Fig. 5.2), using thermocouples embedded into the setting times specimens. All mixtures showed initially high internal temperature (21 to 27°C) which can be attributed to the resulting heat from using a high-speed drill mixer and initial hydrolysis of cement. Subsequently, all mixtures experienced progressive drop in internal temperature, due to the rapid rate of heat loss to the surrounding environment (-5°C), which was relatively high compared to the heat emitted from the hydration reactions. However, up to 16 h, the range of temperatures was mostly above the freezing threshold of water (up to 13°C at 16 h), and the hardening of mixtures was achieved between 5.5 to 10.6 h depending on the dosages of nano-silica and fly ash, alluding to the continuity of hydration reactions under such freezing conditions. Afterward, there was a notable rise in the internal temperature of all mixtures due to the commencement of the low temperature curing period (+5°C), which boosted the kinetics of hydration reactions. Thus, the loss of internal temperature was discounted during this portion of the cycle, and the peaks of the curves (12 to 20°C) were obtained at the end of the 5°C curing portion at 24 h, followed by deceleration and steady-state intervals. It is worth noting that the second freezing period (24 to 40 h) did not interrupt the continuity of the hydration reactions since the internal temperature of the mixtures was in the range of 2.5 to 7°C without reaching equilibrium with the adiabatic environment (-5°C). The binders tested were at its utmost reactivity during the first seven days, as shown by the TG trends.
Figure 5.2: Internal temperature profile of the mixtures during the first 40 h.

Complying with the setting time trends, the nano-modified binary binder (cement and NS) mixtures were capable of maintaining the highest internal temperatures between 9 to 14°C during the first 16 h (first freezing period). The peak temperatures of N2 and N4 at 24 h were 12.5% and 25%, respectively higher than that of the GU mixture, which was 16°C. This substantiated the catalytic effect of nano-silica on the hydration process at early-age as discussed earlier, especially with the coexistence of CNAI; thus, mixtures N2 and N4 had the fastest rates of hardening among the mixtures tested. Comparatively, ternary binder mixtures comprising cement, nano-silica and fly ash showed a steeper drop in internal temperature, which reached 0 to 1°C during the first freezing period. The peak temperatures at 24 h of F25N2 and F25N4 were 33% and 35%, respectively lower than that of the corresponding binary binder mixtures N2 and N4. Despite that inclusion of fly ash in the ternary binder decelerated the kinetics of hydrations reactions, the peak
Chapter 5: Nano-modified Concrete as a Repair Material in Cold Weather

Temperatures of all nano-modified fly ash mixtures were above 10°C due to the vigorous reactivity of nano-silica, which partially balanced the delaying effect of fly ash.

5.4.2 Compressive Strength and Hydration Development

The compressive strength of the different mixtures was assessed at early- (1, 3 and 7 days) and late- (14, 28, 56 and 91 days) ages (Fig. 5.3). ACI 306R (2016) stipulates that the strength of concrete cast in cold weather should achieve at least 3.5 and 24.5 MPa before being exposed to one cycle and multiple freezing-thawing cycles, respectively. The compressive strength of most nano-modified concrete mixtures, which were cast and cured under the freezing/cold regime without insulation, met these limits after 1 and 3 days, respectively. In addition, all mixtures achieved compressive strength in the range of 33.6 to 54.6 MPa at 28 days, which qualifies them for various concrete applications including construction/repair of buildings, bridges and pavements, which require strength grade of 25 to 40 MPa (MacGregor et al. 1997).

During early-age, the average results of compressive strength of mixtures at 1, 3 and 7 days varied between 3.4 to 10.7 MPa, 20.9 to 32.5 MPa and 26.9 to 43.5 MPa, respectively. This, for example, meets strength requirements for partial depth repair of concrete pavements, which stipulate a strength of at least 15-20 MPa before opening roads for traffic (CW3310 2015). The incorporation of nano-silica in concrete significantly improved the rate of strength gain at early-age, especially with increasing the dosage to 4%. For example, the incorporation of 4% nano-silica in mixture GU to produce mixture N4 increased the compressive strength by 215%, 27% and 19% after 1, 3 and 7 days, respectively. These trends conform to the thermal analysis results as depicted in Fig. 5.4, since mixtures with nano-silica comprised the highest calcium hydroxide (CH) contents, especially at the first day of curing, indicating accelerated
hydration development of the paste. For example, the normalized CH contents of mixture N4 compared to mixture GU were 2.6, 1.39 and 1.64 at 1, 3 and 7 days, respectively. This improved performance, especially with increasing dosage can be ascribed to the function of nano-silica agglomerates to provide hydration products with additional surfaces (nucleation sites) to precipitate on at the very early-age (Ghazy et al. 2016; Madani et al. 2012), leading to noticeable acceleration in the kinetics of hydration. In addition, nano-silica may reduce the apparent w/b due to the absorption of water into their ultra-high nano porosity (Kong et al. 2012) and physically fill out the pore spaces in the paste, resulting in microstructural improvement and thus increasing compressive strength of concrete at early-age.

On contrary, incorporating fly ash in concrete, at constant nano-silica dosages, markedly decreased its strength at early-age. For instance, incorporating 15% fly ash in mixture N4 to produce mixture F15N4 led to compressive strength reduction of 33%, 19% and 23% after 1, 3 and 7 days, respectively. This complies with the lower CH contents in nano-modified fly ash mixtures compared to corresponding nano-modified mixtures. For instance, the incorporation of 15% fly ash in mixture N4 to produce mixture F15N4 led to an average reduction of 24% in CH content in the paste during the first 7 days of curing, indicating slower hydration rate. This can be attributed to the replacement of cement with slow reactivity Class F fly ash, which led to decelerating the kinetics of hydration and delaying strength development of concrete. However, it is worth noting that the compressive strength of all nano-modified mixtures without and with fly ash exceeded that of the GU mixture at 1 day due to the dominant effect of nano-silica in the binder at this age, hence the normalized CH contents in these mixtures relative to that in the GU mixture varied between 1.3 to 2.6 after 1 day. Correspondingly, the
incremental dosage of nano-silica from 2 to 4% was effective at improving the hydration development of paste, and thus the strength of fly ash concrete at 3 and 7 days.

![Graph showing compressive strength over time](image)

**Figure 5.3:** Average results of compressive strength vs. time of curing. (Note: error bars represent standard deviation)

The late-age compressive strength of all mixtures varied between 30.5 to 39.8 MPa, 33.6 to 54.6 MPa, 37.6 to 56.7 MPa and 39.6 to 59.1 MPa after 14, 28, 56 and 91 days, respectively. Complying with the early-age strength results, increasing the dosage of nano-silica in the binder notably improved later-age strength. For instance, the incorporation of 4% nano-silica in mixture GU to produce mixture N4 improved later-age strength by 21%, 25%, 30% and 27% at 14, 28, 56 and 91 days, respectively. This could be attributed to the filler effect and delayed pozzolanic activity of nano-silica under this cold temperature curing regime, producing secondary calcium silicate hydrate (C-S-H). This is shown by the TG results, as after 7 days nano-modified mixtures showed continual consumption of CH up to 91 days. For instance, the normalized CH contents of mixture N4 relative to mixture GU were 1.64, 1.23, 0.79, 0.67 and 0.63 after 7, 14, 28, 56
Chapter 5: Nano-modified Concrete as a Repair Material in Cold Weather

and 91 days, respectively. This trend confirmed nano-silica delayed pozzolanic effect on the cementitious systems, under the low curing temperatures, which is reported to start within 1 to 3 days under normal temperatures (Ghazy et al. 2016; Hou et al. 2013).

Figure 5.4: Termogravimetry results for the CH contents with time. (Note: the table shows exemplar normalized ratios).

Incremental addition of fly ash led to reduction of later-age strength of concrete compared to mixtures without fly ash. For instance, the incorporation of 15% fly ash in mixture N4 to produce mixture F15N4 reduced the strength of concrete by an average of 18% between 14 to 91 days, due to the dilution of cement with fly ash. However, the fly ash concrete mixtures showed progressive rate of hydration development and strength increase with time, from 7 to 91 days, owing to the synergistic effects of nano-silica (improved reactivity of the ternary binder comprising fly ash at earlier age) and fly ash (long-term reactivity of the ternary binder). For instance, the normalized CH contents in mixture F15N4 to mixture N4 were increasing up to 28 days, and then it decreased to
0.78 at 91 days. The stepwise slope of CH curves after 28 in the nano-modified fly concrete reflected efficient continuity of the pozzolanic activity in this ternary binder, owing to the functionality of nano-silica and CNAI in maintaining the reactivity of fly ash under this cyclic freezing/cold curing regime. While ACI306R (2016) does not recommend the use of slowly reactive SCMs in cold weather concrete applications due to the expected delay of strength development, the results presented herein indicate that the technical limitations of fly ash concrete cast and cured under cold weather can be alleviated by the addition of adequate dosages of nano-silica.

5.4.3 Durability and Microstructural Features

The conditions and mass loss of the specimens due to combined freezing-thawing cycles and de-icing salt are shown in Fig. 5.5 and 5.6, respectively. Ministry of Transportation of Ontario (MTO LS-412 1997) and Bureau du normalisation du Quebec (BNQ NQ 2621-900 2002) stipulate that failure limits in salt-frost scaling tests at 500 and 800 g/m², respectively, but both jurisdictions use a less aggressive solution of 3% sodium chloride. In addition, the absorption and pore structure features (Table 5.2) of the mixtures were determined to corroborate the trends from the surface scaling test.

The single binder mixture (GU) showed acceptable performance with a total mass loss of 362 g/m² and visual rating of 1. This can be attributed to the mix design parameters (low w/b, adequate cement content, CNAI) selected, which led to sufficient hydration development (CH evolution and strength of 43.6 MPa) after 28 days of curing under the freezing/low temperatures regime. This was also reflected by the development of microstructure of this mixture, with a total porosity of 14.5% and proportion of micropores of 56% (Table 5.2).
Incorporating nano-silica in binary binder mixtures led to noticeable reduction in surface scaling of concrete. Binary binder mixtures N2 and N4 had the lowest scaled mass (211 and 104 g/m², respectively with visual rating of 0) with 71% and 42% reduction in mass loss compared to that of the reference mixture (GU). This enhanced resistance to salt-frost scaling conformed to the marked reduction of fluid absorption, porosity, and threshold pore diameter as well as the increase in the proportion of micro-pores of these nano-modified mixtures. For instance, the addition of 4% ultrafine silica nanoparticles to mixture GU to produce mixtures N4 decreased the fluid absorption, porosity, and threshold pore diameter by 20, 16, 81%, respectively and increased the proportions of micro-pores by 27%. The low absorption of these mixtures, which can be ascribed to the refined pore structure as well as nano-silica pore blocking action, discounted the ingress of salt solution into concrete surface, and in turn its vulnerability.
to critical saturation. In addition, the higher strength of concrete due to addition of nano-silica after 28 days (51 to 55 MPa) improved its resistance to stresses resulting from hydraulic and osmotic pressures induced by frost action (Karagöl et al. 2015; Prado et al. 1998; Powers and Helmuth 1953). This was indicated by the higher degree of hydration and pozzolanic reactivity of nano-modified binders within 28 days (Fig. 5.4).

![Figure 5.6: Cumulative mass loss of slabs tested according to ASTM C672 (2012).](image)

Except for mixture F15N4, adding fly ash to nano-modified concrete (ternary binders) adversely affected its resistance to salt-frost scaling, especially at the higher dosage of fly ash. This can be ascribed to the relatively lower degree of microstructural development (Fig. 5.4) and coarser pore structure, and thus higher fluid absorption of fly ash mixtures at 28 days. For instance, the incorporation of 15% fly ash in mixture N2 to produce mixture F15N2 increased fluid absorption, porosity and threshold pore diameter by 37, 12 and 178%, respectively relative to that of mixture N2; correspondingly, there was 15% decrease in the proportion micro-pores. Correspondingly, irrespective of the
nano-silica dosage, the incorporation of higher fly ash dosage (25%; maximum limit of fly ash permitted by ACI 318 (2019) in salt frost-scaling exposures), produced cold weather concrete mixtures with higher propensity to surface scaling only after 10 cycles of freezing-thawing. For example, incorporation of 25% fly ash in mixture N2 to produce mixture F25N2 led to high surface scaling of 872 g/m² after 15 freezing-thawing cycles, exceeding both the MTO and BNQ limits (Fig. 5.6). The performance was improved by increasing the dosage of nano-silica to 4%, but mixture F25N4 still failed the MTO and BNQ limits after 15 and 30 cycles, respectively.

### Table 5.2: Summary of absorption and MIP results

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Absorption (%)</th>
<th>Apparent Total Porosity (%)</th>
<th>Threshold Pore Diameter (µm)</th>
<th>Proportion of Micro-pores (&lt;0.1 µm)</th>
<th>Proportion of Meso-pores (&lt;0.05 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU</td>
<td>2.29</td>
<td>14.5</td>
<td>0.27</td>
<td>56</td>
<td>50</td>
</tr>
<tr>
<td>N2</td>
<td>2.02</td>
<td>13.6</td>
<td>0.09</td>
<td>68</td>
<td>64</td>
</tr>
<tr>
<td>N4</td>
<td>1.84</td>
<td>12.2</td>
<td>0.05</td>
<td>71</td>
<td>68</td>
</tr>
<tr>
<td>F15N2</td>
<td>2.76</td>
<td>15.2</td>
<td>0.23</td>
<td>58</td>
<td>53</td>
</tr>
<tr>
<td>F15N4</td>
<td>2.52</td>
<td>14.2</td>
<td>0.18</td>
<td>61</td>
<td>57</td>
</tr>
<tr>
<td>F25N2</td>
<td>3.08</td>
<td>16.9</td>
<td>0.3</td>
<td>50</td>
<td>44</td>
</tr>
<tr>
<td>F25N4</td>
<td>2.81</td>
<td>15.6</td>
<td>0.28</td>
<td>53</td>
<td>48</td>
</tr>
</tbody>
</table>

In a previous study at the University of Manitoba, nano-modified concrete mixtures cast and cured under normal temperatures for 28 days, had high resistance to salt-frost scaling (Ghazy et al. 2016). However, most nano-modified fly ash concrete mixtures herein had inferior resistance to the same exposure due to the slower reactivity (Fig. 5.4), and hence coarser microstructure (Table 5.2) at 28 days, reflecting the need for extended curing (56 or 91 days) before aggressive exposures. Whereas all nano-modified fly ash mixtures had strength more than 30 MPa at 28 days, exceeding the limit suggested by ACI 306R (2016) to resist multiple cycles of freezing-thawing, the surface scaling test projected their potential risks in the field, in case of early exposure to similar aggressive
Chapter 5: Nano-modified Concrete as a Repair Material in Cold Weather

conditions. Therefore, there is a need to supplement the strength thresholds of cold weather concrete with durability indicators, if the concrete element/repair patch will be subjected to severe exposures such as salt-frost scaling (e.g. pavements and bridges in cold regions).

5.4.4 Compatibility with Substrate Concrete

5.4.4.1 Restrained Shrinkage

To investigate the suitability of the nano-modified concrete mixtures for repair applications, restrained shrinkage test was performed. Large deformations of the repair layer relative to substrate concrete can result in surface cracking and debonding at the interface (Li et al. 1999), compromising the durability and quality of the repair assembly. Table 5.3 lists the total restrained shrinkage results up to 154 days, including 28 days in cold weather curing and 126 days in hot/arid conditions (Figs. C.3 and C.4 show detailed results), with relevant mechanical properties of the mixtures. It is conceivable that field conditions such as frequent rise of RH and precipitation may reduce the total shrinkage of nano-modified concrete compared with the more aggressive drying conditions implemented. However, this extreme scenario was chosen to project performance risks that may arise with nano-modified concrete in the field.

After one day of curing, the repair concrete exhibited shrinkage values between 44 to 73 microstrain, which were approximately 25% of the corresponding 28 days values. This could be linked to autogenous shrinkage, imparted by the low water content and coexistence of CNAI (accelerating/antifreeze system), which sped up the binder reactivity in all mixtures. During early-age, desiccation of mixing water in low w/b concrete and negative volumetric change are critical because of the low tensile capacity and modulus of elasticity of concrete, which can result in significant shrinkage and
cracking (Slatnick et al. 2011). The rates of shrinkage noticed herein compiled with internal heat evolution and TG trends, in the sense that nano-modified mixtures had the highest shrinkage due to the accelerated nucleation effect of nano-silica; conversely, higher dosages (25%) of fly ash, which showed low internal heat evolution and slower reactivity, led to the lowest shrinkage rates of repair concrete. Only GU and F25N2 mixtures exhibited web-cracking after 1 day, as shown in Fig. 5.7, which could be ascribed to their relatively low tensile strength (0.3 and 0.35 MPa, respectively) and modulus of elasticity (3.5 and 3.9 GPa, respectively), compared to that of other mixtures.

Table 5.3: Summary of tensile strength, modulus of elasticity and restrained shrinkage of repair mixtures

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Tensile Strength (MPa)</th>
<th>Modulus of Elasticity (GPa)</th>
<th>Shrinkage (microstrain)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>7 days</td>
<td>28 days</td>
</tr>
<tr>
<td>GU</td>
<td>0.3</td>
<td>3.4</td>
<td>4.1</td>
</tr>
<tr>
<td>N2</td>
<td>0.9</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>N4</td>
<td>1.2</td>
<td>4.4</td>
<td>5.5</td>
</tr>
<tr>
<td>F15N2</td>
<td>0.7</td>
<td>3.1</td>
<td>3.9</td>
</tr>
<tr>
<td>F15N4</td>
<td>0.75</td>
<td>3.4</td>
<td>4.6</td>
</tr>
<tr>
<td>F25N2</td>
<td>0.35</td>
<td>2.6</td>
<td>2.9</td>
</tr>
<tr>
<td>F25N4</td>
<td>0.6</td>
<td>2.9</td>
<td>3.3</td>
</tr>
</tbody>
</table>

At 28 days of curing under the adopted regime, the shrinkage significantly increased between 202 to 296 microstrain. The shrinkage rates mainly depended on the reactivity of the binders, governed by the contents of nano-silica and fly ash; this was aggravated by the windy conditions (25 km/h) in the chamber as the polyethylene covers were removed after three days. Mixtures N2, N4 and F15N4 showed higher shrinkage values (a maximum of 17%) compared to that of the reference mixture GU (252 microstrain), whereas mixtures F15N2, F25N2 and F25N4 showed lower deformations (maximum of 20% reduction compared to that of GU). The relatively higher shrinkage of
some nano-modified concrete mixtures can be ascribed to the accelerated rates of cement hydration (combined nano-silica and CNAI) and pozzolanic reactivity of nano-silica, which commenced after 7 days as shown in the TG curves, resulting in higher rates of chemical shrinkage. For nano-modified fly ash concrete, lower dosage of nano-silica and/or higher content of fly ash slowed down binder reactivity (Fig. 5.4), resulting in less shrinkage value up to 28 days. For instance, the incorporation of 25% fly ash in mixtures N2 and N4 to produce mixtures F25N2 and F25N4, reduced the 28 days shrinkage deformation by approximately 26%. Except for the crack pattern observed in repair mixtures GU and F25N2 at one day, no mixture showed signs of surface cracking up to 28 days. This indicated adequate level of hydration development between 1 and 28 days, which was reflected by the significant improvement in the tensile strength and modulus of elasticity of repair concrete at 28 days (Table 5.3), which could resist shrinkage stresses.

After 28 days in the cyclic freezing/low temperature curing regime, these mixtures were exposed to drying conditions at 40±1°C and 35±5% RH for additional 126 days. According to Table 5.3, the total restrained shrinkage values of the repair mixtures varied between (330 to 463 microstrain). Similar trends were obtained to that of the first 28 days. Mixtures N2 and N4 reached the highest shrinkage values with marginal increase of (5 and 8%, respectively) compared to that of mixture GU (427 microstrain). This can be attributed to the microstructural densification of these nano-modified matrices, which led to marked increase in the proportion of meso-pores (28 and 36%, respectively, Table 5.2) and consequently higher capillary stresses and drying shrinkage rates. However, the continual increase in the tensile strength of mixtures N2 and N4 (e.g. 18% and 32% at 91 days) and modulus of elasticity (e.g. 18% and 23% at 91 days) due to
the continued binder reactivity, even under cold conditions as implicated by the TG curves (Fig. 5.4), sustained the higher capillary stresses and impeded drying shrinkage cracking compared to the reference GU mixture (e.g. Fig. 5.7b vs. Fig. 5.7a).

Figure 5.7: Patterns of restrained shrinkage cracking in: (a) GU, (b) N4, (c) F25N2, and (d) F25N4 repair slabs after 154 days (28 days curing in cold/freezing temperatures plus 126 days in hot/arid conditions).

At the end of the drying exposure, mixture F15N2 showed tendency to minor surface cracking. However, despite the higher shrinkage value of mixture F15N4 at the first 28 days compared to the reference mixture (GU), the total deformation of this mixture at the end of the hot/dry exposure was slightly lower by 3%. This can be ascribed to the better long-term tensile strength and modulus of elasticity of mixture F15N4 (e.g.
increase of 14% and 11%, respectively at 91 days) compared to that of mixture GU, which alleviated the effect of slightly higher proportion of meso-pores (57%) compared to that of mixture GU (50%). Nano-modified mixtures comprising higher dosage of fly ash (F25N2 and F25N4) yielded the lowest drying shrinkage values (330 and 351 microstrain, respectively). This can be linked to the slower reactivity of this binder and the reduction in the proportion of meso-pores compared to other binders. For instance, mixtures F25N2 and F25N4 respectively achieved 26% and 24% reduction in total shrinkage compared to that of mixtures N2 and N4, with corresponding reduction in the proportion of meso-pores of 31% and 29%, respectively. However, similar to mixture F25N2, mixture F15N2, was vulnerable to drying shrinkage cracking by the end of exposure. This signifies the positive effect of the higher dosage (4%) of nano-silica at maintaining the dimensional stability of cold weather repair concrete (Fig. 5.7b and 5.7d), by continually improving its mechanical properties during warmer periods.

5.4.4.2 Bonding

One of the key factors in the partial depth repair applications is the bond strength between repair material and parent concrete (substrate). Due to differences in properties, such as modulus of elasticity, these components/layers may deform at different rates leading to failure at the interface (Li et al. 1999). Hence, the bond strength between the proposed repair mixtures and substrate concrete was assessed before and after combined cyclic temperatures to reliably characterize the assembly under severe conditions and project field performance. The temperature profile was a combined exposure of 50 consecutive freezing-thawing cycles followed by 50 cycles of wetting-drying mimicking successive winter and summer seasons. The bond strength was assessed by a direct tension test to represent a worst-case loading configuration. As shown in Fig. 5.8, the bond strength
values varied between 1.18 to 2.10 MPa and slightly increased to 1.49 to 2.18 MPa after the combined exposure. As shown in (Fig. 5.9), failure of the assembly mostly occurred in the substrate layer (10 to 70 mm below the interface), except for mixtures GU and F25N2, which indicated high compatibility between the two layers and soundness of the proposed repair systems.

As shown in (Fig. 9a) The single binder mixture (GU) showed unfavorable mode of failure (0 to 5 mm below the interface), which can be attributed to its early-age low tensile capacity and modulus of elasticity; thus, it suffered from restrained shrinkage cracking during the freezing/low temperature curing, as discussed earlier. Binary nano-modified mixtures achieved the highest bond strength at 28 days. The incorporation of 2 and 4% nano-silica in mixture GU to produce mixture N2 and N4, increased the bond strength by 13 and 37%, respectively. This can be ascribed to the effect of nano-silica on speeding up the kinetics of hydration due to its nucleation effect during the first day of
curing as well as the production of secondary C-S-H through its pozzolanic effect after 7 days of curing, as explained in the TG results. Thus, the development of concrete microstructure at the interface was improved resulting in higher bond with the substrate. On contrary, fly ash concrete (ternary binders) had noticeable reduction in the bond strength due to the previously discussed factors of diluting the cement content and slow reactivity up to 28 days. For instance, the incorporation of 15 and 25% fly ash in mixture N2, reduced the bond strength by 16% and 31%, respectively. It is worth noting that mixture F25N2, with the lowest bond strength, failed at the interface likely due to restrained shrinkage cracking during the freezing/low temperature curing, as discussed earlier.

Figure 5.9: Typical modes of failure under pull-off test: (a) GU and F25N2, and (b) other mixtures

The combined exposure led to increasing the bond strength between the repair mixtures, especially the nano-modified fly ash mixtures, and parent concrete, with substrate concrete failure being the dominant mode. The evolution in bond strength of the mixtures without and with fly ash varied between 4 to 6% and 18 to 30%,
respectively. This can be attributed to the continual hydration of cement grains in the binders, as discussed in the compressive strength and hydration development section, especially during the thawing and wetting portions of the combined exposure, due to the increased temperature and saturation conditions. In particular, the presence of fly ash significantly enhanced the bond strength between the two layers due to its long-term pozzolanic reactivity (Fig. 5.4). This prolonged pozzolanic effect resulted in chemically consuming the portlandite, available within the repair layer and substrate layer interface to produce secondary C-S-H leading to higher mechanical interlock and bond strength, which mitigated effects of swelling/shrinkage micro-cracks associated with the combined exposure projecting long-term integrity of the repair assembly.
CHAPTER 6: CONCRETE INCORPORATING NANO-SILICA CURED UNDER FREEZING TEMPERATURES USING CONVENTIONAL AND HYBRID PROTECTION METHODS

The preceding chapter presented an extensive evaluation of the performance of nano-modified concrete, cast and cured under cyclic freezing low temperatures 5/-5°C, to investigate the suitability of these mixtures for repair applications. This chapter elucidates the performance of concrete, cured under lower freezing temperatures down to -20°C, using two different protection methods, conventional (insulation blankets) and hybrid system (insulation blankets + phase change material mat).

6.1 Introduction

Concrete is indispensable for restoring/building vital infrastructure required for sustaining the economic growth and quality of life worldwide. Guidelines and codes for concrete (e.g., ACI 306R (2016) and CSA A23.1 (2019) set a threshold of 4 to 5°C as the ambient temperature benchmark for cold weather concreting practices to maintain continual hydration of cement. As the temperature reaches these values, the hydration development progresses at a slower rate and completely stops when the temperature reaches -2.8°C due to freezing of mixing water (Karagöl et al. 2015; Ratinov and Rozenberg 1996; Korhonen et al. 1992). Under such conditions, concrete has heterogenous and cracked matrix due to the pressures associated with freezing of water within inadequately hydrated paste, leading to early damage of concrete (Prado et al. 1998; Powers and Helmuth 1953).

Both ACI 306R (2016) and CSA A23.1 (2019) have stringent stipulations for cold weather applications such as mixing, placement and curing temperatures, which can be acquired by multiple procedures including heating of concrete constituents (water and
aggregates) between 40 to 80°C and using voluminous heated enclosures during the protection/curing period. However, in addition to being energy consuming, heating practices incur substantial costs and may lead to durability problems of concrete such as carbonation. For instance, in the United States, it is estimated that one billion dollars are spent annually on heating practices to cast concrete in cold weather (Barna et al. 2011). The high expenditures and CO₂ emissions associated with these practices, due to the required materials/skilled labour and energy consumption impede concrete works under freezing temperatures (i.e., -20°C). This typically limits the construction season to warmer periods (commonly from May to September), resulting in significant socioeconomic losses due to the backlogged construction schedules. Consequently, there is a constant need to extend construction periods in cold regions by considering innovative materials and strategies to allow concrete to be cast and cured at freezing temperatures.

Since the last decade, the effects of nano-silica (ultrafine and vigorously reactive pozzolan) on concrete hydration, hardened properties, and microstructural characteristics have been the subject of extensive investigation in the cementitious materials field (Ghazy et al. 2016; Belkowitz et al. 2015; Madani et al. 2012). However, most of these investigations were done under normal temperatures (20 to 30°C), and the potential use of nano-silica to produce concrete under cold weather is largely unexplored. In Chapters 3, 4 and 5, experimental work and statistical modelling were performed to investigate the potential of concrete, produced using various combinations of water-to-binder ratios (w/b), nano-silica, fly ash and cold weather admixture systems (CWAS: antifreeze/accelerating admixtures). These mixtures were cast and cured under either cyclic (5/-5 °C) or constant low temperature (-5 °C) without any protection nor heating
Chapter 6: PCM Protected Nano-modified Concrete Under Freezing Temperatures

procedures. Mixtures incorporating nano-silica, calcium nitrate-nitrite solutions (CNAI) and low w/b (0.32), with and without fly ash (15%), showed promising success to achieve balanced performance in terms of acceptable hardening rates, strength development and durability properties. However, the performance of such mixtures when cured under lower freezing temperatures, i.e., -10 and -20°C, which are common during the winter periods in many cold regions, is still uncertain and needs to be further investigated.

Phase change materials (PCM) are latent energy storage reservoirs, which can reversibly store (from surroundings) and emit heat based on their solidifying/melting temperatures (Aguayo et al. 2016). There are several ways to produce concrete with PCM, including direct incorporation during mixing (Liu et al. 2017; Fernandes et al. 2014), macro-(e.g., in tubes) (Farnam et al. 2015) and micro-encapsulation (Liu et al. 2017), or saturation of lightweight aggregates (Farnam et al. 2015), nano-silica (Li et al. 2015), and carbon nanotubes (Dorigato et al. 2017). Organic PCM, paraffin or non-paraffin, are preferable to other types (e.g., salt hydrants) with concrete, despite their low thermal conductivity, due to their stability, non-corrosive nature and functional ranges of operating temperatures (Baetens et al. 2010). Incorporating PCM in concrete may mitigate the risk of thermal cracking (Kim et al. 2015) and improve the resistance to freezing-thawing by delaying ice formation (Meshgin and Xi 2012). However, PCM can impart negative effects on concrete (e.g., reduction of strength/elastic modulus (Farnam et al. 2015), higher porosity (Aguayo et al. 2016) and drying shrinkage (Meshgin et al. 2012), which may limit their use to non-structural applications (Cao et al. 2017; Memon et al. 2015). Despite the potential of PCM to control ice formation through heat fusion, thus aiding the continuity of cement hydration under cold weather by acting as an external curing agent, this strategy has not been explored.
6.2 Research Significance

The combination of nano-modified concrete comprising CWAS and PCM as a curing aid may offer a viable and sustainable option to produce and cure concrete under freezing temperatures without the need for voluminous enclosures or extensive heating. Yet, this needs to be systematically substantiated, which is a major motive for the current research. In comparison to a conventional protection method (insulation blankets), this study aimed at exploring the efficacy of using a hybrid protection system (insulation blanket + PCM mat) on the fresh, hardened and durability properties of nano-modified mixtures (without and with fly ash) comprising CNAI cured under freezing temperatures (-10 and -20°C). The bulk trends were supplemented by thermal and microstructural studies to capture the hydration development of the cementitious matrix. The success of such innovative mixtures and protection methods may provide an integrated strategy for alleviating heating requirements and improving the quality of winter concrete production in cold regions.

6.3 Experimental Procedure

6.3.1 Materials and Mixtures

The materials used in this chapter were similar to that used in Chapters 3 and 4 (refer to Sections 3.4.1 and 4.3.1). In addition, high-early strength (HE) portland cement, complying with CAN/CSA-A3001 (2018), was used as an alternative to GU cement.

Similar to the previous chapters, the CNAI dosage was kept constant at 15% by mass of the mixing water, to depress the freezing point of mixing water down to -5°C to prevent mixing water from freezing during the first 2 to 4 hours, to allow for mixing, transporting and placement operations before applying any protection. The proportions of
the mixtures tested are listed in Table 6.1. In the mixture ID, the letters GU, HE, F, N denote GU cement, HE cement, fly ash and nano-silica, respectively.

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Cement (kg)</th>
<th>Fly Ash (kg)</th>
<th>Nano-silica (kg)</th>
<th>Water (kg)</th>
<th>CNA/CNI (kg)</th>
<th>Coarse Aggregate (kg)</th>
<th>Fine Aggregate (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>105.6</td>
<td>14+32</td>
<td>1156</td>
<td>622</td>
</tr>
<tr>
<td>HE</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>105.6</td>
<td>14+32</td>
<td>1156</td>
<td>622</td>
</tr>
<tr>
<td>GUN</td>
<td>376</td>
<td>-</td>
<td>48</td>
<td>81.6</td>
<td>14+32</td>
<td>1151</td>
<td>620</td>
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<tr>
<td>HEN</td>
<td>376</td>
<td>-</td>
<td>48</td>
<td>81.6</td>
<td>14+32</td>
<td>1151</td>
<td>620</td>
</tr>
<tr>
<td>GUFN</td>
<td>296</td>
<td>80</td>
<td>48</td>
<td>81.6</td>
<td>14+32</td>
<td>1137</td>
<td>612</td>
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<td>296</td>
<td>80</td>
<td>48</td>
<td>81.6</td>
<td>14+32</td>
<td>1137</td>
<td>612</td>
</tr>
</tbody>
</table>

*Adjusted amount of water considering the water content of nano-silica (aqueous solution with 50% solid content of SiO₂) and CNI (aqueous solution with 30% solid content).

bThe CNA admixture was in solid form with 70% active ingredient.

6.3.2 Procedures

Mixing and casting of all mixtures were conducted at -5°C in an environmental chamber, where solid constituents of concrete were stored for 24 h prior to mixing. Cold water conditioned at (5±1°C) was used in mixing to mimic conditions of tap water during winter. These temperatures simulate minimal to low heat conditioning for the main ingredients of concrete and formwork during winter. The different concrete mixtures were mixed and cast as mentioned in Section 3.4.2. After casting, the specimens were immediately transferred and kept inside another environmental chamber for two winter curing scenarios (-10 and -20°C), using the protection methods described in the subsequent section. To simulate wind conditions, the curing chamber was equipped with a fan to circulate air at a speed of 25 km/h. After 24 h, all specimens were demolded and kept covered using the protection methods until testing. Such freezing temperatures were selected to cover the common and practical range of winter temperatures for construction in many regions in North America and Europe.
6.3.3 Protection Methods

Two methods of protection, conventional and hybrid, were adopted during curing under freezing temperatures. In the conventional method, insulation blankets (designated as ‘I’) were used to cover the specimens. They were selected based on the $R$-value (capacity of an insulating material to resist heat flow; higher numbers designate greater efficiency) as recommended in ACI-306R (2016) to protect ordinary concrete sections above ground level with thickness $\leq$200 mm for 7 days. However, a reduction factor of 25% was applied to the $R$-values considering the satisfactory performance of the adopted mixtures under -5°C without protection [Chapters 3-5]; thus, the $R$-values of the insulation blankets were 5 and 7 for -10 and -20°C curing temperatures, respectively.

Moreover, the efficacy of applying paraffin-based PCM as a renewable and sustainable curing aid for the mixtures was explored. A reusable PCM (Table 6.2) mat was attached to the insulation blanket without/with a reflective layer as a hybrid system (designated as ‘IP’) as schematically shown in Fig. 6.1. The PCM melting point is constant at approximately 5°C, thus releasing stored energy (187 J/g) at the cold weather threshold stipulated by ACI 306R (2016) and CSA A23.1 (2019). With PCM, the $R$-values of the supporting insulation blankets were selected at 2.5 and 3.5 (i.e., 50% reduction relative to the reference insulation ‘I”) for the curing temperatures of -10 and -20°C, respectively. At -20°C, 0.3 mm reflective layer was attached to the insulation blankets in all cases (i.e., ‘I’ and ‘IP”) to improve heat storage at this deep-freezing temperature. At the two curing temperatures, the PCM mat in the hybrid system was replaced with another melted one after 3 and 7 days to act as an external heating source.
Table 6.2: Properties of phase change material

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>5°C</td>
</tr>
<tr>
<td>Heat storage capacity</td>
<td>187 J/g</td>
</tr>
<tr>
<td>Thermal conductivity (liquid/solid)</td>
<td>0.15/0.25 W/m°C</td>
</tr>
<tr>
<td>Density (liquid/solid)</td>
<td>0.88/0.96 g/ml</td>
</tr>
<tr>
<td>Specific heat (liquid/solid)</td>
<td>2.26/1.78 J/g°C</td>
</tr>
<tr>
<td>Number of cycles before instability</td>
<td>10,000 cycles</td>
</tr>
<tr>
<td>Expected service life with daily usage</td>
<td>27 years</td>
</tr>
</tbody>
</table>

Note: Data was provided by the manufacturer.

Figure 6.1: A schematic representation of the hybrid protection system used at -20°C.

6.3.4 Testing

The internal temperature of each mixture was monitored for the first 7 days after casting by thermocouples, which were embedded within the top 10 mm of 100 mm cubic specimens. Moreover, the hardening rates of the different mixtures were assessed based on the initial and final setting times, which were determined according to ASTM C403 (2016). This test was performed inside the environmental chamber set at the curing temperatures and employing the protection methods described earlier. The early- and later-age compressive strength of the different mixtures were determined by testing triplicate cylinders (100×200 mm), as per ASTM C39 (2020), after 7 and 28 days of curing, respectively under the adopted curing regimes and protection methods.

In addition, after 28 days, the fluid transport and durability properties of the mixtures were assessed based on absorption and freezing-thawing tests. The absorption test was performed on triplicate concrete discs (75×50 mm) as described by Tiznobaik and Bassuoni (2018). In addition, for each mixture, the resistance of triplicate prisms
(50x50x285 mm) to freezing-thawing cycles was assessed, following the guidelines ASTM C666 (2015) procedure A (freezing-thawing in water), based on the durability factor, assessed by the dynamic modulus of elasticity, as per ASTM C215 (2019). Additional triplicate prisms (50x50x285 mm) were exposed to a de-icer (13.6% calcium chloride solution) instead of water in the freezing-thawing test. This concentration was selected to incorporate the chemical/physical degradation effects of the salt (solution with ice) based on the calcium chloride phase diagram (Ghazy and Bassuoni 2019). For both testing conditions, two freezing-thawing cycles per day were adopted to allow for potential chemical reactions with hydrated paste, if any. One freezing-thawing cycle (12 h) consisted of freezing for 7 h at −18±1°C, thawing for 3.5 h at 4±1°C, and 45 min to ramp up and down to the target freezing or thawing temperatures. This exposure regime continued for 150 days (300 cycles). Furthermore, the bulk tests were corroborated by thermal and microstructural studies (TG and MIP), following the procedures mentioned in Chapter 3 (Section 3.4.3)

6.4 Experimental Results

6.4.1 Internal Temperature

The internal temperature change in the specimens of exemplar (all GU and one HE) mixtures cured under -10 and -20°C for 7 days is shown in Figs. 6.2 and 6.3, respectively (other mixtures' internal heat evolution are shown in Figs. D.1 and D.2). All mixtures initially attained high internal temperature (19 to 29°C) due to mechanical mixing (at -5°C) and initial hydrolysis of cement. Subsequently, a continual drop in internal temperature was recorded in all mixtures, due to heat loss to the ambient curing environments (-10 or -20°C), despite the heat emitted from the cement hydration process.
catalysed by CNAI with HE cement and/or nano-silica. The internal temperature of mixtures exposed to -10 and -20°C curing regimes, dropped below the freezing point of water (0°C) after 12 to 42 h and 14 to 33 h, respectively and reached a minimum range of -5 to -7°C and -8 to -13°C, respectively at 7 days. This indicates that the temperature during the protection period did not comply with ACI 306R (2016) recommendations of maintaining a surface temperature of 10°C for 7 days, albeit the R-values of the insulation blankets were selected based on ACI 306R (2016) recommendations. However, reduction factors of 25% and 50% in case of conventional (I) and hybrid (IP) protection methods, respectively, were applied considering the higher reactivity of the mixtures tested compared with ordinary concrete prescribed in that table.

Despite the lower (50% reduction) R-values of the insulation used in the hybrid system compared to the conventional insulation method, the specimens covered by this
method showed higher retention of internal heat. During the first 7 days, the internal temperatures of the specimens protected by the hybrid system were higher (2 to 5°C) compared to that of similar specimens covered by the insulation blankets. This can be linked to the addition of PCM mat in the hybrid system, which was substantiated by the prompt rise in temperature of mixtures when the PCM mat was replaced after 3 and 7 days. Therefore, the internal heat loss of the different mixtures was reduced owing to this heat boosting process, for example raising the peak temperatures up to 1°C and -0.5 °C in case of mixtures cured at -10 and -20°C, respectively; the impact of this process was observed for approximately 8 and 6 h, respectively. In Chapters 3-5, these temperature ranges were shown to be sufficient for continuity of hydration in binders containing low w/b, GU cement, nano-silica, and CNAI, suggesting the efficacy of the hybrid protection system.

![Figure 6.3: Internal temperature profile of exemplar mixtures cured at -20°C during 7 days.](image)
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For both protection and curing regimes, nano-modified binary binder mixtures showed the lowest heat loss during the first 7 days of curing. For instance, at -10°C, the temperature of mixture GUN-IP was 2 to 4°C higher than that of the corresponding reference mixture GU-IP during the first 24 h (Fig. 6.2). This alluded to the high heat of hydration of nano-modified concrete due to the catalytic effects of nano-silica, with high surface area and vigorous reactivity, on the kinetics of hydration at early-age. Indeed, the incorporation of CNAI (accelerating/anti-freeze admixture) was essential to keep functionality of nano-silica, under the freezing curing regimes herein. On contrary, nano-modified fly ash mixtures (ternary binder) experienced higher loss in internal temperature compared to nano-modified (binary binder) mixtures. This can be ascribed to the replacement of cement with 20% Class F fly ash, which has lower lime content, and consequently, lower rates of calcium ions dissolution. However, the adverse effects of fly ash on internal temperature, and thus hydration at early-age, was partially alleviated by the incorporation of nano-silica and maintained it to levels comparable to single binders.

Expectedly, the HE mixtures attained higher early internal temperatures relative to corresponding GU mixtures. This can be attributed to the higher tricalcium (C₃S) content and fineness of HE cement, resulting in faster reactivity of binder and higher heat emission associated with the accelerated hydration process (Neville 2011). For instance, at -20°C with the hybrid protection system, the temperature difference between mixtures HEN-IP and GUN-IP was between 2 and 4°C during the first 24 h of curing (Fig. 6.3). However, HE mixtures showed higher rates of heat loss after 6 days of curing compared to GU mixtures, indicating slower hydration rates at later-ages, as will be discussed in the TG section.
6.4.2 Setting Times

As shown in Figs. 6.4 and 6.5, the mixture design variables as well as the protection methods significantly affected the rigidity behavior of the mixtures. Both initial (IST) and final (FST) setting times varied between 0.8 to 2.2 h and 3.8 to 8.2 h, respectively, coinciding with the above-zero temperatures period for all mixtures within the first 8 h (3 to 12°C at 8 h). The FST is similar to the typical hardening times (4 to 8 h) of concrete cast and cured under normal temperatures (Neville 2011), which highlights the practicality of these mixtures, considering the protection methods implemented, for construction applications under freezing temperatures down to -20°C. For both curing temperatures, the hybrid protection method led to faster rates of concrete hardening due to the PCM, complying with the internal heat results. For example, at -20°C, mixture HEN-IP had 33% and 29% reduction in both initial and final setting times, respectively relative to the values achieved for the same mixtures using the conventional insulation method.

The incorporation of nano-silica markedly decreased both IST and FST compared to counterpart mixtures without nano-silica, under the same curing temperature and protection method. For instance, at -10°C, the incorporation of 6% nano-silica in mixture GU-IP to produce mixture GUN-IP shortened both IST and FST by 22 and 18%, respectively. This conforms to the previous chapters, which showed the contribution of nano-silica to shorten the hardening time of concrete at low temperatures (down to -5°C). This is linked to acceleration in the hydration process as implicated by the high internal heat of nano-modified mixtures with binary binders, and thus faster rates of hardening.
Conforming to their low internal temperature, mixtures incorporating fly ash attained the longest IST and FST due to the replacement of cement with slow reactivity supplementary cementitious material (SCM). However, the presence of silica nanoparticles and CNAI, mitigated the slow reactivity of fly ash mixtures; hence the IST of ternary binder mixtures (GUFN and HEFN) were comparable to single binder mixtures (GU and HE), conforming to the negligible difference in their internal temperatures. For instance, at -10°C, the IST and FST of mixture GUFN-I were only 4% and 10%, respectively, more than that of the corresponding single binder mixture GU-I. The use of HE cement significantly reduced the setting times of the mixtures compared to the corresponding GU mixtures. For example, at -10°C, changing the cement type in mixture GU-IP to produce mixture HE-IP reduced both IST and FST by 33% and 21%, respectively. This can be attributed to the previously mentioned accelerating effect of HE cement on the hydration process.
6.4.3 Compressive Strength

Despite the continual reduction of internal temperature below 0℃ within the first 12 to 42 h, all concrete mixtures showed progressive strength gain with time at both curing temperatures. As shown in Figs. 6.6 and 6.7, the 7 and 28 days compressive strength of the mixtures varied between 15 to 42 MPa and 25 to 56 MPa, respectively. The strength range of the mixtures at 28 days, comply with the strength requirement of concrete (20 to 40 MPa) for various construction applications such as concrete pavements, sidewalks, buildings, bridges (MacGregor et al. 1997). Changing the protection method had a pronounced effect on the strength development of concrete mixtures at both curing temperatures. Accordingly, the compressive strength of concrete protected by the hybrid system was higher than that of similar concrete covered with conventional insulation by an average of 40% and 23% at -10℃ and -20℃, respectively. This can be attributed to the additional effect of the PCM mat, which acted as an external heating source, which
temporarily raised the internal temperature of concrete; thus, it contributed to boosting hydration and strength development, especially at early-age.

Regardless of the cement type, the incorporation of nano-silica notably enhanced the strength development of concrete cured under freezing temperatures. This trend is similar to that observed in Chapters 3-5. For example, at -20°C, incorporating nano-silica in mixture GU-I to develop mixture GUN-I increased the 7 and 28 day strengths by 38 and 33%, respectively. The performance of nano-modified mixtures can be linked to the vigorous reactivity and ultra-fineness of nano-silica maintained by CNAI, conforming to the setting time trends.

![Figure 6.6: Compressive strength of the mixtures at 7 days. (Note: error bars represent standard deviations)](image)

Under normal (20 to 30°C) curing temperatures, Class F fly ash, slowly reactive pozzolan, has a well-documented delaying effect on the development of concrete strength up to 28 days (Neville 2011), which would be expected to exacerbate under the freezing regimes adopted herein. However, similar to the trends of setting time, the presence of
nano-silica alleviated this effect on concrete protected by both methods (I and IP). Ternary mixtures comprising fly ash and nano-silica yielded strength values comparable to the reference single binder mixtures (GU and HE). For instance, incorporating 20% fly ash with 6% nano-silica led to marginal reduction (averages of 8% and 6%, respectively) in strength at 7 and 28 days. While according to ACI-306R (2016) the use of slowly reactive SCMs is not recommended for cold weather concrete, the presence of fly ash is beneficial to achieve long-term durability and mitigate potential shrinkage and thermal cracks associated with the coexistence of high dosages of CWAS, HE cement and/or vigorously reactive materials such as nano-silica.

Complying with the internal temperature and setting time results, changing the type of cement to HE positively affected concrete strength at early-age, due to its rapidly reactive nature. For instance, the 7 days strength of mixtures HEFN-IP (cured at \(-10^\circ\)C) and HE-IP (cured at \(-20^\circ\)C) were 55% and 30%, respectively higher than that of the corresponding GUFN-IP and GU-IP mixtures. However, this effect diminished with time as the strength of HE mixtures at 28 days were marginally higher (3 to 11%) than that of corresponding GU mixtures.
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6.4.4 Durability Performance

Irrespective of curing temperatures, mixture design and protection methods, all the mixtures achieved the 3 and 24.5 MPa strength stipulations by ACI 306R (2016) to resist one and multiple cycles of freezing-thawing, respectively after 7 or 28 days. The durability of the mixtures was assessed by absorption (Fig. 6.8) and durability factor \((DF)\) of specimens in freezing-thawing tests in water (Fig. 6.9) and calcium chloride solution (Fig. 6.10). Complying with the previous results, mixtures protected by PCM (hybrid system) achieved lower absorption values and higher resistance to frost damage. For instance, at -20\(^\circ\)C, mixture GU-IP showed decreased (10\%) absorption and increased (31\% under freezing-thawing in water) \(DF\) compared to that of mixture GU-I. This can be ascribed to the better microstructural development, as will be discussed in the subsequent section, and strength grade (Figs 6.6 and 6.7) of concrete protected by the hybrid system.
Generally, single binder mixtures incorporating HE cement showed comparable absorption and $DF$ to correspondence GU mixtures, conforming to the compressive strength trends at 28 days. These mixtures (GU and HE) achieved the lowest $DF$ in both freezing-thawing regimes, which corresponded to higher absorption values of these mixtures. Although these mixtures achieved the strength stipulations (24.5 MPa) of ACI 306R (2016) to resist freezing-thawing cycles, they failed to resist frost damage due to physical/chemical degradation in water and salt solution after 190 to 220 and 15 to 30 freezing-thawing cycles, respectively. In addition, the $DF$ of the GU and HE mixtures in the salt solution exposure varied between 0 and 7%, failing the relative dynamic modulus of elasticity limit (60%) stipulated by ASTM C666 (2015). This highlights the importance of durability testing, if concrete would be exposed to similar conditions in service.
Compared to single binder mixtures, nano-modified concrete showed high resistance to frost action under both exposure regimes as the $DF$ was higher than 85%, irrespective of the curing temperature and protection method. For example, at -10°C, mixture GUN-I had 45% and 2200% higher $DF$, in water and salt solution, respectively compared to that of mixture GU-I. This can be linked to improving the maturity of concrete (Fig. 6.7) and discounting the penetrability of concrete, as reflected by reduction of absorption (Fig. 6.8). In addition, nano-silica contributed to increasing the chemical resistance of concrete, which was beneficial in the case of frost action combined with the chloride-based solution.

Figure 6.9: Durability factors of concrete mixtures after 300 cycles of freezing-thawing in water. (Note: error bars represent standard deviations)
The role of nano-silica at improving the durability of concrete was maintained, even when combined with fly ash. Hence, nano-modified fly ash (ternary binder) mixtures showed low absorption at similar strength values compared to reference single binder mixtures. For instance, at -10°C, mixture GUFN-IP had 16% lower absorption value, and increase of 34% and 1617% in $DF$, in water and salt solution, respectively compared to that of mixture GU-IP. This highlights the ability of nano-silica to catalyze the indolent reactivity of fly ash even under freezing temperatures; subsequently, high resistance to frost action (average reduction of 10% of $DF$ up to 300 freezing-thawing cycles under both exposure regimes).

### 6.5 Discussion

To characterize the hydration and microstructural development of concrete, and thus interpret the trends from bulk tests, the portlandite/calcium hydroxide (CH) contents in
exemplar hardened pastes were determined by TG up to 91 days of curing under the adopted curing temperatures and protection methods (Figs. 6.11 and 6.12), other mixtures’ CH contents are shown in Figs. D.3 and D.4. In addition, the MIP test was performed on concrete samples from all mixtures at 28 days (Table 6.3). Irrespective of the type of cement or protection method, all mixtures showed progressive hydration and pozzolanic reactivity (in case of nano-silica without and with fly ash) over 91 days, despite their low internal temperature.

Mixtures protected by the conventional insulation system had lower rates of CH production and/or consumption in comparison to similar mixtures protected by the hybrid system. For instance, the normalized CH contents of mixtures GU-I and GU-IP yielded an average of 0.61 and 0.87 at 1 and 91 days, respectively, under both curing temperatures. Correspondingly, the use of hybrid protection improved the microstructure of concrete. For instance, at -10°C, mixture HEN-IP had reduced porosity and threshold pore diameter by 9% and 38%, respectively, and increased proportion of micro-pores by 9% relative to that of corresponding mixture HE-I (Table 6.3). This can be ascribed to the latent thermal energy storage function of PCM, which acted as an external heat source underneath the insulation blankets with reduced R-values (2.5 and 3.5). The reusable PCM mat provided the concrete specimens with thermal energy of 187 J/g during its solidification process from the liquid state at 5°C, releasing heat that increased the internal temperature of concrete within 6 to 8 h, thus improving the reactivity of the binders. Indeed, replacement of solidified PCM mat with melted one after 3 and 7 days, re-boosted the kinetics of hydration due to reintroducing the PCM heat release process. This explains the better performance of concrete mixtures protected by the hybrid system.
in terms of faster hardening rates, earlier/higher strength development, and better frost resistance.

Figure 6.11: Exemplar thermogravimetry results and normalized CH contents up to 91 days of curing at -10°C.

Binders produced using HE cement was at their utmost reactivity at early-age by producing higher contents of CH compared to corresponding GU binders. This can be ascribed to the rapid rates of calcium ions dissolution from HE cement due to the higher C₃S content (64%) and fineness (500 m²/kg) compared to that of GU cement (50% and 320 m²/kg, respectively). For example, the normalized CH contents in mixture HE-I and GU-I after 1 day of curing at -10°C and -20°C were 1.72 and 1.64, respectively. This explains the higher internal temperatures, shorter setting times, and higher early-age strength of these mixtures. Subsequently, the rate of HE cement hydration reduced up to 91 days, due to formation of thicker hydration shells at early-age, thus discounting the diffusivity of water towards unhydrated cement grains (Mehta and Monteuro 2014). Consequently, the effect of binder type on concrete properties over longer-term was
negligible, as comparable performance of HE and GU mixtures were observed in terms of later-age strength, absorption, and freezing-thawing resistance. This is ascribed to the comparable microstructural development under similar freezing conditions and protection methods as reflected by the MIP results (Table 6.3). For instance, at -10°C, changing the binder type in the mixture GU-I to produce mixture HE-I had the same porosity (15%) at 28 days.

For example, the average normalized CH contents in mixture GUN-I were 53, 24, and 32% higher than that in the corresponding mixture GU-I at 1, 3, and 7 days, respectively, at both curing temperatures (Figs. 6.11 and 6.12). This complies with the shortened setting times and increased early-age strength of these mixtures. With coexistence of CNAI and protection systems, nano-silica maintained its functionality under these conditions.

Figure 6.12: Exemplar thermogravimetry results and normalized CH contents up to 91 days of curing at -20°C.
freezing temperatures by providing additional surfaces for the hydration products to precipitate [nucleation effect (Madani et al. 2012)], leading to further acceleration in the kinetics of hydration reactions, as reflected by the higher internal temperatures and hardening rates, leading to notable strength development at early-age.

Comparatively, the incorporation of Class F fly ash in concrete mixtures resulted in lower CH contents compared to the nano-modified mixtures at early-age, as depicted in Figs. 6.11 and 6.12. For instance, the average CH contents in the ternary mixture GUFN-I were 47, 22, and 18% lower than that in the binary mixture GUN-I at 1, 3, and 7 days, respectively, under both curing regimes. This can be linked to the dilution of cement with a slow reactivity SCM with low lime content. Accordingly, the ternary binder mixtures incorporating fly ash had relatively longer setting times and slow strength development at early-age. However, the coexistence of nano-silica with its nucleation process partially offset the delaying effect of fly ash. Hence, the CH contents in the ternary mixtures were approximately the same as the corresponding single binder mixtures (normalized CH contents varied between 1 to 1.15 during the first 7 days), which links to the comparable early-age performance of both ternary and single binder mixtures.

After 7 days of curing at -10°C, the nano-modified mixtures showed notable consumption of CH up to 91 days (Fig. 6.11). For example, at -10°C, the normalized CH contents in mixture GUN-I relative to mixture GU-I were 0.73 and 0.57 at 28 and 91 days, respectively. This trend can be ascribed to delayed pozzolanic reaction of nano-silica, due to this freezing temperature, by consuming CH from the hydration reactions to produce additional C-S-H gel. The pozzolanic reaction of nano-silica was further delayed under -20°C as conspicuous consumption of CH started after 14 days (Fig. 6.12). This
can be linked to the higher heat loss from concrete specimens cured under this lower freezing temperature, resulting in slower production of CH necessary to commence the pozzolanic reaction of nano-silica. However, when adequate amounts of CH were produced after 14 days, the pozzolanic reactivity of nano-silica was continual, as for example indicated by the normalized CH contents in mixtures GUN-I, which reached 0.80 and 0.63 after 28 and 91 days, respectively compared to mixture GU-I. The notable positive effect of nano-silica on the later-age performance of concrete was supported by the MIP results, as the nano-modified mixtures showed significant improvement in the pore structure features at both curing temperatures. For instance, at -20°C, the addition of 6% nano-silica in mixture GU-IP to produce mixture GUN-IP decreased the 28 days porosity and threshold pore diameter by 21% and 88%, respectively, and increased the proportion of micro-pores by 39%. These trends verified the functionality of nano-silica under these freezing temperatures due to the coexistence of CWAS and protection methods implemented herein; consequently, the concrete produced had adequate degree of hydration and thus improved hardened and durability properties.

Correspondingly, the dominant effect of nano-silica on the pore structural development of nano-modified fly ash concrete was highlighted by the MIP results. The ternary mixtures showed refined pore structure characteristics compared to reference single binder mixtures at 28 days. For example, at -10°C, mixture GUFN-I achieved 7% and 43% reduction in porosity and threshold pore diameter compared to that of mixture GU-I; also, there was 13% increase in the proportion of micro-pores. After 28 days of curing, the nano-modified fly ash concrete mixtures showed higher consumption rates of CH up to 91 days relative to their corresponding binary binder mixtures, reaching
normalized CH ratios less than 0.75. This alluded to the contribution of nano-silica to catalyzing the indolent pozzolanic reactivity of fly ash, under such freezing temperatures.

The nucleation, filler and pozzolanic effects of nano-silica led to improvement and densification in the microstructure of concrete, which was reflected by the lower absorption values of nano-modified mixtures after 28 days of curing. This led to higher resistance to freezing-thawing cycles in water due to discounting the susceptibility to saturation (physical resistance). Indeed, the thawing periods during freezing-thawing...
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cycles (higher temperature of 4±1°C) had a positive effect on the reactivity of nano-modified binders, in terms of further improving the microstructure and durability of concrete with time. In addition, compared to concrete mixtures made from single binders (GU and HE), the nano-modified concretes had high chemical resistance to the freezing-thawing exposure involving the de-icing salt, due to consuming CH in the pozzolanic reaction. The CH contents in the single binder mixtures were 43% to 67% higher than that in the corresponding binary and ternary mixtures, resulting in favorable reaction conditions for calcium oxychloride formation (Balonis et al. 2010), which led to aggravated chemical degradation of cementitious matrix and loss of concrete stiffness.
CHAPTER 7: INTERACTION BETWEEN NANO-MODIFIED CONCRETE CAST AND CURED UNDER FREEZING TEMPERATURES AND STEEL: EXPERIMENTAL AND MODELING

This chapter expands on the previous chapter and aims at investigating the efficacy of using conventional (insulation blanket) and hybrid protection system (insulation blanket + PCM mat) on concrete-steel interface hydration development and bonding behavior with steel re-bars of different concrete mixtures cured under freezing temperatures (-10 and -20℃), based on experimental work and numerical modeling to capture and predict temperature stratification in concrete and resulting bonding strength with steel re-bars.

7.1 Introduction

The capacity of reinforced concrete elements is affected by the concrete-steel bonding, which defines their structural and ductility performance (MacGregor et al. 1997). However, concrete placement and curing under cold weather negatively affect its hydration development, mechanical properties, and consequently the concrete-steel bond strength (Neville 2011; Rixom and Mailvaganam 2002). Guidelines and codes for concrete (e.g., ACI 306R 2016, CSA A23.1 2019 and CS164 2016) set 4 to 5℃ as the benchmark for cold weather precautions. When the ambient temperature reaches these values, hydration of cementitious binders proceeds at very slow rates and ceases when the temperature drops to -2.8℃ due to freezing of mixing water (Karagöl et al. 2015; Ratinov and Rozenberg 1996; Korhonen et al. 1992). Concrete produced under such conditions suffers from heterogonous microstructure and cracked matrix, which negatively affects its structural performance and service life (Prado et al. 1998; Powers and Helmuth 1953).
Both ACI 306R (2016) and CSA A23.1 (2019) have stipulations for cold weather concreting, including limitations on mixing, placement and curing temperatures, which can be achieved by heating concrete constituents (aggregates and water) between 40°C to 60°C, and building voluminous and heated enclosures to maintain concrete temperature at an acceptable threshold (more than 10°C) during placement and protection periods. In addition, ACI 306R (2016) recommends to heat any metallic embedments to at least 0°C when the ambient temperature is at or below -12°C to avoid ice formation at the interface and ensure adequate development in bond strength with concrete. However, such heating practices incur considerable costs due to massive energy consumption, required coverings/skilled labour and increased carbon footprint of construction (Barna et al. 2011). Consequently, in cold regions, the construction season is limited to warmer periods (from May to September in North America), leading to significant socioeconomic losses due to busy construction and backlogged repair schedules. Therefore, extending the construction season in cold regions is a critical issue, which necessitates continual advent of innovative strategies to cast and protect concrete efficiently under freezing temperatures.

In cold weather applications, the bonding between concrete and steel maybe inferior, because of the development of inadequately hydrated interfacial zone (Schroeder and Wood 1996). For instance, Schroeder and Wood (1996) investigated the effect of using calcium nitrite and sodium nitrite (cold weather admixture system; CWAS) at dosages of 2% and 6% by mass of cement, respectively on concrete (cement content of 370 kg/m³ and water-to-cement ratio of 0.48) bond strength with 20 mm steel bars. After casting specimen, using hot water (54°C) and room temperature steel bars, they were cured at average temperatures of -5 and -10°C. The bond strength of the specimens after
15 days of curing was less than 1 MPa and increased to 5.5 MPa after 28 days, which was markedly lower than that of similar concrete cured at normal temperatures (8 to 17 MPa) (Tondolo 2015; Diab et al. 2014).

Since the last decade, the effects of vigorously reactive nanoparticles (e.g. nano-silica) on improving the hydration and microstructural development of concrete and its hardened properties have been the subject of extensive investigations (e.g. Ghazy et al. 2016; Belkowitz et al. 2015; Madani et al. 2012). However, most of these studies were conducted for concrete produced and cured under normal temperatures (20 to 30°C), while research on the use of nanoparticles in cold weather concrete applications is still in early stages. In Chapters 3 and 4, statistical modelling associated with experimental work were performed to develop winter concrete, using combinations of various water-to-binder ratios (w/b), fly ash, nano-silica and different antifreeze/accelerating CWAS, which was cast and cured under low temperatures down to -5°C without any heating or protection. It was found that low w/b (0.32) concrete mixtures incorporating 2 to 6% nano-silica and calcium nitrate-nitrite solutions (CNAI), without and with fly ash, achieved acceptable performance in terms of hardening rates, hydration development, strength and durability properties. However, the bonding behaviour of these mixtures with unheated metallic reinforcement at freezing temperatures has not been investigated, which warrants further studies in this direction.

On the other hand, incorporating phase change materials (PCM), energy absorbing/release reservoirs that can reversibly store and emit heat through solidifying/melting processes processes (Aguayo et al. 2016; Fernandes et al. 2014), in concrete is a relatively new technique capable of enhancing concrete’s thermal energy storage capacity. PCM can be integrated into concrete matrices by direct incorporation
Chapter 7: Bonding Behaviour of Nano-Modified Concrete with Steel
during mixing (Liu et al. 2017; Fernandes et al. 2014), micro (Liu et al. 2017), or macro-encapsulation (Farnam et al. 2015) as well as saturation of lightweight aggregates (Farnam et al. 2015), or nano-materials such as nano-silica (Li et al. 2015), and carbon nanotubes (Dorigato et al. 2017). Among all types of PCM, organic PCM, paraffin or non-paraffin, are preferred to be used in concrete applications due to their noncorrosive and stable nature as well as operating temperatures (Baetens et al. 2010). These materials have been commonly utilized to improve the resistance of concrete to freezing-thawing cycles by delaying ice formation (Meshgin and Xi 2012), and mitigating thermal cracking (Kim et al. 2015). However, the incorporation of PCM in concrete has its own drawbacks; it has marked negative effects on concrete mechanical and physical properties [reduction of strength/elastic modulus (Farnam et al. 2015), and high porosity (Aguayo et al. 2016) and drying shrinkage (Meshgin and Xi 2012)], which may limit the applications of PCM-modified concrete to non-structural applications (Cao et al. 2017; Memon et al. 2015). Despite the potential of PCM to retain concrete internal temperature and delay ice formation between concrete and unheated metallic embedment and/or forms through its heat of fusion, the viability of using PCM as external curing aids in order to protect newly poured concrete under freezing temperatures has not been explored.

7.2 Research Significance
Nano-modified concrete incorporating CWAS and protected using PCM as an external curing agent may offer a sustainable and cost-efficient option for cold weather concreting applications, without the need for extensive heating practices. Yet, this needs to be systematically investigated, which was the motive for this research. In comparison to a conventional protection method (insulation blankets), this study aimed at exploring the
efficacy of using a hybrid protection system (insulation blanket + PCM mat) on hydration development and bonding behavior with steel of nano-modified concrete cured under freezing temperatures (-10 and -20°C), without heating. The experimental work included internal temperature, mechanical properties, bonding, thermal, and microstructural studies to evaluate the hydration development of the cementitious matrix at the concrete-steel interface. In addition, thermal and mechanical finite-element models were developed to numerically capture temperature stratification in concrete and resulting bonding strength with steel. The success of such protection methods and mixtures designs may provide an integrated strategy for alleviating heating requirements and improving the quality of winter concrete production in cold regions.

7.3 Experimental Procedure

7.3.1 Materials and Mixtures

The materials used in this chapter were similar to that used in Chapters 3 and 4 (refer to Sections 3.4.1 and 4.3.1). The proportions of the mixtures tested in this chapter are shown in Table 7.1. In the mixture ID, the letters GU, F, N denote GU cement, fly ash and nano-silica, respectively.

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Cement (kg)</th>
<th>Fly Ash (kg)</th>
<th>Nano-silica (kg)</th>
<th>Water* (kg)</th>
<th>CNA*/CNI* (kg)</th>
<th>Coarse Aggregate (kg)</th>
<th>Fine Aggregate (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>105.6</td>
<td>14+32</td>
<td>1156</td>
<td>622</td>
</tr>
<tr>
<td>N</td>
<td>376</td>
<td>-</td>
<td>48</td>
<td>81.6</td>
<td>14+32</td>
<td>1151</td>
<td>620</td>
</tr>
<tr>
<td>FN</td>
<td>296</td>
<td>80</td>
<td>48</td>
<td>81.6</td>
<td>14+32</td>
<td>1137</td>
<td>612</td>
</tr>
</tbody>
</table>

*Adjusted amount of water considering the water content of nano-silica (aqueous solution with 50% solid content of SiO₂) and CNI (aqueous solution with 30% solid content).
†The CNA admixture was in solid form with 70% active ingredient.
7.3.2 Procedures

The procedures followed in this chapter were similar to that used in Chapter 6 (refer to Sections 6.3.2).

7.3.3 Protection Methods

The protection methods used in this Chapter were similar to that used in Chapter 6 (refer to Sections 6.3.3).

7.3.4 Testing

Concrete mechanical properties were assessed based on compressive strength, tensile strength and modulus of elasticity, which were determined by testing triplicate cylinders (100×200 mm) as per ASTM C39 (2020), ASTM C496 (2017) and ASTM C469 (2014), respectively after 28 days of curing under the adopted temperatures and protection methods. In addition, the bond strength of the different mixtures, under different curing temperatures and protection methods, with steel reinforcement at 28 days, were assessed through pull-out tests which were performed on duplicate 200 mm cubic specimens, which were designed following RILEM 7-II-128 (1994) guidelines. Each cube contained a 15M (16 mm) steel re-bar, which had an initial temperatures equal to the curing temperatures (-10 or -20°C), inside concrete cubes with an embedment length of 12.5 times the bar diameter (Fig. 7.1). Half of the bars embedded length (100 mm) was debonded using polyvinyl chloride tubing to reduce the concrete-steel contact area to limit the failure load below the machine loading capacity. Two linear variable displacement transducers (LVDTs) were attached to each specimen to monitor the steel bars free and loaded ends slippage under a constant loading rate of 0.5 kN/s. The LVDTs as well as the machine load were collected using a data acquisition system and used to draw the force-slippage relationships of the different mixtures.
Moreover, the internal temperature of concrete was monitored up to 28 days by Type T thermocouples which were embedded inside the bond test specimens in four different locations; steel-concrete interface, concrete edge, and 1/3 and 2/3 the distance between the concrete edge and steel re-bar, as shown in Fig. 7.1.

To capture the hydration development of binders, thermogravimetry (TG) at 10°C/min constant heating rate was conducted in nitrogen gas environment on powder samples, extracted from the different concrete specimens under the adopted temperatures and protection methods. The portlandite (CH) content of the different mixtures was calculated by multiplying the percentage drop of an ignited mass of the TG curves at the endothermic range of 400 to 450°C by 4.11 (CH-to-water molecular mass) after 1, 3, 7, 14, 28, 56 and 91 days of curing. In addition, the total hydration products at 28 days was expressed by determining the percentage drop of an ignited mass of the TG curves between 105 to 1050°C (Cassagnabère et al. 2009). Furthermore, environmental scanning electron microscopy (ESEM) with elemental dispersive X-ray (EDX) analysis were performed on fracture pieces extracted from the interface between steel bars and different

Figure 7.1: Schematic drawing of the bond strength specimens (all dimensions are in mm).
concrete specimens after the bond test to capture the effect of changing the mix design parameters and protection methods on the quality of the steel-concrete interfacial transitional zone (ITZ).

**7.4 Model I: Modeling of Heat Evolution in the Assembly**

7.4.1 Theoretical Formulation and Model Parameters

Fundamentally, the heat exchange between two objects, which is governed by the energy conservation and Fourier’s laws (Bergman et al. 2011; Mills 1999), occurs through one or combinations of three main mechanisms: conduction, convection and radiation. By definition, conduction is the energy transfer between different objects through direct contact, while convection is the transfer of energy through the movement of fluids, whereas the radiation is the energy transfer by electromagnetic emission such as light (Bergman et al. 2011; Mills 1999). In this study, the main objective of the thermal modeling was to determine the different elements’ heat exchange with surrounding environment due to the conditions imposed on their boundaries. In this case, the heat transfer by convection and radiation were assumed to be null. Hence, capturing the temperature variation within the assembly (insulation, concrete and steel) is beneficial at defining the temperature of any position at specific time by conduction based on energy conservation and Fourier’s laws (Bergman et al. 2011; Mills 1999). Assuming a homogeneous medium as well as temperature distribution \( T \) represented in Cartesian space \( (x, y, z) \), the general heat transfer equation, excluding convection and radiation, is determined by the heat flow through the assembly, as expressed in Eq. 7.1(Bergman et al. 2011; Mills 1999). The right and left hand sides of the equation represent the rate of change in stored energy and energy transferred by conduction, respectively.
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\[ k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) = C_p \rho \frac{\partial T}{\partial t} \]  
(Eq. 7.1)

where, \( K \) and \( C_p \) are the material thermal conductivity (W/m°C) and specific heat capacity (kJ/kg°C), respectively while \( \rho \) is its density (kg/m³).

However, if the material produces heat, such as concrete (through binder reactivity) and PCM, the influence of another term, \( Q \) (kJ/m³) representing the amount of heat generated per unit volume, should be added to the previous equation (Bergman et al. 2011; Mills 1999):

\[ k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + Q = C_p \rho \frac{\partial T}{\partial t} \]  
(Eq. 7.2)

Eq. 7.2 implies that at any position in the studied assembly, the energy transfer net rate by conduction to the interior of a unit volume in addition to the volumetric rate of thermal energy generation equals to the rate of variation of the thermal energy accumulated inside this volume (Kim et al. 2001). In case of concrete, the amount of heat generated from binder reactivity can be calculated from Eq. 7.3:

\[ Q \left( \frac{kJ}{m^3} \right) = \beta C_p \rho \left( 1 - e^{\alpha t} \right) \]  
(Eq. 7.3)

where, \( t \) is concrete age (days), while \( \beta \) and \( \alpha \) are constants which were chosen (Tanabe et al. 1985) based on binder content, \( w/b \) as well as the placement temperature.

The finite element modeling was performed based on hourly time steps, then concrete rate of heat generation, \( q' \) was calculated by Eq. 7.4:

\[ q' \left( \frac{kJ}{m^3h} \right) = \frac{1}{24} \beta C_p \rho \alpha e^{\frac{\alpha t}{24}} \]  
(Eq. 7.4)

The required parameters to construct the model and thus determine the assembly’s temperature gradient are shown in Table 7.2. For concrete, \( \rho \) was determined as per ASTM C138 (2017). The thermal conductivity, \( k \) of the different concrete mixtures was
calculated using a heat flow meter apparatus (HFMA) (ASTM C1784 2020; Ruuska et al. 2017), with an accuracy of ±1%. Slab specimens (200×200×55 mm) were sandwiched between the apparatus plates, which were equipped with a solid state cooling and heating system capable of independently controlling the induced heat flow in either downward or upward direction. Thin (76×76×1.78 mm) heat flux transducers (HFTs) were permanently attached to each of the plates surfaces and a Type E thermocouple was attached to the plates surface, close to the test specimen to monitor the specimen’s surface temperature. The plates’ temperatures and HFT output were continuously recorded every 1.3 s up to 512 consecutive data points, which were used to calculate the mean plates’ temperatures and heat fluxes. Once the thermal equilibrium of the system was achieved (temperature and transducers’ signal equilibrium) (FOX 314 Instrument Manual 2015), the thermal properties of concrete were calculated. The thermal diffusivity, \( \delta \) (m\(^2\)/sec) and specific heat, \( C_p \) (J/g°C) of concrete were calculated based on Eqs. 7.5 and 7.6:

\[
\delta = L^2 \frac{\Delta \ln Q_v}{\Delta t \pi^2}
\]

(Eq. 7.5)

\[
C_p = \frac{k}{\delta \times \rho}
\]

(Eq. 7.6)

where, \( L \) is the sample thickness (m), and \( \Delta \ln Q_v/\Delta t \) is the slope of straight line in the graph of natural logarithms of the heat flow signals \( Q_v \) (μV) vs. time \( t \) (s).
Table 7.2: Thermal conductivity, specific heat and density input used in the model

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity, k (W/m°C)</th>
<th>Specific Heat, C_p (J/g°C)</th>
<th>Density, ρ (kg/m³)</th>
<th>Heat Generation (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Bar</td>
<td>45</td>
<td>502</td>
<td>7800</td>
<td>--</td>
</tr>
<tr>
<td>Concrete</td>
<td>By testing</td>
<td>By testing</td>
<td>By testing</td>
<td>Eq. 3</td>
</tr>
<tr>
<td>Plywood</td>
<td>0.12</td>
<td>1210</td>
<td>540</td>
<td>--</td>
</tr>
<tr>
<td>PCM</td>
<td>0.20</td>
<td>2</td>
<td>920</td>
<td>187^b</td>
</tr>
<tr>
<td>Reflective Layer</td>
<td>0.01</td>
<td>1000</td>
<td>5</td>
<td>--</td>
</tr>
<tr>
<td>Insulation Blanket</td>
<td>0.03</td>
<td>1200</td>
<td>18</td>
<td>--</td>
</tr>
</tbody>
</table>

^aData was provided by the manufacturer of each material.
^bAmount of energy emission when PCM temperature reaches 5°C.

7.4.2 Numerical Simulation

To capture the effect of changing the mixtures design parameters as well as protection methods on the assembly, twelve 3D (three dimensional) models were created using Ansys 19.2 Workbench platform (2020), with identical dimensions and geometries to laboratory specimens. The software used the finite volume method to solve the partial differential energy equations based on energy conservation and initial conditions of the different elements. To simulate casting and placement conditions, the initial temperature of steel bars and formwork was set to match ambient temperature (-10 or -20°C), while PCM and insulation blankets started at 20°C (brought from storage at room temperature). The concrete mixtures initial temperatures were set based on their placement temperatures after mixing, i.e. 23, 26 and 22°C for single, binary and ternary mixtures, respectively.

The total number of nodes and elements in the models varied between 346193 to 378109 and 1364994 to 1510930, respectively. The mesh was structured as space discretization by tetrahedral elements with maximum size of 5 mm and average aspect ratio (the measure of mesh element's deviation from having equal lengths of all sides) of 1.87; an aspect ratio of 1 indicates a perfectly shaped tetrahedral mesh element. The different models convergence was defined based on residual energy precision of 6
decimals. Fig. 7.2 shows a general representation of the geometry input of each model. The input material parameters ($K$, $C_p$, $\rho$ and $Q$) were identified as per the above description. The presented model output includes temperature gradient of the different assemblies at any time ($t$) and the final results were presented as net internal heat at the concrete-steel interface after 28 days of curing, $Q_{28}$ ($^\circ$C-h). This term was integrated with respect to time, representing the area under the temperature-time curve, considering a datum temperature of -10$^\circ$C, at which the hydration development was negligible based on the phase diagram of the CWAS used (Fig. 3.1).

Figure 7.2: Finite element geometry of the thermal evolution model: (a) top view; (b) side View; and (c) meshing.
7.5 Model II: Modeling of Concrete-Steel Bonding

7.5.1 Theoretical Formulation and Model Parameters

The concrete-steel interface behavior under pull-out loading is governed by stress-strain relationships (Yankelevsky et al. 2008). Hence, the relative displacement, \( dl \) (mm) of a steel bar embedded at distance, \( dy \) (mm) in a concrete is equal to the relative displacement of concrete, \( \delta_c \) (mm) and steel, \( \delta_s \) (mm) as shown in Eqs. 7.7 and 7.8. However, the concrete displacement can be neglected due to its high area and low internal stresses compared to that of steel and by differentiation of both sides of the equation with respect to \( dy \), Eqs. 7.9 and 7.10 can be derived (Yankelevsky et al. 2008; Yankelevsky et al. 1985).

\[
dl = \delta_s - \delta_c \quad \text{(Eq. 7.7)}
\]

\[
dl = \left( \frac{\sigma}{E} \right)_s dy - \left( \frac{\sigma}{E} \right)_c dy \quad \text{(Eq. 7.8)}
\]

\[
\frac{dl}{dy} = \left( \frac{\sigma}{E} \right)_s \quad \text{(Eq. 7.9)}
\]

\[
\frac{d^2l}{dy^2} = \left( \frac{1}{E_s} \right) \frac{d\sigma_s}{dy} \quad \text{(Eq. 7.10)}
\]

where, \( \sigma \) and \( E \) are internal stress and modulus of elasticity (MPa), while \( s \) and \( c \) subscripts refer to steel and concrete, respectively.

Hence, the steel and bond stresses over a segment \( dy \) are correlated from the equilibrium condition shown in Eq. 7.11:

\[
(\sigma_s + d\sigma_s) A_s = \sigma_s A_s + \tau \ dy \ \pi \ d \quad \text{(Eq. 7.11)}
\]

Simplifying, Eq. 7.11 to produce Eq. 7.12:

\[
\frac{d\sigma_s}{dy} = \tau \left( \frac{\pi \ d}{A_s} \right) \quad \text{(Eq. 7.12)}
\]
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By substantiation from Eqs. 7.10 and 7.12, the contact surface between the two materials can be modeled analytically by a force-slip relationship which can be simply defined in Eq. 7.13 (Yankelevsky et al. 2008; Yankelevsky et al. 1985) based on the circumferential shear stress, $\tau$ (MPa) acting at the contact surfaces between concrete and steel bar:

$$\left( \frac{d^2 l}{dy^2} \right) = \tau_y \frac{\pi d}{E_s A_s}$$  \hspace{1cm} (Eq. 7.13)

where, $\tau_y$ is the shear stress (MPa), $l$ is the slippage (mm) between concrete and steel in $y$ ordinate (direction of loading), while $d$ and $A_s$ are the steel bar diameter (mm) and cross sectional area (mm$^2$), respectively.

The input parameters for concrete compressive strength, tensile strength and modulus of elasticity required to construct the model to predict concrete-steel bond strength and plot the force-slip relationship were obtained by testing as mentioned in the Testing section. Concrete Poisson’s ratio was assumed as 0.2 for the different concrete mixtures (Neville 2011). The steel bar Poission’s ratio, yield and ultimate stresses and modulus of elasticity were input as 0.3, 360 MPa, 520 MPa and 200 GPa, respectively.

7.5.2 Numerical Simulation

Twelve 3D models were developed using Ansys 19.2, Mechanical APDL platform (2019) to predict concrete-steel force-slip relationship. To model the actual bonded length of the steel bar, the cross sectional dimension of the concrete block were kept similar to the actual experimental specimens (200×200 mm) with only 100 mm embedded length, which represents the bonded length with steel bars without sleeve as shown in Fig. 3. The total number of nodes and elements were 4861 and 4020, respectively at a maximum mesh size of 10 mm. The ‘Solid65’ finite element, which is defined by eight nodes and
has isotropic properties, was used to represent concrete blocks in the numerical analysis, while “Beam188” with 16 mm diameter was selected to represent the steel bar. The concrete-steel contact interface was defined using “Combin39”, which is a 2-node spring element. Fig. 7.3 shows a general representation of the geometry of the model.

To simulate the actual testing conditions, the model assembly was constrained in all directions and the steel bar had one degree of freedom in the loading direction. The input parameters of the two materials were integrated into the model, and by applying an axial tension force at a rate of 0.5 kN/s, similar to the experimental loading rate in the direction of the steel bar embedded length, the model generated the force-lip relationship. Hence, the concrete-steel bond strength was determined based on Eq. 7.14:

\[
\tau_b = \frac{T}{\pi d L_e}
\]  
(Eq. 7.14)

where, \( \tau_b \) is the bond strength (MPa), \( T \) is the ultimate failure load (N), \( d \) is the steel bar diameter (mm) and \( L_e \) is the embedment length in contact with concrete (100 mm).

Figure 7.3: Geometry of the finite element model for concrete-steel bond.
7.6 Results and Discussion

7.6.1 Experimental

7.6.1.1 Internal Heat Evolution

Figures 7.4 and 7.5 present the internal temperature evolution at the concrete-steel interface in specimens during the first 7 days of curing under -10 and -20°C, respectively. Also the net heat produced ($Q_{28}$), after considering heat generation and losses to adiabatic environment, at this interface in the different mixtures during the first 28 days of curing are tabulated in Figs. 7.4 and 7.5. All steel bars had an initial temperature of -10 or -20°C based on the curing regime (initial condition). After 15 min of casting concrete, the concrete-steel interface temperature increased to reach 20 to 24.5°C due to rapid heat exchange through thermal conduction between the two materials. Afterwards, the interface temperature showed continual drop in all mixtures, which can be ascribed to heat loss to the surrounding environment (-10 or -20°C). Hence, the interface temperature, reached the freezing point of water (0°C) after 14 to 38.5 h and 13 to 26 h and dropped to a range of -5.2 to -7.6°C and -9.2 to -14.1°C, after 7 days of curing at -10 and -20°C, respectively. The different mixtures reached an average minimum temperature of -8.8 to -9.5°C and -17.6 to -19°C after 28 days of curing at -10 and -20°C, respectively, indicating near-equilibrium with adiabatic temperatures irrespective of mix design or protection method.
Although the hybrid protection system had 50% lower $R$-values of insulation compared to the conventional insulation method (refer to the Protection methods section), concrete mixtures protected by the hybrid system showed higher capability of internal heat retention. Hence, after 7 days of curing, the concrete-steel interface temperatures of mixtures protected by the hybrid system were higher (2 to 4°C) compared to the corresponding mixtures protected by the insulation blankets. This can be attributed to the energy release phenomenon of the PCM mat, which re-boosted the reactivity of different binders, resulting in higher internal temperature and $Q_{28}$ as shown in Figs. 7.4 and 7.5. This process was also reflected by the rise (3 to 7°C) at the concrete-steel interface temperature in the different mixtures after 4 to 6 h upon the replacement of the PCM mat after 3 and 7 days of curing. For example, using the hybrid protection method for mixture
GU-IP instead of the conventional method led to an average increase in $Q_{28}$ by 51% and 84% at -10 and -20 °C curing temperatures, respectively.

Regardless of the protection method and curing temperature, binary mixtures incorporating nano-silica achieved the highest temperatures at the concrete-steel interface. For instance, at -20°C, the temperature of mixture GUN-IP was 2 to 5°C higher than that of the corresponding reference mixture GU-IP during the first 3 days of curing with 45% higher $Q_{28}$ (Fig. 7.5). This can be linked to nano-silica nucleation and pozzolanic effects on improving the kinetics of binder reactivity, as will be discussed in the Hydration Development section. In contrast, ternary mixtures comprising fly ash with GU and nano-silica experienced higher temperature loss at the concrete-steel interface compared to the corresponding nano-modified binary mixtures. For example, at -10°C, incorporating 20% fly ash in mixture GUN-I to produce mixture GUFN-I reduced $Q_{28}$ by
Nevertheless, the coexistence of nano-silica in the ternary binder partially mitigated the negative effects of fly ash on delaying the internal heat evolution of the binder; hence, the ternary mixtures maintained internal temperatures close to that in the single binders at the concrete-steel interface. For instance, mixture GUFN had an average reduction of 12% and 5% in $Q_{28}$ (Figs. 6 and 7) compared to that of corresponding mixture GU when protected using the hybrid and conventional methods, respectively at both curing temperatures.

7.6.1.2 Mechanical Properties and Bond Strength

The force-slip relationships of the different concrete mixtures, cured under both temperatures -10 and -20°C, with steel are shown in Figs. 7.6 and 7.7. Moreover, the mechanical properties, compressive strength ($f'_c$), tensile strength ($f_t$), modulus of elasticity ($E$), and the bond strength ($\tau_b$), which was calculated based on Eq. 7.14, of the mixtures after 28 days are shown in Table 7.3. In the bond test, the splitting failure of concrete was the dominant mode, consequently the bond strength was governed by the mechanical properties of concrete (Butler et al. 2011; Gjørv et al. 1990). The bonding failure load of the specimens at 28 days varied between 39.8 to 70.5 kN corresponding to 7.9 to 14 MPa concrete-steel bond strength, which conforms to the bond strength values for concrete with similar strength grade and re-bar size, but cast and cured under normal temperatures (Tondolo 2015; Diab et al. 2014). Bond strength of concrete is governed by the mode of failure which is a function of concrete confinement, mechanical interaction, friction, and chemical adhesion with steel re-bars (Gjørv et al. 1990). When the re-bar embedded length is high enough, the splitting mode of failure of concrete dominates the bond test due to surrounding concrete failure by cracking (Gjørv et al. 1990), which is affected by the degree of hydration of the cementitious matrix. This is prudent to the
current case to substantiate the evolution of mechanical properties of the mixtures, under different freezing temperatures and protection methods, with respect to bonding with steel.

![Load-slip relationship (at the free end) of mixtures after 28 days of curing at -10°C.](image)

Figure 7.6: Load-slip relationship (at the free end) of mixtures after 28 days of curing at -10°C.

Changing the protection method had a marked effect on the mechanical properties and in turn bond strength of concrete mixtures cured at both freezing temperatures. Accordingly, concrete mixtures protected by the hybrid system achieved higher bond strength than that of similar concrete covered with conventional insulation by an average of 18% at both curing temperatures. This conformed to the higher compressive strength, tensile strength and modulus of elasticity of mixtures protected using the hybrid system compared to that of similar concrete protected by the conventional method. For instance, after 28 days of curing at -20°C, mixture GU-IP achieved 10, 32, 36 and 32% higher bond, compressive and tensile strengths and modulus of elasticity, compared to that of
mixture GU-I. This complies with the higher internal heat of mixtures protected by the hybrid system, indicating better development in paste microstructure and ITZ with steel bars as will be discussed in the subsequent section.

![Graph](image_url)

Figure 7.7: Load-slip relationship (at the free end) of mixtures after 28 days of curing at -20°C.

Irrespective of the curing temperature and protection method, nano-modified concrete (binary mixtures) achieved the highest mechanical properties. For example, at -20°C, incorporating 6% nano-silica in mixture GU-IP to produce mixture GUN-IP increased the bond, compressive, and tensile strengths and modulus of elasticity by 20, 30, 43, and 31% respectively. Comparatively, Class F fly ash, which is a slowly reactive pozzolan, has a well-documented delaying effect on the development of concrete mechanical properties at 28 days under normal (Mehta and Monterio 2014; Neville 2011) and low temperatures down to -5°C (Chapters 3-5). Albeit this effect would be expected to exacerbate under the freezing regimes (-10/-20°C) adopted herein, the coexistence of
nano-silica in mixtures comprising fly ash alleviated this negative effect on concrete, regardless of the protection method. Hence, ternary mixtures comprising nano-silica and fly ash yielded mechanical properties close to the corresponding single binder mixtures. For example, at -20°C, the incorporation of 6% nano-silica and 20% fly ash in mixture GU-IP to produce mixture GUFN-IP led to marginal reduction in bond and compressive strengths by 5% and 3%, respectively with 3% increase in tensile strength and similar modulus of elasticity at 28 days.

<table>
<thead>
<tr>
<th>Mixture ID.</th>
<th>Compressive Strength, $f'_c$ (MPa)</th>
<th>Tensile Strength, $f_t$ (MPa)</th>
<th>Modulus of Elasticity, $E$ (GPa)</th>
<th>Bond Strength, $\tau_b$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10°C Curing Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GU-I</td>
<td>33.9 (1.3)</td>
<td>3.3 (0.2)</td>
<td>31 (1.5)</td>
<td>11.4 (0.3)</td>
</tr>
<tr>
<td>GU-IP</td>
<td>44.7 (2.1)</td>
<td>4.5 (0.2)</td>
<td>41 (1.9)</td>
<td>12.5 (0.5)</td>
</tr>
<tr>
<td>GUN-I</td>
<td>39.5 (1.6)</td>
<td>4.7 (0.2)</td>
<td>39 (1.2)</td>
<td>12.7 (0.3)</td>
</tr>
<tr>
<td>GUN-IP</td>
<td>51.5 (2.6)</td>
<td>6.1 (0.3)</td>
<td>50 (1.9)</td>
<td>14 (0.3)</td>
</tr>
<tr>
<td>GUFN-I</td>
<td>33.1 (1.2)</td>
<td>3.1 (0.1)</td>
<td>29 (1.0)</td>
<td>8.8 (0.2)</td>
</tr>
<tr>
<td>GUFN-IP</td>
<td>43.4 (1.5)</td>
<td>4.7 (0.1)</td>
<td>39 (0.8)</td>
<td>12.1 (0.3)</td>
</tr>
<tr>
<td>-20°C Curing Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GU-I</td>
<td>30.1 (1.2)</td>
<td>3.2 (0.1)</td>
<td>27 (1.0)</td>
<td>8.5 (0.1)</td>
</tr>
<tr>
<td>GU-IP</td>
<td>34.6 (1.8)</td>
<td>3.5 (0.2)</td>
<td>32 (0.9)</td>
<td>10.1 (0.2)</td>
</tr>
<tr>
<td>GUN-I</td>
<td>35.6 (1.4)</td>
<td>3.7 (0.2)</td>
<td>32 (1.2)</td>
<td>10.7 (0.1)</td>
</tr>
<tr>
<td>GUN-IP</td>
<td>45.0 (2.2)</td>
<td>5.0 (0.1)</td>
<td>42 (2.0)</td>
<td>12.1 (0.4)</td>
</tr>
<tr>
<td>GUFN-I</td>
<td>29.3 (0.9)</td>
<td>3.4 (0.2)</td>
<td>27.5 (0.8)</td>
<td>7.9 (0.2)</td>
</tr>
<tr>
<td>GUFN-IP</td>
<td>33.6 (1.3)</td>
<td>3.6 (0.1)</td>
<td>32 (1.0)</td>
<td>9.6 (0.3)</td>
</tr>
</tbody>
</table>

Note: numbers in parentheses represent standard deviations.

7.6.1.3 Hydration Development and Microstructure Characteristics

Figure 7.8 shows the mass of hydration products after 28 days of curing under -10 and -20°C. The different mixtures showed continual hydration, despite the gradual drop in internal temperature that reached 0°C after 13 to 38.5 h of curing, as discussed in the previous section. Mixtures protected using the hybrid system achieved 12% average increase in the mass of hydration products compared to corresponding mixtures protected
using the conventional method, which complies with enhanced performance of mixtures protected using the hybrid system.

Figure 7.8: Mass of hydration products in mixtures at 28 days. (Note: error bars represent standard deviations)

Figure 7.9 shows exemplar portlandite (calcium hydroxide, CH) trends in some mixtures up to 91 days. It supports the superior performance of mixtures comprising nano-silica due to its vigorous reactivity associated with its ultra-fineness, as nano-modified mixtures (GUN-IP at -10 and -20°C) produced higher CH contents at early-age. This can be ascribed to the nucleation effects of nano-silica on the kinetics of cement hydration at early-age by providing the hydration products with additional surfaces to precipitate on (Madani et al. 2012), even under low temperatures. Indeed, the coexistence of CWAS (accelerating/anti-freeze admixture) kept the functionality of nano-silica, under the freezing temperatures adopted herein. This conforms to the higher internal heat of binary binder mixtures compared to that of single binder mixtures. In addition, the nano-modified mixtures showed consumption of CH after 7 and 14 days of curing at -10 and -
20°C, respectively, indicating the initiation of delayed pozzolanic reactivity by reacting with CH to produce secondary C-S-H gel. This pozzolanic reactivity was accompanied by the filler effect in the matrix (Ghazy et al. 2016; Belkowitz et al. 2015; Madani et al. 2012), which explains the marked improvement in mechanical properties, including bond strength with steel re-bars, of these mixtures at 28 days. This corresponded to higher mass (average of 12% higher) of hydration products in nano-modified mixtures at 28 days compared to that in single binder mixtures (Fig. 7.8).

Likewise, the mass of hydration products (Fig. 7.8) in ternary mixtures were 14% lower than that in binary mixtures but comparable to that in the single binder mixtures. Furthermore, as shown in Fig. 7.9, ternary mixtures showed continual hydration development, even with the existence of 20% Class F fly ash, due to the synergistic effects of nano-silica and CWAS which catalyzed the indolent reactivity of fly ash. Hence, nano-modified fly ash concrete, cast and cured under freezing temperatures down to -20°C showed acceptable performance in terms of hydration development and mechanical properties. This highlights that ACI 306R (2016) and CSA A23.1 (2019) recommendations against the use of slow reactivity supplementary cementitious materials in cold weather concreting can be mitigated by the addition of nano-silica.

To corroborate the findings from the TG test, exemplar mixtures were selected to perform ESEM on fracture pieces extracted from the concrete-steel interface in specimens after the bond test (Fig. 7.10). In addition, the average calcium-to-silicate ratio (C/S) within the concrete-steel ITZ was determined by EDX, which was performed at multiple points. Detwiler et al. (1996) reported that the C/S of secondary/pozzolanic and conventional C-S-H were approximately 1.1 and 1.7, respectively. The microstructural features of the different mixtures were dissimilar, which indicated the dominant effect of
changing the mix design and/or protection method on concrete cast and cured at the freezing temperatures adopted herein. It is worth noting that the micro-cracks appearing in the images are associated with mechanical loading during the pull-out test which led to concrete failure as will be discussed in Model II results.

![Graph](image_url)

Figure 7.9: Exemplar thermogravimetry results for the portlandite contents in some mixtures up to 91 days of curing.

Complying with the previous findings, mixtures protected using the hybrid system produced denser cementitious matrix than that of similar mixtures protected by the conventional method [Figs. 7.10 (b), (d), (f) vs. Figs. 12 (a), (c), (e)]. This can be attributed to the heat release phenomenon of the PCM mat, which has a latent energy storage process. The PCM mat acted as a sustainably external heat source by emitting thermal energy at a rate of 187 kJ/kg in the hybrid system through its solidification process from the liquid state at 5ºC. This explains the relatively higher internal concrete-steel interface temperature of mixtures protected by the hybrid system. Consequently, it
maintained concrete hydration development rate at higher level compared to the conventional protection method. This led to better cementitious matrix quality, lower $C/S$ and improved ITZ with steel bars, and consequently higher mechanical bonding.

Figure 7.10: Exemplar ESEM micrographs for mixtures cured at -10°C: (a) GU-I (avg. $C/S = 1.8$), (b) GU-IP (avg. $C/S = 1.6$), (c) GUN-I (avg. $C/S = 1.3$), (d) GUN-IP (avg. $C/S = 1.1$), (e) GUFN-I (avg. $C/S = 1.7$), and (f) GUFN-IP (avg. $C/S = 1.4$). Note: The $C/S$ was calculated based on the marked locations.
Chapter 7: Bonding Behaviour of Nano-Modified Concrete with Steel

The inclusion of nano-silica in concrete cast and cured under freezing temperatures adopted herein produced more homogenous microstructure, regardless of the protection method. For instance, the incorporation of 6% nano-silica in mixture GU-I to produce mixture GUN-I reduced the C/S from 1.8 to 1.3 as shown in Figs. 7.10 (a) and (c), respectively, which highlights the pronounced effect of nano-silica pozzolanic reactivity, even under freezing temperatures, on densifying concrete-steel ITZ by producing secondary C-S-H gel, which improved the bond strength of the binary binder mixtures. Accordingly, as shown in Fig. 7.10 (e) and (f), the negative effects of incorporating 20% slowly reactive material such as Class F fly ash was alleviated by the co-existence of nano-silcia. Hence, nano-modified fly ash mixtures showed better microstructure characteristics (densified concrete-steel ITZ) and lower (C/S) compared to single binder mixtures, especially when protected using the hybrid system. This supports the previously discussed synergistic effect of nano-silica and fly ash which produced concrete mixtures with comparable/ better performance than the corresponding single binder mixtures.

7.6.2 Modeling

7.6.2.1 Model I: Modeling of Heat Evolution in the Assembly

Table 7.4 lists the thermal conductivity ($k$), specific heat ($C_p$) and density ($\rho$) input values for the different mixtures at both curing temperatures. While Figs. 7.11 and 7.12 show the predicted temperature-time profiles up to 7 days as well as the predicated $Q_{28}$ at the interface of the concrete-steel in the assembly based on the numerical results for both curing temperatures.
Table 7.4: Average values of thermal conductivity, specific heat and density used in Model I

<table>
<thead>
<tr>
<th>Mixture ID.</th>
<th>Thermal Conductivity, $k$ (W/m°C)</th>
<th>Specific Heat, $C_p$ (J/g°C)</th>
<th>Density, $\rho$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU-I</td>
<td>1.37</td>
<td>870</td>
<td>2270</td>
</tr>
<tr>
<td>GU-IP</td>
<td>1.27</td>
<td>948</td>
<td>2315</td>
</tr>
<tr>
<td>GUN-I</td>
<td>1.22</td>
<td>1001</td>
<td>2305</td>
</tr>
<tr>
<td>GUN-IP</td>
<td>1.14</td>
<td>1050</td>
<td>2350</td>
</tr>
<tr>
<td>GUFN-I</td>
<td>1.38</td>
<td>857</td>
<td>2245</td>
</tr>
<tr>
<td>GUFN-IP</td>
<td>1.3</td>
<td>911</td>
<td>2300</td>
</tr>
</tbody>
</table>

-10°C Curing Temperature

<table>
<thead>
<tr>
<th>Mixture ID.</th>
<th>Thermal Conductivity, $k$ (W/m°C)</th>
<th>Specific Heat, $C_p$ (J/g°C)</th>
<th>Density, $\rho$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU-I</td>
<td>1.56</td>
<td>852</td>
<td>2170</td>
</tr>
<tr>
<td>GU-IP</td>
<td>1.39</td>
<td>878</td>
<td>2205</td>
</tr>
<tr>
<td>GUN-I</td>
<td>1.41</td>
<td>933</td>
<td>2210</td>
</tr>
<tr>
<td>GUN-IP</td>
<td>1.31</td>
<td>971</td>
<td>2250</td>
</tr>
<tr>
<td>GUFN-I</td>
<td>1.63</td>
<td>845</td>
<td>2150</td>
</tr>
<tr>
<td>GUFN-IP</td>
<td>1.47</td>
<td>867</td>
<td>2190</td>
</tr>
</tbody>
</table>

-20°C Curing Temperature

The temperature profiles and net heat values were in good agreement with the experimental results (Figs. 7.4 and 7.5). For example, at -10°C, the predicted $Q_{28}$ values of single, binary and ternary mixtures protected using the conventional method were 1302, 1702 and 1236 °C-h, respectively corresponding to experimental values of 1359, 1775 and 1312 °C-h, respectively. The thermal stratification from the models (e.g. Figs. 7.13 and 7.14) at a horizontal plane located in the middle of the assembly conformed to the previously discussed effects of changing the protection method and mix design on the internal temperature evolution of concrete.
The developed models were used to predict the time required to melt any ice lensing at the concrete-steel interface, which might negatively affect the concrete-steel bonding. The judgement criterion adopted herein was to increase the internal temperature of the outer surface of the steel re-bars, which is in contact with freshly placed concrete, to above 0°C. It was found that only a thin crust (1 to 2 mm) of concrete around the unheated steel re-bar was affected by the thermal difference between both materials. Regardless of the mix design or the protection method, the time required to reach above 0°C in this crust was very rapid between 17 and 37 s for both curing regimes. This highlights that efficient winter concrete mixture designs, especially the ones comprising nano-silica, incorporating CWAS and protected using the proposed systems can be cast against metallic embedments (up to 200 mm²) with an initial temperature down to -20°C.
without the need for any heating procedures. This alleviates ACI 306R (2016) requirements, which recommends to heat any metallic embedments in contact with concrete when the ambient temperature is below -12°C.

Figure 7.12: Predicted temperature profiles at concrete-steel interface in mixtures cured at -20°C up to 7 days.
Figure 7.13: Temperature stratification with respect to time in different mixtures cured under -10°C.
7.6.2.2 Model II: Modeling of Concrete-Steel Bonding

The model input parameters are compressive ($f_c'$), tensile strengths ($f_t$) and modulus of elasticity ($E$) which were obtained experimentally (Table 7.3). To eliminate the need for
performing lab tests to run the concrete-steel bonding finite element model, a nomogram (Fig. 7.15) was also developed by implementing regression analysis to correlate $Q_{28}$, (output of the thermal model), mass of hydration products at 28 days and the mechanical properties of concrete based on the results of the previous sections. The nomogram consists of three parts: the bottom part represents the relationship between $Q_{28}$ and hydration products content (%), in the range of the curing temperatures adopted herein, the top right part correlates between the hydration products content (%) and 28 day compressive strength of concrete ($f_c'$), while the top left part links the latter parameter to both tensile strength ($f_t$) and modulus of elasticity (E) of concrete. Exponential, power and linear correlations were established among the different parameters with high coefficients of determination ($R^2$) (0.95 to 0.97), indicating that the predicted properties varied systematically with experimentation. Thus, using the output of thermal modeling, the mechanical parameters needed for the bond strength predictions can be directly obtained from the nomogram, as for example shown by the guideline arrows in Fig. 7.15.

Figures 7.16 and 7.17 present the predicted force-slip relationships as well as the bond strength ($\tau_b$) of the different mixtures cured at -10 and -20 °C, respectively. The predictions conformed to the experimental trends. For instance, at -10°C, the model predicted $\tau_b$ values of the single, binary and ternary mixtures protected by the hybrid system as 11.4, 12.5 and 11.4 MPa in comparison with 12.5, 14 and 12.1 MPa from the experimental results, respectively. The differences between the numerical and experimental bond strength results can be linked to the fact that numerical model was based on solving the mathematical equations, described in the numerical simulation section, and thus the results will be affected by assumptions such as linearity of stress and strain distributions. On the other hand, experimental results are affected by multiple
factors including nonlinearity of the actual material behavior, errors in devices and instrumentation, specimens’ deficiencies and potential eccentricity of re-bars. Nevertheless, the accuracy of the bonding model was acceptable as will be shown in the subsequent section. The numerical results indicated the same trends observed in the laboratory with respect to concrete-steel bonding. Mixtures protected using the hybrid system achieved higher bond strength compared to that of similar mixtures protected using the conventional method. Moreover, nano-modified binary mixtures achieved the highest bond strength while ternary mixtures showed comparable bond strength to that of single binder mixtures, under similar curing temperatures and protection methods.

\[
f_{c} = 5.79e^{0.11H} \\
R^2 = 0.95
\]

\[
Q_{28} = 117.7e^{0.15H} \\
R^2 = 0.95
\]

\[
Q_{28} = 9.91e^{0.25H} \\
R^2 = 0.95
\]

Figure 7.15: Nomogram correlating the net heat from the thermal model \((Q_{28})\) to content of hydration products \((H)\) and mechanical properties at 28 days for concrete cast and cured under freezing temperatures.
Figure 7.16: Predicted load-slip relationship of concrete mixtures cured at -10°C.

Figure 7.17: Predicted load-slip relationship of concrete mixtures cured at -20°C.
In addition, the developed models simulated cracking of concrete and mode of failure. As shown in Figs. 7.18 (a)-(b), the model suggested that the first-crack patterns, representing failure of concrete as the induced principle stresses reached capacity of concrete, were mainly perpendicular and parallel to the loading direction. In Fig. 7.18(a), the cracks propagated perpendicular to the loading direction (circles represent cracks propagation direction) due to the wedging action of the steel bar; thus the bond forces were directed outward from the bar surface resulting in tensile stresses higher than concrete tensile strength. Then, as shown in Fig. 7.18(b), these cracks propagated vertically (circles crossed with vertical lines) along the depth of concrete block leading to anchorage failure and concrete splitting (Butler et al. 2011; Gjørv et al. 1990), which was the dominant mode of failure in this study [Fig. 7.18(c)].

![Figure 7.18: Exemplar cracking patterns at the failure load of mixture GUFN-IP cured at -20°C: (a) top view, (b) side view, and (c) experimental mode of failure.](image)

### 7.6.2.3 Models’ Performance

Figures 19(a)-(b) show the numerical models output to predict $Q_{28}$ and $\tau_b$, respectively relative to their corresponding experimental values. For the thermal model, the points were located primarily on the line of equity or in the vicinity of this line. However, the datasets were mostly skewed under the line of equity for the bonding model, indicating
that the numerically predicted bond strength values were conservative. Moreover, the performance of models was evaluated by calculating the average absolute error (AAE), which is the average magnitude of errors, according to \((\text{Eq. 7.15})\) (Montgomery 2017) to quantify the accuracy of calculated values from the models relative to the measured ones. The AAE for the thermal and bond models were 6.94\% and 8.98\%, respectively and the corresponding \(R^2\) \((\text{Eq. 7.16})\) (Montgomery 2017) values were of 0.99 and 0.93, respectively. This indicated strong association between the predicted and experimental data sets (less than 10\% error), which substantiated the reasonableness of the assumptions, parameters and algorithms adopted to establish the thermal and bonding models.

\[ AAE = \frac{100}{n_d} \sum_{i=1}^{n} \left| \frac{x - y}{x} \right| \]  
\hspace{1cm} (\text{Eq. 7.15})

\[ R^2 = \left( \frac{n_d (\sum xy) - (\sum x)(\sum y)}{\sqrt{n_d (\sum x^2 - (\sum x)^2)[n_d (\sum y^2 - (\sum y)^2)]}} \right)^2 \]  
\hspace{1cm} (\text{Eq. 7.16})

where, \(n_d\) is the total number of data points, while \(x\) and \(y\) are the experimental and predicted values, respectively.

The models presented herein can be beneficially used for similar field concrete mixtures cast and cured under similar freezing conditions. Since, the accuracy of the models was high, the developed thermal model may have an adequate generalization capacity to predict concrete-steel interface temperature evolution, which can be used to calculate the net heat \((Q_{28})\), and corresponding degree of hydration and mechanical properties of concrete from the nomogram developed in Fig. 7.15. Subsequently, these mechanical properties can be integrated into the bonding model to project the concrete-steel force-slip relationship to estimate the bond strength \((\tau_b)\) of the assembly.
Figure 7.19: Response of numerical models to predict the 28 day: (a) net heat ($Q_{28}$), (b) bond strength ($\tau_b$).
8.1 Summary

Concrete placement and curing under cold weather is one of the most challenging problems that face concrete practitioners in North America. In this thesis, experimental and statistical/finite element modeling were performed to gain fundamental understanding of the factors affecting cold weather concreting (e.g. mix designs and protection methods) as well as identifying cost-efficient concrete mixtures and protection methods suitable for different cold weather scenarios down to -20°C.

The response surface method, a statistical modeling approach, was applied on a total of 40 concrete mixtures cast and cured under freezing (-5°C) or cyclic low/freezing (5/-5°C) temperatures, without any heating procedures nor protection methods, to capture the influence of water-to-binder ratio (w/b), nano-silica and fly ash dosages as well as cold weather admixture system (CWAS) type on concrete fresh, hardened and durability properties. In addition, the effect of different parameters on concrete cementitious matrices was assessed by microstructural analysis. Multi-objective optimization was then implemented to determine optimal combinations of parameters to produce concrete mixtures suitable for different cold weather applications at low temperatures down to -5°C.

Based on the outcomes of the aforementioned numerical optimization scenarios, optimized concrete mixtures were selected to implement a comprehensive study to further understand the behavior of these mixtures, cast and cured at cyclic freezing/low temperatures (5/-5°C), to examine their suitability for repair applications. Seven concrete mixtures, comprising GU cement, (0-4%) nano-silica, (0-25%) fly ash and calcium nitrate-nitrite (CNAI) as CWAS, were cast as repair mixtures. The mixtures were tested
in an integrated manner exploring fresh (setting times), hardened (compressive strength, tensile strength and modulus of elasticity) and durability properties (absorption and surface scaling), as well as compatibility with substrate concrete (restrained shrinkage and bond).

For concrete mixtures cured at lower freezing temperatures (-10 to -20°C), two types of protection methods, conventional protection method (insulation blankets) and hybrid protection system (insulation blanket + PCM mat) were adopted. Six mixtures, comprising General Use (GU) and High Early Strength (HE) cements, fly ash (20%), nano-silica (6%) and CNAI as CWAS, were cured under (-10 to -20°C) using the aforementioned protection methods and tested in terms of fresh (setting times) hardened (compressive strength) and durability properties (absorption and freezing-thawing resistance) as well as thermal and microstructural studies to capture the hydration development of the cementitious matrices.

Furthermore, three GU mixtures (part from the above mentioned experimental work) were selected to perform extended investigation by assessing concrete tensile strength and modulus of elasticity as well as bond strength with un-heated steel reinforcement and their effects on the internal temperature evolution at concrete-steel interface under freezing temperatures of -10 and -20°C. The hydration degree of the cementitious matrices was assessed by thermal and microstructural analysis at concrete-steel interfacial transition zone (ITZ). In addition, thermal and mechanical finite-element models were developed to numerically capture temperature stratification in concrete and resulting bonding strength with steel. A nomogram was developed to link between the developed finite element models through the correlations among the experimental results.
8.2 Conclusions

8.2.1 Factors Affecting Cold Weather Concrete Performance (Chapters 3 and 4)

- The derived statistical models can be used as mix design and optimization tools to capture the trends and effects of changing any of the adopted factors (w/b, fly ash content, nano-silica dosage and CWAS type); thus, they are reliably capable of simulating various responses that represent fresh (setting time), hardened (compressive strength), and durability (freezing-thawing resistance or fluid absorption) properties of normal and nano-modified concrete cast and cured under constant freezing (-5°C) or cyclic freezing/low temperatures (-5/5°C).

- Increasing the calcium nitrite (CNI) dosage in CWAS improved the overall performance of concrete; consequently, calcium nitrate-nitrite (CNAI) had balanced performance in terms of depressing the freezing point of mixing water, accelerating solidification of concrete and improving the kinetics of binder hydration compared to other antifreeze admixtures.

- The inclusion of higher contents of either water and/or fly ash resulted in prolonging the setting times, decreasing the compressive strength, increasing the fluid absorption as well as inferior resistance to freezing-thawing cycles of concrete, due to insufficient level of hydration and formation of coarse microstructure in the hardened paste.

- The addition of nano-silica markedly improved the performance (shortened setting times, increased compressive strength, enhanced resistance to fluid penetrability and frost action) of concrete produced under both curing regimes, especially when combined with CNAI which maintained the functionality of nano-silica at the sub-zero temperature.
The thermal analysis results highlighted the role of nano-silica in markedly improving microstructural evolution of the cementitious matrix at very-early age (nucleation effect) and at later ages through its pozzolanic activity which started after 7 to 14 days. Together with its physical filler effect, this caused the nano-modified mixtures to attain discontinuous and dense microstructure (MIP and BSEM/EDX trends) after 28 days under these cold curing regimes.

The applicability of these results are limited by the curing temperatures adopted in this stage (-5°C or 5/-5°C). It worth noting that, despite the exposure to daily freezing and thawing cycle within immature cement paste since the first day of casting, the cyclic freezing low temperature cured mixtures showed enhanced mechanical, continuity of hydration and pozzolanic reactivity compared to the constant freezing regime.

Based on the analysis of results from experimental work and models, the incorporation of at least 2% nano-silica with single or blended binders (maximum of 15% fly ash), especially with low \( w/b \) and CNAI, achieved balanced performance in terms of fresh, hardened and durability properties. Thus, it may present a cost-efficient and viable option for cold weather concreting down to -5°C, without the need for conventional heating practices and/or insulation, thus allowing for versatile construction schedules in late fall and early spring periods.

8.2.2 Repair Mixtures Under Cold Weather (Chapter 5)

The developed single, binary and ternary mixtures gave ample hardening times (5.5 to 10.5 h) without protection, which might be acceptable for a suite of applications including repair under cold weather (5/-5°C). The presence of CNAI
(antifreeze/accelerator) allowed for efficient and continual hydration of the binders under freezing/low temperatures, especially when combined with nano-silica. Accordingly, nano-modified concrete mixtures had accelerated hardening and high ability to retain internal heat during early-age.

- The TG trends substantiated the ability of nano-silica, even with the presence of fly ash, to significantly increase CH production and strength gain at early-age due to its nucleation and filler effects. Thus, the 1 and 7-day strength of all nano-modified concrete mixtures exceeded the 3.5 and 24.5 MPa limits recommended by ACI 306R-16 to resist one and multiple cycles of freezing-thawing, respectively. At 3 days, all nano-modified concrete applications exceeded 20 MPa, which qualifies them for various repair applications including pavements and bridges.

- After 7 days, the additional, but delayed relative to normal curing temperatures, pozzolanic effect of nano-silica helped all binders, including with 25% fly ash, to maintain later-age strength gain under freezing/low temperatures; hence, the compressive strength range at 28 days was between 34 to 55 MPa making them suitable for various construction applications.

- The MIP and absorption test results conducted at 28 days showed marked improvement in nano-modified concrete (N2, N4, F15N4) pore structure, resulting in satisfactory performance in the frost scaling test. However, the presence of fly ash (especially at the high dosage of 25%) and/or low dosage (2%) of nano-silica led to excessive surface scaling due to higher absorption and porosity of these mixtures (F15N2, F25N2 and F25N4). This highlights the need for extended curing of these mixtures and their unsuitability for repair applications involving early exposure to similar aggressive conditions.
Chapter 8: Summary, Conclusions and Recommendations

- According to the tensile strength and modulus of elasticity trends, all the repair mixtures, except GU and F25N2, showed high compatibility with substrate concrete (typical of pavement mix design in Manitoba). There was no or minimal restrained shrinkage cracking during curing and exposure to hot/arid conditions. Correspondingly, the substrate mode of failure was the dominant one in the pull-off bond test, with consistent increase of the bond strength even after exposure to consecutive W/D and F/T cycles, implying long-term dimensional stability and integrity of the repair assembly.

- The synoptic results show that nano-modified concrete, especially with a high nano-silica dosage (4%) and even with the presence of fly ash (15%), can achieve balanced performance in terms of setting, early- and late-strength, durability and compatibility with parent concrete. Hence, it may present a viable option to extend the repair season during early spring and late fall periods in cold regions.

8.2.3 Nano-Modified Concrete Under Low Freezing Temperatures Down to -20°C (Chapter 6)

- Without heating, concrete mixtures protected by the hybrid protection method (insulation with reduced R-values + PCM) showed improved fresh, hardened, and durability performance compared with similar concrete protected by the conventional method (insulation with higher R-values). Under freezing temperatures, the PCM heat release phenomenon acted as a temporary (6 to 8 h), renewable and reusable heating source, which improved the hydration activity of binders and microstructural development of concrete.

- Despite the reduction of internal temperatures of concrete to -7 and -14°C after 7 days of curing at -10 and -20°C, respectively, the setting time (3.8 to 8.2 h) and strength
(25 to 56 MPa at 28 days) results showed the functionality of the mixtures (low w/b, adequate binder content and specialty admixtures, CNAI) and protection methods implemented herein to maintain adequate hydration development as substantiated by TG and MIP analyses.

- Although, all the proposed mixtures achieved the strength stipulation of ACI 306R (24.5 MPa) and CSA A23.1 (7 MPa) to resist freezing-thawing cycles, single binder (GU and HE) mixtures failed to resist frost damage due to physical/chemical degradation in water and salt solution after 190 to 220 and 15 to 30 cycles, respectively. This highlights the importance of additional durability indicators with strength thresholds for cold weather concrete based on expected service conditions.

- Using HE cement instead of GU to produce concrete showed better performance in terms of hardening rates and early-strength. However, complying with the TG and MIP findings, both cements led to similar performance of concrete at later-age properties (28 days strength and resistance to frost damage).

- Under these freezing temperatures, the enhanced performance of nano-modified concrete mixtures, with and without fly ash and CNAI, was due to the nucleation, filler and delayed (7 and 14 days) pozzolanic effects. This resulted in acceptable rates of hardening, higher strength, and improved durability, due to continual hydration/pozzolanic reactivity and microstructural evolution of the matrix with time (physical resistance). In addition, the chemical resistance of nano-modified concrete was reflected by its high resistance to freezing-thawing cycles and salt solution, due to the significant reduction of the portlandite content in the matrix.
8.2.4 Thermal and Mechanical Finite Element Modeling of Nano-Modified Concrete (Chapter 7)

- The results of the bulk tests yielded high coefficient of determination ($R^2 \approx 0.95$) among concrete internal net heat ($Q_{28}$), mass of hydration products, compressive strength ($f_c'$), tensile strength ($f_t$) and modulus of elasticity ($E$) after 28 days of curing at both freezing temperatures.

- The developed thermal analysis model has an adequate generalization capability to predict concrete-steel interfacial temperature evolution, which can be used to calculate the net heat ($Q_{28}$), consequently concrete mechanical properties ($f_c'$, $f_t$, and $E$) can be predicted using the presented nomogram. These properties can be integrated into the bonding model as input parameters to determine concrete-steel force-slip relationship, bond strength ($\tau_b$) as well as concrete cracking pattern. The proposed models showed accurately predicted concrete behavior thermally and mechanically with less than 10% error between predicted and experimental results.

- The synoptic experimental and numerical results herein show that nano-modified concrete comprising CWAS, without or with fly ash (20%) and protected using the hybrid system achieved adequate hydration development, mechanical properties and bonding with steel re-bars due to the nucleation, pozzolanic and filler effects of nano-silica. Therefore, this may provide an integrated strategy for alleviating heating requirements and improving the quality of concrete for various cold weather concreting applications down to -20°C.
Chapter 8: Summary, Conclusions and Recommendations

8.3 Recommendations

- Based on the results obtained from the statistical models, complementary research is required to verify the model predictions with other mixtures and field data.

- The effect of incorporating other CWAS like urea and potash on nano-modified-concrete performance is recommended for further investigations.

- Some durability aspects need to be further studied to understand the behavior of cold weather nano-modified concrete under different mechanisms of attack (e.g. sulphate and combined sulphate and chloride) to evaluate their applicability for foundation construction under cold weather.

- The application of nano-modified concrete mixtures as a partial depth repair overlay in concrete pavements or bridge decks at late fall or early spring is recommended to confirm the experimental behaviour of these mixtures.

- Further studies are required to understand the effect of incorporating PCMs in cold weather nano-modified concrete mixtures by saturating the powdered form nano-silica to enhance concrete thermal resistance.

- With respect to modeling, a supplemental study is required to investigate the effect of increasing the re-bar diameter on concrete $Q_{28}$ and $\tau_0$.

- Large-scale elements need to be constructed using the proposed materials and protection methods to investigate the effect of this integrated strategy on the structural performance of reinforced concrete under different loading scenarios.
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APPENDIX A: SUPPLEMENTAL RESULTS FOR CHAPTER 3

Figure A.1: Fine and coarse aggregates particle size distribution.
Figure A.2: Exemplar cost isoresponse plots (CAD). (a) 0.4CNA, (b) 0.4CNAI, (c) 0.32CNA, (d) 0.32CNAI.
Figure A.3: Walk-in Environmental Chamber.

Figure A.4: Exemplar Box-Cox Plot tool to determine the optimum transformation power for the different responses.
Figure A.5: Exemplar pore size distribution of concrete, incorporating CNAI, cast and cured at -5°C after 28 days.
APPENDIX B: SUPPLEMENTAL RESULTS FOR CHAPTER 4

Table B.1: Numerical optimization criteria, goals, and results.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Goal</th>
<th>Weight</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>non-structural Applications</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly Ash</td>
<td>Within range from 0 to 25%</td>
<td>-</td>
<td>19%</td>
</tr>
<tr>
<td>Nano-silica</td>
<td>Within range from 0 to 4%</td>
<td>-</td>
<td>1.85%</td>
</tr>
<tr>
<td>CAN:CNI</td>
<td>Within Range</td>
<td>-</td>
<td>CNAI</td>
</tr>
<tr>
<td>IST</td>
<td>Within range from 30 to 60 minutes</td>
<td>3</td>
<td>85 minutes</td>
</tr>
<tr>
<td>FST</td>
<td>Minimize</td>
<td>3</td>
<td>350 minutes</td>
</tr>
<tr>
<td>$f'_c$ 3d</td>
<td>Maximize</td>
<td>3</td>
<td>19 MPa</td>
</tr>
<tr>
<td>$f'_c$ 28d</td>
<td>within range 30 to 35 MPa</td>
<td>5</td>
<td>35 MPa</td>
</tr>
<tr>
<td>absorption</td>
<td>Minimize</td>
<td>3</td>
<td>2.50%</td>
</tr>
<tr>
<td><strong>structural Applications</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly Ash</td>
<td>Within range from 0 to 25%</td>
<td>-</td>
<td>0%</td>
</tr>
<tr>
<td>Nano-silica</td>
<td>Within range from 0 to 4%</td>
<td>-</td>
<td>2.40%</td>
</tr>
<tr>
<td>CAN:CNI</td>
<td>Within Range</td>
<td>-</td>
<td>CNAI</td>
</tr>
<tr>
<td>IST</td>
<td>Within range from 30 to 60 Minutes</td>
<td>3</td>
<td>60 minutes</td>
</tr>
<tr>
<td>FST</td>
<td>Minimize</td>
<td>3</td>
<td>304 minutes</td>
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<td>$f'_c$ 3d</td>
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<td>4</td>
<td>28.5 MPa</td>
</tr>
<tr>
<td>$f'_c$ 28d</td>
<td>within range 35 to 45 MPa</td>
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<td>43 MPa</td>
</tr>
<tr>
<td>absorption</td>
<td>Minimize</td>
<td>5</td>
<td>2.10%</td>
</tr>
</tbody>
</table>

Figure B.1: Contour plots of the desirability function for: (a) non-structural applications (b) structural applications.
APPENDIX C: SUPPLEMENTAL RESULTS FOR CHAPTER 5

Figure C.1: Parent concrete surface before and after roughening

Figure C.2: Configuration of repair and substrate concrete assembly for shrinkage test
Figure C.3: Restrained shrinkage of the different mixtures up to 28 days of curing under the freezing/low temperatures regime.
Figure C.4: Restrained shrinkage of the different mixtures up to 154 days.
APPENDIX D: SUPPLEMENTAL RESULTS FOR CHAPTER 6

Figure D.1: Internal temperature profile of complementary mixtures cured at -10°C during 7 days.

Figure D.2: Internal temperature profile of complementary mixtures cured at -20°C during 7 days.
Figure D.3: Complementary thermogravimetry results and normalized CH contents up to 91 days of curing at -10°C.

Figure D.4: Complementary thermogravimetry results and normalized CH contents up to 91 days of curing at -20°C.