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Abstract

This investigation is based on the novel technique of Ice Formwork where ice is used as moulding material for cementitious materials. Its assets are manifold; a stark decrease in manual labour at many stages of the process including creation of the ice mould and demoulding, no non-recylcable waste production. This research examines the effects of antifreeze, namely Calcium Chloride and Sodium Chloride, on the mechanical properties of mortar samples. In total, three experiments are conducted. Firstly, mortar samples with a solution of 0-3wt% of CaCl2 as antifreeze are cured at temperatures of -20°C, -2°C, and 23°C. Secondly, two Calcium Chloride and Sodium Chloride solutions are investigated with percentages of 9% and 6% and 15% and 5% respectively. These are used in mortar and cured at temperatures of -11°C and 23°C. Each of the aforementioned samples in the two first experiments are tested at three different ages; after 3, 7, and 14 days. The third experiment consists of exploring the hydration curve of mortar samples cured at subfreezing temperatures. This entails two different samples being cured at two different temperatures during 24 hours: a 3% CaCl2 sample at -2°C and a 15% CaCl2 and 5% NaCl samples at -11°C. The mechanical properties investigated are the bending and compression stresses at failure point. The tests are comprised of a 3-point bending and compression tests, in which the data being processed are the failure points.

Keywords: ice moulding, concrete, structural behavior

Introduction

Concrete is the most used building material in the world. Since 2019, a technique has been developed and researched known as ‘Ice Formwork’ in which the moulding material for concrete is ice, see Figure 1.1. This practice may seem counter-intuitive since curing of concrete produces heat involving the issue of potential premature melting of said cast. However, compatibility with conventional practices is virtually impossible. A new method needs to be created which may bring different implications as opposed to the already existing precast concrete procedures. Firstly, the water used for the moulds stays in the cycle and can be reused completely. Secondly, CNC milling ensures precise, customised, and unique pieces with dramatically less labour involved [15]. Thirdly, the demoulding process occurs automatically as the ice melts away where the concrete object also stays in tact [15].

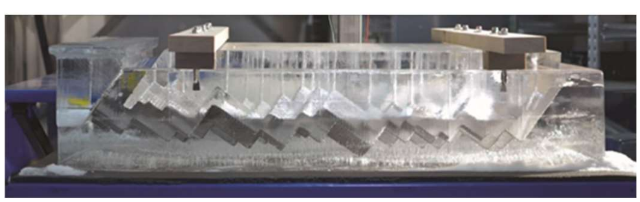


Figure 1.1: Example of a CNC machined Ice Mould [38].

Although, these advantages seem enticing, there are critiques. Firstly, during the time in which the concrete is curing, the cool houses need to be continuously fed with energy. Secondly, much research is still needed about the different influences of the chemicals added and the specific chemical reactions taking place. Ice Formwork is still in development and its applications are, as of yet, limited. In Figure 1.2, an artistic specimen with a precise geometric shape using Ice Formwork can be seen.

Figure 1.2: Example of a Finished Specimen made using Ice Formwork [38].

Due to the novelty of this practice, there is a clear gap in literature concerning curing at subfreezing temperatures. Albeit, the use of admixtures is not uncommon and documentation thereof already bring forth good speculation material. This research encompassing the topic of Ice Formwork is stated as follows. Along different samples of mortar with antifreeze chemicals namely Calcium Chloride and Sodium Chloride which are cured at various sub-freezing temperatures, the compressive and bending strength are measured and a final advice is given concerning the optimal combination of aforementioned factors.

2 Materials and Methods

In this paragraph, the materials used are listed and the sample preparation is elaborated upon where the specific mortar varieties and the mixing and molding process is explained. Next, the methods are described for both bending and compression tests.

2.1Materials

The material used for the mortar samples:

• Cement; CEM I (100% cement), Grade 42.5 N,

• Sand; individually packaged in 1350g bags, maximum thickness of 2mm

• Water; Tap water

• Calcium Chloride Dehydrated; VWR International BV (CaCl2x2H2O)

• Sodium Chloride; VWR International BV (NaCl)

To ensure a safe environment and process precautions, the following material should also be used: • Lab coat

• Safety glasses

• Latex gloves

• Ear muffs for hearing protection during the vibration stage

The tools used for mixing, see Figure 2.1:

• Mixing machine; KitchenAid mixer 6,9 L - Type: Heavy Duty 5KSM7591X

• Weighing scale; 0.1g accuracy with a minimum limit of 1g

• Timer; to keep track of the precise timing when mixing

• Scraper; Mix the contents during the 90-second interval, explained in Section 2.2.2, and used to equalize the surface of the samples

• Molds; Styrofoam molds with three 40x40x160 millimeter cavities

• Bowl; the complete mixture should fit

• Measurement beaker; 250 ml beaker for water

• Measurement beaker; 30 ml beaker for antifreeze

Figure 2.1: Setup for Sample Preparation

Other:

• Freezer with a range of -11 to -25°C - Type: ZFC51400WA

• Weiss Climate Chamber; Chamber regulating temperature and humidity - Type: SB22 300

• Rotronic Instrument; Datalogger for Temperature and Humidity for Hydration Experiment and to check temperature in the freezer - Type: Hygrolog HL-1D

2.2 Sample preparation

The specific contents of each mortar mixture can be seen in Table 2.1. These chemicals are also called admixtures which refers to any material added besides water, aggregates, or cementitious materials which can induce modifications in setting or hardening properties [4]. In this case, the chemicals added are Calcium Chloride dihydrate and Sodium Chloride which are considered negligeable volume-wise due to the addition being small in comparison to the total volume. As a consequence, the water to cement ratio stays constant for all samples made. The flakes of the Calcium Chloride dihydrate compound consist for 25% of water [13], so the amount of water to be added was determined with Equation 2.1. Water Content = 225grams − 0.25 ∗ weight of Calcium Chloride dihydrate. (2.1) The Calcium Chloride Dihydrate concentrations ascend in increments of 0.5 percent (in relation to weight percent of cement) for the variations in Table 2.1. The maximum percentage of antifreeze added is 3%. This cap is set due to the following reasoning. There should be an investigation on the feasibility of above 2% CaCl2 added to mortar. Above 4% admixture should be avoided, due to excessively fast setting. In addition, at 3.5% CaCl2, the peak of acceleration is achieved before becoming detrimental to its mechanical properties [13].

Table 2.1 Varieties of Mortar containing CaCl2.

#	Sand (g)	CEM I (g)	Water (g)	wt% A (C)	wt% A (W)	$CaCl_2$ (g)
1	1350	450	225	0	0.00	0.00
2	1350	450	222.75	0.5	0.74	1.69
3	1350	450	220.5	1	1.48	3.38
4	1350	450	218.25	1.5	2.20	5.06
5	1350	450	216	2	2.91	6.75
6	1350	450	213.75	2.5	3.61	8.44
7	1350	450	211.5	3	4.31	10.13

Note that 'A' stands for antifreeze, which in this case refers to Calcium Chloride, with column 5 the weight percentage, with regards to cement, of Calcium Chloride dihydrate and column 6 the weight percentage, with regards to water, of Calcium Chloride dihydrate. Next up, elaboration on the mixtures considering both chemicals, Calcium Chloride and Sodium Chloride is presented. The percentages are taken from literature [2] and verified by placing them in the freezer as solution to clarify whether they freeze over. See 4 for elaboration on the results.

Table 2.2 Solutions of Combination of CaCl2 and NaCl.

#	Water (g/%)		$CaCl_2$x$2H_2O$		NaCl (g/%)	
8	225	100	0	0	0	0
9	222.2	89	11.2	4 (3 of which CaCl2)	19.6	7
10	216.6	82	33.7	12 (9 of which CaCl2)	16.8	6
11	211	75	56.2	20 (15 of which CaCl2)	14	5

Each of the described mortar mixes in Table 2.1 and mixes #10 and #11 from Table 2.2, which from theory should be compatible at -11°C, are made for three different ages; ages 3 days, 7 days, and 14 days. The total volume of the ingredients accounts for the volume of three rectangular prisms with dimensions 40x40x160 millimeters, see Figure 2.2. The boundaries for the curing temperatures are from 23°C to -21°C. These extremities are chosen because the hardening process cannot happen below -25 °C [6]. By having a benchmark in normal curing conditions, the strength discrepancy can be measured when curing temperature is changed and how much of an effect the latter has in combination with the chemicals added. Control samples with 0% antifreeze assess whether its effects are considerable. At the chosen curing periods, a compressive strength of around 40%, 68%, and 90% respectively [1] of the final compressive strength without admixtures cured at room temperature is measured.

2.3 Methods

In this section, the tests are described alongside the setup specifications which were predetermined by the Laboratory.

2.3.1 3-Point Bending Test

The brick is centered based on eyeball judgment. By placing the top surface on the side, it establishes more equal level on the pressure of the surfaces connected to the 3 points of the 3-point bending machine because this 'top surface' can be subject to asymmetry during curing. See Figures 2.5 and 2.7.

2.3.2 Compression Test

The second test is the compression test. The data retrieved indicate the force at which the block fails under compression.

Figure 2.5: Bending Test Setup. Figure 2.6: Compression Test Setup.

Figure 2.7: Result of Bending Test. Figure 2.8: Result of Compression Test.

3 Testing of cement based concrete.

Typical ingredients making up cement are limestone, chalk, shells, iron, ore, and silica sand [9]. Known as Bogue's compounds, the four main chemical components which can be found in most types of cement are Tricalcium Silicate (C3S, 30-50%), Dicalcium Silicate (C2S, 20-45%), Tricalcium Aluminate (C3A, 8-12%), and Tetracalcium Alumino Ferrite (C4AF, 6-10%) [10] [7]. Within this research, mortar samples are made. Refer to Table 3.1 to compare the differences of the three main cementitious mixtures.

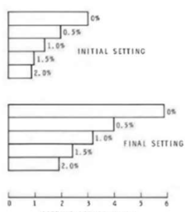
Table 3.1: Comparison between Cementitious Mixtures [2].

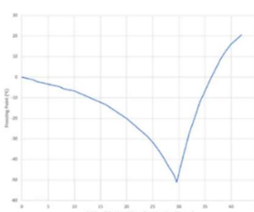
Type	Ingredients	Uses
Cement paste	Cement, Water	The matrix material binding the aggregates
Mortar	Cement, Water, Sand	The 'Glue' holding structural elements together
Concrete	Cement, Water, Sand, Gravel	Foundations for buildings, roads, sewers etc.

Type Ingredients Uses Cement paste Cement, Water The matrix material binding the aggregates Mortar Cement, Water, Sand The 'Glue' holding structural elements together Concrete Cement, Water, Sand, Gravel Foundations for buildings, roads, sewers etc.

3.2 Calcium Chloride

One of the chemicals used within the domain of this research is Calcium Chloride, its chemical formula being CaCl2. Its use is widely known in the cement industry and it is the most used chemical since the use of admixtures within this industry. Some reasons include the low price and its high efficiency [3]. The decision was made to move forward with this chemical as antifreeze, to observe the accelerating and the antifreeze effects and how it behaves with regards to cement at various low temperatures. In general, there are three groups of antifreeze: primary (freeze depressant); binary and ternary (combination of freezing depressant and hydration accelerators; other (water reducers and superplasticizers) [11]. An adverse effect is represented in corrosion. In reinforced concrete, chloride is mostly avoided. It interacts with the chloride, damaging the structural integrity. Depending on the amount added (by wt% of cement), the freezing point is decreased by several degrees [12]. See Figure 3.5. On a molecular level, the compound has an electrical charge. Since the covalent bond of water is much stronger compared to the ionic bond in Calcium Chloride, it breaks down into three alone standing ions which act as a barrier for crystallization of water [14].





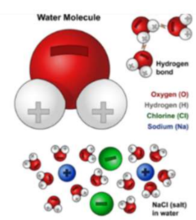


Figure 3.4: Initial and final setting times with different amounts of Calcium Chloride [33].

Figure 3.5: Freezing point of concentrations of Calcium Chloride and Water [40].

Figure 3.6: Molecular Level of Salt Ions and Water [14].

Regarding its influence on mechanical properties, after 1.5 days the same strength is measured with 2% CaCl2 as opposed to after 3.5 days for a slab of concrete without admixture [13]. Hence, after only one day compressive strength is doubled. Curing at lower temperatures even increases the accelerating effect [9]. The maximum amount lies at 3.5% CaCl2, where the peak of acceleration, before it becomes detrimental to its mechanical properties, is achieved [13].

3.2.2 Sodium Chloride

Sodium Chloride, also known as table salt, has two main effect which are discussed here. More commonly used as a substance to depress the freezing point of water is sodium chloride. The salt dissolves in the water creating an alone standing particles of sodium and chloride, see Figure 3.6. In short, the salts make it difficult for ice to form from the water molecules due to the charge in the water [34]. This chemical is 'neutral' in the sense that it does not react with any compounds of cement. It had been used in concrete since the ancient roman times and has proven to actually increase its strength as opposed to not using salts [8]. An amount of Sodium Chloride dihydrate is proposed for a depression of -22.9°C. However, in research usually freezing points are only lowered a few degrees, down to -5°C

[41]. Furthermore, optimum salinity for maximum strength seems to be between 30% and 36% as a result of experimenting with different W/C ratios [5]. The same result was seen when using sea water instead of just NaCl. At 3wt% NaCl at 15°C, high early compressive strength development is recorded, but at 28 days there is barely any difference in comparison to the control sample [3]. The latter proves an accelerating characteristic for Sodium Chloride.

3.2.3 Combination of Calcium and Sodium Chloride

In general, it is complicated to distinguish between the influence of Calcium Chloride, Sodium Chloride, and sub-freezing curing temperatures. There is a clear intermingling of reactions taking place which are hard to isolate from each other. A noticeable contradiction is obviously taking place; Calcium Chloride reduces the time of initial setting whereas Sodium Chloride forces a prolonging of such. Literature does not offer much insight in these two chemicals combined. In [2], a combination of these is found together with their freezing points, however, not much interpretation is enlightened. All in all, a balance must be found. Too much of any chemical could induce an adverse effect.

4 Results and Discussion

In this section, the outcome of the various experiments will be elaborated on and discussed. The structure will follow chronological order of experiments in which the mechanical properties are individually analyzed. Table 4.1 exhibits a brief summary of the types of mortar samples cured at specific temperatures.

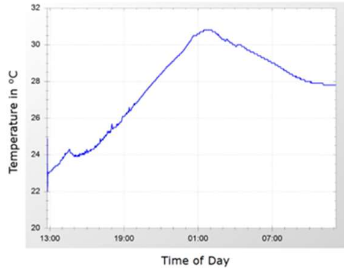
Table 4.1: Summary of Cement Samples per Experiment.

Experiment	Antifreeze Variety[1]	Curing Temperatures (°C)	Age (Days)
Investigating $CaCl_2$	0% $CaCl_2$	-20, -2, 23	3, 7, 14
	0.5% $CaCl_2$	-20	
	1% $CaCl_2$	-20, -2, 23	
	1.5% $CaCl_2$	-20	
	2% $CaCl_2$	-20, -2, 23	
	2.5% $CaCl_2$	-20	
	3% $CaCl_2$	-20, -2, 23	
Investigating combinations of $CaCl_2$ and $NaCl$	9% $CaCl_2$, 6% $NaCl$	-11, 23	3, 7, 14
	15% $CaCl_2$, 5% $NaCl$	-11, 23	
Investigating influence of $CaCl_2$ and $NaCl$	9% $CaCl_2$, 5% $NaCl$	-11	3
	15% $CaCl_2$, 6% $NaCl$	-11	

The CaCl2 percentages in the first experiment are with regard to weight of cement and the other two experiments are weight percentage with regard to water.

4.2 Hydration Curve Analysis

Looking at Figure 4.1, the first stage and onset of the second stage of hydration, which is initial hydrolysis and dormancy, can be seen from the steep slope leading in to a negatively steeped line. There is a total increase of 8°C, see Figure 4.1 or Appendix B. This slight temperature gain is to be expected; the mortar samples are relatively small, implying little heat generation by hydration. For the sample at -2°C, albeit, in a Styrofoam mold, the temperature dropped from 30°C to 5°C over the first 3h, with a slight decrease over time to finally 1.8°C at the end. A temperature of around 2°C was kept quite constant. This graph implies hydration took place. What is more, hydration is the reason the sample did not dip below 0°C. In the case of the curing sample at -2°C, it is hard to tell in which stage hydration is or even if these stages exist at subfreezing temperatures.



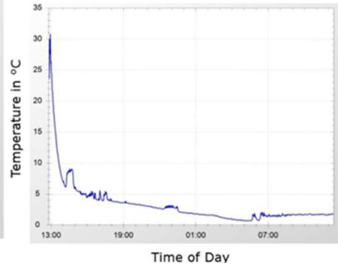
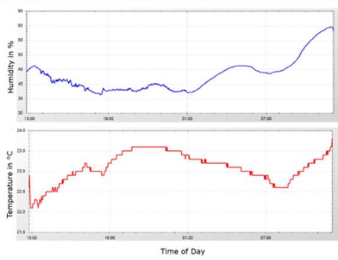


Figure 4.1: Temperature Level over 24 hours in the Sample at 23°C.

Figure 4.2: Temperature Level over 24 hours in the Sample at -2°C.

The data collected from the surrounding environment had the purpose of checking whether this could have had an influence on the temperature picked up by the sensor located in the sample. The temperatures varied from 22.1°C to 23.8°C in the lab which can only assume to be hardly influential to the insulated sample. It's safe to assume that the W/C ratio was respected due to proper insulation, indicating that the humidity of the lab, which varied from 36.3% to 59.7%, had close to no effect on hydration and same thing goes for the temperature in the lab, see Figure 4.12.



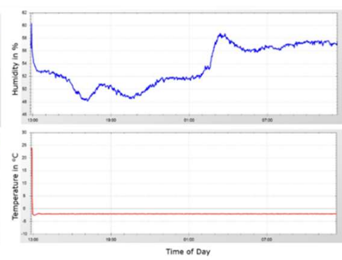


Figure 4.3: Temperature and Humidity Levels over 24 hours in the Laboratory.

Figure 4.4: Temperature and Humidity Levels over 24 hours in the Climate Chamber at -2°C.

The following conclusions can be taken from the results with regards to hydration. The higher the quantity of admixture (considered in this research), the sooner the initial strength peak occurs at room temperature. For the samples with variations of Sodium Chloride and Calcium Chloride, presumably the initial peak is reached much earlier at room temperature. In addition, the higher initial strength gain is, the sooner strength development flattens out. Leaving the final strength to be lower. In general, the hydration curve is more curved at room temperature and flatter at sub-freezing temperatures.

5 Conclusion and Acknowledgements

The goal of this research is to investigate the feasibility of the technique called Ice Formwork. This technology is a very recent innovation and can be considered a more sustainable way to produce precast concrete.

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