COLD WEATHER CONCRETE: CURRENT PRACTICES AND INNOVATIVE MIX DESIGNS AND PROTECTION METHODS

By

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Abstract

Concreting in cold weather can be challenging because low temperatures can slow down the hardening processes of the concrete. Reducing the heating requirements for cold weather concreting is an area where further research and development are needed. This study allows for a thorough exploration of the effects of multiple variables on the properties of concrete under cold weather conditions.

In Phase I, two commercial winter concrete mixtures of Type 6 (supplier I (L) and supplier II (C)) were chosen for testing, and the curing process was conducted at four different temperatures: -5, 0, +5, and +23°C. The protection was done using a commercial tarp as per current field practices for pavements. According to the results, the C and L concrete mixtures exhibited better mechanical and durability properties at temperatures of 0 and +5°C, and the tarp was inadequate at -5°C temperature.

In Phase II, the impact of two antifreeze additives: calcium nitrate-based (CN) and urea, on the performance of concrete containing nano-silica, was assessed. The concrete was cast and cured at -5°C. The concrete specimens modified with nano-silica and containing CN exhibited the highest mechanical strength and durability properties, but the counterparts prepared with urea also exhibited satisfactory performance.

In Phase III, internal curing of concrete was achieved by Lightweight Aggregates (LWA): expanded shale (ES) and slag-based (SB) aggregates, that were saturated with phase change material (PCM). The test variables included the use of different LWA contents (15% and 30% as a replacement for normal aggregate) and sizes (fine and coarse aggregates). The mixtures were prepared, cast, and cured at -15°C. The properties of concrete were directly affected by the size, type, and amount of LWA. The mixtures with 30% ES exhibited superior mechanical and durability properties compared to the SB mixtures and mixtures with 15% replacement, respectively. The size of LWA led to a divergent trend between the ES and SB mixtures. While the mixtures containing expanded shale fine aggregate (ESFA) demonstrated superior performance compared to those containing expanded shale coarse aggregate (ESCA), the trend was reversed for SB mixtures, depending on the absorption capacity to PCM.

Dedication

I would like to dedicate this thesis to my beloved family - my mother, father, brother and my cherished girlfriend, whose unwavering love, support, and encouragement have been a constant source of inspiration throughout my academic journey.

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Abbreviation/Nomenclature

AE - Air entrainment

C – Supplier II

CA – Coarse aggregate

$CaCl_2$ – Calcium chloride

C_2S - Dicalcium silicate (belite), $2CaO.SiO_2$

C_3A - Tricalcium aluminate, $3CaO.Al_2O_3$

C_3S - Tricalcium silicate (alite), $3CaO.SiO_2$

C_4AF - Tetracalcium aluminoferrite, $4CaO.Al_2O_3.Fe_2O_3$

CH - Calcium hydroxide

CNI - Calcium nitrite

CNA- Calcium nitrate

CNAI - Calcium nitrate: Calcium nitrite (1:1)

COW- City of Winnipeg

C-S-H - Calcium silicate hydrate

CWAS - Cold weather admixture system

DSC - Differential scanning calorimetry

DF – Durability factor

ES – Expanded shale

ESCA – Expanded shale coarse aggregate

ESFA – Expanded shale fine aggregate

FA – Fine aggregate

FST- Final setting time

GU – General use cement

HE – High Early strength

HRWRA - High range water reducer admixture

IST - Initial setting time

L – Supplier I

LWA – Lightweight aggregate

NS - Nano-silica

OVF – Overflow

PCM – Phase change material

RCPT – Rapid chloride penetrability test

RH – Relative humidity

SCMs - Supplementary cementitious materials

SB – Slag-based

SBCA – Slag-based coarse aggregate

SBFA – Slag-based fine aggregate

TG – Thermogravimetry

TGA - Thermal gravimetric analysis

UPV - Ultrasonic pulse velocity

Chapter 1: Introduction

1.1. Overview

Concrete is one of the widely used construction materials, due to its suitable formability, cost effectiveness and availability of raw materials, fire resistance and convenient production. Cement, as one of the main constituents of concrete, begins to hydrate when it is mixed with water and acts as a binder for aggregates, which is also responsible for strength and durability evolution with time (maturity). The relative humidity (RH) and temperature conditions have a major impact on this hydration process. Standard curing conditions for concrete are defined as 20 to 23°C and >95% relative humidity, respectively, as these values are optimal for the hydration process (Neville 2011). The cement hydration decelerates under low temperatures (less than 10°C), and it stops at -2.8 °C (Abayou et al. 2019).

Under cold weather, the mixing water in the immature paste may freeze, resulting in volume expansion by about 9% and cracking of concrete (Abayou et al. 2019). The compressive strength and frost resistance of concrete will be reduced by up to 40 and 60%, respectively when the fresh concrete freezes (Zhang et al. 2020a). To mitigate the challenges of cold weather concreting, different techniques such as hot air curing, heating of concrete constituents, enclosures, insulation, etc. are recommended by codes/guides for concrete (e.g., ACI 306R-16 (2016)). However, these methods involve high energy consumption, CO_2 emission, cost, and detrimental effects on the durability of concrete [e.g., carbonation, coarse microstructure] (Ryou and Lee 2012, 2013; Zhang et al. 2020b). Using efficient and economic anti-freeze admixtures can be an effective solution to alleviate the costs incurred by heating practices. Another solution can be the internal curing by pre-saturated lightweight aggregate (LWA) with Phase Change Materials (PCM), which do not require energy consumption for its function.

1.2. Research Needs and Significance

Winter construction of concrete is a big challenge for Northern countries such as Canada, Russia, northern China, and Europe. Because these countries deal with short seasons of construction due to cold weather conditions, they spend a lot of money to facilitate concrete placement and extend the construction season (Karagöl et al. 2013). According to the ACI 306R-16 (2016) cold weather is ‘‘a period at which the average daily outdoor temperature drops below + 4°C for three or more successive days and is not greater than + 10 °C for 12 h of any 24 h period”. In this situation, the work environment should be managed by some measures and the concrete should not freeze so that the concrete does not lose its physical and mechanical properties, to attain the target strength and durability properties. Some solutions have been recommended to prevent concrete from freezing at early-age. Two of them are investigated in this thesis: using economical anti-freeze additives and internal curing, which are optimized with the coexistence of nano-silica in concrete to eliminate the need for heating operations.

Cold weather admixture systems (CWAS), also known as antifreeze admixtures, have been developed as a practical and affordable way to decrease the negative effects of cold weather concreting (Ratinov and Rozenberg 1996; Korhonen 1990). Owing to antifreeze admixtures, concrete can be cured at low temperatures, particularly down to -7°C while maintaining the desired physical and mechanical properties (Korhonen 1990; Ratinov and Rozenberg 1996; Karagöl et al. 2013; Polat 2016). Various antifreeze admixtures, including sodium nitrite, calcium nitrite, sodium nitrate, calcium nitrate, urea, calcium chloride, sodium chloride, potash, and their combinations, have been shown to be effective in combating cold weather adverse effects (Korhonen 1990). However, some chemical additives have detrimental effects on the mechanical and durability properties of concrete. Also, even though many studies have mainly focused on how they affect the workability and compressive strength of the concrete, they have paid little attention to their effects on the durability features of concrete (Karagöl et al. 2015; Demirboğa et al. 2014; Karagöl et al. 2013). As a result, it is unclear how CWAS may affect concrete's microstructure and durability properties.

The aim of concrete curing is to uphold optimal moisture and temperature conditions within the recently mixed concrete. This facilitates the process of hydration and potential pozzolanic reactions, enabling the concrete to attain its desired properties. Currently, there are two main methods for internal curing of concrete: pre-soaked LWA and super-absorbent polymers. However, none of them has been explored for cold weather concrete production and curing. Hence, this study investigated the efficacy of internal curing with pre-soaked LWA with PCM, which are sensible and latent thermal energy storage materials that depending on their melting and solidifying temperatures, can both store and expel heat as energy (Aguayo et al. 2016). They can increase the thermal energy storage capacity of concrete and reduce its temperature fluctuations (Yaghoob et al. 2016; Cao et al. 2017). By delaying the formation of ice, it may reduce the chance of thermal cracking and increase resistance to freezing-thawing. However, the use of PCM may be limited to non-structural applications due to the negative impacts on concrete, such as increased porosity, drying shrinkage, and a reduction in strength/elastic modulus (Meshgin and Xi 2012; Kim et al. 2015; Memon et al. 2015; Aguayo et al. 2016; Farnam et al. 2016; Cao et al. 2017). Nanoparticles have been reported to improve the properties of concrete produced at low and freezing temperatures, due to multiple mechanisms including nucleation, particle packing, and pozzolanic reactive. Previous studies at the University of Manitoba showed that hydration and strength development rates were accelerated when nano-silica was added to masonry cement mortars that contained 30% inert filler and were cast and cured at 5°C without the use of any protective measures including heating or CWAS (Abayou et al. 2019; Yasien and Bassuoni 2022). Therefore, the incorporation of pre-soaked LWA may help alleviate the limitations of PCM and establish a sustainable and effective method for cold weather concreting, without requiring additional heating. However, this needs to be systematically investigated.

1.3. Research Objectives

The specific objectives of this master's thesis are to:

- ✓ Assess the efficacy of current cold weather practices for concrete pavements in Winnipeg, Manitoba.
- ✓ Explore the potential for new winter concrete mixture designs including economic CWAS and test their interaction with nanoparticles.
- ✓ Investigate the effectiveness of LWA (expanded shale) saturated with PCM, as an internal curing aid for concrete cast and cured under a freezing temperature.
- ✓ Investigate the effectiveness of LWA (slag-based) saturated with PCM, as an internal curing aid for concrete cast and cured under a freezing temperature.

1.4. Scope of Work

To achieve the specific objectives of this thesis, the scope of work was divided into three phases as described below.

Phase I: Cold Weather Practices in Winnipeg, Manitoba

This phase involved testing two ready mixed winter concrete mixtures (Type 6 concrete, CW 3310, 2022) that are currently used to cast concrete pavement in Winnipeg, during cold seasons. In comparison to standard curing at +23°C, the concrete mixtures were cured at three low temperatures: -5, 0, and 5°C, and covered with a commercially available tarp (non-*R*-rated) similar to current practices in Winnipeg. The fresh, mechanical, and durability properties of the produced mixtures were determined to assess the efficacy of this protocol.

Phase II: Nano-modified Concrete Containing Anti-Freeze Additives at -5°C

This phase involved the development of four winter concrete mixtures in the laboratory. The mixtures were prepared using GU cement, nano-silica (up to 6%), calcium nitrate-based admixture and urea. Casting and curing operations were done at a freezing temperature (-5°C), which corresponds to the average temperature in late fall and early spring in cold regions. The tests included the fresh, hardened, and durability properties, which were corroborated by the thermal analysis to capture the hydration/pozzolanic development in these mixtures.

Phase III: Lightweight Aggregates Saturated with PCM as Internal Curing Aid for Concrete at -15°C

In this phase, the internal curing for winter concrete was made by LWA (expanded shell and slag-based) aggregate, saturated with PCM. Nine concrete mixtures involving key variables were developed and characterized. The test variables were using different contents of LWA (15 and 30% replacement of normal aggregate), and different sizes of LWA (fine and coarse aggregates). The mixtures were prepared by combining cement, nano-silica, LWA with PCM, and calcium nitrate/nitrite. They were mixed, cast, and cured under -15°C, to evaluate the fresh, hardened and durability properties of the concrete produced.

1.5. Thesis Structure

There are seven chapters in this thesis, which are as follows:

The first chapter (Introduction) of this thesis contains an overview, research significance, objectives, and scope of this research.

The second chapter provides a comprehensive literature review about concreting in cold weather. Additionally, it discusses potential innovative solutions to cold weather issues as well as the limitation of conventional approaches.

The third chapter presents detailed information on materials and concrete mixtures of Phases I, II, and III that were used in this study. Besides, it provides the mixing and curing conditions and the details of test methods adopted in all phases.

In the fourth chapter, the results of Phase I (commercial concrete and current curing practices in Winnipeg) are presented and analyzed for the fresh, hardened and durability tests.

In the fifth chapter, the results of Phase II (innovative winter concrete mixtures with economic CWAS at -5°C) are presented, along with the discussion of the effect of test variables on the fresh, hardened, and durability properties, in relation to the hydration/pozzolanic development of the paste.

The findings from Phase III of this investigation are reported in the sixth chapter. The results were analyzed and discussed for the fresh, hardened, and durability properties of the concrete cast and cured at -15°C, using LWA with PCM as an internal curing aid.

In the seventh chapter, the research program is summarized, conclusions are presented, and recommendations for future research are provided.

Chapter 2: Literature Review

2.1. Background

Both mortar and concrete are composite materials comprised of paste and aggregate. The paste is typically prepared with water and portland cement. When these two substances (water and cement) are combined, a chemical reaction known as the hydration reaction begins. This reaction becomes slower as the air temperature drops. If the temperature is low enough to cause the liquid water to freeze, hydration may completely stop. Due to the rise in water-to-ice volume, strength growth becomes extremely slow and cement paste may damage. This is the main issue with building with concrete in cold weather. The main countries impacted by the issue of cold weather concreting include Canada, Russia, North of Europe, China, etc. Each of these countries has its own practices, some of which are more restrictive than others. According to ACI 306R-16 (ACI., 2016) and CSA A23.1/A23.2 (2019), the definition of cold weather is when the air temperature drops, or is expected to drop, below 4 or 5°C during the protection period required for concrete to develop mechanical and physical properties capable of withstanding exposure to such harsh conditions.

The first step in the solutions provided for this issue by many guidance documents [e.g., ACI 306R-16 (2016)] is to heat the materials. Water is typically the easiest ingredient to heat, but if water heating is insufficient, heating may also be applied to sand and aggregate. Some suggestions include utilizing Type High Early strength (HE) cements, increasing the cement dosage, or employing accelerating admixtures. In extreme circumstances, it may be necessary to use heated enclosures to condition the entire work area. This solution is proven to be expensive, and the cost might not be appropriate for small projects. As a result, it has been necessary to research and find other strategies to get over the difficulties of pouring concrete in cold weather. The code requirements in North America, the most recent research on cold weather concrete, mixture components, innovative solutions, and techniques for concrete curing under low temperatures are all introduced in this literature review chapter.

2.2. Challenges Associated with Concrete Placement and Curing in Cold Weather

Water, cement, and aggregates are the main ingredients of both concrete and mortar. Lime, silica, alumina, and iron oxide make up the majority of the ingredients of Portland cement. During the manufacturing process, these chemical components interact with each other to create a more complex product until a state of chemical equilibrium is reached. The final cement product consists of four main components: Tricalcium Aluminate (C_3A), Tricalcium Silicate (C_3S), Tetracalcium Aluminoferrite (C_4AF), and Dicalcium Silicate (C_2S). This composite material reacts with water and changes from a plastic to a solid state as a result of a cement and water chemical process known as "the hydration reaction".

During cement hydration, three heat peaks occur. The first peak occurs immediately after water is added to the cement, corresponding to the initial hydrolysis at the surface of cement particles. Less than an hour passes between the high temperature and the first heat peak, which is largely caused by the response of C_3A. After that, concrete enters a stage known as the latent period, which under normal circumstances lasts for one to two hours and is still workable. After six to ten hours, when it reaches its second highest, the heat of hydration rises gradually. The second step is when the hydration products interact, the concrete gets stronger, and the final setting happens. A third heat peak that is also connected to a reactivated C_3A reaction appears between 18 and 30 hours after the first (Neville 2011). The rate of a hydration process is proportional to temperature, just like any other chemical reaction. The hydration reaction slows down when the temperature drops, resulting in less strength gain. When the temperature falls below the freezing point, or about -3°C, more than 90% of the liquid water in the pore structure will freeze (Korhonen 1990). If the temperature continues to decrease, the hydration process will be stopped. Theoretically, cement can continue to hydrate at -20 °C as long as the water is kept from freezing, but in reality, this rarely happens (Brook 1988).

When fresh concrete experiences a very low temperature and the majority of its pores are filled with water, the water freezes and forms ice. The pores in the concrete are able to accommodate this expansion because water expands by approximately 9% in volume when it freezes into ice. The effect is that the increased water will cause internal hydraulic strains that can damage the hardened mortar or concrete permanently (Prado et al. 1998). The kind of ice that formed depends on how quickly the temperature decreases. For rapid cooling, the water cannot travel to colder regions quickly enough during rapid cooling, resulting in a uniform dispersion of microscopic ice crystals. However, water can migrate to cooler areas and freeze there for slow cooling. The fresh material is negatively impacted by both rapid and slow freezing, which can cause a loss of up to 50% of its ultimate compressive strength (Suprenant 1992).

The most frequent examples of durability problems in cold weather include corrosion, freezing and thawing, and exposure to de-icing salts. The difference in temperature below and above the freezing point has a direct impact on freezing and thawing. The volume of water changes when it changes from its liquid phase to its solid phase, increasing by 9%, which may help to explain how the material deteriorates. Scaling and spalling are caused by the tension this volume shift causes to build up inside the cementitious matrix (Kosmatka 2002). On surfaces where the concrete is more likely to be saturated, the impact of freezing and thawing is especially noticeable, as seen in Figure 2.1.

Figure 2.1: Effect of freezing and thawing on concrete (Sacco 2014; Fritz 2019; Saha 2019).

The literature has identified another issue that is not specific to cementitious materials and is connected to how effectively people, materials, and equipment work when it's cold outside. The study examines how men's productivity is impacted by the psychological and physical effects of cold weather. The primary psychological problem is identical to that which arises when working in any other severe circumstance, and includes, among other things, being impatient, undisciplined, depressed, losing sleep, quickly becoming exhausted, and becoming distracted. The physiological impacts were divided into two groups: those that involved tissue damage, like frostbite, immersion foot, lung chilling, and skin blistering; and those that did not involve tissue damage, like dehydration, hypothermia, respiration, and caloric needs (Havers 1972).

2.3. Codes' Provisions in North America

2.3.1. American Standards

The standard specification ACI 306.1-90 (1990) outlines the very minimum requirements for concrete preparation and protection. ACI 306R-16 (2016) is a thorough document that lists broad standards and approaches to meet them. In the literature on cold weather concreting, these two references are the most frequently mentioned. The major goals of the ACI 306R-16 (2016) report are to limit sudden temperature changes, ensure strength growth, and prevent damage at an early age. Concrete that reaches a compressive strength of 3.5 MPa can withstand one cycle of freezing, according to the main idea presented in this document. Protection should be given for several cycles until the concrete reaches a minimum compressive strength of 24 MPa.

The usage of cold weather admixture systems (CWAS) as one of the thirteen classed chemical admixtures used in concrete is first mentioned in the 2010 edition of ACI 212.3. CWAS are referred to as water freeze depressants, accelerators, and occasionally water reducers. The publication cites ASTM C1622 (2016) as the recommended standard test procedure to use when assessing the admixtures. The first standard document in North America to establish minimum guidelines for the usage of

CWASs in concrete construction is ASTM C1622 (2016). This standard's objective is to outline the minimal parameters needed for concrete with CWAS when its temperature is as low as -5°C prior to initial set. These requirements include the following: the initial setting time must not exceed twice that of the control specimen, the compressive strength must not fall below 40%, 80%, and 90% at 7, 28, and 90 days, respectively, the maximum shrinkage must not exceed 135%, and the relative durability factor must not fall below 80%.

2.3.2. Canadian Standards

In this standard CSA A23.1 (2019) which deals with the use of concrete in buildings, there is a section on working with concrete in cold climates. When the air temperature is forecasted to drop below +5°C, it is imperative to shield fresh concrete during the entire curing process. To ensure proper concrete placement, it is necessary to clear all snow and ice from the designated areas and de-ice the forms with proper method. The use of heated enclosures, covers, insulations, or a combination of these are acceptable forms of protection. In addition, concrete can be placed at temperatures as low as -5°C owing to the use of non-chloride, non-corrosive accelerating admixtures.

2.4. Conventional Cold Weather Concreting Practices

Since the early 1930s', recommendations for dealing with cold weather building have been implemented (Korhonen 1997) that some of them mentioned below:

2.4.1. Heating of Concrete Ingredients

Typically, the first piece of advice is to plan ahead so that everything is prepared 24 hours before the job begins. The building supplies should be stored and protected from rain, snow, and ice. Any surface that comes into touch with concrete needs to be cleared of snow and ice. Steel that is embedded serves as a cooling conductor. Therefore, before pouring, it is typically advised to heat and insulate imbedded metals. Another traditional method for combating the detrimental effects of cold weather on concrete is heating the water and aggregates (both coarse and fine). It is worth noting that flash set and cement balls in mixers can result from the premature contact of excessively hot water with large amounts of cement. Although it is possible to use water that is at or above the boiling point, specific precautions should be followed to prevent detrimental effects. It is necessary to mention that extra heating is not regarded as a desirable cpractice since it frequently results in a number of unfavorable side effects, including quick heat loss, increased water use, higher rates of slump loss, and the potential for thermal and plastic shrinkage (Scanlon 1989).

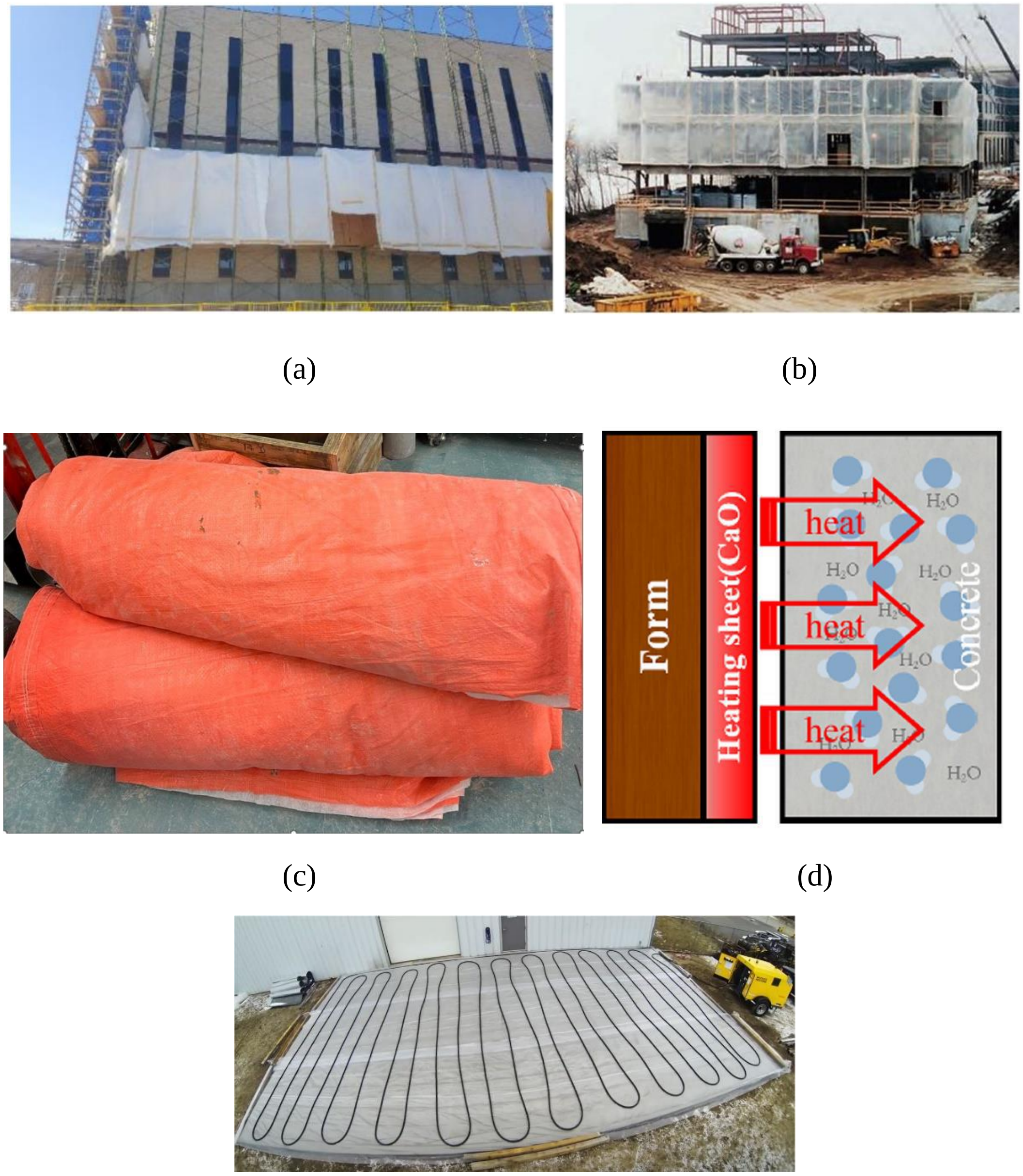
2.4.2. Materials

The use of HE cement, high cement content (without the requirement for a minimum cement content), and accelerators can expedite the setting time of concrete, allowing it to swiftly attain the compressive strength required to endure freezing and thawing cycles. Moreover, it is advisable to steer clear of excessive water bleeding, which can amplify the impact of freezing-thawing cycles, by employing low *w/c* along with lower slump values. By using CWAS, antifreeze, and/or accelerating admixtures, the freezing point of mixing water can be decreased to -5°C, which can minimize the influence of low temperatures on both concrete placement and strength gain. However, no specific guidance on constituent materials is provided for temperatures below this threshold.

2.4.3. Protection

Curing is a crucial component in the formation of concrete's long-term strength and durability. Heat and moisture have the most effects on curing. For cold weather concreting, using a heated enclosure is the best option because it can simulate lab conditions. The primary issue with this method is its price. Because steam supplies both heat and moisture simultaneously, it is a very effective curing treatment. To safeguard concrete, it is enclosed within heated enclosures that must be both waterproof and windproof to maintain the desired temperature across the entire designated area. Additionally, they must be capable of withstanding snow loads. The enclosures are heated using ventilated combustion heaters; however, it is crucial to avoid direct heating or drying of the concrete by the heaters to prevent evaporation of the mixing water (ACI 306R-16, 2016). Fresh concrete may sustain damage from carbonation when it comes in contact with the carbon dioxide generated by heater exhaust. Based on the exhaust gas concentration, concrete temperature, and relative humidity, carbonation softens and crazes concrete surfaces. Utilizing heated enclosures has additional drawbacks, such as risks to workers from high carbon dioxide levels, harm to the environment from exhaust gas emissions, and potential fire hazards from overheated enclosures. Figure 2.2 shows the protection enclosures method.

Both ACI and CSA documents reference the usage of insulating blankets and covers. It may not always be necessary to externally heat freshly placed concrete to prevent freezing as the hydration of cement is an exothermic process that generates heat, particularly in the initial three days. To sustain the heat produced by cement hydration and ensure adequate strength development, protective and insulating covers are employed for the concrete. To minimize heat loss, the insulation cover should be kept in close contact with the surface of the protected concrete. The quantity of insulation needed is determined by several factors, including the expected temperature during the protection period, moisture resistance, wind chill, size and shape of the concrete structure, and thermal resistance (R-value) of the insulating material used.



(a) (b)

(c) (d)

(e)

Figure 2.2: Protection methods: a) enclosure b) hot air curing c) Insulation blanket d) Heating sheet e) Embedded heating elements (Morrical 2011; Bill and Mary 2018; Yasien 2020).

2.4.4. Internal Curing for Construction in Cold Weather Temperature

It has been crucial to focus research on creating specialized strategies and procedures to cure concrete placed at sub-zero temperatures. An innovative approach to regulating temperature fluctuations is to incorporate phase change materials (PCMs) into concrete, which can absorb and release thermal energy. PCMs, which combine sensible and latent thermal energy storage materials, can store energy and release it as heat, based on their melting and solidifying temperatures (Aguayo et al. 2016). Studies have shown that the use of PCMs in concrete has the potential to reduce the likelihood of thermal cracking and enhance concrete's resistance to freezing and thawing (Šavija & Schlangen 2016). There are several methods for incorporating PCMs into concrete, including direct inclusion and microencapsulation, which can be added directly during the concrete mixing process (Fernandes et al. 2014; Liu et al. 2017). The macro encapsulation method, which involves saturating the pores of lightweight aggregates, is another option to use PCMs in concrete (Farnam et al. 2016). PCMs fall into two categories: organic and inorganic. Because of their non-corrosive properties and application, Organic PCMs—paraffin or nonparaffin—are preferred to be zutilized within concrete (melting and solidifying temperatures range) (Kalnæs & Jelle 2015). Although PCMs significantly reduce the occurrence of thermal cracks in concrete, there is conflicting evidence on their impact on the mechanical performance of concrete. For instance, the impact of liquid phase-change material on the mechanical properties of concrete, such as elastic modulus and compressive strength, has been investigated. According to the findings, the strength and elastic modulus significantly decreased as the proportion of PCMs increased. Additionally, as PCMs content increased, concrete drying shrinkage also increased (Yang et al. 2016).

2.4.5. Chemical Admixtures

Using chemical admixtures is often more economical than using cement-based combinations for thermal protection. Utilizing chemical admixtures can result in significant cost savings on labour, heat, electricity, and material costs (Dolgikh & Rapoport 2005). In order to lower the freezing point of water, calcium chloride and sodium chloride were first utilized as antifreeze admixtures in concrete in the early 1950s in the former Soviet Union. Later, they found that these two chemical species also aid in the corrosion of steel reinforcing (Korhonen 1990). Then, other chloride-free admixtures, including sodium nitrite, calcium nitrate, and calcium nitrite-nitrate, were successfully tested. Finland released the first ready-mix antifreeze concrete on the market in 1985. Most recent developments in China have been concentrated on testing fly ash as a mineral supplement to determine its impact on freezing protection (Huo 2013; Zhang et al. 2014).

Accelerators are chemical admixtures that can be added to cementitious materials in the form of powder or liquid and speed up the cement's hydration and setting times. Accelerators do not raise the mortar mixture's temperature or lower the freezing point. As a result, accelerators might not completely replace the necessity for insulations (Throop 2005). There are two main categories of accelerators: soluble inorganic salts and soluble organic salts. The calcium-based salts calcium chloride and calcium nitrate are the most efficient soluble inorganic salts for accelerating cement hydration. Triethanolamine, calcium formate, and calcium acetate are examples of organic accelerators used in cementitious materials. However, investigations have shown that if the correct dosage is not employed, organic accelerators could result in flash setting or retardation (Mindess 2003).

In order to minimize the water requirement for the appropriate workability, water-reducing admixtures are typically added to cementitious materials. At all ages, the mixture's compressive strength is enhanced by the reduced *w/c* ratio. Additionally, it decreases porosity and improves the cementitious matrix's long-term durability. It may be possible to decrease the impact of cold weather on strength development by taking into account the higher compressive strength at early ages (1 and 3 days).

Cementitious materials may freeze before setting in extremely cold temperatures. Due to the fact that accelerators do not stop the mortar mixture from freezing in this condition, their usage may not be adequate to reduce the negative effects of cold weather on concrete (Korhonen 2002). As a result, admixtures that lower water's freezing point have been created. The addition of antifreeze admixtures, which are often alcohol-based (for example, polyethylene glycol), allows the cementitious matrix to be set at low temperatures.

Chemical admixtures called CWAS are applied to cement-based building components during cold weather construction. These admixtures are used to simultaneously lower the freezing point and speed up the hydration of cement paste. It has also been discovered that high doses of the accelerator’s chlorides, nitrates, and nitrites have a favourable effect on lowering the freezing point of water. As a result, calcium-based accelerators (calcium nitrate, calcium nitrite, and calcium chloride) are occasionally utilised as CWAS. For instance, researches have shown that a high dosage of calcium nitrate (6% by mass of cement) can lower the freezing point and speed up the cement's hydration (Mindess 2003). Karagöl et al. (2013) examined the effects of adding calcium nitrate to concrete mixtures at a dose of 6% by mass of cement when the temperature ranged from -5 to -20℃. The combinations including calcium nitrate showed higher compressive strengths, according to the results of the 7-day cold-curing process. As an illustration, at -5°C, the compressive strength of the mixes containing calcium nitrate was approximately 453% higher than the control mixtures. However, as the temperature dropped, the impact of the calcium nitrate was lessened. For instance, when the curing temperature was -20℃ compared to the control mixture, the improvement of the compressive strength was reduced to roughly 230%. Table 2.1 lists the various antifreeze admixtures that were employed.

Table 2.1: Anti-freeze admixtures' different types

Antifreeze Type	**Percent by Cement Weight**	**Strength[1] (%)**	**Temperature (℃)**
Calcium nitrate	6	65	-5
	6	21	-10
	9	67	-5
	9	11	-10
Urea	6	32	-5
	6	14	-10
	9	56	-5
	9	20	-10
Calcium nitrate+sodium sulphate	6.6	56	-10
Calcium nitrate+urea	8.8	29	-10
	9	34	-20
Calcium nitrite+urea	9.5	55	-10
	11	35	-15
Sodium nitrite	6	70	-5
	8	57	-10
	10	36	-20
Sodium nitrite+sodium sulphate	9	62	-10
Potassium carbonate	6	75	
	8	70	-5
	10	65	-10
	10	47	-15
	12	55	-20
Ammonium hydroxide	5.2	93	-20
Calcium chloride	7	50	-15
Sodium chloride	5.7	80	-5
Sodium chloride+calcium chloride	7.7	85	-20
Sodium nitrite+calcium chloride	9	42	-20

[1] percentage of the control sample's strength after a 28-day cure at room temperature.

The impact of various chemical admixtures was evaluated on the setting time and compressive strength of mortar mixtures at -5℃ (Korhonen 2001). The findings showed that the freezing point of the mortar mixture was lowered to around -5℃ with the use of two distinct kinds of commercial accelerators and water reducing agents, while the control sample froze at about -2°C. The mixture's initial and final setting times were roughly 2 h longer than those of the control mixture due to the water reducing agent's delaying effect. Because of this, adding a variety of chemical admixtures may lower the freezing point of water without necessarily accelerating hydration or removing the requirement for heat and safety. In another studied, concrete's response to the effects of mixing various chemical admixtures concluded that the freezing point of concrete may be lowered to -5°C by mixing the admixtures (accelerators, water reduction agents, etc.) (Barna & Korhonen 2012). The efficiency of CWAS is dependent on the ambient environment, though, because differing ambient temperatures affect the setting time and compressive strength values (Karagöl et al. 2013).

2.5. Effects of Antifreeze Admixtures on Concrete Properties

Antifreeze admixtures are added to concrete mixtures to reduce the freezing point of the water and accelerate early strength development, thereby improving frost resistance. The function of antifreeze admixture is different. Antifreeze admixtures can significantly accelerate the hydration process by increasing the solubility of C_3S and C_2S. This is achieved by adding admixtures that have the same ions as the cement. When electrolytes come into contact with C_3S and C_2S, the ionic strength and density of the pore solution are modified. As a consequence, the greater surface area of the cement paste leads to an improved contact area between the paste and the aggregates (Ratinov and Rozenberg 1996).

Any additives that may be added to concrete have an impact on its fresh, harden, and durability. Antifreeze admixtures can be used without the need for particular knowledge; nonetheless, there are some suggestions on when to use the admixtures. This section primarily discusses a few features that anti-freezing admixtures have an impact on.

2.5.1. Workability and Air Content

The effort necessary to maintain homogeneity of the concrete during mixing, pouring, compacting, and finishing is thought to be largely dependent on the workability of the concrete. Fresh concrete should have the right consistency for the application in order to make high-quality concrete. Otherwise, inadequate workability may result in decreased compressive strength and durability problems. According to research, for every 11°C drop in temperature, concrete loses approximately 2 cm of slump (Tattersall 2003). Regarding workability, the majority of chloride-based admixtures function as weak plasticizers, which reduces the need for water. Some additional salts are mixed with plasticizers or superplasticizers since they do not have a plasticizing action. The concrete slump was raised from 40 to 60 mm when utilizing 6% by weight of cement calcium nitrate. This conclusion was related to calcium nitrate's activity as a plasticizer, which improved the workability of concrete (Karagöl et al. 2013). Furthermore, research has shown that increasing the dosage of calcium nitrate from 4 to 8% by weight of cement slightly improves concrete slump, regardless of whether the concrete is air-entrained or not (Franke et al. 2014). Moreover, the workability of concrete was improved using antifreeze admixtures. Specifically, by adding 9% calcium nitrate, 9% urea, or a combination of 4.5% urea and 4.5% calcium nitrate by weight of cement, the workability increased from 40 mm to 60, 120, and 220 mm at room temperature, respectively (Karagöl et al. 2015). Improvement in the workability of concrete can be achieved by increasing the doses of various antifreeze admixtures, such as polyhydroxy amine, calcium nitrate, and a combination of 30% calcium nitrate + 5% hydroxy ethoxy amine.

For example, increasing the amount of calcium nitrate from 0.5% to 1%, 1.5%, and 2% by weight of cement resulted in a rise in the workability of concrete from 70 mm to 80 mm, 95 mm, and 100 mm, respectively (Arslan and Durmus 2011).

Regardless of the concrete mix design specifications, a significant air content (typically 4-8% by volume) is necessary to increase concrete resistance to freezing and thawing cycles. For concrete compositions subjected to freezing and thawing cycles, 6% is the ideal air void percentage (Barna and Korhonen 2012). The utilization of calcium nitrate at 4 and 8% as antifreeze admixtures do not affect either the capillary pores or the air-entrained voids of fresh concrete at 20°C (Franke et al. 2014). While a different study found that adding more antifreeze additives at room temperature increased the amount of air in the concrete (Arslan and Durmus 2011). The studies demonstrated that antifreeze admixtures do not always stop air from being entrained in concrete; in some instances, with sustained mixing, air content can even rise (Korhonen 1990).

2.5.2. Setting Time

A cement paste's pace of transition from a fluid to a rigid state is referred to as the setting time, which is a word used to indicate how stiff the cement paste becomes. The initial and final set of paste can be measured in accordance with ASTM C403 (2016), which are the two arbitrarily separated stages that are used in practice to describe setting. A shorter protection period and a lower chance of mixing water freezing result from a shorter concrete setting time. For every 6°C drop in ambient temperature, the setting time increased by approximately 30% to 35% (Tattersall 2003). Antifreeze admixtures can be used to lower the freezing point of mixing water, preventing the production of ice. As a result, concrete hydration may continue, leading to faster hardening and setting of the concrete and ultimately increasing its strength. For example, the addition of antifreeze admixtures by weight of cement decreased the initial setting periods by 4% and 5%, respectively, from 413 minutes to 336 and 315 minutes, while the ultimate setting times were reduced from 585 minutes to 503 and 482 minutes (Wang et al. 2012).

2.5.3. Compressive Strength

Compressive strength is a commonly used indicator of the quality of hardened concrete, which has been proven to be cost-effective, reliable, and easy to test. The standard states that until concrete reaches a compressive strength of 3.5 MPa, it cannot undergo even one freezing-thawing cycle. Additionally, concrete needs to reach a 24 MPa compressive strength before it can be subjected to repeated freeze-thaw cycles (ACI 306R-16 2016). As a result, it is crucial to consider how utilizing CWAS affects concrete's rate of attaining early and final design strengths while it is cold outside. Antifreeze admixtures have been found to enhance the concrete's physical and mechanical qualities by altering the microstructure and the interfacial transition zone.

Numerous research has been published to examine the impact of adding various admixtures to cold weather concrete on compressive strength. As an example, when concrete was cured for 7 days at -5°C, -10°C, -15°C, and -20°C, the addition of 6% calcium nitrate by weight of cement increased the compressive strength from 7.92 MPa, 7.81 MPa, 6.97 MPa, and 6.55 MPa to 35.93 MPa, 18.23 MPa, 16.1 MPa, and 15.53 MPa, respectively (Karagöl et al. 2013). Additionally, it was observed that even after the concrete specimens were cured in water for an additional 7, 14, and 28 days, calcium nitrate samples consistently exhibited greater strength than plain concrete samples under the same curing conditions. Antifreeze admixtures, such as calcium nitrate and calcium nitrite, not only accelerate the strength gain of concrete due to their acceleration effect but also provide continued strength gain after 28 days, similar to normal concrete. It is worth noting that, unlike antifreeze concrete, which continues to gain strength after 28 days depending on the type and amount of antifreeze admixture and the unconsumed water in the system, concrete cured at room temperature exhibits slower strength gain after 28 days due to the water consumption within the system.

As mentioned earlier, urea acts as a retarder. A study was conducted to investigate the effect of urea on the compressive strength of concrete samples after curing at -5, -10, -15, and -20°C for 7 and 14 days, by applying 6% urea by weight of cement. Urea is a suitable antifreeze additive, even at low temperatures as low as -5°C. Additionally, the impact of increasing the curing time by 7, 14, and 28 days in lime-saturated water at room temperature on the samples' compressive strength was examined. Under all curing settings and temperatures, it was generally claimed that employing urea produced samples with higher strength than control samples (Demirboğa et al. 2014). Furthermore, another study found that the 28-day compressive strength of concrete mixtures cured at 20°C was 91%, 88%, 42%, and 0% of concrete containing 10% urea by weight of cement and 0.45 water-to-cement ratio that was cured at 20°C, -5°C, -10°C, and -20°C, respectively (Bennett 1994). Another study investigated the effect of incorporating 3%, 6%, and 9% of urea on the compressive strength of concrete. The compressive strength of concrete containing 3%, 6%, and 9% urea was investigated in a study, where it was found that the 28-day strengths were 94.1%, 98%, and 92.2% of the control sample's strength at 20°C, 30%, 38.6%, and 60.8% at -5°C, and 13%, 14.6%, and 18.7% at -10°C, respectively, when cured at 20°C (Korhonen 1999). Except for potash and urea, it has been demonstrated that the majority of antifreeze admixtures increase the dynamic elastic modulus. The overall porosity was unaffected; however, the pore structure varied depending on the size of the pore. It appears that the density of the paste-aggregate transition zone is improved by antifreeze admixtures (Ratinov and Rozenberg 1996).

Figure 2.3 illustrates the qualitative compressive strength curves, comparing the control concrete cured at the recommended temperature of 25°C with the one cured at the lowest permitted temperature of 5°C. Additionally, it includes the compressive strength curves of concrete samples containing the best and worst performing antifreeze, all cured at -5°C. It is clear that concrete gains greater long-term strength at low temperatures compared to high temperatures. Furthermore, at the lowest permitted temperature, the concrete samples containing antifreeze demonstrate superior performance when compared to the concrete samples cured at the recommended temperature (Korhonen et al. 2004).

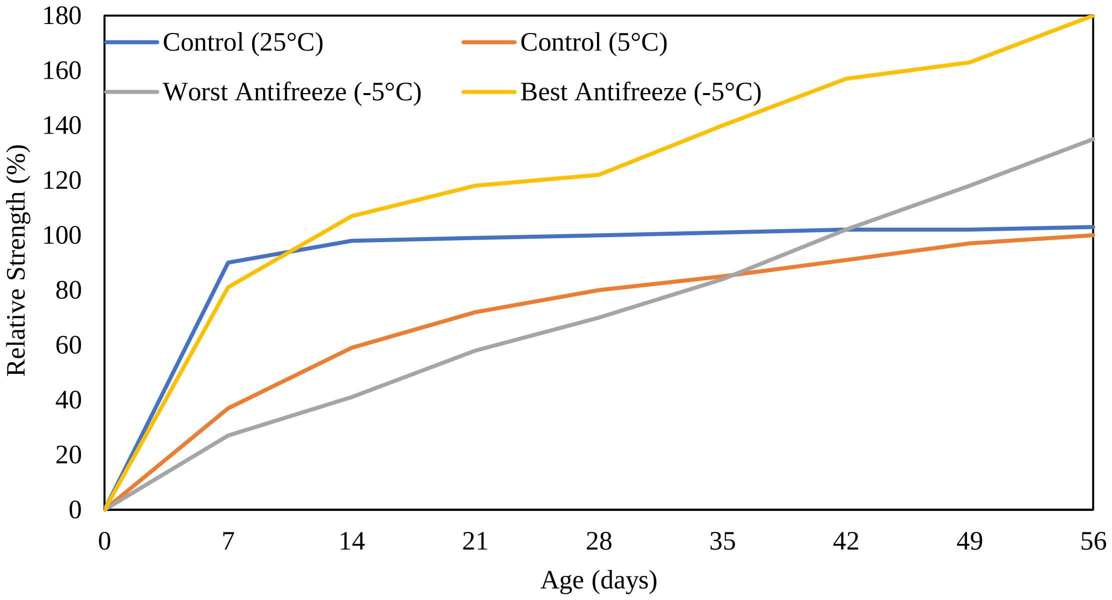


Figure 2.3: Comparative compressive strength of control concrete versus concrete with antifreeze (reproduce from (Korhonen et al. 2004)).

2.5.4. Durability Properties

When assessing the durability of concrete in cold climates, the ability to withstand freeze-thaw cycles is a critical factor to consider. For concrete failure caused by freeze-thaw cycles, two basic theories have been proposed. The first is a local failure mechanism brought on by water-to-ice transition, which results in tensile stresses that are greater than the material's tensile strength (Davison 1970). The second results from the hydraulic pressure that builds up in the liquid pore solution as ice expands, forcing the liquid out of the pores (Setzer 2001). The addition of antifreeze admixtures to concrete has a positive impact on its ability to resist freeze-thaw cycles by lowering the freezing point of water and prolonging the duration of time when water is in its liquid state. Furthermore, antifreeze admixtures have been found to enhance the ability of concrete to withstand freeze-thaw cycles by accelerating the rate of strength development in early-age concrete, in addition to lowering the freezing point of water and extending the duration of water in its liquid state. The effect of using 4% and 8% calcium nitrate alone, air-entraining admixture (AE) alone, and a combination of both on the resistance of concrete to freezing-thawing cycles was investigated. The use of AE, it was determined, is crucial for creating concrete that is highly resistant to freezing and thawing, but it will have a negative impact on the concrete's compressive strength. However, it has been suggested that the use of calcium nitrate can help improve the compressive strength of concrete, which can compensate for any reduction in strength caused by the use of air-entraining admixtures. Additionally, it has been suggested that calcium nitrate could aid in the distribution of air spaces by increasing the number of micro voids and decreasing the number of macro voids, thereby improving the overall performance of air-entrained concrete (Franke et al. 2014). For up to 28 cycles, the impact of urea and calcium nitrate on freeze-thaw durability was studied. In contrast to the 72% strength drop seen in the control sample, samples containing the antifreeze agents showed strength reductions of 53% and 28%, respectively (Polat 2016).

The majority of antifreeze admixtures increase freeze-thaw resistance, some more effectively than others, with complex ones being especially potent. Concrete containing antifreeze admixtures has demonstrated better resistance to freezing and thawing cycles compared to plain concrete when subjected to the same curing conditions. We can draw the conclusion that it is crucial to apply the correct antifreeze admixture and dosage in CWAS. The effectiveness of concrete in withstanding freezing and thawing cycles depends on several factors, such as the type and amount of cement used, water content, supplementary materials, and ambient temperature.

2.5.5. Corrosion of Embedded Steel

Antifreeze admixtures may shorten the service life of concrete by decreasing its durability. For example, steel is shielded from corrosion by the alkaline atmosphere provided by cement. The presence of moisture and oxygen can lead to corrosion of steel, and any additives that can neutralize the alkaline environment of concrete may contribute to this process. According to their ability to encourage steel corrosion, antifreeze admixtures can be divided into three categories: inhibitors (such as sodium nitrite and calcium nitrate), inert (such as potash and calcium nitrate) and aggressive (e.g., calcium chloride, sodium chloride). Admixtures of antifreeze made of sodium or chloride may cause alkali aggregate reaction or corrosion, respectively, which are problems with durability (Karagöl et al. 2013; Karagol et al. 2015). Several studies have reported on the heterogeneous microstructure of concrete, as well as the reduction in strength in concrete that contains potash (Demirboğa et al. 2014). However, some antifreeze admixtures can raise the temperature during concrete placement, which can harm concrete's late-age strength by causing microcracks in the microstructure of the concrete that was created.

2.6. Nanomaterials for Construction in Cold Temperature

To improve the mechanical and durability qualities of cementitious materials, nanoparticles are added. Nucleation sites for chemical reactions are provided by the high surface-to-volume ratio of nanoparticles (specific surface area). Additionally, nanoparticles serve as fillers to minimize porosity and densify the microstructure of cementitious materials (Kawashima et al. 2013). In order to provide the cementitious matrix additional properties, nanoparticles are occasionally added. For instance, they have been introduced to cement-based materials to give them self-healing, self-cleaning, and low electrical resistivity qualities.

The qualities of cementitious materials' fresh, hardened, and durability are improved by nanoscale SiO_2 (NS) particles. Because NS is ultrafine, it has a larger surface area that might act as nucleation sites for hydration processes. Portlandite (CH) is transformed into calcium silicate hydrate (C-S-H) through pozzolanic reaction when NS is added to cement-based materials (Senff et al. 2009). The secondary C-S-H that is produced by pozzolanic activity enhances the durability and hardened characteristics of cement-based products. A study found that adding NS decreased flowability even though superplasticizer was added to the mixtures. Lower flow table values were obtained for the mortar due to increased NS dosages. Compared to the control mixture, the mixes' flow values were lowered by around 33% at 2.5% NS. Additionally, they reported that a 1.5% increase in NS dosage (from 1 to 2.5%) resulted in a 20% decrease in flow value. Along with flowability, the NS-incorporated mixes' setting times were lowered; it was found that the mortar mixture with 2.5% NS was no longer flowable after 75 minutes. The initial and final setting times were reduced by nearly 60% in comparison to the combinations without NS at a dosage of 2.5% NS. Also, thermocouples were used to test the hydration temperatures of the cement pastes, and the results showed that mixtures containing NS took less time to reach their peak temperatures. For instance, the peak was achieved approximately 10 hours earlier for mixtures containing 2.5% NS than for mixtures without NS. This demonstrated that NS speed up the hydration kinetics, which decreased setting times. The apparent density of the mortar mixtures appears to be reduced by NS. The mixtures' air content increased as a result of this. For instance, when comparing mixtures containing 2.5% NS to control mixtures, the air content increased by 79% (Senff et al. 2009). In another study, by replacement of 6% nanosilica with cement, the compressive strength was 18% improvement compared to the control samples, and this relates to the cementitious binder's pozzolanic and physical properties (Said et al. 2012). Different studies show a decrease in the CH level for the NS-containing mixtures at the age of 7 days. Also, the hydration temperature curve showed that the samples with NS had a larger hydration peak than the simple sample. In comparison to the mixture without NS, the micrographs of the mortar mixture with NS revealed a densified and compacted microstructure (Jo et al. 2007).

Few studies have explored the impact of nanoparticles on concrete at low temperatures, and there are still many unanswered questions about how nanoparticles interact with cementitious systems. One study investigated the impact of NS and NA on masonry mortar, which was mixed and cured at a temperature of 5±1°C using dosages of 2, 4, and 6% by weight of cement. The findings of this research indicate that high dosages of both NS and NA lead to increased air content in the mixtures, acceleration of the hydration reactions, reduction in the dormant period, and shortened setting time. According to studies, the improvement in compressive strength was caused by the latent pozzolanic effect at later age and the physical filler effect at early age (Kazempour et al. 2014). In another study, the frost resistance of ordinary concrete containing NS at dosages of 3%, 5%, and 7%, and NA at dosages of 1%, 2%, and 3% by weight of cement was investigated. The results indicated that concrete specimens containing 5% NS and 3% NA performed the best, with a strength loss of 16.2% and 18.2% respectively, after 300 freeze-thaw cycles. The lowest mass loss after 300 freeze-thaw cycles was 4.3% for 5% NS and 11.47% for 3% NS. The included nanomaterials, according to the researchers, enhance concrete's pore structure and densify the microstructure of cement paste while also encouraging the pozzolanic reaction and acting as a filler (Behfarnia and Salemi 2013). Due to a significant decrease in the amount of CH in the matrix, the high resistance of the nano-modified concrete to freezing-thawing cycles and salt solution is a strong indicator of its chemical durability (Abayou et al. 2019).

2.7. Closure

Cold weather concreting is receiving renewed attention from researchers; studies in this area began in the 1950s' and have since evolved. The code requirements for casting concrete at low temperatures in North America have been reviewed, along with the latest research developments and advancements in cold weather admixture systems, as well as concreting practices that utilize state-of-the-art materials and techniques. In order to lessen the difficulties of cold weather concreting, CWAS has been introduced. Many types speed up the pace of cement hydration (accelerator) and lower the freezing point of the mixing water (antifreeze). However, some types of CWAS negatively affect the microstructure of concrete, resulting in losses in freeze-thaw resistance and strength. However, the use of cutting-edge curing techniques, such as PCMs, can improve the microstructure and strength development of concrete by enabling phase transition. PCMs can help delay ice formation in freezing temperatures by releasing heat, without the need to heat the entire construction site, thus potentially saving money, time, and energy for cold weather construction. Additionally, incorporating nanomaterials in winter concrete has proven to improve the mechanical and durability properties of concrete. They can speed up the hydration process and densify the cement matrix.

Some gaps in the literature have been identified. For instance, scarce data is available on the combination of CWAS, nanomaterials, lightweight aggregates, and PCM to alleviate the effects of cold temperatures on concrete placement and curing. Also, further research should be done on the long-term impacts of economic CWAS (urea) on the durability of nano-modified concrete. The objective of this thesis is to enhance the understanding of the effects of utilizing these materials and their combinations on the properties of concrete, which is cast and cured at low temperatures. By utilizing this combination, it is possible to enhance the microstructure and strength development of concrete without relying on conventional heating techniques. This will ultimately save time, money, and energy, i.e., reducing the carbon footprint of the product, while producing durable specialty concrete that is specifically suited for cold climates.

Chapter 3: Experimental Program

The materials and mixture designs, procedures, and tests used in the three phases of this program are all described in this chapter.

3.1. Methodology of Phase I

3.1.1. Mixtures and Procedures

In this phase, two commercial concrete mixtures (Type 6) were selected for testing at four different temperatures for curing: -5, 0, +5, and +23°C. To reach the desired consistency of 150±25 mm, a high-range water reduction admixture (HRWRA) was utilized. Moreover, in order to attain a fresh air concentration of 6±1%, an air-entraining admixture was added. These mixtures were provided by two approved ready-mix suppliers by the City Of Winnipeg (COW), and the specific mixtures' proportions were not revealed by the suppliers due to confidentiality. Each mixture ID starts with a letter L (supplier I) or C (supplier II) representing the different types of concrete, followed by a number which indicated the temperature of curing. For instance, mixture L+5 refers to concrete from L cured at +5°C. As a result, eight mixtures were tested in Phase I (L-5, L0, L+5, L+23, C-5, C0, C+5, and C+23).

After filling the molds with concrete and standard compaction. The specimens were maintained at curing temperatures of -5, 0, +5, and +23°C (standard curing chamber) after casting. The samples at -5, 0, +5°C were stored in three environmental chambers and exposed to circulating air flowing at an average speed of 25 km/h, in order to simulate the chilly environments, until testing. The common method adopted in Winnipeg (non-*R*-rated tarp) was selected to cover the specimens during curing at cold temperatures.

3.1.2. Testing

Concrete cylinders measuring 100×200 mm were tested in triplicates for compressive strength in accordance with ASTM C39 (2020) at both 7 and 28 days. Additionally, according to the temperature profile of ASTM C666 (2015) Procedure A (freezing-thawing in water), the durability of triplicate prisms (50×50×285 mm) was evaluated for each mixture based on the durability factor with ultrasonic pulse velocity (UPV) test. In the freezing-thawing test, additional duplicate prisms (50×50×285) were put in a deicer solution (13.6% calcium chloride solution). Based on the calcium chloride phase diagram, this concentration was chosen to take into account the impacts of the salt's chemical and physical deterioration (solution with ice) (Ghazy and Bassuoni. 2019). Two freezing-thawing cycles per day were used for both testing scenarios in order to account for any potential chemical reactions that might occur in the hydrated paste. The freezing-thawing cycle procedure involved a "12-hour cycle," which included 7 hours of freezing at -18°C, 3.5 hours of thawing at +4°C, and 45 minutes of ramping up and down to the desired freezing or thawing temperatures. For 150 cycles, this exposure protocol was followed.

Based on a test procedure introduced by (Tiznobaik and Bassuoni 2017) on concrete discs (75×50mm), the fluid absorption of concrete was assessed. After being cured for 28 days at the specified temperatures, the concrete discs were dried in an oven with a temperature of 50°C and relative humidity of 40% until they reached a constant mass. Afterward, they were placed in a sealed desiccator operating under vacuum pressure (85 KPa) for 6 hours. Each sample was then freely submerged in 4% calcium chloride ($CaCl_2$) solution, and the amounts absorbed were measured to the nearest 0.01 g after 360 minutes.

The rapid chloride penetrability test (RCPT), in accordance with ASTM C1202 (2012), was carried out at 28 days on triplicate samples from each mixture to assess the penetrability of the pore structure. Between cathodic (3% NaCl solution) and anodic (0.3 N NaOH solution) compartments, concrete discs of 100 mm in diameter and 50 mm thickness were installed for six hours at a potential difference of 60 V DC. During the test period, charges traveling through the discs (measured in coulombs) were automatically captured by the data-collecting equipment, which was attached to the cells. According to Bassuoni et al. (2006), to overcome the electrolysis bias of this method, the penetration depth of chloride ions into concrete, which is closely connected to the physical properties of the pore structure, was determined. To determine the physical depth of chloride ion penetration, the samples were split axially and sprayed with 0.1 M silver nitrate solution, which precipitates silver chloride as a white precipitate in about 15 minutes. The average depth of the white precipitate was calculated by taking readings at five different points along the diameter of each half-sample. Figure 3.1 shows the RCPT equipment.

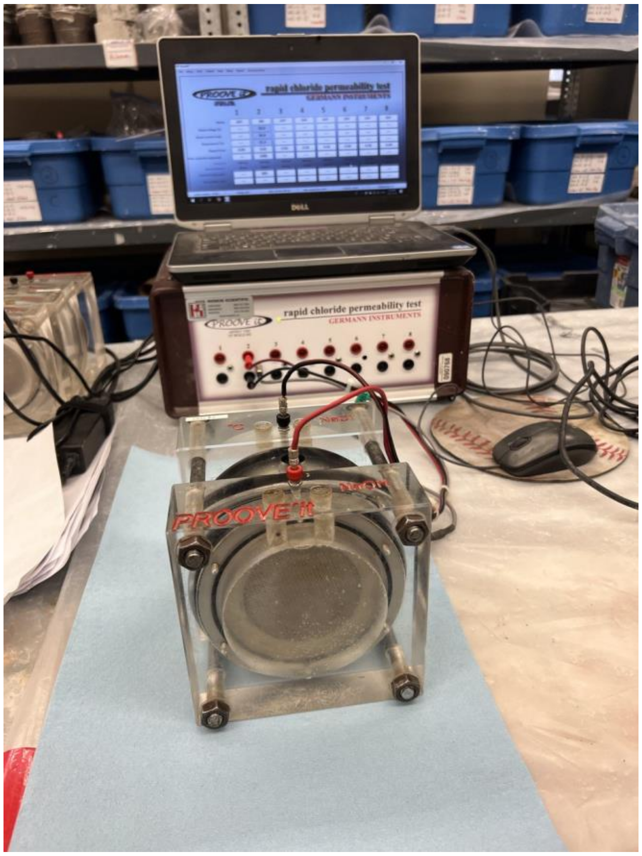


Figure 3.1: The RCPT equipment.

Thermal analysis was used to examine the change in microstructure of samples to determine the hydration development. On powder samples from specimens Thermogravimetry (TG) (Figure 3.2) was performed. This powder was obtained by carefully removing the fractured pieces, except for the coarse aggregate, from the specimens and grinding them into a fine powder that was able to pass through sieve #200 (75 m). The samples were heated to 500°C at a rate of 10°C/min. The portlandite content (CH) was determined by multiplying the percentage decrease of the ignited mass in the TG curves at 400 to 450°C by 4.11, which is the ratio of the molecular mass of CH to that of water.

Figure 3.2: The TG equipment.

3.2. Methodology of Phase II

3.2.1. Materials and Mixtures

All mixtures comprised 400 kg/m^3 General Use (GU) portland cement, which complies with CAN/CSA A3001 (2013) as the main constituent of the binder at a constant water-to-binder ratio (*w/b*) of 0.32. Also, a nano-silica solution with 50% solid content was used to partially replace cement by weight at a constant dosage of 6%. The mean particle size, specific gravity, and surface area of the used nano-silica are 35 nm, 1.4, and 80 m^2/g, respectively. These proportions resulted in a balanced performance in terms of fresh, hardened, and durability properties of concrete that was cast and cured under normal and low temperatures (ranging from 23°C to -5°C) (Yasien and Bassuoni 2020;

Yasien and Bassuoni 2022; Yasien et al. 2019). The coarse aggregate (CA) was 9.5 mm natural gravel with a specific gravity of 2.65 and 2% absorption, while the fine aggregate (FA) was well-graded river sand with a specific gravity of 2.53, a fineness modulus of 2.9, and 1.5% absorption. A polycarboxylic acid-based water-reducing admixture according to ASTM C494/C494M Type F (2019) was added to all mixes to achieve a target consistency/slump of 180±20 mm. Moreover, to achieve a fresh air content of 6%, an air-entraining admixture was utilized following ASTM C260 (2016). All mixtures comprised antifreeze admixtures with/without an accelerating effect: CN (calcium-nitrate-based antifreeze admixture) or urea as cold weather admixture system (CWAS). In this study, the CN and urea were used as 5 and 6% by weight of binding materials (cement + nano-silica), respectively (Yasien and Bassuoni 2020; Polat 2016; Demirboğa et al. 2014; Karagöl et al. 2013). The physico-chemical properties of CN and urea are listed in Table 3.1, whilst the proportions of the concrete mixtures tested are listed in Table 3.2. In the mixture ID, the letters CN, UR, and NS denote calcium nitrate, urea, and nano-silica, respectively.

Table 3.1: Properties of CN and urea

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

Table 3.2: Mixtures proportions per cubic meter

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

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

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

[C] Canadian Dollar.

3.2.2. Procedures

To simulate construction in cold weather, all mixtures were mixed and cast inside an environmental chamber set at -5ºC, while the solid constituents of the concrete were stored at the same temperature for 24 hours prior to mixing. Furthermore, in order to replicate the temperature of tap water during winter, conditioned water at 5ºC was employed in the mixing process. Based on trial batches and prior studies conducted by the authors (Yasien and Bassuoni 2020; Yasien and Bassuoni 2022), a specific mixing sequence was implemented to achieve a uniform dispersion of the constituents in the mixtures. Hence two solutions were prepared; the first one comprised 2/3 of the mixing water containing the nano-silica, air-entraining, and HRWR admixtures, whilst the second solution was the CWAS (CN or urea) diluted in the remaining 1/3 of the mixing water. Both solutions were stirred for one minute to ensure homogeneity. Afterwards, the coarse and fine aggregates were mixed with half of the first solution for one minute, then the cement was added, and mixing continued for another 30 seconds followed by adding the remaining half of the first solution to the pan while mixing for another 30 seconds. Finally, the second solution was added to the pan and then the combined materials were mixed for an additional minute. Concrete mixtures were poured into molds and compacted using a vibrating table at 60 Hz; subsequently, all specimens were covered using economical tarps (Yasien and Bassuoni 2022) mm thick layer of closed cell foam sandwiched between two layers of reinforced polyethylene and kept inside the environmental chamber at -5°C under a 25 km/h fan speed to simulate wind conditions.

3.2.3. Testing

The setting times of each mixture were determined by measuring the penetration resistance of standard needles into 150 mm cubes of the mortar portion, passing sieve #4 (4.75 mm), while inside the environmental chamber set at -5°C. The initial and final setting times were determined in accordance with ASTM C403/C403M (2016). The compressive strength of all mixtures was evaluated at early and later stages by testing triplicate cylindrical specimens (100×200 mm) following ASTM C39/C39M (2020) after 7 and 28 days of curing at -5°C.

In addition, the fluid absorption test was conducted to investigate the penetrability of the proposed mixtures at the age of 28 days following the protocol described by Tiznobaik and Bassuoni (2018). Three concrete discs (75×50 mm) for each mix design were prepared and dried at 45°C. The samples were then vacuumed for 6 h at 85 kPa. The fluid absorption values of specimens were calculated to the nearest 0.01 g after 6 h of immersion in 4% calcium chloride solution. Also, prismatic (50×50×285 mm) specimens were prepared for freezing-thawing test according to ASTM C666/C666M (2015) at the age of 28 days in water and salt solution (13.6% calcium chloride). The concentration of calcium chloride was chosen to induce the chemical and physical degradation effects of the salt (when dissolved in ice) (Ghazy and Bassuoni 2019). All samples were exposed to a total of 300 cycles of freezing-thawing. Each cycle (6 hours) involved freezing at -18°C±1 for 3 hours, followed by a 2-hour thawing period at 4°C±1, and an additional 15 minutes to ramp up and down to reach the desired freezing or thawing temperatures. For this test, the UPV was determined before and after the freeze-thaw test. This test can be used to find changes, such as deterioration brought on by freezing-thawing cycles. Based on the UPV results the durability factor (DF) was calculated for each mix design.

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

3.3. Methodology for Phase III

3.3.1. Materials and Mixtures

GU portland cement, in compliance with CAN/CSA A3001 (2013) standard, was used for the different mixtures. A nano-silica solution with 50% solid content was also incorporated at constant dosage of 4% as partial replacement of cement by weight. The physico-chemical properties of the cement and nano-silica are listed in Table 3.3. A HRWRA based on polycarboxylic acid and complying with ASTM C494/C494M Type F (2019) was added to all mixtures to achieve a target consistency of 180±20 mm. Also, an air-entraining admixture complying with ASTM C260/C260M (2016), was used to achieve a fresh air content of 6 ±1%. The antifreeze admixtures in this study were

Calcium Nitrite (CNI), and Calcium Nitrate (CNA) at a combination ratio of 1:1 by mass (CNAI). The properties of CNI and CNA are presented in Table 3.4.

It should be noted that the concentration of CNAI was selected conservatively according to the phase diagram of this combination that is shown in Figure 3.3. This concentration lowers the freezing point of the mixing water to -5°C, preventing it from freezing during the initial two to four hours, which provides sufficient time for mixing, transportation, and placement procedures before implementing any protective measures. The coarse aggregate (CA) had a maximum size of 9.5 mm with a specific gravity of 2.65 and 2% absorption. Besides, the fine aggregate (FA) had a fineness modulus of 2.9 with specific gravity of 2.53 and 1.5% absorption. In this study expanded shale (ES) and slag-based (SB) lightweight aggregates were used as a partial replacement of coarse and fine aggregates. The dry loose bulk density for expanded shale coarse aggregate (ESCA) and expanded shale fine aggregate (ESFA) are 704 and 881 kg/m^3, respectively. The specific gravity of ESCA was 1.3, while that of ESFA was 1.55. The absorption of ESCA was approximately 20% after one week, whereas ESFA showed an absorption of around 17.5% during the same period. In addition, slag-based coarse aggregate (SBCA) and slag-based fine aggregate (SBFA) have dry loose bulk densities of 881 and 1121 kg/m^3, respectively. The specific gravity and absorption rates of SBCA were 1.74 and 8%, respectively, whereas SBFA had a specific gravity of 2.22 and an absorption rate of 7%. Expanded shale lightweight aggregate has a lower density and higher water absorption capacity than slag-based lightweight aggregate.

Table 3.3: Physico-chemical properties of cement and nano-silica

Parameter	**Cement**	**Nano-silica**
SiO_2 (%)	19.8	99.17
Al_2O_3 (%)	5	0.38
Fe_2O_3 (%)	2.4	0.02
CaO (%)	63.2	-
MgO (%)	3.3	0.21
SO_3 (%)	3	-
Na_2O_{eq}. (%)	0.6	0.20
Specific gravity	3.17	1.4
Mean particle size (μm)	13.15	35×10^{-3}
Fineness (m^2/kg)	390	80000

Table 3.4: Properties of CNI and CAN

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

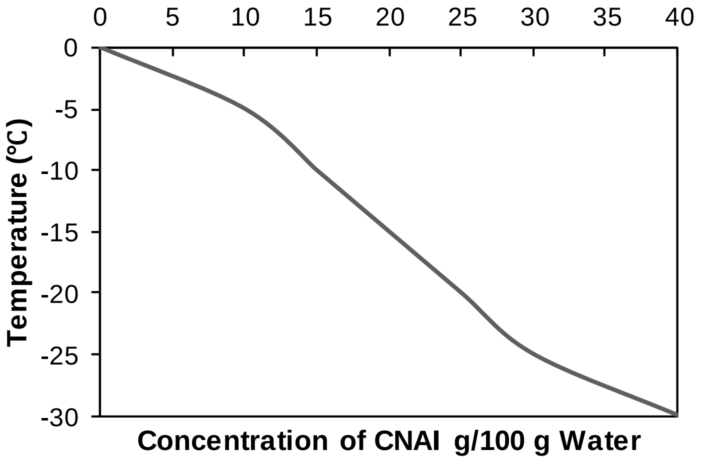


Figure 3.3: Phase diagram of calcium nitrate-nitrite with ratio of 1:1 by mass.

The mixtures were prepared by replacing the fine and coarse aggregates with ES and SB, at different proportions of 15 and 30%, designated at ESFA-15, ESFA-30,

ESCA-15, ESCA-30, SBFA-15, SBFA-30, SBCA-15, and SBCA-30. The amount of binder and w/b were kept fixed at 400 kg/m3 and 0.32, respectively. It should be noted that the amount of nano-silica and the ratio of CNI to CNA (were chosen based on the previous research (Yasien and Bassuoni, 2019). In addition, the amount of air-entraining admixture and superplasticizer were determined based on the trial batches. Table 3.5 displays the proportions of the mixtures.

Table 3.5: Mixtures proportions (kg/m^3)

Mixture ID.	**Cement (kg)**	**Nano-silica (kg)**	**Water[a] (kg)**	**CNA[b]/CNI (kg)**	**CA/LWCA (kg)**	**FA/LWFA (kg)**
C	384	32	90	14+32	1135	613
ESFA-15	384	32	90	14+32	1135	521/31
ESFA-30	384	32	90	14+32	1135	429/62
ESCA-15	384	32	90	14+32	965/45	613
ESCA-30	384	32	90	14+32	794/90	613
SBFA-15	384	32	90	14+32	1135	521/39
SBFA-30	384	32	90	14+32	1135	429/78
SBCA-15	384	32	90	14+32	965/57	613
SBCA-30	384	32	90	14+32	794/114	613

[a] Adjusted amount of water considering the water content of nano-silica (aqueous solution with 50% solid content of SiO_2) and CNI (aqueous solution with 30% solid content).
[b] The CNA admixture was in solid form with 70% active ingredient.

3.3.2. Procedures

For determining the effects of internal curing on the mechanical and durability properties of concrete, phase change material (PCM) has been used as a material that can store heat and release it at the cold temperature. The properties of PCM are mentioned in Table 3.6. The lightweight aggregate was immersed in PCM for 24 h followed by drying the surface for 48 h. Drying of the aggregate was done in such a way that the aggregates were taken out of the PCM and then spread on clean clothes to dry the surface completely. In order to control the additives for a uniform mixture, two solutions were prepared: first, the whole amount of nano-silica, air-entraining and superplasticizer admixtures were added to two-third of the calculated water; subsequently, the CNI and CNA additives were diluted in the remaining water, which both solutions were stirred for 1 minute to form homogenous mixtures (Figure 3.4).

Figure 3.4: Solutions prepared.

To ensure a uniform dispersion of the constituents in the mixtures, a specific mixing sequence was followed, based on trial batches conducted in previous studies. The mixing process involved first mixing the whole aggregate with half of the first solution for 1 minute, followed by the addition of cement and mixing for 45 seconds, during which the remaining half of the first solution was also added to the pan. Then, the mixing continued until obtaining a uniform mixture. At the end, the second solution was added followed by mixing for about 1 minute till achieving a consistent mixture. The final mixture was transferred into a certain mold that was compacted by the vibrating table. It should be noted that to simulate the cold weather conditions, all mixtures were mixed and cast at -15℃ inside an environmental chamber. In addition, after casting the concrete, the specimens were cured at -15℃ temperature in an environmental chamber with the circulation air till the age of testing. For concrete and formwork, this temperature simulates minimal to low heat conditioning in the winter season.

Table 3.6: Properties of PCM

Parameter	**Value**
Melting point	5℃
Heat storage capacity	187 J/g
Thermal conductivity (liquid/solid)	0.15/0.25 W/m℃
Density (liquid/solid)	0.88/0.96 g/ml
Specific heat (liquid/solid)	2.26/1.78 J/g℃
Number of cycles before instability	10,000 cycles
Expected service life with daily usage	27 years

Note: Data was provided by the manufacturer.

3.3.3. Protection Methods

To protect the samples from freezing, two different methods were applied: 1) conventional (insulation blanket), and 2) internal curing with PCM, where the latter was one of the aims of this research. The conventional method was selected based on the R-values, which are used as a measure of how effectively an insulating material can resist heat flow. Higher R-values are deemed more efficient, as recommended by ACI-306R (2016) for protecting ordinary concrete sections above ground level with a thickness of 200 mm for seven days.

The internal curing method may provide effective thermal heating for completing the hydration process in concrete at sub-zero temperatures and prevent it from freezing. In this study, the internal curing was supplied by pre-soaked lightweight aggregate in PCM as a partial replacement of normal aggregate. It should be noted that the PCM is used in several ways in concrete, including incorporation into a mixture, in the form of microencapsulation, or saturation of aggregate, etc., and in this study, the method of saturation of lightweight aggregate was used. In fact, the PCM could store and release the heat. Besides, the PCM can be improved the freeze-thawing resistance by retarding ice formation and reducing thermal cracking risk.

3.3.4. Testing

Thermocouples were embedded within the top 10 mm of 100 mm cubic specimens to monitor the internal temperature of each mixture during the first seven days after casting. The initial and final setting times were tested based on the ASTM C403/C403M (2016). The setting time test was conducted in the environmental chamber by measuring the penetration resistance of specific needles into the 150 mm cubes of mortar that pass from a #4 sieve. To investigate the compressive strength, triplicate cylinders specimens (100×200 mm) were tested according to ASTM C39/C39M (2020) by the age of 7 and 28 days for each mix design. It should be noted that the average of the measurements for three samples is presented in the results.

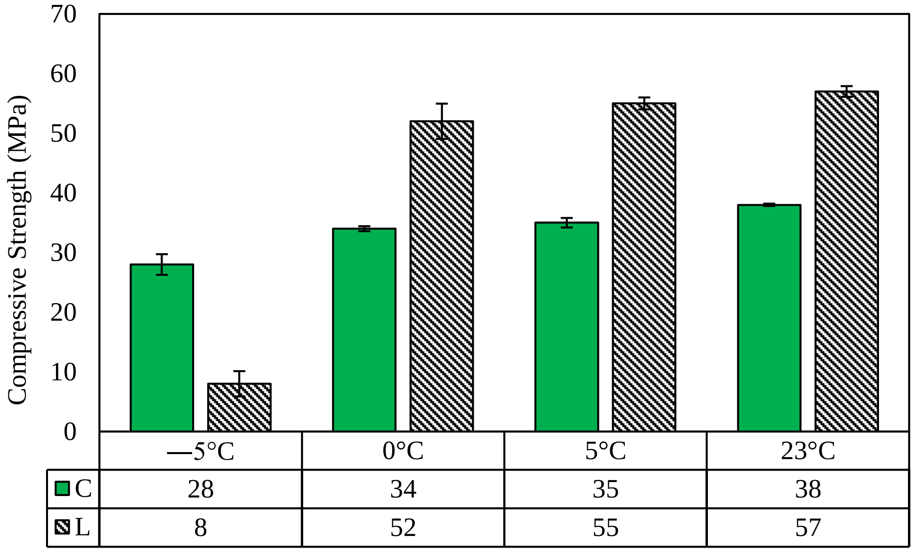
The fluid absorption test at the age of 28 days was carried out based on a method described by Tiznobaik and Bassuoni (2018). For each mix design, three concrete discs (75×50 mm) were prepared and after 28 days, the samples were dried at 45°C. Then, the samples were vacuum pressured at 85 kPa for 6 h. After that, the samples were weighed and submerged in a 4% calcium chloride solution for 6 h and again their weights were noted. For freeze-thaw test, the prismatic (50×50×285 mm) samples were prepared based on ASTM C666/C666M (2015) temperature profile, in two different solutions: pure water and deicer water (13.6% calcium chloride solution) at the age of 28 days. To consider the chemical and physical degradation effects of the salt solution with ice, the concentration of calcium chloride was selected based on a previous study by Ghazy and Bassuoni (2019). Three millimeters of the sample was submerged into the solution and the rest of the sample was exposed to the air. The samples were subjected to a total of 300 cycles with temperatures ranging from -18℃ to +4℃. Each cycle (12 h) included freezing at -18°C±1 for 7 hours, thawing at 4°C±1 for 3.5 hours, and ramping up and down to the target temperature for 45 minutes. For this test, the UPV result of each mix design was reported before and after freeze-thaw test.

To study the hydration of development in the mixtures, the thermal analysis test at the ages of 1, 3, 7, 14, 28 and 90 days was done on selected samples. Powder from fracture pieces passing through sieve #200 was prepared and heated at 10℃/min in the TG equipment until 500℃. To determine the CH amount, the percentage drop of an ignited mass of the TG curves at 400℃-450℃ was multiplied by 4.11, which is the CH to water molecular mass ratio.

Chapter 4: Results and Discussion of Cold Weather Practices in Winnipeg, Manitoba

4.1. Compressive Strength

Figures 4.1 and 4.2 show that the compressive strengths of the concrete cylinders (100×200 mm) at 7 and 28 days ranged from 8 to 57 MPa and 13 to 69 MPa, respectively. According to ACI 306R (2016), concrete cast in cold weather must be at least 3.5 and 24.5 MPa before it is subjected to one freezing-thawing cycle and multiple cycles, respectively. Most of the mixtures used in this Phase had compressive strengths that were well above these thresholds at an early-age. Additionally, most mixtures attained compressive strengths between 33 and 69 MPa at 28 days, making them suitable to be used in different concrete applications, such as the construction and repair of buildings, bridges, and pavements, all of which require strength grades between 25 and 40 MPa (MacGregor et al. 1997).



	—5°C	0°C	5°C	23°C
🟩 C	28	34	35	38
▨ L	8	52	55	57

Figure 4.1: Compressive strength at 7 days.

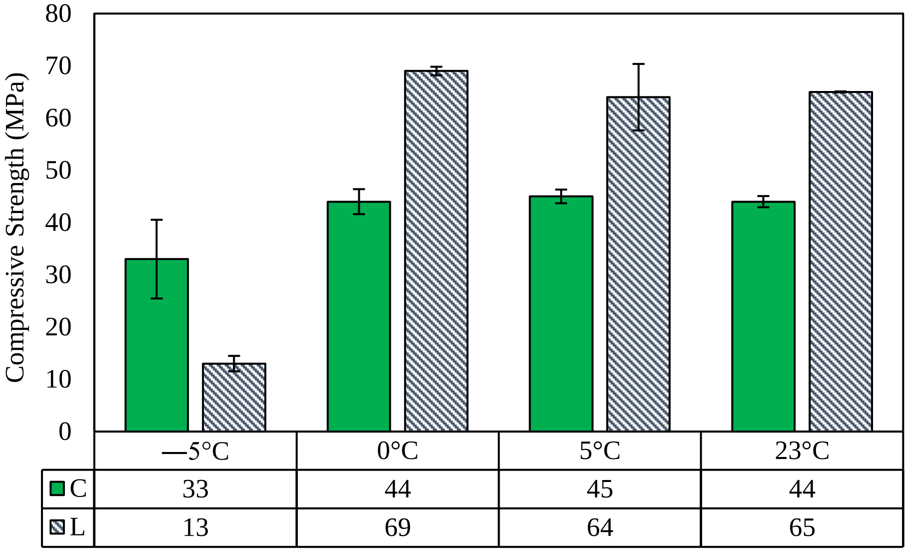


Figure 4.2: Compressive strength at 28 days.

According to the 28 days results, both the C and L concrete mixtures gain higher compressive strength at temperatures of +5 and 0°C, respectively. By looking at the standard deviation bars plotted in the compressive strength results, it can be observed that some overlapping happens at specific spots, mainly in 0 and +5°C temperatures. Hence, the coverage with the commercial tarp was efficient at maintaining the hydration and strength development of the C mix which achieved more than the COW strength requirement at 28 days (35 MPa). Likewise, the L mixture achieved an average high strength of 69 and 64 MPa at 28 days for the 0 and +5°C, respectively. However, the commercial trap was inadequate for attaining the target strength for the C and L mixtures, albeit to different extents, at the -5°C, alluding to its unsuitability for freezing conditions.

The supplier I (L) concrete mixture seemed to be more influenced by the lowest (-5°C) curing temperature, showing a loss of 86 and 80% at days 7 and 28, respectively, relative to that of the same mixture cured at the standard temperature (23°C).

Comparatively, the supplier II (C) concrete mixtures demonstrated that when the concrete was cured at -5°C rather than 23°C, the 7- and 28-day compressive strengths were reduced by approximately 26% and 25%, respectively. The worst-case scenario is when freezing happens after the concrete has set but has not yet established enough strength to support the expansion caused by ice formation, leading to an irreversible loss of strength. It seems that the L mix suffered from ice formation at early-age, and the protection by the commercial tarp (non-R-rated) was insufficient to continue the hydration process and hence development of mature paste; thus, this mix had very low strengths at 7 and 28 days (8 and 13 MPa, respectively).

Based on the compressive strength results, the trend of gaining strength was mixed at 7- and 28-days. By inspecting the results of the C mixture at 7 days, the compressive strength increased by 11% at 0, +5, and +23°C in order, while at 28 days, the compressive strength was constant at the three temperatures. This might be related to the use of accelerating additive in the C mixture, which caused gaining strength at an early-age. In general, accelerating admixtures can increase the early strength of concrete, but there may be a trade-off in terms of the late compressive strength development. This is because the rapid strength gain facilitated by the accelerator can result in denser and more impermeable hydration shells rapidly forming around cement grains, which may lead to coarse microstructure and difficulty of water diffusing into these shells (Mansell et al. 2021). Indeed, this phenomenon is affected by the curing temperature, the C mixture had comparable strengths (average of 44 MPa) at 0, +5, and +23°C at 28 days.

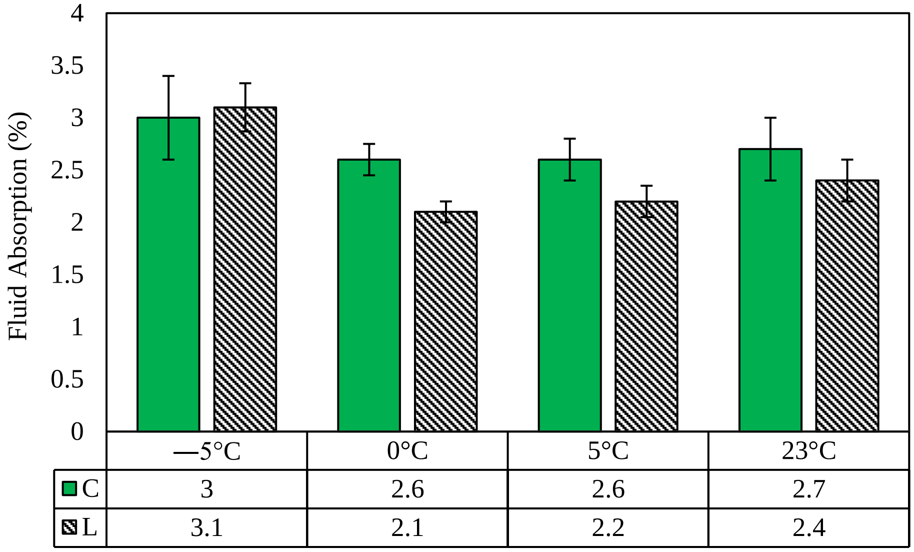
The L mixture achieved higher compressive strengths than that of the C mixture likely due to the use of higher binder content. The compressive strength of L mixtures at

0, +5, and +23 was increased continuously by 9% at 7 days, while at 28 days the compressive strength was slightly decreased by 8% at +5 and +23 relative to 0 C temperature. Again, this might be related to the fact that concrete with accelerators and or rich/rapid hardening binders, cured at lower temperatures (such as 0°C) can experience more homogenous hydration development of the paste resulting in higher compressive strength at later ages compared to the same concrete cured at higher temperatures. At lower curing temperatures, the rate of hydration of these reactive mixtures is balanced, allowing for homogenous C-S-H gel to form and creating a denser, stronger matrix, resulting in higher compressive strength at the late age than concrete cured at room temperature (Escalante-García and Sharp 1998).

4.2. Durability Performance

4.2.1. Fluid Absorption

According to Figure 4.3, the fluid absorption of the various mixtures ranged from 2.1% to 3.1%. Taking into account the strength results, it can be observed that each mixture with a higher compressive strength exhibited a lower fluid absorption, and vice versa. For instance, mixture L-5 (L mixture cured at -5°C) had the highest absorption rate of 3.1%, which was consistent with its lowest compressive strength of 13 MPa at this age (28 days). Nevertheless, the other L mixtures (L mixture cured at 0, +5 and +23°C) had comparably low fluid absorption of (2.1, 2.2, and 2.4%) indicating that the microstructure of the concrete was adequately developed to resist the capillary suction of the salt solution into concrete. Similarly, the C-5 exhibited the highest fluid absorption (3%), with a difference of approximately 15% compared to the other mixtures, while the amount of fluid absorption for the C0, C+5, and C+23 mixtures were comparable, which is consistent with the compressive strength results.



	—5°C	0°C	5°C	23°C
🟩 C	3	2.6	2.6	2.7
▨ L	3.1	2.1	2.2	2.4

Figure 4.3: Fluid absorption results.

By comparing the results of C mixtures with L mixtures, two trends could be observed. Firstly, all L mixtures, except L-5, exhibited lower fluid absorption compared to C mixtures, which is consistent with their higher compressive strength at 28 days. Secondly, both C and L mixtures cured at 0°C and +5°C temperatures had absorption values slightly lower than that the mixtures cured at +23°C. This could be attributed to the fact that at lower temperatures, the rate of fluid absorption decreases due to the better quality of the microstructure of these mixtures containing accelerator and rich/rapid hardening binders, as explained in Section 4.1.

4.2.2. RCPT

Since the ready mixed concrete were provided by the two suppliers, complying with Type 6 CW 3310 – R18 (2022), the mixtures proportions are unknown to the author of this thesis. The results of RCPT are affected by electrolysis bias in the pore solution due to the addition of anionic species in admixtures (e.g. accelerators, plasticizers), or addition of supplementary cementitious materials (SCMs) (e.g. fly ash). Hence, outlier points were excluded from the calculation of average results, which are based on at least two replicate specimens.

After finishing the RCPT, concrete specimens made from all the combinations had their physical chloride ion penetration depths assessed. As demonstrated, for example, in Figure 4.4, the whitish precipitate indicated the depth of chloride ions penetration. Table 4.1 lists the combinations' average passing charges, chloride ion penetrability class in accordance with ASTM C1202 (2012), and average penetration depth. It can be observed that the passing charge and penetrability class trends are linked to the penetration depth trend in the sense that high passing charge values corresponded to high penetration depth values, and vice versa.

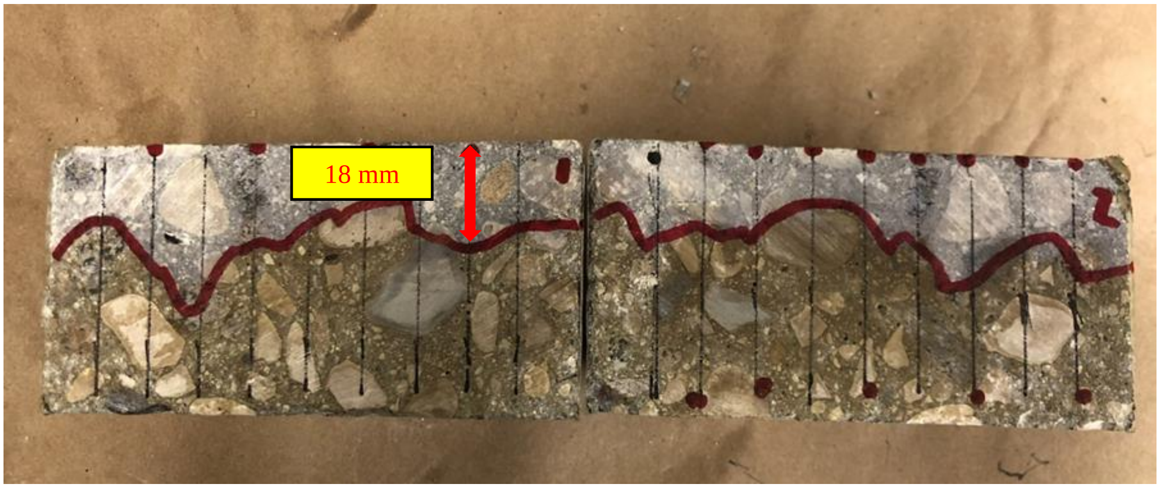


Figure 4.4: Penetration depth after the RCPT for C+5 mixture.

Table 4.1: RCPT results

Mixture ID.	Charges Passed (coulombs)	Chloride Ions Penetrability Class (ASTM C1202)	Average Penetration Depth (mm)	Standard Error of Penetration Depth
C-5	6397	OVF*	--	--
C0	3085	Moderate	18	0.95
C+5	3078	Moderate	18	1.2
C+23	3321	Moderate	21	1.9
L-5	6448	OVF*	--	--
L0	2620	Moderate	16	0.9
L+5	2479	Moderate	15	1.7
L+23	3685	Moderate	22	0.5

*OVF: overflow due to high temperature in the cell.

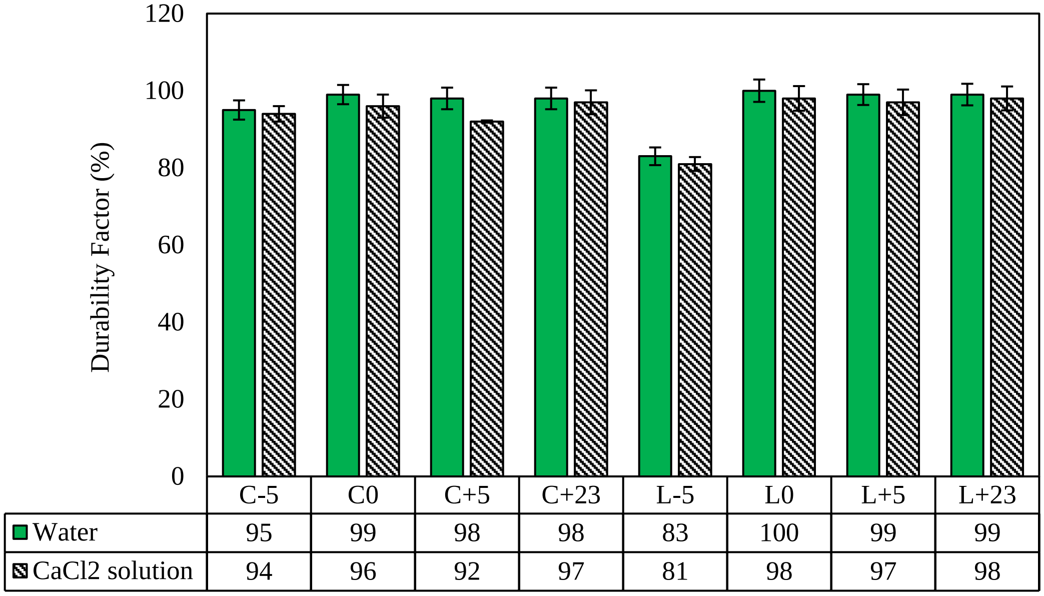
These RCPT results are consistent with those obtained from fluid absorption and compressive strength tests. According to Table 4.1, the specimens at the sub-zero temperature (L-5 and C-5) had overflow (OVF) chloride ions penetrability. This shows that these mixtures had very high penetrability, and they may be vulnerable to premature deterioration in the field. For the C mixtures, the sample of C0 and C+5 had comparable penetration depth (18 mm) and passing charges (approximately 3100 coulombs). The C+23 yielded marginally higher passing charges values of approximately 3300. However, all the C0, C+5, and C+23 was classified as having a “Moderate” level of chloride ions penetrability. The same trends were replicated for the L mixtures. This indicated that all the concrete cast and cured herein did not meet the maximum 1500 coulombs criterion, as required by the COW.

4.2.3. Freeze-Thaw Cycles

The durability of the mixtures was also assessed by the durability factor (DF) of specimens to freezing-thawing cycles in water and a calcium chloride ($CaCl_2$) solution.

After 150 cycles, the DF varied between 81 and 100% (Figure 4.5) for all the mixtures. It is important to note that the results one replicate from C+5 mixture did not align with the findings for the compressive strength and fluid absorption. Since C0 had comparable strength, air content and transport properties to C+5, this inferior performance of a C+5 replicate could be related to over or under consolidation of these specimens, which made it susceptible to reduction of air content and/or supersaturation and consequently frost damage. Hence, the result of this outlier was excluded. When a concrete sample is immersed in $CaCl_2$ solution coupled with freeze-thaw cycles, the solution can penetrate the porous structure of the concrete causing the salts to accumulate in the concrete matrix. This accumulation can lead to a process known as “salt crystallization,” where the salt crystals form within the pores of the concrete and exert a significant amount of pressure on the surrounding concrete material. Also, the concentration of salt and conditions selected herein promote the chemical deterioration of the matrix due to oxychloride formation, especially that these mixtures contain calcium hydroxide (Section 4.3). These processes make the concrete expand, crack and deteriorate (Jiang et al. 2022).

Overall, the C and L mixtures exhibited resistance to frost action after 150 cycles, with the majority of mixtures having a similar percentage DF. The L mixtures exhibited slightly higher DF to that of the C mixtures in both water and $CaCl_2$ solution, with the exception of L-5, which had the lowest compressive strength and penetrability at 28 days. In general, the results of the freezing-thawing testing did not have a conclusive pattern among the mixtures so far, and it is recommended to extend the duration of this test.



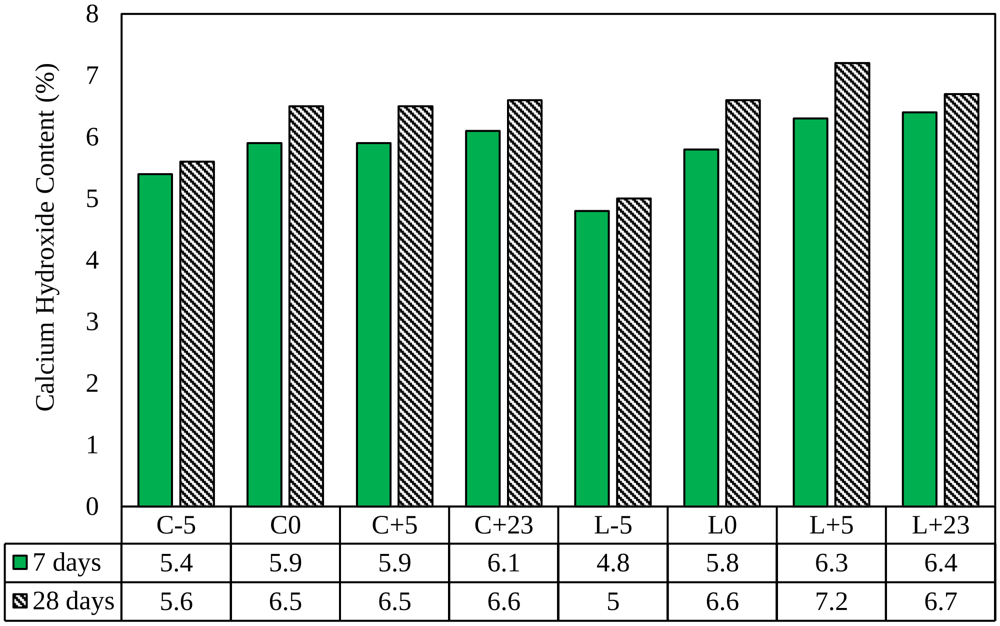
	C-5	C0	C+5	C+23	L-5	L0	L+5	L+23
🟩 Water	95	99	98	98	83	100	99	99
▨ CaCl2 solution	94	96	92	97	81	98	97	98

Figure 4.5: Durability factors of concrete mixtures after 150 cycles of freezing-thawing in water and $CaCl_2$ solution.

4.3. Thermal Analysis

Despite the difficulty in analyzing these commercial mixtures, as mentioned earlier, the thermogravimetry (TG) trends could potentially indicate the progress of hydration/pozzolanic reactions within the system. Figure 4.6 showed that the concentration of CH in the L-5 mixtures was the lowest among the other mixtures at 7- and 28- days, which is consistent with the compressive strength and penetrability results. As discussed earlier, this was ascribed to the inadequacy of the commercial trap at maintaining the progression of binder reactivity and hence strength development at the freezing temperature. Conversely, the L0, L+5 and L+23 mixtures displayed higher and increasing CH contents at 7- and 28-days, respectively. This complied with the high strength and low penetrability of these mixtures, due to the progression of the hydration process.

Similarly, the C-5 mixture contained a lower amount of CH compared to the other C mixtures at 7 and 28 days, explaining the lowest mechanical capacity of this group. The results at 28 days indicated that the amount of CH in samples C0, C+5, and C+23 was the same, which is consistent with the compressive strength results obtained at the age of 28 days. It is worth noting that the CH contents increased with time, indicating the lack or absence of reactive SCMs (e.g., silica fume) in the C and L binders. For slowly reactive SCMs, their pozzolanic activity commences beyond 28 days, which was not assessed herein.



	C-5	C0	C+5	C+23	L-5	L0	L+5	L+23
🟩 7 days	5.4	5.9	5.9	6.1	4.8	5.8	6.3	6.4
▨ 28 days	5.6	6.5	6.5	6.6	5	6.6	7.2	6.7

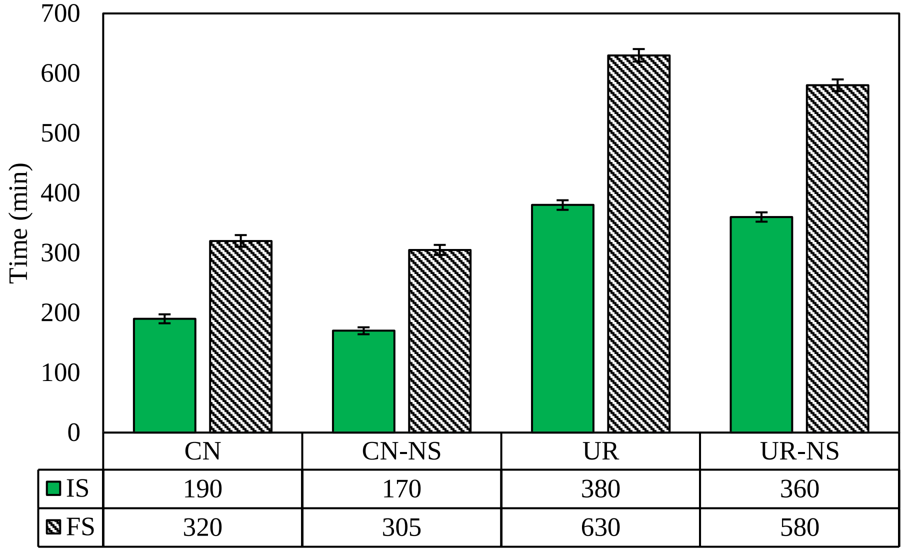
Figure 4.6: TG results for CH contents. (Note: the error range of the TG is within ±0.25%)

Chapter 5: Results and Discussion of Nano-modified Concrete Containing Anti-Freeze Additives at -5°C

5.1. Setting Time

Both initial setting (IS) and final setting (FS) times were determined in accordance with ASTM C403 (2016) requirements as the mortar portion of each mixture reached penetration resistance of 3.5 and 27.6 MPa, respectively. As shown in Figure 5.1, the IS and FS occurred within 2.8 to 6.3 and 5.2 to 10.5 hours, respectively. This highlights the significant impact of the investigated parameters in this study (anti-freeze admixtures type and nano-silica) on the hardening behavior of concrete that was mixed, cast, and cured at -5°C. Generally, the IS and FS of the concrete mixtures tested herein, comply with the period of time needed for concrete placement and finishing operations, indicating the applicability of these mixtures for cold weather construction. The adopted cold weather admixture system (CWAS) types and dosages were capable of depressing the freezing point of mixing water and speeding up the kinetics of cementitious materials' reactivity.

Generally, mixtures comprising Calcium nitrate (CN) had shorter setting times compared with the counterpart mixtures incorporating urea. The IS and FS of mixture CN were 190 and 320 minutes, respectively, while for the UR mixture, they were 380 and 630 minutes, respectively. This can be attributed to the function of CN, as an antifreeze and accelerator, and consequently it shortened the setting time of concrete at freezing temperatures. The CN contains the same cations as C_3S, catalyzing hydration by acting as nuclei, thus speeding up the process of hydrate crystallization (Ratinov and Rozenburg 1996; Yasien et al. 2021). Comparatively, the setting time of concrete was extended with the addition of urea, which is an organic compound that absorbs the heat emitted by cement hydration; and consequently, retards hydration kinetics and skeletal rigidity (Wang et al. 2020).



	CN	CN-NS	UR	UR-NS
🟩 IS	190	170	380	360
▨ FS	320	305	630	580

Figure 5.1: Initial and final setting times of all mixtures.

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

5.2. Compressive Strength

Figure 5.2 shows the compressive strengths of all mixtures, which were cast and cured at -5°C without heating. The compressive strength results varied from 31 to 42 MPa and 46 to 59 MPa after 7 and 28 days of curing, respectively. Regardless of the mix design parameters, it is worth noting that all mixtures developed and tested herein achieved the 24 MPa, after 7 days of curing at -5°C without heating, as stipulated in ACI-306R (2016) to resist multiple cycles of freezing-thawing. Also, the 28 days strength range of all mixtures complies with the strength requirement of various concrete applications (35 to 45 MPa) (MacGregor 1997).

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

The well-documented positive influence of nano-silica on the strength development of cement-based materials (Hou et al. 2013; Haruehansapong et al. 2014; Ghazy et al. 2016; Sneff et al. 2009) was observed in this study. Accordingly, concrete mixtures incorporating nano-silica yielded higher mechanical capacity than that of corresponding mixtures without nano-silica after 7 and 28 days of curing. For instance, the addition of 6% nano-silica by weight of cement to mixture CN to produce mixture CN-NS increased the 7- and 28-days strengths by 20% and 18%, respectively. This can be attributed to multiple mechanisms such as the filler effects, nucleation, pozzolanic, and apparent water reduction effect of nano-silica aggregates on cementitious systems (Haruehansapong et al. 2014; Ghazy et al. 2016; Hou et al. 2013; Sneff et al. 2009; Yasien and Bassuoni 2022); thus, additional calcium silicate hydrate (C-S-H) gel with higher stiffness and consequently denser microstructure characteristics was achieved. Indeed, the coexistence of the adopted CWAS was critical to maintaining the hydration development/pozzolanic development and functionality of nano-silica in cementitious systems.

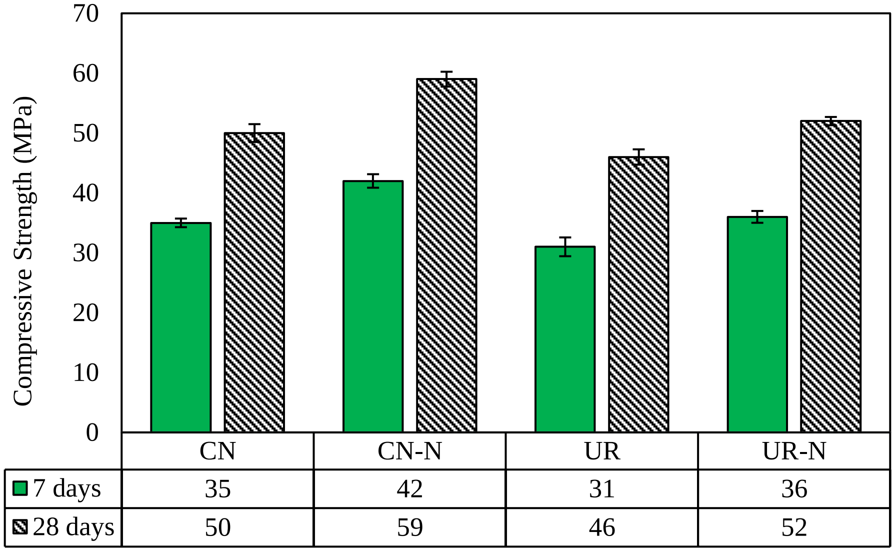


Figure 5.2: Compressive strength of all mixtures cast and cured at -5°C.

5.3. Durability Performance

Fluid absorption (Figure 5.3) and the durability factor (*DF*) of specimens in the freezing-thawing tests in water and a calcium chloride solution $CaCl_2$ solution (Figure 5.4) were used to evaluate the durability of the different mixtures. The results of fluid absorption tests were used to evaluate the different concrete mixtures' penetrability. The fluid absorption results varied from 2.0 to 2.6%, while the *DF* ranged from 90 to 100% after 300 cycles of freezing-thawing.

Generally, the type of antifreeze admixture as well as the amalgamation of nano-silica were essential determinants of the mass transport properties. Hence, the use of urea as CWAS resulted in 18% accretion in the fluid absorption, but marginal (3%) reduction in the resistance to frost action of the produced concrete compared with the counterpart mixtures comprising CN. This can be attributed to the capability of CN to accelerate the hydration process of the binder and level of maturity of the hardened paste, as indicated earlier by the setting time and compressive strength trends. Also, it is reported that calcium-based antifreeze admixtures improve the interfacial zone of contact between the cement paste and aggregates; and consequently, reducing the penetrability of concrete, complying with the presented absorption values herein, leading to the shift in the cement paste's pore size towards the zone of micro capillaries and gel pores (Polat 2016).

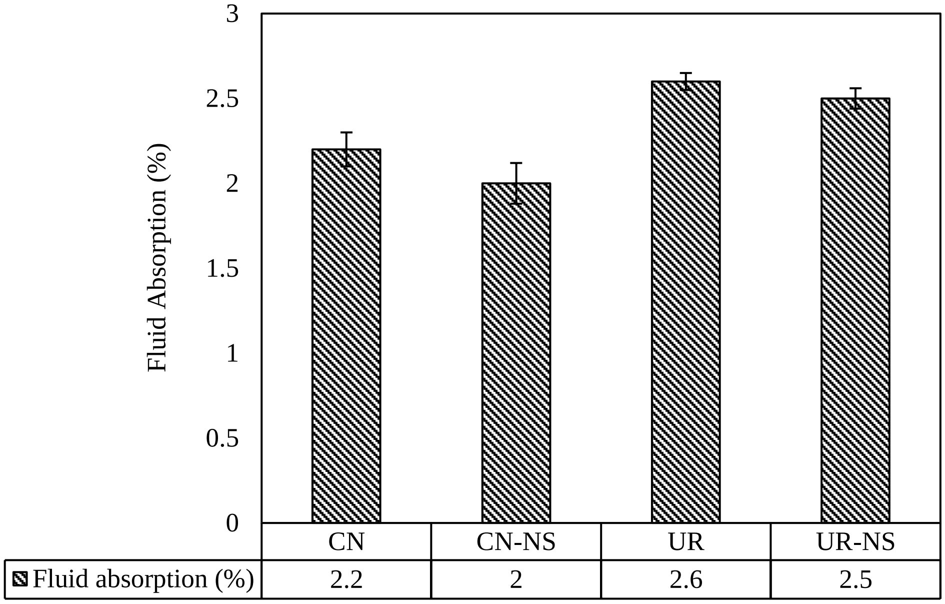
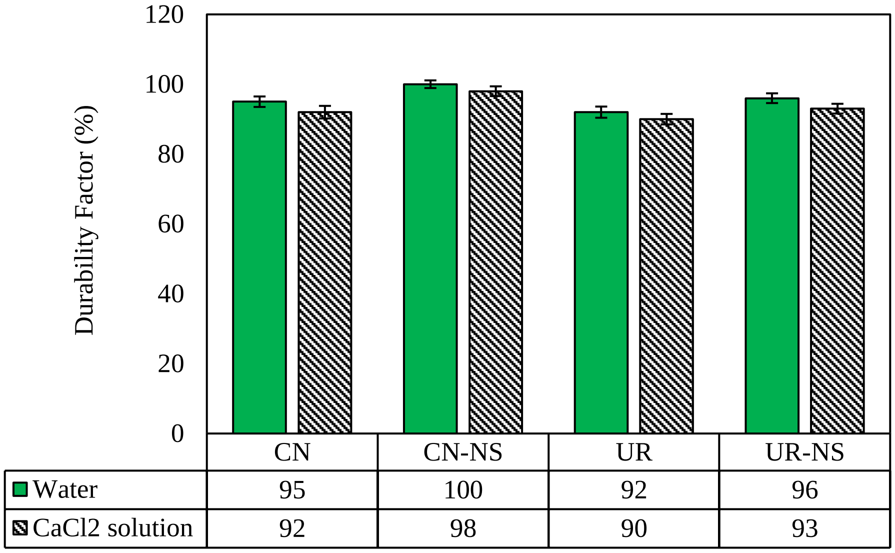


Figure 5.3: Fluid absorption of the different mixtures after 28 days of curing under -5°C.

The addition of nano-silica had a positive impact on lowering the fluid ingress and enhancing the freezing-thawing resistance of concrete, cast and cured under -5℃. For instance, the absorption values were reduced by an average of 7%, when nano-silica was added to mixtures UR and CN to produce mixtures UR-NS and CN-NS, respectively. While the frost resistance of nano-modified mixtures was marginally (5%) higher than the counterpart mixtures without nano-silica after 300 cycles of freezing-thawing. This alluded to the synergistic influence of nano-silica on the acceleration of the hydration process and development of concrete microstructure through the filler, nucleation, pozzolanic effects as well as reducing the apparent *w/b* (Ghazy et al. 2016; Senff et al. 2009; Yasien and Bassuoni 2022), as will be discussed in the TG section. Accordingly, concrete mixtures comprising nano-silica attained denser microstructure and mechanical capacity faster.



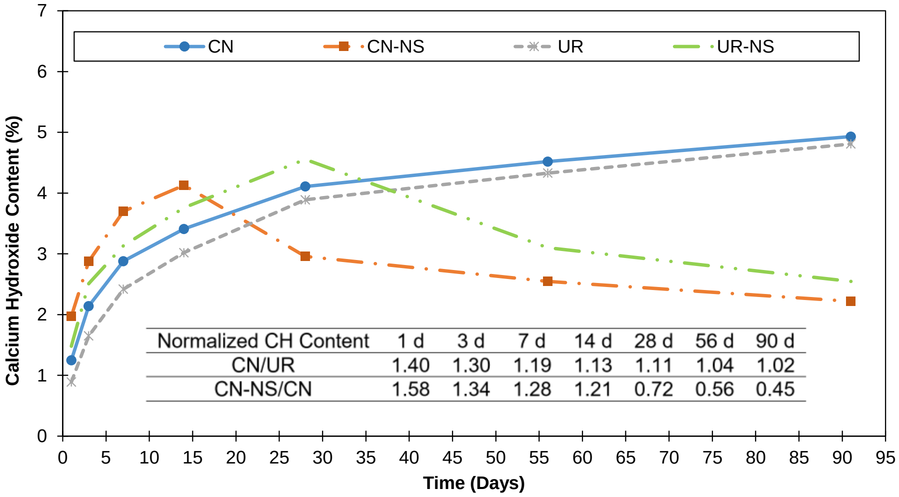
	CN	CN-NS	UR	UR-NS
🟩 Water	95	100	92	96
▨ CaCl2 solution	92	98	90	93

Figure 5.4: Durability factors of concrete mixtures after 300 cycles freezing-thawing cycles in water and $CaCl_2$ solution.

5.4. Thermal Analysis

TG analysis was performed to monitor the production and consumption of portlandite (CH) in the concrete mixtures at various ages (1, 3, 7, 14, 28, 56, and 90 days) of curing at -5°C. The CH results, shown in Figure 5.5, agree with the aforementioned bulk results. Hence, at early-age, the addition of CN increased the quantities of CH in the mixtures relative to urea, which explains the considerably quicker hardening rates of CN mixtures than those incorporating urea. For instance, the normalized CH content of mixture CN compared to the counterpart mixtures incorporating urea reached 1.4, 1.3, 1.19, 1.13, and 1.11 after 1, 3, 7, 14, and 28 days of curing. This can be attributed to the substantial acceleration effect of CN on speeding up cement hydration. This corresponded to the shorter setting times, higher mechanical capacity, and better resistance to ingress of fluids of mixtures comprising CN. However, the effect of CWAS type on the longer-term properties of concrete was insignificant, as comparable performance of CN and urea mixtures was observed in terms of freezing-thawing resistance (only 4% difference). This was ascribed to the comparable hydration degree of both mixtures as reflected by the TG results (Figure 5.5). For instance, changing the CWAS type in mixture CN to produce mixture UR achieved comparable CH contents at 56 and 91 days of curing, respectively.

Furthermore, in comparison to counterpart mixtures without nano-silica, nano-modified concrete produced larger CH amounts at an early-ages. For example, at 1, 3, and 7 days, the normalized CH contents of the nano-modified mixture CN-NS in comparison with its corresponding mixture without nano-silica (CN) were 1.58, 1.34, and 1.28, respectively. This is in agreement with the noticeably improved early-age hardening rate and compressive strength of the nano-modified mixtures, which can be linked to the filler as well as the nucleation effects of nano-silica by acting as nuclei sites for the early-age precipitation of hydration products (Hou et al. 2013; Sneff et al. 2009; Yasien and Bassuoni 2022; Yasien et al. 2019). Afterwards, the consumption of the CH up to 90 days of curing was noted in all the nano-modified concrete mixtures after 14 and 28 days, in the case of CN and urea mixtures, respectively, as showed by the sharp decline in the CH contents. This indicated the initiation of a delayed pozzolanic reaction of nano-silica, due to the adopted freezing temperature, which densified the pore structure of concrete by consuming with CH to produce high-stiffness secondary calcium silicate hydrate (C-S-H) gel (Haruehansapong et al. 2014; Yasien and Bassuoni 2022; Yasien et al. 2019). This explains the higher late-age mechanical capacity as well as lower absorption values of concrete mixtures amalgamating nano-silica compared with reference mixtures without nano-silica. This signifies the benefit of incorporating nano-silica particles in concrete for cold weather applications. Indeed, the selection of CWAS was critical to maintaining the functionality of nano-silica, although at different delaying rates.



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

Figure 5.5: TG results for CH contents up to 90 days of curing at −5°C. (Note: the error range of the TG is within ±0.25%)

Chapter 6: Results and Discussion of Lightweight Aggregates Saturated with PCM as Internal Curing Aid for Concrete at -15°C

6.1. Internal Temperature

Figure 6.1 shows the internal temperature changes in all mixtures cured at -15°C for 7 days. All mixtures achieved high internal temperatures, initially (within one to two hours) ranging between 22 to 34°C, which can be attributed to the mixing process and initial hydrolysis of cement. Afterwards, all mixtures exhibited a continuous decrease in internal temperature due to dissipation of heat to the ambient curing environments (-15℃); however, the rate of heat loss varied across the different mixtures. Over the early-age time interval (seven days), the specimens containing LWA exhibited higher internal temperatures (ranging from 1 to 9℃) compared to the C mixture. This variation in heat loss among these mixtures depended on the type, content, and size of LWA, in terms of their relation to the volume of PCM absorbed and released.

It was observed that the mixtures containing ES aggregate had a greater effect on the internal temperature compared to the C and majority of mixtures containing SB. For instance, after two hours, it was observed that the ESFA-15, ESFA-30, ESCA-15, and ESCA-30 mixtures had a higher internal temperature by approximately 50%, 72%, 47%, and 65%, respectively compared to that of the C mixture, and the amount of internal heat increased with the content of ES. During the entire seven days, the ESFA-15 and ESFA-30 mixtures consistently exhibited higher internal temperatures (from 0.5 to 1.3℃ and from 0.7 to 1.8℃) than that in the ESCA-15 and ESCA-30, respectively. This indicated that the size of ES had an effect on the binder reactivity, in the sense that mixtures comprising fine ES exhibited higher internal temperatures.

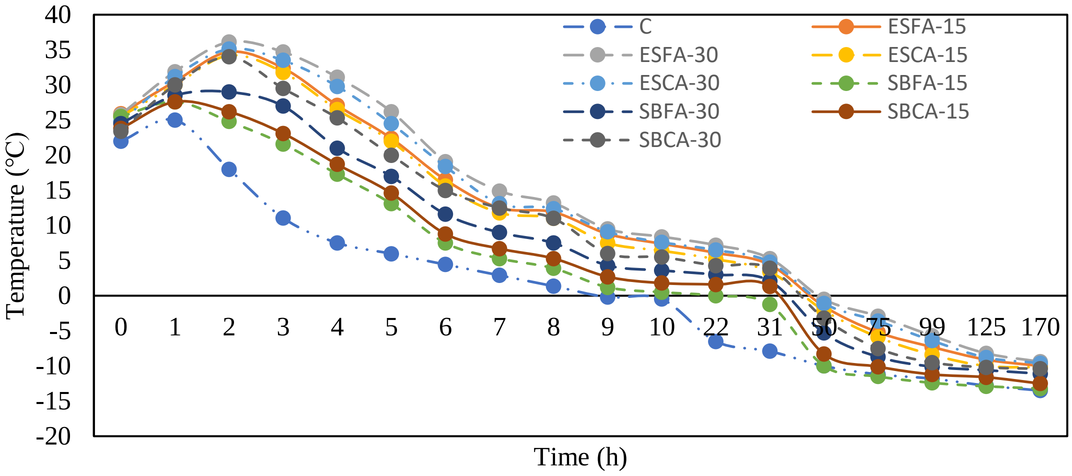


Figure 6.1: Internal temperature profile of exemplar mixtures cured at -15℃.

Similar to the ES, increasing the content of SB resulted in consistent rise in internal temperature in the mixtures. Over the course of seven days, both the SBFA-30 and SBCA-30 mixtures consistently maintained higher internal temperatures (from 0.9 to 5.4℃ and from 0.8 to 7.8℃) than that of their counterparts with lower content of SB (SBFA-15 and SBCA-15). Contrary to the ES trend, the SBCA-30 and SBCA-15 consistently exhibited higher internal temperatures from 0.4 to 5℃ and from 0.7 to 2.5℃ than that of the SBFA-30 and SBFA-15, respectively.

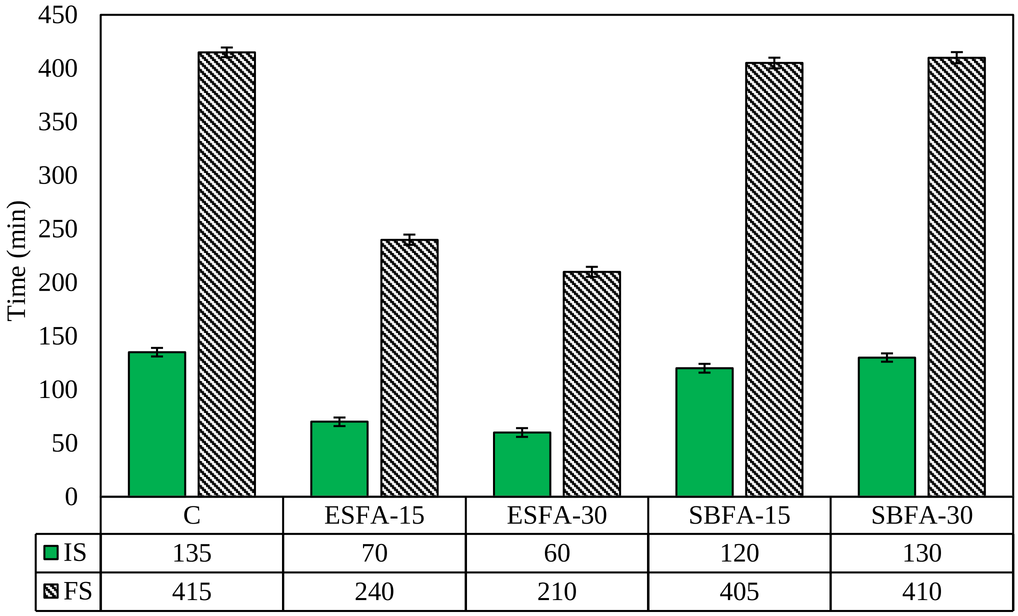
In general, the mixtures containing ES and SB, which underwent curing in -15℃, showed a decrease in internal temperature below the freezing point of water (0℃) after 25 to 48 hours and 21 to 48 hours, respectively. This indicated that the temperature during the protection period did not adhere to the recommendations set forth by ACI

306R (2016), which require maintaining a surface temperature of 10°C for seven days. However, these mixtures still performed better than the C mixture, as the C mixture experienced a drop in internal temperature below freezing point after only 8 to 9 hours. It is worth noting that other factors, such as CNAI and nano-silica, can also contribute to the exothermic heat generated by the cement hydration process. However, in all mixtures, these materials were used in equal amounts.

6.2. Setting Time

The rigidity behavior of the mixtures was significantly influenced by the different types and proportions of LWA comprising PCM, as depicted in Figure 6.2. The trends described herein are only relevant to the lightweight fine aggregate replacement method, as the penetration test is done on the mortar fraction of concrete; hence, testing the mixtures containing lightweight coarse aggregate (CA) did not apply to this case.

The initial setting times (IST) varied from 60 to 135 minutes, with the C mixture reaching the longest IST. Mixtures containing LWA exhibited lower IST compared to the C mixture because the release of heat from PCM accelerated the hardening of concrete, which corresponded to the higher internal temperatures (Figure 6.1). The ES mixtures yielded the shortest setting times, which reduced with content. For example, the IST of the ESFA-30 mixture was approximately 17% lower than that of the ESFA-15 mixture, which was 70 min. However, this trend differed slightly for mixtures containing SB LWA, as the IST of SBFA-15 was approximately 8% lower than that of SBFA-30. Furthermore, mixtures containing ESFA demonstrated lower IST when compared to those containing SBFA. This can be attributed to the fact that expanded shale LWA has a lower density and higher porosity compared to slag-based LWA, which enabled it to absorb more PCM and thus release more heat for the reactivity of the binder.



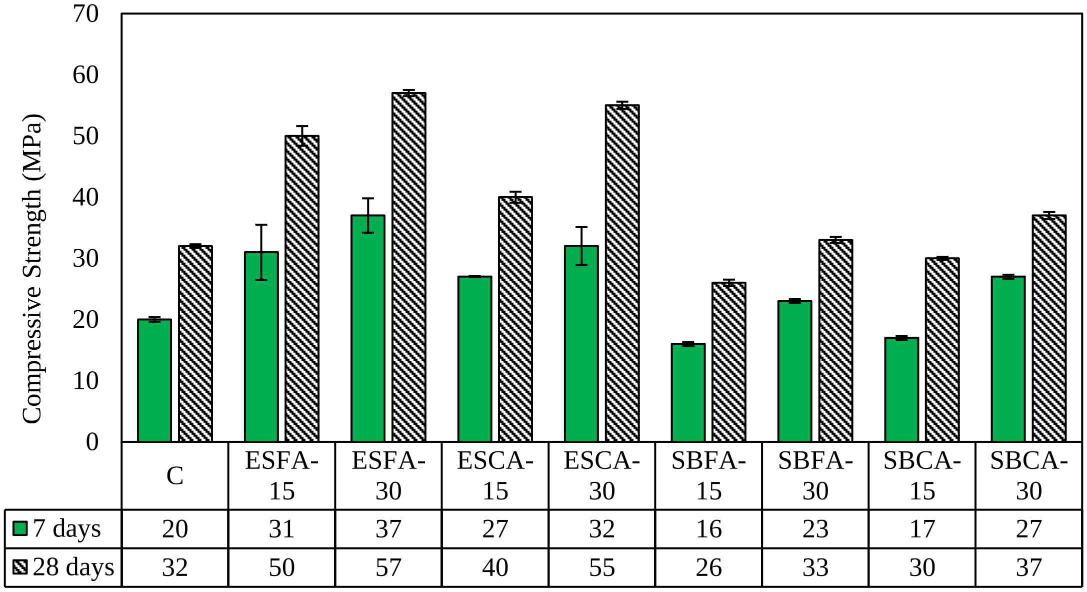
	C	ESFA-15	ESFA-30	SBFA-15	SBFA-30
🟩 IS	135	70	60	120	130
▧ FS	415	240	210	405	410

Figure 6.2: Initial and final setting times of all mixtures.

As shown in Figure 6.2, the final setting time (FST) of mixtures varied between 210 to 415 minutes, which is favorably comparable to the average hardening durations (4 to 7 hours) of concrete cast and cured at normal temperatures. This demonstrates that these mixtures have practicable hardening rates for construction applications in sub-zero temperatures down to -15°C. Most trends observed for the FST results were similar to that of IST, and they were consistent with the results of the internal temperature. For instance, mixture ESFA-30 had the shortest FST (210 min), which was 14% less than that of mixture ESFA-15, due to the inclusion of more PCM. Despite that the internal temperatures, of SB LWA were higher than that of the C mixture within the first 8 hours, all these mixtures had FST of approximately 7 h, which suggested the equivalency of both protocols (insulation with higher R-value blanket, and insulation with lower R-value blanket plus SB fine aggregate saturated with PCM) in terms of hardening rates. It should be emphasized that all the mixtures had an equal amount of nano-silica and CNAI, and these two materials accelerate the hydration process under cold weather resulting in a fast rate of hardening (Yasien and Bassuoni 2022; Abayou et al. 2019).

6.3. Compressive Strength

The compressive strength results (Figure 6.3) ranged from 16 to 37 MPa at 7 days and from 26 to 57 MPa at 28 days. Most mixtures (with the exception of SBFA-15 and SBCA-15) yielded higher compressive strengths than that of the C mixture at 7 (20 MPa) and (32 MPa) 28 days. The results indicated that the compressive strength of mixtures containing ES fine aggregate was higher than that of mixtures containing ES coarse aggregate at 7 and 28 days. For example, the compressive strengths of the ESFA-15 and ESFA-30 mixtures were approximately 15% and 16%, respectively higher than that of the ESCA-15 and ESCA-30 mixtures at 7 days. In conformance with the internal temperature and setting times trends, mixtures with higher contents of LWA achieved higher compressive strengths. For instance, at 28 days, the compressive strengths of the ESFA-30 and ESCA-30 mixtures were 14% and 37% higher than that of the ESFA-15 and ESCA-15 mixtures, respectively. This could be attributed to the higher PCM in the mixtures, which contributed to increased level of maturity and hence strength development, by acting as an internal heating source that elevated the temperature inside the concrete above the freezing point, especially at early-age (up to 31 hours).



	C	ESFA-15	ESFA-30	ESCA-15	ESCA-30	SBFA-15	SBFA-30	SBCA-15	SBCA-30
🟩 7 days	20	31	37	27	32	16	23	17	27
▧ 28 days	32	50	57	40	55	26	33	30	37

Figure 6.3: Compressive strength of all mixtures cast and cured at -15°C.

Unlike ES aggregates, only the higher content of SB LWA mixtures achieved higher compressive strengths (average of 25% and 13% higher at 7 and 28 days, respectively) relative to that of the C mixture. The trend of higher compressive strength of mixtures comprising higher amounts of SB aggregate was consistent over 28 days, with the SBFA-30 and SBCA-30 mixtures exhibiting approximately 26% and 23% greater compressive strength than that of the SBFA-15 and SBCA-15 mixtures, respectively.

The strength range of the nano-modified concrete mixtures at 28 days complies with the requirement for various construction applications, such as concrete sidewalks, parking lots, buildings, and bridges, which typically range from 20 to 40 MPa (MacGregor et al. 1997). Nano-silica has various effects on the hardened characteristics of concrete. It enhances hydration reactions, pozzolanic, and filler effects, as well as reduces the apparent water-to-binder ratio (w/b) in cementitious systems by absorbing water onto its ultrafine surface (Haruehansapong et al. 2014; Ghazy et al. 2016; Senff et al. 2009). The results indicated that even under freezing temperatures, nano-silica retained its effectiveness to improve the level of paste maturity due to the coexistence of CNAI. This functionality was particularly enhanced when adequate amounts of PCM, hosted by ES aggerates or the high content of SB aggregates, were released in the matrix. These concrete mixtures achieved 28 days compressive strengths in the range of 33 to 57 MPa, indicating a high degree of paste maturity within 28 days, rendering them appropriate for vital transportation infrastructure applications, including concrete bridges and pavements, even when cast and cured under freezing conditions, without heating.

6.4. Durability Performance

To assess the durability of the various mixtures, the fluid absorption (Figure 6.4) and durability factor (DF) of the specimens subjected to freezing-thawing tests in both water and a calcium chloride ($CaCl_2$) solution (Figure 6.5) were evaluated. Based on the results, all mixtures except for SBFA-15 and SBCA-15 demonstrated decreased fluid absorption relative to the C mixture, aligning with the compressive strength results. In general, it is worth noting that the mixtures containing ESFA and ESCA exhibited lower fluid absorption compared to those containing SBFA and SBCA. As mentioned in the compressive strength section, this could be attributed to the fact that ES aggregate absorbs more PCM and releases more heat at subzero temperatures. Thus, the mixtures containing ES aggregate exhibited a denser matrix and lower absorption.

The absorption values for both types of aggregate were lower in the mixtures containing 30% LWA aggregates comprising PCM. For instance, mixtures ESFA-30 and ESCA-30 had approximately 18 and 16%, respectively lower fluid absorption compared to that of ESFA-15 and ESCA-15 mixtures. This can be linked to the higher proportion of LWA containing PCM, which led to progression of binder reactivity with time, and consequently denser microstructure and decreased penetrability.

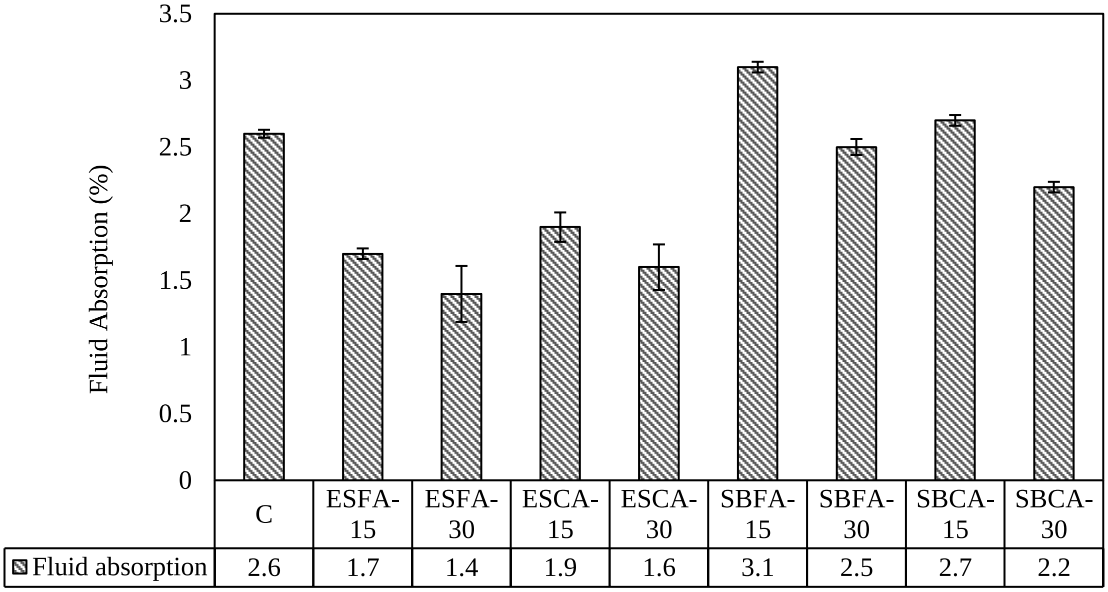


Figure 6.4: Fluid absorption of the mixtures after 28 days of curing at -15°C.

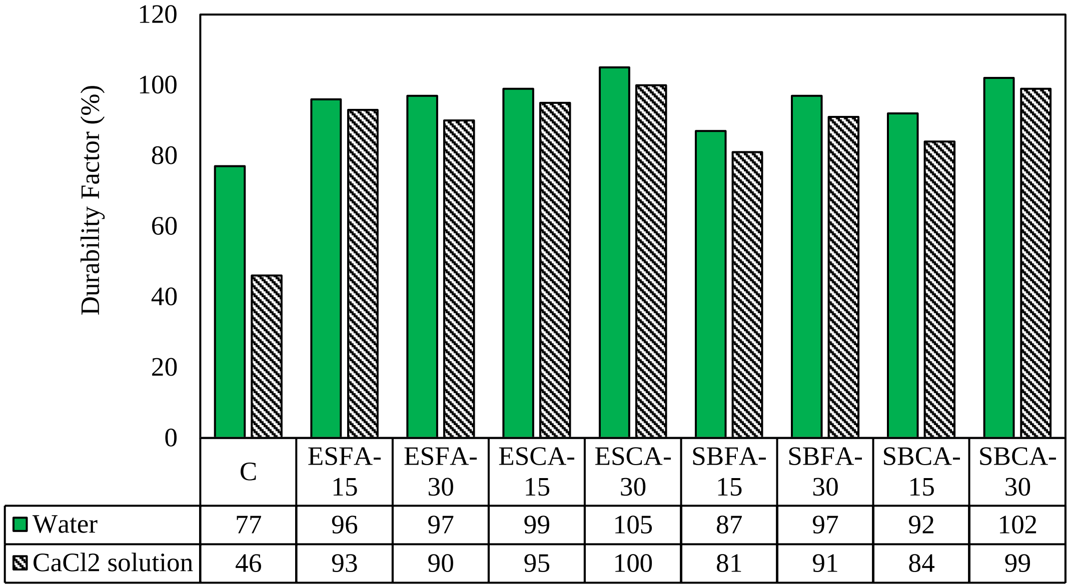
Mixtures incorporating ESCA at the same amount exhibited higher absorption compared to samples with ESFA. For instance, ESCA-15 and ESCA-30 mixtures had 12% and 14% higher absorption than that the ESFA-15 and ESFA-30 mixtures. This can be attributed to the fact that fine aggregate hosting PCM, which was more evenly distributed in the specimens, relatively improved the binder reactivity at sub-zero temperatures, leading to denser matrix, higher strength, and greater resistance to fluid ingress. The trend was different for the SB aggregates, as mixtures containing SBCA had lower fluid absorption compared to those with SBFA. For instance, when compared to the SBFA-15 and SBFA-30 mixtures, the SBCA-15 and SBCA-30 mixtures showed 13 and 12% lower fluid absorption, respectively. The lower density and higher absorption of SBCA, as determined by the aggregate properties discussed in Chapter 3, indicates that it can absorb a greater amount of PCM and release more heat compared to SBFA. Since SBCA can release more heat, it can facilitate cement hydration and result in a denser mixture, which in turn reduced fluid absorption.

Specimens in the $CaCl_2$ solution were more vulnerable to damage (Figure 6.5), due to the combined physical (frost action) and chemical (oxychloride formation) attacks (Farnam et al. 2015). Based on Figure 6.6, all mixtures containing LWA comprising PCM had higher DF (above 80%) than that of the C mixture in water and $CaCl_2$ solution. This is attributed to the continual role of PCM absorbing energy during the thawing stage, and releasing it during the freezing stage, hence increasing internal temperatures of concrete and alleviating the impact of frost action on specimens. In fact, the PCM boosts the kinetics of hydration in the samples by releasing heat, resulting in a denser sample that exhibits reduced absorption and increased durability properties. Additionally, the PCM has the ability to enhance the thermal energy storage capacity of concrete, thereby reducing the fluctuations in temperatures. This can improve resistance to freezing-thawing by delaying the formation of ice (Meshgin and Xi 2012; Cao et al. 2017).

The mixtures containing ES aggregate generally had higher DF than that of the control and SB mixtures. For instance, the DF of ESFA-30 and ESCA-30 mixtures were approximately 26 and 36%, respectively higher than that of the C mixture in the water, which was 77%. The ESFA-30 and ESCA-30 mixtures had marginally higher DF in water than that of ESFA-15 and ESCA-15, complying with the absorption results. However, the trend was inconsistent in the $CaCl_2$ solution for the ESFA-30, which still achieved a DF of 90%. It was observed that specimens containing higher amounts of ES aggregate and hence PCM, which released more heat (Figure 6.1), and consequently higher potential for thermal stresses, expansion and surface cracking the surface of specimens during the protection period (Figure 6.7). Some replicates of ESFA-30 showed this behavior, and hence they were susceptible to more fluid penetration and saturation during this long-term test. To prevent thermal cracking in concrete due to PCM, it is important to select a PCM that has a suitable melting and freezing point that is compatible with the expected temperature range in which the concrete will be exposed. Additionally, the amount and distribution of the PCM within the concrete should be carefully controlled to ensure that the heat generated during the phase change is distributed evenly throughout the concrete.

(a) (b)

Figure 6.5: (a): The C specimen after undergoing 300 freeze-thaw cycles in water, (b) The C specimen after undergoing 300 freeze-thaw cycles in $CaCl_2$ solution.



	C	ESFA-15	ESFA-30	ESCA-15	ESCA-30	SBFA-15	SBFA-30	SBCA-15	SBCA-30
🟩 Water	77	96	97	99	105	87	97	92	102
▨ CaCl2 solution	46	93	90	95	100	81	91	84	99

Figure 6.6: Durability factors of concrete mixtures after 300 cycles of freezing-thawing in water and $CaCl_2$ solution.

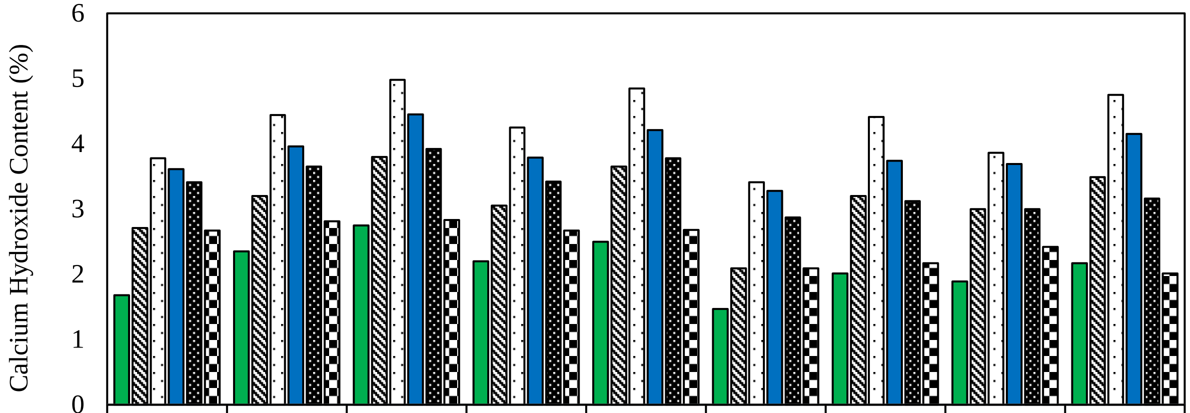
Figure 6.7: Thermal stress and surface cracking.

The DF of the mixtures comparing SB was better than that of the C mixture. For example, SBFA-30 and SBCA-30 mixtures had higher DF than that of the C mixture by approximately 26% and 32%, respectively in water; in the $CaCl_2$ solution, these increases were 98% and 115%, respectively. The mixtures that included the SB aggregate showed improved performance in the freeze-thaw tests, in both water and $CaCl_2$ solution environments, when the LWA content was increased. For example, in water, the increase in DF for SBFA-30 and SBCA-30 was approximately 11% compared to that of the SBFA-15 and SBCA-15; correspondingly, in the $CaCl_2$ solution, these increases were approximately 12% and 18%, respectively. The mixtures containing SB coarse aggregates, SBCA-15 and SBCA-30, exhibited relatively higher DF than that of the counterparts SB fine aggregates conforming to their higher compressive strength and lower penetrability. LWCAs typically have a lower thermal conductivity compared to LWFA. This means that when PCM is applied to the surface of LWCA, the heat transfer between the PCM and the concrete is slower. As a result, the PCM has more time to absorb and release thermal energy during phase changes, leading to better temperature regulation and energy efficiency (Real et al. 2016). According to the SB properties, the SBCAs generally have a higher absorption capacity compared to SBFA. If the aggregates absorb an excessive amount of PCM, it can result in the release of more heat at freezing temperatures, thereby enhancing the cement hydration process.

6.5. Thermal Analysis

The hydration and microstructural development of concrete were characterized by measuring the amount of portlandite/calcium hydroxide (CH) in the hardened pastes using thermogravimetry (TG) over a period of 90 days. Figure 6.8 indicates that owing to the application of nano-silica in concrete, marked CH contents were obtained in the matrix at earl-age. In addition to its physical filling effect, the coexistence of CNAI enabled nano-silica to maintain its functionality under freezing conditions in terms of providing additional surfaces for the precipitation of hydration products through the nucleation effect. This corresponded to the accelerated hardening rates and notable strength development observed at an early-age (up to 7 days). Most mixtures comprising appropriate types of LWA and PCM content had further acceleration of hydration kinetics due to the heat release mechanism during the first 30 hours, as indicated by the higher CH contents relative to the C mixture, which resulted in higher maturity levels of the hardened paste, and hence improved strength and durability of concrete.

After 7 days, the contents of CH decreased in all the mixtures consistently up to 90 days. This indicated that at sub-zero temperatures, the mixtures had a delayed pozzolanic reaction of nano-silica, which densified the pore structure of concrete by consuming CH to produce high-stiffness secondary calcium silicate hydrate (C-S-H) gel (Yasien et al. 2019, Yasien and Bassuoni 2022). At normal curing temperatures (20 to 30°C), this reaction commences within the first day of reaction (Ghazy et al. 2016). For the majority of mixtures comprising LWA and PCM, the CH contents dropped at faster rates up to 90 days.



	C	ESFA-15	ESFA-30	ESCA-15	ESCA-30	SBFA-15	SBFA-30	SBCA-15	SBCA-30
🟩 1 day	1.68	2.35	2.75	2.2	2.5	1.47	2.01	1.89	2.17
▧ 3 days	2.71	3.2	3.8	3.05	3.65	2.09	3.2	3	3.49
☐ 7 days	3.78	4.44	4.98	4.25	4.85	3.41	4.41	3.86	4.75
🟦 14 days	3.61	3.96	4.45	3.79	4.21	3.28	3.74	3.69	4.15
▩ 28 days	3.41	3.65	3.92	3.42	3.78	2.87	3.12	3	3.16
▣ 90 days	2.67	2.81	2.83	2.67	2.68	2.09	2.17	2.42	2.01

Figure 6.8: TG results for the CH contents up to 90 days of curing at −15°C. (Note: the accuracy of TG is within ±0.25%).

It was found that the ESFA-30 mixture had the highest CH contents compared to the other mixtures at all ages, followed by ESCA-30. The reason behind this could be the larger surface area of the ES fine aggregate comprising the highest amount of PCM, allowing for greater thermal energy storage capacity and consequently enhancing the reactivity of the binder. This finding explained the shortest setting times and highest early-age strength of this mixture. It is worth noting that all mixtures containing ES aggregate demonstrated a higher percentage of CH at all ages, compared to the C mixture. At all ages, the mixtures containing ESFA, such as ESFA-15 and ESFA-30, exhibited a higher percentage of CH content compared to the ESCA-15 and ESCA-30 mixtures, respectively, owing to the homogeneous distribution of fine aggregate in concrete. The results of the setting time, compressive strength and absorption were found to be consistent with the TG test results.

For the SB mixtures, mixtures with a higher content of SB aggregate had higher CH contents, similar to the trends observed in mixtures containing ES. Based on the data, it is evident that at most ages, SBFA-30 and SBCA-30 mixtures had a higher CH content compared to SBFA-15 and SBCA-15 mixtures, respectively. Furthermore, the mixtures containing coarse aggregates, such as SBCA-15 and SBCA-30, had a higher CH content compared to the SBFA-15 and SBFA-30 mixtures, respectively. These trends suggest these mixtures had higher levels of paste maturity, which explained their higher compressive strength and durability.

Chapter 7: Summary, Conclusions and Recommendations

7.1. Summary

Placing and curing concrete in cold weather is one of the most challenging issues faced by concrete contractors in North America. Although research on the use of antifreeze additives for concrete dates back to the 1950s, a literature review on cold weather practices for construction with cementitious materials revealed that the use of antifreeze admixtures is still not a common practice in North America. Relative to conventional protection methods, the experiments conducted in this thesis aimed to identify cost-effective concrete mixtures and protection techniques that are suitable for various cold weather scenarios, including temperatures as low as -15°C. The experimental program of this thesis was divided into three phases.

The evaluation of the two Type 6 commercial concrete mixtures (supplier I (L) and supplier II (C)) in Phase I of the experimental program involved testing eight different mixtures (L-5, L0, L+5, L+23, C-5, C0, C+5, and C+23) for hardened properties (compressive strength), durability (fluid absorption, rapid chloride penetrability test (RCPT), and freezing-thawing resistance), and thermal analysis to monitor the hydration development.

Phase II of the experimental program was designed to evaluate the effectiveness of two commercial admixtures (calcium-nitrate-based and urea) when used in nano-modified mixtures for cold weather applications. The primary objectives of Phase II were to develop and assess the performance of a commercially available cold weather admixture system (CWAS) for concrete, utilizing the two admixtures tested in nano-modified mixtures. For mixing, casting, and curing until testing, a temperature of -5°C was employed, which is representative of the late fall and early spring weather conditions in Winnipeg. The mixtures were assessed for their fresh properties (setting times), hardened characteristics (compressive strength), and durability (fluid absorption and freezing-thawing resistance). Thermal analysis was employed in Phase II to complement the results of the bulk tests.

Phase III of the experimental program involved utilizing lightweight aggregate (LWA) comprising phase change material (PCM) as a protection technique for concrete mixtures cured at lower freezing temperatures (-15°C). Three key variables, namely the type, size and amount of LWA, were incorporated into the mixture designs for Phase III, as they were believed to have a significant impact on the performance of the concrete when cured in cold weather. Phase III involved evaluating the fresh and hardened properties of the concrete by measuring the internal temperature, setting time, and compressive strength. In addition, experiments were conducted in Phase III to assess the durability characteristics of the concrete through fluid absorption and freezing-thawing tests. Thermal analysis was also performed to examine the hydration development of the mixtures.

7.2. Conclusions

The following conclusions were deduced from Phase I:

- The performance of L concrete mixtures appeared to be more significantly affected by the lowest curing temperature (-5°C) compared to C concrete mixtures, but both mixtures failed the 35 MPa required limit by the COW, which suggested the inadequacy of the commercial tarp to protect winter concrete at freezing temperatures However, it is worth noting that the L mixtures, when cured at 0, +5, and +23°C, exhibited higher performance levels in comparison to the C mixtures.

- The C mixtures exhibit higher mechanical properties during the early stages of curing as compared to the later stages. This trend may be attributed to the presence of accelerating admixtures in the C mixtures.
- Winter concrete mixtures containing accelerators and/or a high content of binder exhibited increased compressive strength at an early age when subjected to different temperatures at or above 0°C. However, this relationship did not hold at the later stages of curing. Specifically, the data suggested that while the L and C mixtures cured at 23°C had higher compressive strength at 7 days, those cured at 0°C and +5°C reached greater strength at 28 days, due to the effect of more homogenous hydration development.
- The durability properties were consistent with the mechanical strength, and it has been observed that the L mixtures exhibited better durability performance compared to the C mixtures, with the exception of the L mixture at -5°C. However, both mixtures failed the RCPT limit of 1500 coulombs required by the COW.

The following concluding remarks were drawn from Phase II of the experimental program:

- Despite the low curing temperature utilized in the experimental program, the results of the setting time (ranging from 5.1 to 10.5 hours) and strength (ranging from 46 to 59 MPa at 28 days) indicate that the adopted mix design (characterized by low water-to-binder ratio, adequate binder content, and CWAS) was capable of achieving an adequate level of maturity of the hardened paste. These findings were supported by the thermal gravimetric analysis (TGA) performed on the samples.

- The use of calcium nitrate (CN) as the CWAS in comparison to urea resulted in better concrete performance, as evidenced by faster hardening rates, greater strength development up to 28 days, greater resistance to fluid ingress, and greater initiation of nano-silica pozzolanic reactivity. However, consistent with the TGA findings, both mixtures achieved comparable performance in later-age properties such as resistance to frost damage.
- The addition of nano-silica to concrete produced at -5°C led to significant improvements in performance, as evidenced by shorter setting times, increased compressive strength, lower absorption, and enhanced resistance to frost action. These improvements were particularly notable when nano-silica was combined with CN, which helped preserve the functionality of nano-silica at sub-zero temperatures. TGA analysis showed that the early-age nucleation, latent pozzolanic, and filler effects of nano-silica contributed significantly to the improved hydration development of the concrete mixtures.
- The findings of this study suggest that nano-modified concrete mixtures, particularly those incorporating commercial grade CN or urea, may offer a practical and cost-effective solution for cold weather concreting down to -5°C. These alternatives may prove more efficient than conventional methods such as heating materials and insulation blankets with high thermal resistance.

The following conclusions were drawn from Phase III:

- Utilizing LWA comprising PCM can be a highly effective approach for concrete work in cold weather conditions. However, it is important to keep in mind that the type, size, and quantity of LWA used have a significant impact on the properties of the concrete produced.
- According to this study, the ES LWA demonstrated superior performance in terms of fresh, hardening, and durability properties compared to the SB LWA.
- Higher internal temperature, shorter setting times, greater compressive strength, and less fluid absorption of concrete were all achieved by increasing the LWA content of concrete from 15% to 30%. This was explained by the fact that more PCM led to the release of more heat, thus improving the reactivity of the binder. It is worth noting that the ESFA-30 and SBCA-30 mixtures were able to achieve the highest levels of strength and durability properties.
- Mixtures containing ESFA demonstrated better performance than those containing ESCA, due to the more homogenous distribution in the matrix. However, this trend was reversed for the mixture containing SB LWA, due to the higher absorption, i.e. PCM, in the coarse aggregate.
- Overall, the use of PCM can have both positive and negative impacts on winter concrete. On the positive side, PCM can help the fast setting and increase the mechanical strength at early-age by releasing heat. However, there are also potential drawbacks to using PCM in concrete such as thermal cracking which could alter the durability of the concrete over the long term and reduce the frost resistance of concrete. Overall, the use of PCM in concrete for freeze-thaw testing is an area of ongoing research and development, and the effectiveness and feasibility of this approach will depend on a variety of factors, including the

specific type of PCM used, the composition of the concrete, and the environmental conditions under which it is tested.

7.3. Recommendations

Based on the findings of this research, the following recommendations are presented:

- It is recommended to conduct further investigation on the impact of anti-freeze admixtures, supplementary cementitious materials, and nano materials on the L and C mixtures.
- For Phase I, it is recommended to conduct compressive strength and thermal analysis tests at 56 and 90 days to evaluate the later age performance of the concrete.
- To validate the results obtained in Phase II, it is recommended to conduct further research, including field trials and cost-benefit analyses that compare the effectiveness of the nano-modified concrete mixtures with conventional construction methods, such as enclosures and insulations.
- To evaluate the suitability of cold weather concrete for foundation construction under varying mechanisms of attack such as sulphate and combined sulphate and acid, further investigation is required to understand the behavior of these durability aspects.
- To examine the impact of various nano-materials in concrete, such as nano-alumina and nano-clay, at different dosages under cold exposure conditions, it is suggested similar to Phases II of this program.

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Appendix A

Figure A.1: Walk-in environmental chamber.

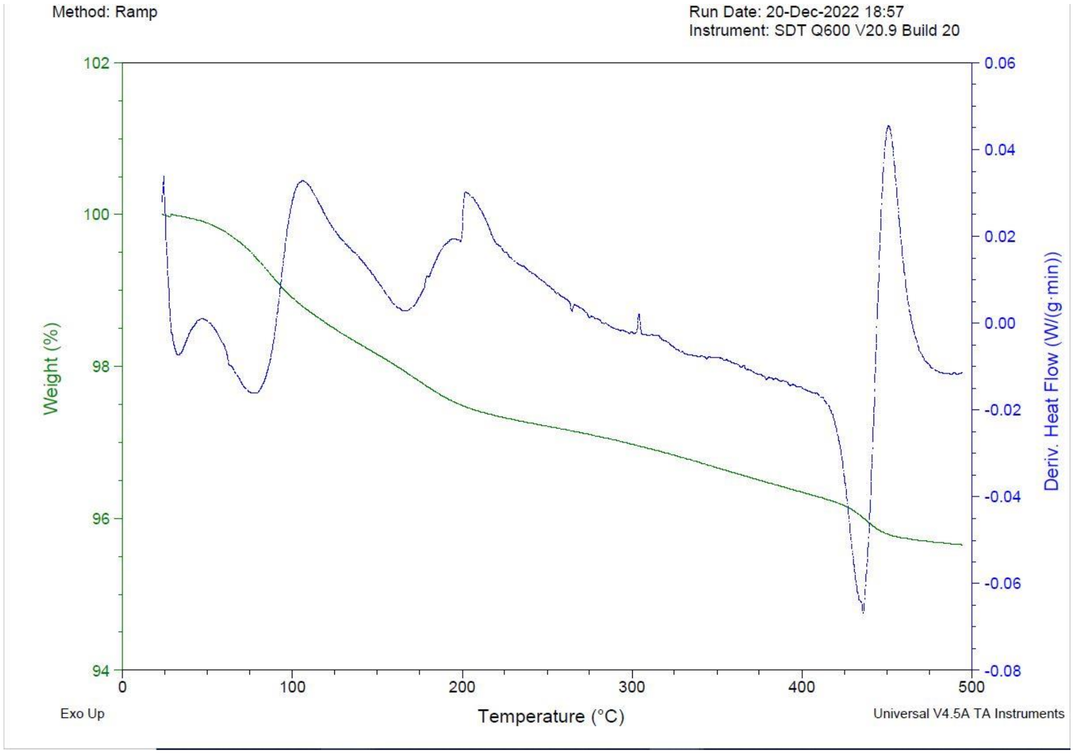

Figure A.2: Thermogravimetry result of UR-NS in 90 days at -5°C.

(a) (b)

Figure A.3: (a) The ESFA-15 specimen after undergoing the 100 cycles in water, (b) The ESFA-15 specimen after more than 300 cycles in water.