Master's thesis

NTNU
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Faculty of Engineering
Department of Civil and Environmental Engineering

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Measuring the ice melting rate of deicers with a calorimeter

Master's thesis in Cold Climate Engineering
Supervisor: Alex Klein-Paste; Eyal Levenberg
July 2020

NTNU
Norwegian University of
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DTU

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Abstract

Deicers such as sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) play an important role in winter road maintenance. To apply deicers on winter maintenance in more efficient way, the properties of deicers including ice melting capacity and ice melting rate should be evaluated accurately.

The purpose of this thesis is to develop the test of measuring ice melting rate of deicers with a calorimeter. The calorimeter was successfully used to measure the ice melting capacity in an accurate way and attempted to measure the ice melting rate with extreme assumptions on the salt concentration during the melting process in the previous study. So, the objective of this thesis is to explore the real salt concentration during the melting process, which could fill the gap of knowledge and improve the tests on measuring melting rate with calorimetry.

In this study, both tests that directly tracing the concentration in the calorimeter during the melting process and exploring the law of concentration development in more general conditions are attempted. Tracing directly was not successful due to the limitations of calorimeter and the failure reasons are analyzed for the future study. Regard tests that exploring in more general conditions, two deicers (NaCl and $MgCl_2$) are designed to be tested at three different temperatures (-5°C, -10°C, -15°C). The salt concentration in meltwater and temperature of the samples are measured at different time points.

Based on the results, it is possible to find that the concentration would get closer to the freezing point concentration gradually and away from the solubility concentration during the melting. Also, at a specific temperature, the Percentage Value might start around a certain value and end with a certain value during the melting process. New assumptions are proposed and applied on the tests at -15 °C. Compared with the results of previous assumption, new assumptions can achieve some improvements.

Key words: Calorimetry, deicer, ice melting rate, winter maintenance.

Preface and acknowledgments

This report is the final work of my Nordic Master in Cold Climate Engineering (Land Track) at NTNU and DTU. The work has been performed at the Department of Civil and Environmental Engineering in NTNU. The subject, road and ice are what I am interested in. Thanks NTNU for providing me such an awesome topic and laboratory.

Little experience of lab work and unexpected COVID-19 pandemic makes the work harder in this spring. I would like to say thanks to my parents who have always supported me during my life. Without you, I will not be able to achieve anything.

I would thank my supervisor Alex klein-Paste, for patient help and guidance through this year. I want to thank Sergey Kulyakthin and Mateusz Piotr Trzaskos who give me a lot of help in the lab work. I also want to thank my best friend Zihan Yu for your perfect support during this semester.

Trondheim, Norway
15 July 2020

Yuxuan Liu

Summary

Deicers such as sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) play an important role in winter road maintenance. Large amount of de-icing chemicals is applied in the winter maintenance to keep the road safe and trafficable. Due to the environmental aspects, it is necessary to apply the deicers in an efficient way through better understanding on their properties, including ice melting capacity and ice melting rate. In the previous study, the melting capacity already could be evaluated in a high accuracy with the calorimetry. Therefore, the motivation for this thesis is to develop a better method for determining the melting rate with the calorimetry.

Researchers in NTNU conducted a test for the measurement of ice melting rate with a customized calorimeter recently. However, two extreme assumptions on the salt concentration during the melting process were applied on the calculation models. Hence, the objective of this thesis is to explore the real salt concentration during the melting process, which fills the gap of knowledge in the previous study and improve the tests on measuring melting rate with calorimetry.

In this study, both tests that directly tracing the concentration in the calorimeter during the melting process and exploring the law of concentration development in more general conditions are designed. However, limited lab time due to the Corona Virus pandemic in this semester and limitations of experimental equipment cause a failure on the test of tracing directly. Failure reasons are analyzed for the future study. Regarding the second test plan, two deicers (NaCl and MgCl2) are designed to be tested at three different temperatures (-5°C, -10°C, -15°C). The salt concentration in meltwater and temperature of the sample are measured at different time points. Another supplementary test for the preparation of measuring the concentration with reflectometer is also performed.

A parameter called Percentage Value is defined for the result analysis in this thesis,

which illustrates how close the salt concentration is to the freezing point concentration. Based on the results, it is possible to find that the concentration would be closer the freezing point concentration and away from the solubility concentration as the melting processing. Also, at a specific temperature, the Percentage Value might start around a certain value and end with a certain value during the melting process. With these findings, new assumptions of concentration during the melting for NaCl and MgCl2 at three temperatures, which can be applied on the calculation model of measuring the ice melting rate with calorimetry are proposed.

New assumptions are applied on the tests at -15°C. Compared with the results of previous assumption, new assumptions achieve some improvements. For the future work, both more repetition tests to verify the findings in this study and working on developing the tests of direct measurement in calorimeter should be conducted.

Table of Contents

Abstract I

Preface and acknowledgments III

Summary IV

List of figures X

List of tables XII

1. Introduction 1

  1.1. Background 1

  1.2. Objective, scope and limitations 3

  1.3. Report outline 3

2. Theory 5

2.1. Thermodynamics 5

2.2. Calorimetry 6

2.3. Melting Process 6

    2.3.1. Phase transition of water 6

    2.3.3. De-icing with salt 8

  2.4. Ice Melting Capacity vs Ice Melting rate 9

3. Literature review 11

4. The application of calorimeter on measuring ice melting rate in NTNU 13

  4.1. Snow laboratory in NTNU 13

  4.2. The customized calorimeter 14

  4.3. Can calorimetry be used to measure the melting rate of deicers 17

    4.3.1. Calculation in theory 17

    4.3.2. Assumptions on the concentration of salt solution 20

5. Methods and tests 22

  5.1. Direct measurement - Tracing the concentration directly in the calorimeter during the melting process (Failed) 22

5.1.1. Test design 22

5.1.2. Failure analysis 24

5.2. Improved assumption - Exploring the law of salt concentration development during the melting process 27

5.2.1. Methods... 27

5.2.2. Materials 29

5.2.3. Test procedure... 31

5.3. Refractometer calibration... 33

6. Results and analysis... 35

6.1. Refractometer calibration... 35

6.1.1. Calibration for NaCl solution... 35

6.1.2. Calibration for $MgCl_2$ solution 36

6.2. Exploring the law of salt concentration changing during the melting process 38

6.2.1. NaCl tests at -5℃... 40

6.2.2. MgCl2 tests at -5℃... 44

6.2.3. NaCl tests at -10℃... 47

6.2.4. MgCl2 tests at -10℃... 50

6.2.5. NaCl tests at -15℃... 53

6.2.6. MgCl2 tests at -15℃... 56

7. Discussion 59

7.1. $MgCl_2$ tests... 59

7.1.1. Law of Percentage Value development 59

7.1.2. New assumption of MgCl2 solution concentration during the melting process 63

7.2. NaCl tests 64
    7.2.1. Data fluctuation analysis 64
    7.2.2. Law of Percentage Value development 66
7.3. Improved assumption applied on the calculation model of calorimeter 67
7.4. Attempt to Apply the improved assumption 69
8. Conclusion 71
9. Future work 73
10. References 74
Appendix 1: Results of the application of new improved assumption 77

List of figures

Figure 1 Phase transition of water (Delapaz, 2015) 7

Figure 2 Phase diagram of Sodium Chloride in water (Klein-Paste et al., 2018) 8

Figure 3 Ice melting rates measured on solid deicers at -20°C (Koefod et al., 2015) . 10

Figure 4 Temperature sensor installed above the test desk 13

Figure 5 Snow lab operation system 14

Figure 6 Overview of Calorimeter 15

Figure 7 Reactor of the calorimeter 15

Figure 8 Elements inside the reactor 16

Figure 9 Operation system of calorimeter 17

Figure 10 Phase diagram of sodium chloride in water (Klein-Paste et al., 2018) 21

Figure 11 Pipette used in tests 23

Figure 12 Modified pipette tips used in tests 25

Figure 13 Modified tips working in the calorimeter 25

Figure 14 Meltwater stick on the wall of the plastic reactor separately (30 mins, NaCl) 26

Figure 15 Plastic bottles for preparing ice cylinders 29

Figure 16 Illustration of small hole drilled in the ice 30

Figure 17 NaCl coarse particles used in tests 31

Figure 18 Thermal sensor used in tests 32

Figure 19 Digital refractometer used for measuring the concentration 33

Figure 20 Relationship between the concentrations of NaCl solution and RI values .. 36

Figure 21 Relationship between the concentrations of $MgCl_2$ solution and the RI values 38

Figure 22 Illustration of the parameter Percentage Value 39

Figure 23 Concentration development of NaCl test at -5°C 42

Figure 24 Percentage Value over time for NaCl test at -5°C 43

Figure 25 Concentration development of $MgCl_2$ test at -5°C 46

Figure 26 Percentage Value over time for $MgCl_2$ test at -5°C 46

Figure 27 Concentration development of NaCl test at -10°C 49

Figure 28 Percentage Value over time for NaCl test at -10°C 49

Figure 29 Concentration development of $MgCl_2$ test at -10°C 52

Figure 30 Percentage Value over time for $MgCl_2$ test at -10°C 52

Figure 31 Concentration development of NaCl test (-15°C) 55

Figure 32 Percentage Value over time for NaCl test at -15°C 55

Figure 33 Concentration development of $MgCl_2$ test at -15°C 58

Figure 34 Percentage Value over time for $MgCl_2$ test at -15°C 58

Figure 35 Percentage Value vs Time ($MgCl_2$) 59

Figure 36 Percentage Value development of $MgCl_2$ tests (Before "disappeared time") 61

List of tables

Table 1 Results of calibration test for NaCl solution 35

Table 2 Results of calibration test for $MgCl_2$ solution 37

Table 3 Results of NaCl Test 1 (-5℃) 40

Table 4 Results of NaCl Test 2 (-5℃) 41

Table 5 Results of $MgCl_2$ Test 1 (-5℃) 44

Table 6 Results of $MgCl_2$ Test 2 (-5℃) 45

Table 7 Results of NaCl Test 1 (-10℃) 48

Table 8 Results of NaCl Test 2 (-10℃) 48

Table 9 Results of $MgCl_2$ Test 1 (-10℃) 51

Table 10 Results of $MgCl_2$ Test 2 (-10℃) 51

Table 11 Results of NaCl Test 1 (-15℃) 54

Table 12 Results of NaCl Test 2 (-15℃) 54

Table 13 Results of $MgCl_2$ Test 1 (-15℃) 57

Table 14 Results of MgCl2 Test 2 (-15℃) 57

Table 15 Parameters of trendlines of MgCl2 tests 62

Table 16 Percentage Value of $MgCl_2$ tests at different time points 62

Table 17 Percentage Value of NaCl tests at different temperatures 66

Table 18 Percentage Value of $MgCl_2$ tests in the new assumption 69

Table 19 Percentage Value of NaCl tests in the new assumption 69

Table 20 Results of melted mass calculations (-15℃) 70

1. Introduction

1.1. Background

In cold climate areas such as Norway, winter road maintenance is a significant task. A large amount of snow and ice seriously affects the mobility and safety of the transport infrastructure, which causes great inconvenience to the society. Thus, lots of de-icing chemicals are adopted on the winter road maintenance and the most common one is NaCl. According to the data in paper, about 250000 tons of road salt are applied in Norway and some 2 million tones are used in the UK, while in the US, the consumption could up to 17 million tones (Wåhlin and Klein-Paste, 2017). Obviously, the cost of de-icing chemicals is very huge. In addition, the extensive use of salt could damage the road structure and pollute the environment surrounding the roads. So how to maintain roads in with de-icing chemicals in an efficient way has become a problem need to be solved.

In order to evaluate the performance of deicers on winter road maintenance, conducting some field tests could be a solution. For example, in Hossain's study, a mechanistic-empirical model was developed to determine the recommended application salting rates based on the snow melting performance data, maintenance and weather data collected in the real-world environment (Hossain et al., 2015). Field tests could directly reflect the performance of the deicer products in the practice and provide a straightforward overall guide for the application. However, field tests could be affected by many factors, such as weather condition, traffic type, test time and so on. It is impossible to keep all influencing factors the same in field tests. Hence, the complexity and uncertainty sometimes could lead to an inaccurate conclusion.

Another method is to evaluate a specific property of deicers by performing tests in laboratories where all other factors can be controlled. There are two properties of de-icing chemicals which are important for the winter road maintenance. One is the ice melting capacity that can be defined as the amount of ice that one gram of chemical can melt (Chappelow et al., 1992). It is a constant value when the specific chemical and temperature are given (Wåhlin and Klein-Paste, 2017). Many studies have been conducted to improve the test methods for ice melting capacity measuring in lab. Research group in NTNU also worked a lot on this. Nilssen introduced a new method based on calorimetry that avoids the sources of inaccuracy in SHRP method (Chappelow et al., 1992), which is the most common method in USA. The results through this method shows an average error of 4% compared with the theoretical ice melting capacity (Nilssen, 2017), which is a significant improvement and will be very helpful to evaluate the efficiency of deicing chemicals.

The other property is the ice melting rate, which is used to describe the speed of ice melting caused by a certain chemical. Ice melting rate is more complex than melting capacity which depends only on the temperature. In addition to the temperature, ice melting rate is also influenced by factors such as grain size of chemical particles, the distribution of chemicals, contact form between chemicals and ice, presence of mixing and so on. In order to better evaluate how fast a chemical can melt the ice on roads in reality, a relatively accurate lab test for measuring the ice melting rate needs to be established. Inspired by the ice melting capacity measurement by Nilssen (2017), calorimetry could be one solution to measure the ice melting rate in an accurate way.

Research group in NTNU have been devoted to the study of deicers for road operation. A customized calorimeter was developed and successfully applied on the measuring the melting capacity of deicers. Recently, Kulyakthin and Klein-Paste (2020) managed to use this calorimeter to evaluate the ice melting rate under extreme assumptions. This Master’s thesis is based on the study from Kulyakthin and Klein-Paste. It conducts a study on the development of salt concentration in meltwater during the melting process and improving the test for measuring the ice melting rate with calorimetry.

1.2. Objective, scope and limitations

This Master's thesis focuses on the development of the laboratory experiments for evaluating de-icing chemicals. NTNU's researchers developed a test for the measurement of ice melting rate of deicers with a customized calorimeter. However, two extreme assumptions on the salt concentration during the melting process were applied in order to quantify the ice melting rate. Details about this study is described in Chapter 4. So, the objective of this thesis is to explore the real salt concentration in meltwater during the melting process, which can fill the gap of knowledge in the previous study and improve the tests on measuring melting rate with calorimetry.

This Master's work consists of the theory part and the laboratory part. The theory part includes the preparation of the theory behind the ice melting process with salts and calorimetry, literature review about tests for measuring the ice melting rate and the introduction of NTNU calorimetry tests. The laboratory work is conducted in NTNU's snow laboratory to explore the salt concentration development during the melting process. Tests are performed on three temperatures (-5°C, -10°C, -15°C) and two de-icing chemicals are selected (sodium chloride and magnesium chloride).

This study was conducted in the spring 2020. Unexpected epidemic shut down the campus completely for two months. In the case of very limited lab time, the tests focus more on exploring the changes of salt concentration in meltwater. And tests only consider the influences from the temperature and chemicals. Other factors could influence the results, including size and shape of chemical particles, ice samples and mixing are not explored deeply.

1.3. Report outline

This report is structured first with the introduction of the theory behind the melting ice with deicers and calorimeter in Chapter 2. Existing studies and tests of measuring ice melting rate are summarized in Chapter 3. The customized calorimeter used in this study and the calculation model based on it are introduced in Chapter 4. Chapter 5 illustrates the methods and procedures of designed tests in this study. In Chapter 6, results of all the tests and some analysis are conducted. In Chapter 7, the results are discussed deeply and new assumptions for the concentration during the melting process are proposed. An attempt to apply the new assumption is also performed. Chapter 8 highlights the main conclusion of this study. The possible future work is summarized in Chapter 9.

2. Theory

2.1. Thermodynamics

Thermodynamics describes the relationship between the temperature, heat, work and energy. It reveals the basic principles behind the melting process and calorimetry. Hence, some thermodynamics theory related to this study is presented. The definitions below refer to the textbook "Physical Chemistry" (Atkins and De Paula, 2014).

Internal energy (U) is the *total kinetic and potential energy of constituents (the atoms, ions, or molecules) of the system.*

Enthalpy (H) is defined as:

$$H = U + pV \tag{1}$$

Where p is the pressure of the system and V is its volume.

Entropy (S) is a quantitative measure of disorder in a system. Among the three phases of a matter, solid has the least entropy and liquid has less entropy than gas.

Internal energy (U), Enthalpy (H) and Entropy (S) are **State functions.** That means they only depend on the current equilibrium state of the system and do not depend on how that state has been prepared.

First Law of thermodynamics: *The internal energy of an isolated system is constant.* In addition, the internal energy of a system can be transferred either by heat or work. So, the changes of internal energy of a system can be expressed as:

$$\Delta U = q + w \tag{2}$$

Where q is the heat transferred to the system, and w is the work done on the system.

Hess's Law: *The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions.* In addition, it states that the change of enthalpy only depends on the initial and final states and independent of the of the pathway. The Hess's law provides a way to calculate the total change of enthalpy in the calorimeter.

2.2. Calorimetry

Calorimetry is the process that measuring the heat transfer between the system and surroundings. The heat transaction can be caused by the chemistry rection, physical reaction or phase transition. **Calorimeter** is the device which used to perform calorimetry. It is possible to know the quantity of heat transferred between the system and surroundings through calorimeter. A customized calorimeter is constructed in NTNU's Snow lab and is applied in this study. The description of this calorimeter is presented in Section 4.2.

2.3. Melting Process

2.3.1. Phase transition of water

It is well known that water has three phases, including solid (ice), liquid (water) and vapor (gas). At standard atmospheric pressure, the freezing point of pure water is 0℃ (273.15K) and the boiling point is 100℃ (373.15K). Figure 1 shows the phase transitions of water. In this study, the transition between ice and water is followed with interests, where the process of freezing is an exothermic rection and the melting is an endothermic reaction.

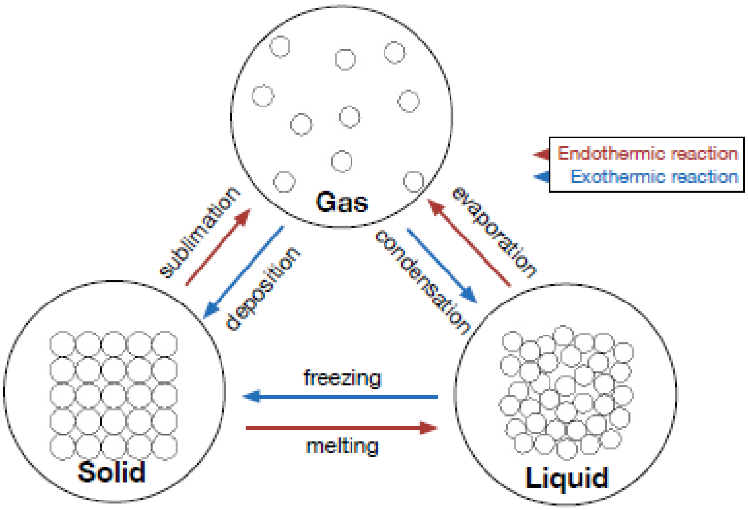


Figure 1 Phase transition of water (Delapaz, 2015)

2.3.2. Freezing point depression

The freezing point of water is depressed when foreign molecules or ions are dissolved in the water (Atkins and De Paula, 2014). Rewarding to the low concentration solution and ideal solution, this property can be considered as a colligative property, which means that the degree depends on the number of particles in the solution. For the real solution, it is possible to describe it with a phase diagram. Figure 2 shows the phase diagram of Sodium Chloride (NaCl) in water.

As shown in Figure 2, there are two curves in the phase diagram. The left branch is the **freezing curve**, which illustrates the freezing points for the different solution concentration. Freezing curve the is the equilibrium for melting and freezing. Along the freezing curve, the freezing point can drop until approximately -21℃ when the concentration is about 23%. This lowest point is called **eutectic point**, which indicates the temperature and concentration (w%) corresponding to the lowest freezing point. Beyond this point, the curve in the right is the **solubility curve**, which indicates the maximum solubility of the solution. In other words, the phase transition at this curve is caused by the limitation of solubility.

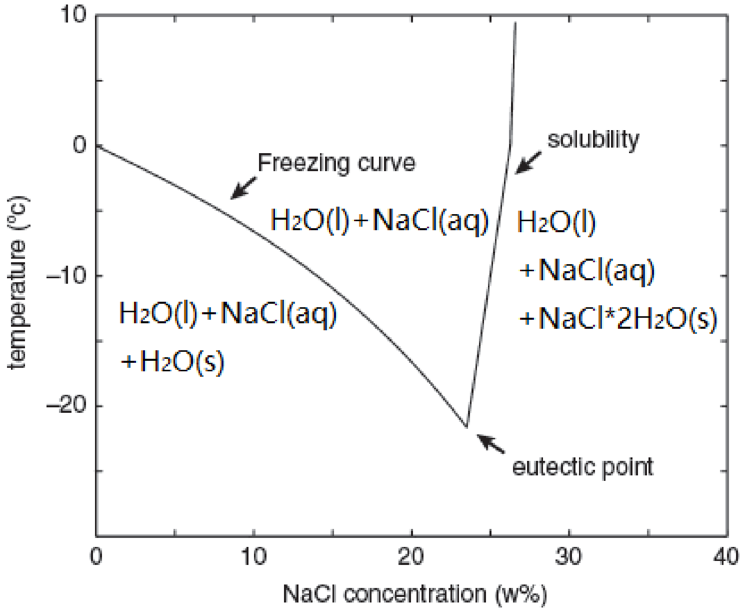


Figure 2 Phase diagram of Sodium Chloride in water (Klein-Paste et al., 2018)

Freezing curve and solubility curve divide the diagram to three parts. In middle part where the temperature is higher than the freezing point, the water keeps liquid and all the NaCl is in the solution (H2O(l) + NaCl(aq)). If the temperature is lower than the freezing point, the mixture would locate in the left part in the diagram. Some of the liquid water will be transformed to solid ice, and the concentration of the remaining NaCl solution will be higher (H2O(l) + NaCl (aq) + H2O(s)). Under this circumstance, the salt solution is trapped in pockets inside the ice and weakens it (Klein-Paste and Wåhlin, 2013). For the right part in the diagram, when adding more salt to the solution, after the concentration arrives the solubility, some undissolved crystals will be formed (H2O(l) + NaCl(aq) + NaCl·2H2O(s)).

2.3.3. De-icing with salt

For solid state, the ice molecules are bonded with other neighbor molecules and situated in a fixed position. For the liquid sate, the water molecules are more energetic and could move relatively freely. So, to allow a fixed ice molecule convert to a “freely” water molecule, energy is needed which could accelerate the molecule.

When there is no salt present, the ice molecules adjacent to the water molecules could “steal” energy from their neighbor molecules, leading to move freely and melt. Meanwhile, the neighbor molecules which are stolen would move slower and cool down, causing freeze. At 0°C (freezing point), the freezing and melting keeps equilibrium. So, the composition of ice and water would not change.

Where there is salt present, the ice molecules could “steal” energy from water molecules and salt molecules in the solution. The salt molecule in the solution cannot be forced to freeze and prevent the water molecule from freezing. However, the “steal” energy continues, the temperature of ice and solution drops. As the melting process continues, more and more molecules from ice enter the liquid, which means that the meltwater increases and the solution will dilute. Hence, the freezing point will increase due to the drop of the concentration. When the solution is so dilute until the freezing point drops to the given surrounding temperature.

2.4. Ice Melting Capacity vs Ice Melting rate

Ice melting capacity and ice melting rate are the two important properties to evaluate the effectiveness of deicers. It is important to distinguish between these properties. Ice melting capacity can be defined as the amount of ice that one gram of chemical can melt (Chappelow et al., 1992) and is a physical constant value. While the rate is not constant value for a certain chemical, which is influenced by many factors. The rate can be calculated as the amount of ice has been melt in a certain time period. Both the capacity and rate are commonly measured by the SHRP H-205.1 (for solid deicers). For the original SHRP H-205.1 tests provided in the handbook (Chappelow et al., 1992), the capacity test is conducted for 1 hour. While for the rate tests, the result would be measured in different time point. For example, in a test, the amount of meltwater could be measured on 15 min, 30 min, 45 min and 60 min. Thus, the average melting rate in the different time period could be obtained.

In the study from Koefod et al. (2015), a SHRP test for Solid NaCl, $CaCl_2$ and $MgCl_2$ was performed at -20°C. Koefod used this test to describe the importance of distinguishing between ice melting capacity and ice melting rate. The result is shown in Figure 3.

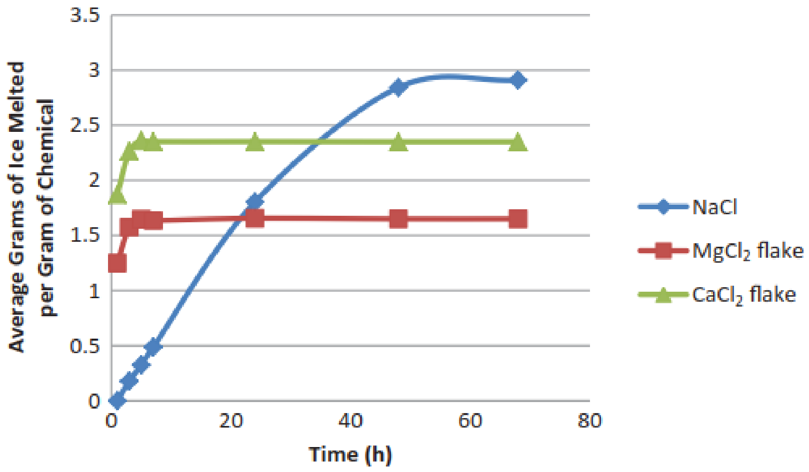


Figure 3 Ice melting rates measured on solid deicers at -20°C (Koefod et al., 2015)

The typical test length is 1 hour for measuring ice melting capacity with SHRP test. As shown in Figure 3, at 1 hour, NaCl melts very little ice. While, the $MgCl_2$ and $CaCl_2$ are much higher. So, if 1 hour is adopted, the capacity of NaCl will be much lower than the capacity of $MgCl_2$ and $CaCl_2$. However, if the time length is set longer than 40 hours, the quantity of meltwater for NaCl is much larger than the other two chemicals. So, in this case, NaCl has relatively large capacity at 20°C. To sum up, theoretically, the ice melting capacity should be the maximum amount of ice that one gram chemical can melt. While the ice melting rate depends on the time period. One hour is relatively short for SHRP test to measure ice melting capacity. It is not very reasonable, although it was provided in the handbook. In this Koefod's study, one-hour results show NaCl have a very low effectiveness, which is actually low on the ice melting rate, not the ice melting capacity. $CaCl_2$ and $MgCl_2$ have higher rate than NaCl, while they have lower capacity than NaCl as shown in the results after 60 hours.

3. Literature review

Regarding with the tests of ice melting rate, the most commonly used tests are SHRP H-205.1 (Solid deicing chemicals) and SHRP-H205.2 (Liquid deicing chemicals) (Chappelow et al., 1992). They are the standard tests for measuring the melting capacity in USA provided in the handbook of test methods for evaluating chemical deicers. By measuring the amount of melted water at different intervals, ice melting rate can be assessed. However, the SHRP tests for measuring melting rates have some obvious defects. In SHRP tests, all melted water is supposed to be collected by syringe, which is very hard to achieve. The deficiency in the melted water extracting and pouring back the melted water would lead to an inaccurate result. The study (Klein-Paste and Potapova, 2014) also pointed out that the amount of ice melted with a certain time (the ice-melting rate) is very sensitive. And the poorly control of heat flow in the SHRP tests affects the accuracy of results greatly. Based on the original SHRP tests, modified SHRP tests were performed in the later research. Alin and Shi (2012) developed the tests with using smaller petri dishes (3.5 cm in diameter) and less deicers (1 g solid or 0.9 ml). In addition, four simultaneous tests are conducted, of which three involve the test deicer and one uses 23 % NaCl solution as control. The less amount of ice and deicers allows more tests to be conducted side-by-side simultaneously, all of which helped to reduce the variability in the obtained results. The control dish is helpful on indicating the completion of tests. The disadvantage of this modification is the volume of generated melted water reduced which makes it hard in tests operation. But as proposed by Wåhlin and Klein-Paste (2017), the ice melting rate is a non-equilibrium property and can be different despite similar external conditions. Hence, simply testing chemicals to determine which chemical is the fastest as in the SHRP tests could produce inconsistent results between different labs and test instances. That is, there would be a large uncertainty if testing the deicers melting rate with SHRP or modified SHRP tests.

Koefod et al., (2015) proposed that focus understanding the fundamental properties which affect the ice melting rate could make the ice melting rate be more useful. From this approach, some studies were performed. Yatsenko and Chudotvortsev (2002) found that an increased concentration led to more rapid melting. Solutions with lower eutectic point correlated with a higher melting rate. Wåhlin and Klein-Paste (2016) also found that solutions with lower freezing points leaded to a faster melting. In this study, for melting the amount of melted ice, Wåhlin and Klein-Paste (2016) develop a test that tracks the ice-solution interface with DSLR camera. The highlight of this method is that using sample holders with very narrow depths to reduce the ice melting to practically two dimensions. Hence, the amount of melted ice could be evaluated.

The DSLR method gave a more accurate way on measuring the melting rate. According to Wåhlin and Klein-Paste (2017), the accuracy of ice melting rate is approximately ±0.025 g/h over 5-minute intervals and ±0.013 g/h over 10-minute intervals. Koefod (2017) developed a method that the ice-melting rates were determined by measuring the change in the concentration of ions in the ice melt as tracers. However, both these two methods could only test the liquid deicers. Hence, a good method for evaluating the ice melting rates, especially for the solid deicers needs to be developed and the calorimetry could be a solution.

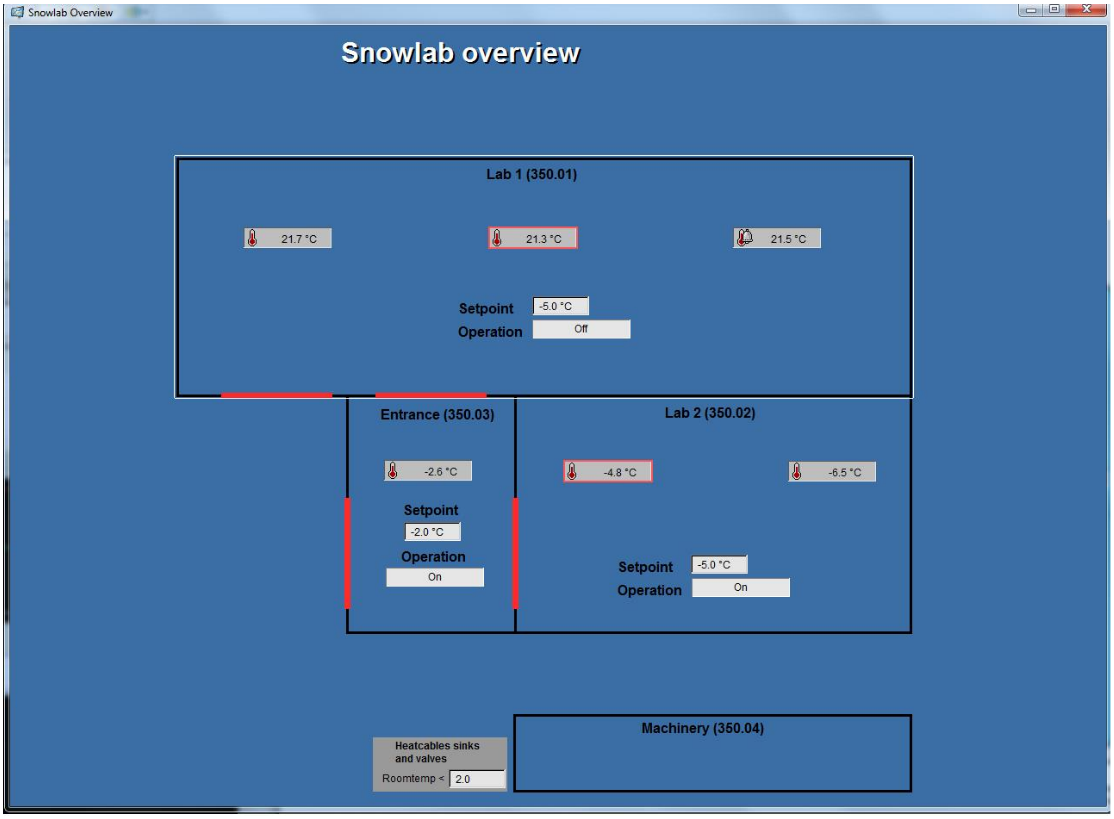
4. The application of calorimeter on measuring ice melting rate in NTNU

4.1. Snow laboratory in NTNU

NTNU has a snow laboratory with two cold rooms, which can used to perform tests at a certain temperature. The walls around the rooms are filled with insulated materials to reduce the heat transfer from outside, which could ensure the stability of in the indoor temperature as much as possible. Figure 4 shows the overview of the snow lab where to perform the tests. As shown in the figure, thermal sensor is installed above the test desk to monitor and stabilize the temperature.

Figure 4 Temperature sensor installed above the test desk

Figure 5 shows the overview of the lab operation system. Room temperature can be set through this system. The sensors inside the room could feedback the difference between the actual temperature and the set temperature, which is used to adjust indoor temperature.



Lab 1 (350.01)
Setpoint -5.0 °C
Operation Off

Entrance (350.03)
Setpoint -2.0 °C
Operation On

Lab 2 (350.02)
Setpoint -5.0 °C
Operation On

Roomtemp < 2.0

Figure 5 Snow lab operation system

4.2. The customized calorimeter

As mentioned above, a customized calorimeter was developed. Figure 6 shows the overview of this calorimeter. There are 2 pieces of polystyrene insulation in the calorimeter to ensure the good thermal insulation. The thickness of the insulation layer is 150 mm. 5 PT100 temperature sensors are equipped in the insulation distributed in the different thickness which can monitor the temperature throughout the insulation layer and can be used to calculate heat flux through the walls. On the top of one insulation, there is a chamber that can used for loading the deicing chemicals by a plunger without opening the calorimeter. The calorimeter is put on an electrical motor with wheels which allows to rotate the calorimeter 180° for mixing the ice and deicing chemicals.

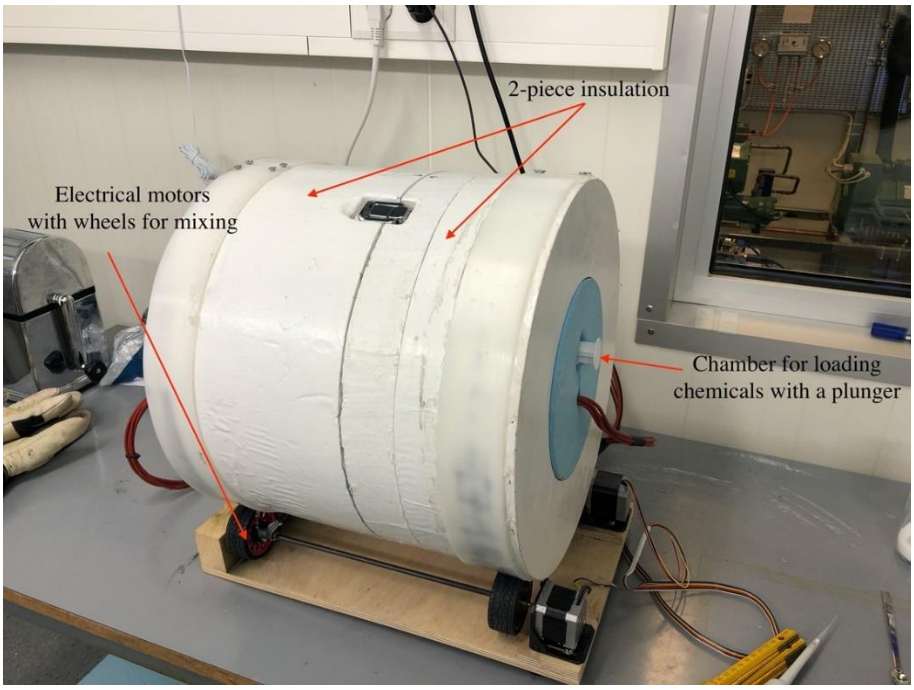


Figure 6 Overview of Calorimeter

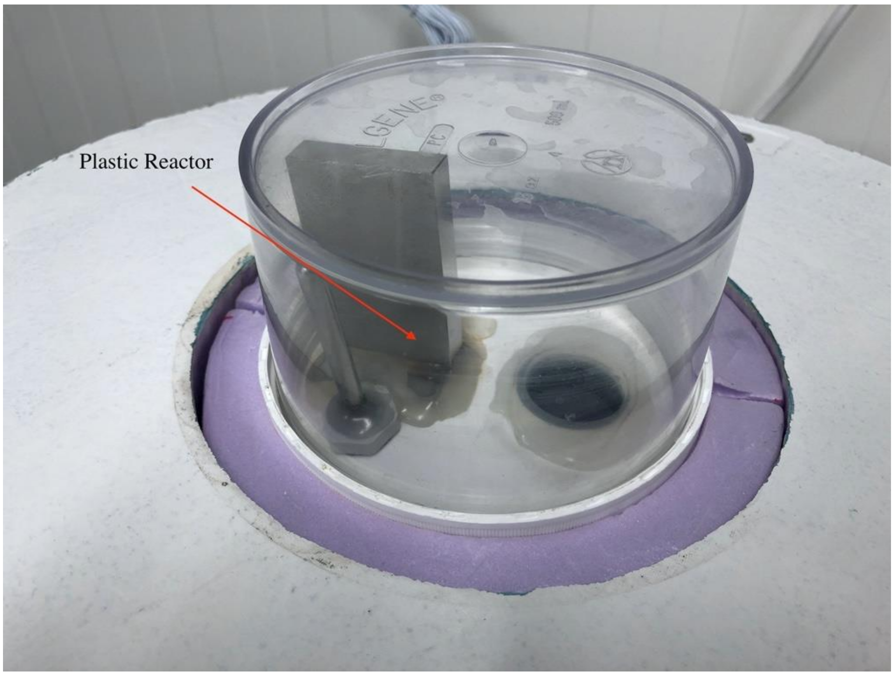


Figure 7 Reactor of the calorimeter

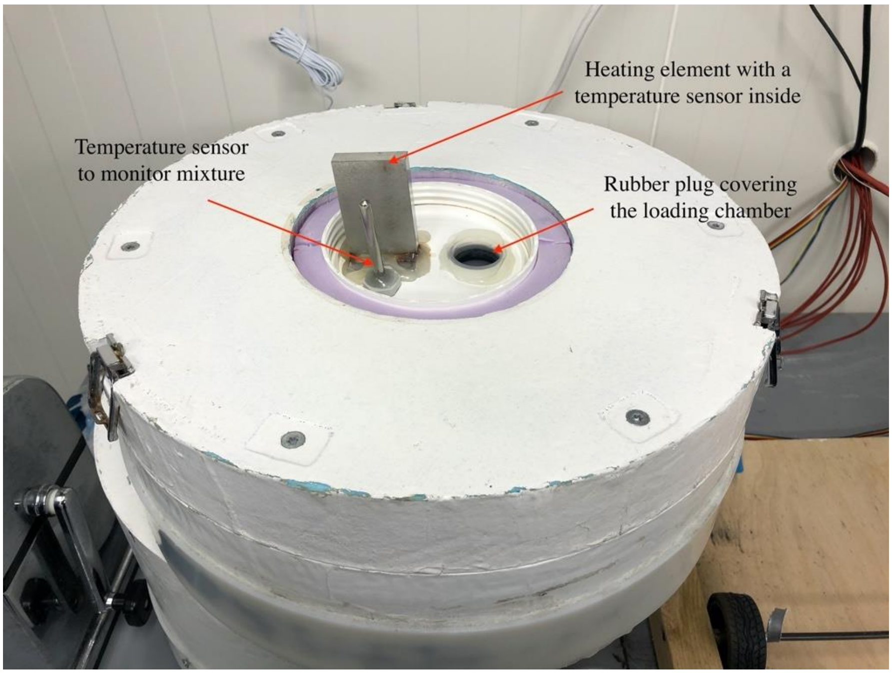
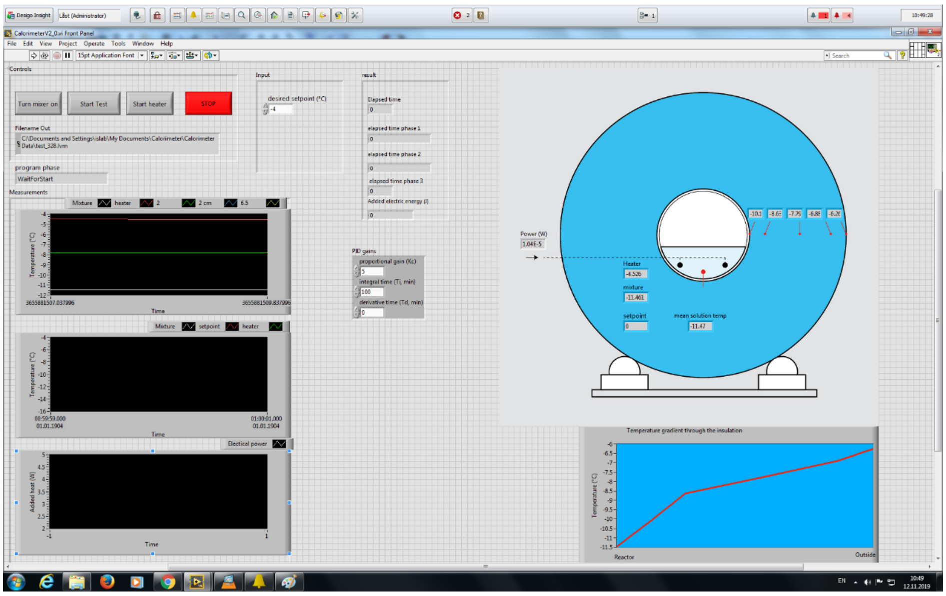


Figure 8 Elements inside the reactor

As shown in Figure 7, the reactor inside the insulation is a 500 ml plastic cylinder that provides the room for the mixing of ice and deicing chemicals.

Inside the reactor, there is temperature sensor that can monitor the temperature of mixtures, as shown in the Figure 8. A cuboid immersible stainless steel heater is also equipped in the reactor and there is also a temperature sensor inside the heater. The heater can provide a 50w heating power. The loading chamber is covered by the rubber plug. During the reaction it can be pushed inside by the deicers input plunger.



CalorimeterV2_0.vi Front Panel

Filename Out: C:\Documents and Settings\islab\My Documents\Calorimeter\Calorimeter Data\test_328.lvm

program phase: WaitForStart

desired setpoint (°C): -4

Elapsed time: 0

elapsed time phase 1: 0

elapsed time phase 2: 0

elapsed time phase 3: 0

Added electric energy (J): 0

proportional gain (Kc): 5

integral time (Ti, min): 100

derivative time (Td, min): 0

Power (W): 1.04E-5

Heater: -4.526

mixture: -11.461

setpoint: 0

mean solution temp: -11.47

Figure 9 Operation system of calorimeter

Figure 9 shows the operation system of calorimeter. The temperature of insulation and mixture can be easily monitored during the experiments. As mentioned above, there is also a temperature sensor inside the heater, which is connected to the power supply (Elektro Automatik PS8160-04). The operation system can control power supply (heating input) based on the practical and preset temperature of the heater. The power supply as well as the temperature log from sensors are recorded by the system every 0.4s automatically.

4.3. Can calorimetry be used to measure the melting rate of deicers

Kulyakthin and Klein-Paste has conducted a research on exploring if the calorimetry can be used to measure the melting rate of deicers based on the calorimeter mentioned above (Kulyakthin and Klein Paste, 2020).

4.3.1. Calculation in theory

Firstly, the thermodynamic calculating model in the reactor can be performed as the follows.

The heat transfer in the reactor which is in an insulated container can cause the temperature changes of the substances in the reactor. The heat source includes the heat added from the heater ΔQ_{add}, the heat through the calorimeter walls due to heat gradient in the different locations inside the walls ΔQ_{walls}, the heat of melting ΔQ_{melt}, the heat of salt dissolution ΔQ_{diss}. While the heat required due to the temperature of ice ΔQ_{ice}, salt ΔQ_{salt}, water ΔQ_{water}, the heating element ΔQ_{heater}. The balance can be expressed as follow and the calculation can be conducted for **each time interval**, which is 0.4s in the system.

$$\Delta Q_{add} + \Delta Q_{walls} + \Delta Q_{melt} + \Delta Q_{diss} = \Delta Q_{ice} + \Delta Q_{salt} + \Delta Q_{water} + \Delta Q_{heater} \quad (3)$$

The heat added from the heater ΔQ_{add} can be recorded by the system.

The heat flux through the calorimeter walls:

$$\Delta Q_{walls} = -h(T_{reactor} - T_{out}) \cdot \Delta t \quad (4)$$

Where $h\ [W/°\mathrm{C}]$ is the heat transfer coefficient for the total area of the calorimeter; $T_{reactor}$ and T_{out} are the temperatures inside the reactor and outside surface of the insulation, which can be recorded by the system; Δt is the time interval, 0.4s.

The heat of melting can be calculated as:

$$\Delta Q_{melt} = -H_{melt}\Delta m_w \quad (5)$$

Where H_{melt} is the heat of fusion of water, $H_{melt} = 333.6\ (J/g)$; Δm_w is the mass of the water melted.

The heat due to the salt dissolution ΔQ_{diss} can be calculated as:

$$\Delta Q_{diss} = -H_{diss}\Delta m_{salt} \quad (6)$$

Where H_{diss} is the enthalpy depending on the de-icing chemicals; Δm_{salt} is the mass increment of dissolved salt. In addition, the relationship between the increase of meltwater mass Δm_w and the increase of dissolved salt mass can be expressed as:

$$\Delta m_{salt} = \frac{x}{1-x}\Delta m_w \quad (7)$$

Where x is the mass concentration of the salt, which is not measured during the test. In addition, it is important to note that the heat change due to the dissolution is only considered, when the salt is not completely dissolved. In the calculation, whether the salt is still present should be determined firstly. If the initial salt mass m_{salt}^{0} larger than the accumulated mass of dissolved salt m_{salt}^{t}, the solid salt is still present and could contribute the heat of dissolution. Otherwise, the heat due to the dissolution would be zero.

Regarding the heat required to cause the temperature change of ice ΔQ_{ice} can be calculated by the specific heat capacity of ice C_p^{ice}, the mass of ice m_{ice} and the temperature change which can be monitored by the system. The equation is shown as the follows.

$$\Delta Q_{ice} = C_p^{ice}(m_{ice}^{0} - m_w^{t-1} - \Delta m_w) \cdot \Delta T \tag{8}$$

The mass of ice m_{ice} is calculated through subtracting the accumulated mass of meltwater the initial mass of ice m_{ice}^{0}.

$$m_{ice} = m_{ice}^{0} - m_w^{t-1} - \Delta m_w \tag{9}$$

Where m_w^{t-1} is the accumulated mass of meltwater before this step of time interval and Δm_w is the increment of meltwater in this time step.

Considering that the mass of salt used in the tests is so small compared with the mass of ice, the heat required to change the temperature of salt ΔQ_{salt} could be neglected.

The heat required to cause the temperature change of meltwater can be calculated by

$$\Delta Q_{water} = C_p^{w}(m_w^{t-1} + \Delta m_w) \cdot \Delta T \tag{10}$$

The heat required to cause the temperature change of heating element can be calculated by the specific heat capacity of stainless steel in the calorimeter C_p^{steel}, mass of it

m_{heater} and the temperature change of heater ΔT_{heater}.

$$\Delta Q_{heater} = C_p^{steel} m_{heater} \Delta T_{heater} \tag{11}$$

Substituting Equation (4)-(10) into Equation (3), the increment of meltwater for each step of time interval can be calculated by Equation (12)

$$\Delta m_w = \frac{\Delta Q_{add} + \Delta Q_{walls} + \Delta Q_{heater} - (C_p^{ice}(m_{ice}^0 - m_w^{t-1}) + C_p^w m_w^{t-1}) \cdot \Delta T}{H_{melt} + H_{diss}\frac{x}{1-x} + (C_p^w - C_p^{ice})\Delta T} \tag{12}$$

With the results of Δm_w, the mass of meltwater for every time step can be determined:

$$m_w^t = m_w^{t-1} + \Delta m_w \tag{13}$$

The initial mass $m_w^0$of meltwater is 0. So, the melting rate can be calculated by taking the time **derivative** of the meltwater mass.

4.3.2. Assumptions on the concentration of salt solution

As mentioned above, the concentration of salt solution is not measured during the tests, which is the only unknown parameter for quantifying the ice melting rate. Figure 10 shows the phase diagram of sodium chloride in water. For a given temperature, the deicer can melt the ice until the solution is so diluted where the solution concentration equals to the freezing point solution from the freezing curve. On the other hand, the solution is also limited by the solubility. Hence, the concentration can range between the freezing point concentration and solubility concentration, which is marked in red in Figure 10.

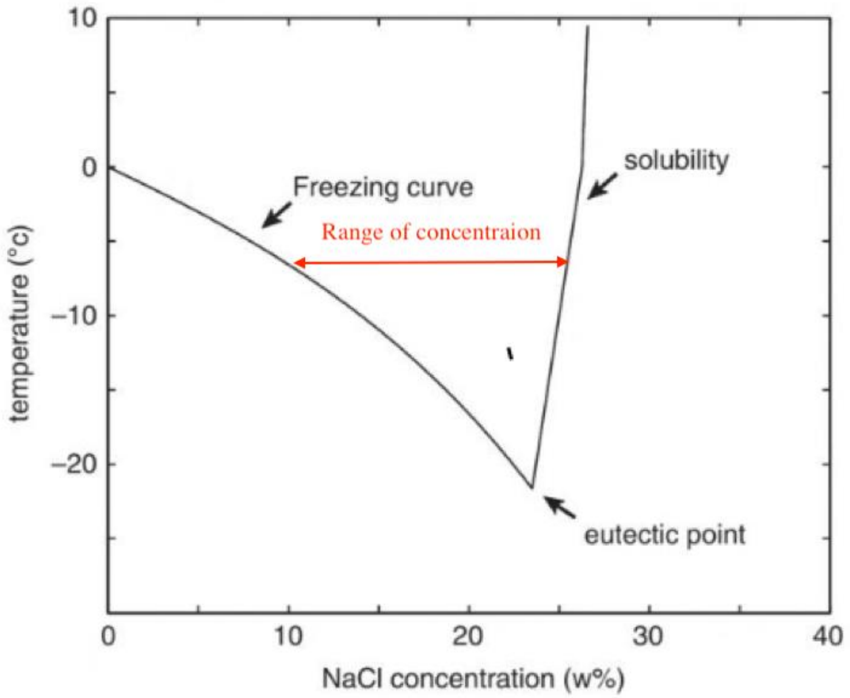


Figure 10 Phase diagram of sodium chloride in water (Klein-Paste et al., 2018)

In Kulyakthin and Klein Paste's study (2020), two extreme assumptions were applied, where the concentration is always equal to the freezing point concentration or the solubility concentration. However, the gap between these two assumptions could be very large, especially for the relatively high temperature. So, in order to fill the gaps in knowledge in Kulyakthin and Klein Paste's study (2020) and have more accurate results, better understanding of the development of concentration during the melting process would be very necessary. Hence, some tests to explore the concentration of salt solution during the melting process are performed in this Master's thesis.

5. Methods and tests

5.1. Direct measurement - Tracing the concentration directly in the calorimeter during the melting process (Failed)

5.1.1. Test design

In order to obtain the concentration of salt solution, the meltwater is supposed to be sampled during the melting process. Extracting the liquid directly from the calorimeter during the test could be the most direct and accurate solution. Hence, the original tests are designed to develop a method to extract the solution from the reactor while the calorimeter is running.

One of the reasons for using calorimetry to measure the ice melting rate is to avoid the unexpected heat pollution during the sampling in the SHRP tests. Hence, the extraction is supposed to be performed without opening the calorimeter by inserting the pipette into the loading chamber and dipping into the mixture located in the reactor. The pipette used in tests is shown in Figure 11, which could extract the liquid ranging from 0-220μl. In order to make sure that the pipette is long enough to reach the melted water, relatively longer pipette tips are supposed to be installed. The concentration measurement would be performed by the refractometer. Hence, the volume of extracted liquid is set as 0.05 ml (one drop). The benefit of digital refractometer is that the result of concentration could be obtained in a very short time and the volume of liquid needed is very little.

Figure 11 Pipette used in tests

Regarding the test materials, the ice cubes are crushed into 3 mm – 10 mm fragments. Typical de-icing chemicals, including NaCl, $MgCl_2$ and $CaCl_2$ are supposed to be tested. Considering the volume of reactor, 100 g ice are applied. The amount of salt is selected to melt 10 g of ice which could be calculated by their theoretical melting capacities at a given temperature.

Since the melting rate throughout the melting process are supposed to be calculated, the measurement of concentration should be performed at different time. 5, 10, 20, 30, 45 and 60 mins after the test starts would be chosen in the study. It is important to note that **measurements at different moments would be performed in the different tests respectively**. Because extracting the meltwater will result the reduce of deicers in the reactor. This will change the melting reaction resulting in inaccurate results. One approach to improve this defect is compensating the reduction in melted water. For instance, in the SHRP tests meltwater is poured back onto the samples. But in this test method, the meltwater would be dropped on the refractometer to measure the concentration, which means that the meltwater could not be returned into the reaction. Even if the meltwater could be returned back, the extra heat in this procedure would significantly affect the melting reaction. Hence, to provide the best undisturbed reaction environment, **one individual test will only measure the concentration data of one**

testing time. In other words, one test would be performed and the sampling would be conducted at 5 minutes. Then, this test would completely stop. Another test for 10 minutes could be prepared and performed later.

5.1.2. Failure analysis

During the first two months of this Master's thesis, the focus was on improving the tests with so that some usable data could be obtained. Unfortunately, for NaCl only some tests on 60 minutes could have available data. The main problem of this method is that extracting the solutions during the test running without opening the calorimeter is very hard to achieve. Some failure reasons are written below.

Pipette tips

It is hard to find appropriate pipette tips which are long enough to reach the bottom of the reactor in the market. Some adapts on the longest available tips were tried to be made. Figure 12 shows the modified pipette tips in the study. Two tips were combined together to have a larger length. Also, as shown in Figure 13, the front tip 1 (marked in red) is bent so that it could reach the corner of the reactor which is supposed to be the gather point of meltwater. However, although the modified tips could reach the "theoretical" gathering point of meltwater in the reactor, it is still very hard to sample enough liquid through one shot. One reason is that the pipette with a modified tip may not have the same suction as the original tip. The other reason is that in practice the meltwater does not gather together due to the gravity.

Figure 12 Modified pipette tips used in tests

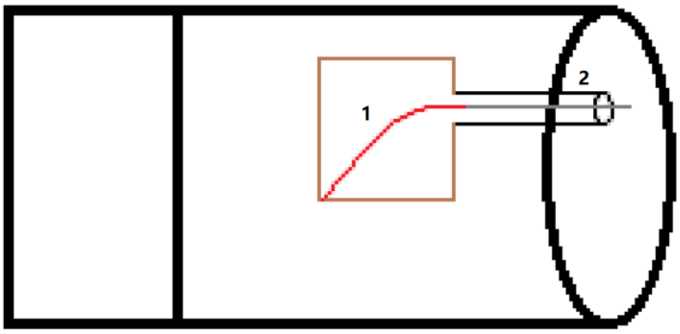


Figure 13 Modified tips working in the calorimeter

Meltwater in the reactor

As mentioned above, during the test the meltwater does not have an obvious gathering as expected, which makes it more difficult to sample enough liquid through pipette. According to the observation, part of meltwater drops stick on the wall of the plastic cylindrical reactor separately. Also, some meltwater is still attached to the ice fragments. Figure 14 Shows the meltwater inside the reactor for the test of NaCl at 30 minutes. Hence, although theoretically maximum 10 ml water could be melted, it is still very hard to sample one drop water from the reactor quickly without open the calorimeter.

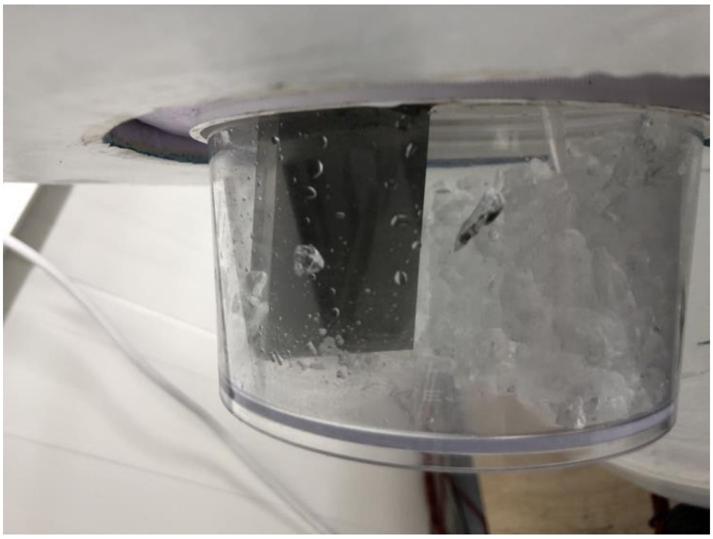


Figure 14 Meltwater stick on the wall of the plastic reactor separately (30 mins, NaCl)

Inefficiency at low temperatures

In theory, 10 ml could be melted in total, which seems to be enough for sampling. However, this calculation is based on the ice melting capacity, which means only when the melting finishes, it would have a result of 10 ml. De-icing chemicals, especially for the NaCl, are usually very inefficient at low temperatures. Part of the tests are supposed to be conducted at -15 °C, where the melting rate of NaCl would be very slow. Hence, very little ice would be melted before 30 min and the sampling would also be impossible. Since the objective is tracing the melting rate during the melting process, data of the concentration at different time points are interested. In fact, the concentration data at the start and middle stage of melting would be more interesting than the final stage. Because in the final stage, the concentration would be close to the freezing point concentration at the given temperature, which is already known by us. In summary, the inefficiency of de-icing chemicals at low temperatures makes it impossible to extract enough meltwater at the start and middle stage of melting process.

In order to solve this problem, increasing the amount of salt was tried. Double or even treble the amount of NaCl still did not work well. On the other hand, due to the volume limitation of reactor, the possible liquid in the reactor could not be very large. In addition, if too much water is present, the water layer would affect the contact between the deicers and ice. The melting process may be influenced.

Time-consuming

As mentioned above, for one individual test, only one chemical at one time point could be tested. As planned, 6 time points in one hour are chosen. At least, considering a two-time repetition, it would be in total $2 \times 6 \times 3 = 36$ individual tests for measuring three deicing chemicals. If tests at different temperature are needed, there would be more tests.

The running time for one individual test would be very short (less than one hour). But the preparation time for the calorimeter would be very long. It takes at least 12 hours to have the thermal equilibrium inside calorimeter after one test is conducted.

The unexpected pandemic in this spring makes the available lab time even more tense. The campus in NTNU was completely shut down from March to May. So, even if there is no problem mentioned above, the available lab hour would not be very abundant. Hence, after having the special access to the lab in May, another method aiming to improve the assumption about concentration instead of measuring it directly was developed.

5.2. Improved assumption - Exploring the law of salt concentration development during the melting process

5.2.1. Methods

The purpose of this test is to improve the assumption about the salt concentration through exploring the law of concentration changing during the melting process. Hence, the method of this test is to simulate the process of ice melting with de-icing chemicals in the lab. The temperature and concentration data would be recorded at different time during the melting. Two chemicals including sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) are supposed to be tested at three different temperatures (-5 ℃, -10 ℃, -15 ℃).

The challenge of this idea is that the salt concentration could not be traced over time in one single test. As mentioned above, the measurement of concentration needs to extract the liquid from the test samples. The extraction of meltwater would decrease the chemicals in the samples (some salt is already dissolved in the meltwater and removed through the extraction) and change the process of melting. More importantly, the removal of meltwater from samples would be kind of "restarting" the melting process. Also, the extra heat from operating might also influence the melting. So, it would be impossible to measure the salt concentration at different time points in one ice sample. With this limitation, the tests are planned to only sample and measure the concentration for one time point from one ice sample. In other words, tracing a melting process is through obtaining the data at different time points. In this study, a group of tests (one chemical at one temperature) is designed to be conducted by collecting data from approximately 15 different time points, which would be measured from 15 individual testing samples.

Another noteworthy consideration is the volume of meltwater. Based on the experience from the previous tests (Section 5.1), the volume of meltwater produced should be in a suitable range. Firstly, the volume should not less than 0.05 ml which is the minimum value that could be used to measure the concentration by refractometer. Then the volume of meltwater should be larger than 0.05 ml as soon as possible, because the concentration data close to the start of melting process are also need. In addition, the loss during the extraction is also needed to be considered. On the other hand, it would be better not to have too much meltwater. Since there is no mixing process for the samples (simulate the natural melting process and avoid the unexpected heat), if the meltwater is too much, the concentration would be uneven at the various depths inside the meltwater pool. So, the amount of salt would be calculated based on the melting capacity and adjusted according to the trail tests. The materials in the tests is introduced in the next section.

5.2.2. Materials

Ice

The ice sample is prepared in the plastic cylinder bottle with a diameter of approximate 4.5 cm, which is shown in the Figure 15. The water volume of each sample is 100 ml. Then, all the samples are placed in the lab (cold room) and waiting to be frozen. After the ice samples are completely frozen, one small hole with a diameter of 10 mm is drilled in the central of each sample. The depth of it is about 6 mm. Figure 16 shows the illustration of the small drilled in the central of the ice sample. The reason for drilling a small hole is that the hole could provide a stable place to set chemicals. It could be also helpful to lead the chemical particles to penetrate into the ice in a relatively vertical direction, which would make the measurement of temperature more convenient. In addition, the snow laboratory is cooled by two sets of refrigerators, which causes that the air temperature actually changes periodically, with a range of about 1°C. For instance, through observation when the set temperature is -15 °C, the real air temperature could change from -14.2 °C to -15.2 °C and period is about 6 minutes. Hence, the small hole could provide a more stable environment, where the temperature would have a relatively smaller variation. That could reduce the inaccuracy of temperature measurement due to the variation of room temperature.

Figure 15 Plastic bottles for preparing ice cylinders

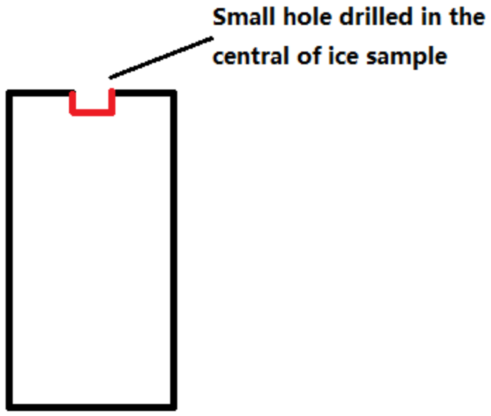


Figure 16 Illustration of small hole drilled in the ice

De-icing chemicals

Two typical de-icing chemicals, NaCl and $MgCl_2$, are tested in this research. Considering the material products in the market, NaCl and MgCl2·6H2O are supposed to be used in the tests. Regarding the Sodium chloride, the coarse particles were selected in this test, which is shown in the Figure 17. All the particles are sieved and the size ranging from 4 mm to 6.3 mm are chosen. The reason why the coarse particles rather than fine powder are selected is that the fine salt powder could have the possibility to enter the pipette tips during the extraction. That could lead the concentration in the tips which are supposed to be measured is higher than the real value in the ice samples. In addition, the contact area of fine salt powder and ice is relatively large. As the melting processes, the melting interfaces would be separated from each other and sometimes even form different holes. That would cause an uneven equilibrium concentration in the meltwater and large difficulties in the measurement of temperature and concentration. While the coarse particle has a relatively small contact area with ice. For one particle, in most cases, it would only form one melting hole. And one particle is enough to provide sufficient meltwater to be measured. Hence, based on the experience from many trial tests, on NaCl tests, **one coarse particle** (the mass is ranging from 0.2 g to

0.3 g) is used for the all three temperatures (-5 ℃, -10 ℃, -15 ℃). As for the $MgCl_2$, since there is no coarse particle product in the lab, MgCl2·6H2O **flakes** are applied. 2 pieces (about 0.1 g), 3 pieces (about 0.15g) and 5 pieces (about 0.25 g) are applied for the temperature of -5 ℃, -10 ℃, -15 ℃ respectively.

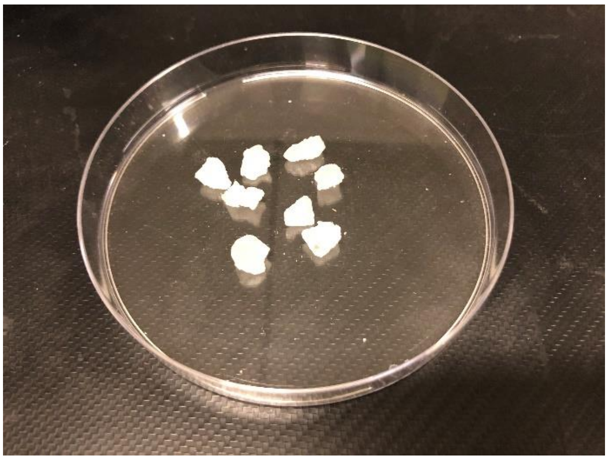


Figure 17 NaCl coarse particles used in tests

5.2.3. Test procedure

Preparation

For each group of tests, 20 ice samples are prepared to be frozen in the lab at the set temperature. After all the ice samples are completely frozen, a small hole is drilled in the central of each ice sample. Wait for at least 6 hours so that the temperature inside ice could be equilibrium and equals to the room temperature. De-icing chemicals are also placed in the lab in advance in order to have the same temperature with ice samples.

Formal tests

Set the deicers on all ice samples and start to record the time. For one group of tests, all the samples are tested at the same time. Each sample would be tested in sequence at its set time, which includes sampling the meltwater and measuring the temperature of melting process. The temperature measurements are conducted by a hand hold thermal sensor, which is shown in Figure 18. The needle of the sensor would be placed at the contact point between the salt and ice. The temperature would be recorded when the value shown is stable for at least 10 seconds. The extraction of meltwater is performed by the pipette shown in Figure 11. In order to have enough liquid to measure, the volume of pipette is set as 0.07 ml.

Figure 18 Thermal sensor used in tests

As for the time points of testing, they are selected based on the experience from trial tests. The first sampling time would be the time when the meltwater is enough for the concentration measurement, and the last time point would be the time when the melting process is finished and the temperature of ice equals to the room temperature. In order to monitor the whole melting process, for each group, about 15 time points of exampling are applied.

After the samples of meltwater are extracted by pipette, they would be stored in the tips and placed in the indoor temperature (about 20 °C) for at least 30 minutes. The standing of samples aims to wait their temperature warming up and be stable. Since the measurement of concentration is conducted by the digital refractometer which is affected by the temperature, the standing would be very important.

5.3. Refractometer calibration

A refractometer is a lab device for measuring the refractive index of solution. Based on the result of **refractive index (RI)**, the concentration of dissolved substances could be determined. For a certain chemical, RI values of different concentrations could be obtained through *Handbook of Chemistry and Physics* (Haynes, 2014). However, considering the specific refractometer used in the lab, to reveal the real relation between RI value and the solution concentration, refractometer calibration tests are performed. Figure 19 shows the digital refractometer used in tests, which is the type of KERN-ORF 1RS.

Figure 19 Digital refractometer used for measuring the concentration

Regarding the NaCl, 12 bottles of solution with different concentrations are prepared (2%, 4%, 6%, 8%, 10%, 12%, 16%, 18%, 20%, 22% and 24%). The solutions are prepared by the distilled water and sodium chloride powder. As for the $MgCl_2$, 11 solutions of different concentrations are prepared by the distilled water and the · **$MgCl_2·6H_2O$** Powder. The concentrations are set at 3%, 6%, 9%, 12%, 15%, 18%, 21%, 24%, 27%, 30% and 33%. All the concentration mentioned in this study is the mass fraction.

The concentration of all the solutions are measured by the refractometer. Hence, the relationship between the Concentration and RI value could be determined by the data analysis. With that, it is possible to determine the concentration through the RI value shown on the refractometer when the measurement is conducted.

6. Results and analysis

6.1. Refractometer calibration

6.1.1. Calibration for NaCl solution

Table 1 shows the results of calibration test for NaCl solution. 12 NaCl solution of different concentrations are prepared and the corresponding RI values are measured by the refractometer. The RI values are determined by the average of at least seven measurements. It is worth noting that the lower limit of measuring by this refractometer is 1.3330. While, the RI value of Bottle H1 (Concentration 1.94%) is 1.3330. So, results of H1 would be neglected.

Table 1 Results of calibration test for NaCl solution

Bottle	Designed Concentration	NaCl (g)	Water (g)	Real Concentration	RI
H1	2%	1.98	100	1.94%	1.3330
H3	4%	4.00	96	4.00%	1.3381
H4	6%	6.01	94	6.01%	1.3413
H5	8%	8.02	92	8.02%	1.3445
H6	10%	10.00	90.1	9.99%	1.3482
H7	12%	11.98	88	11.98%	1.3511
H8	14%	14.00	86	14.00%	1.3545
H9	16%	16.01	84	16.01%	1.3582
H10	18%	18.00	82	18.00%	1.3625
A3	20%	20.06	80	20.04%	1.3664
A4	22%	22.00	78	22.00%	1.3704
A5	24%	24.01	76	24.01%	1.3740

Figure 20 shows the relationship between the concentrations of NaCl solution and the corresponding RI values. The bule curve shows the real data of concentration and RI value measured by the refractometer. Data analysis is performed by Excel and the trendline could be determined, which is also the calibration curve of NaCl solution (Red curve). Regarding the trendline, quadratic polynomial regression is applied and the coefficient of determination R^2 is 0.9995. The relationship between the concentration and the RI values can be expressed as

$$Y = -23.243X^2 + 68.565X - 50.09 \qquad (14)$$

Where Y is the concentration and X is the RI value.

Through Formula (14), it is possible to determine the concentrations of NaCl solution with the RI values obtained from refractometer.

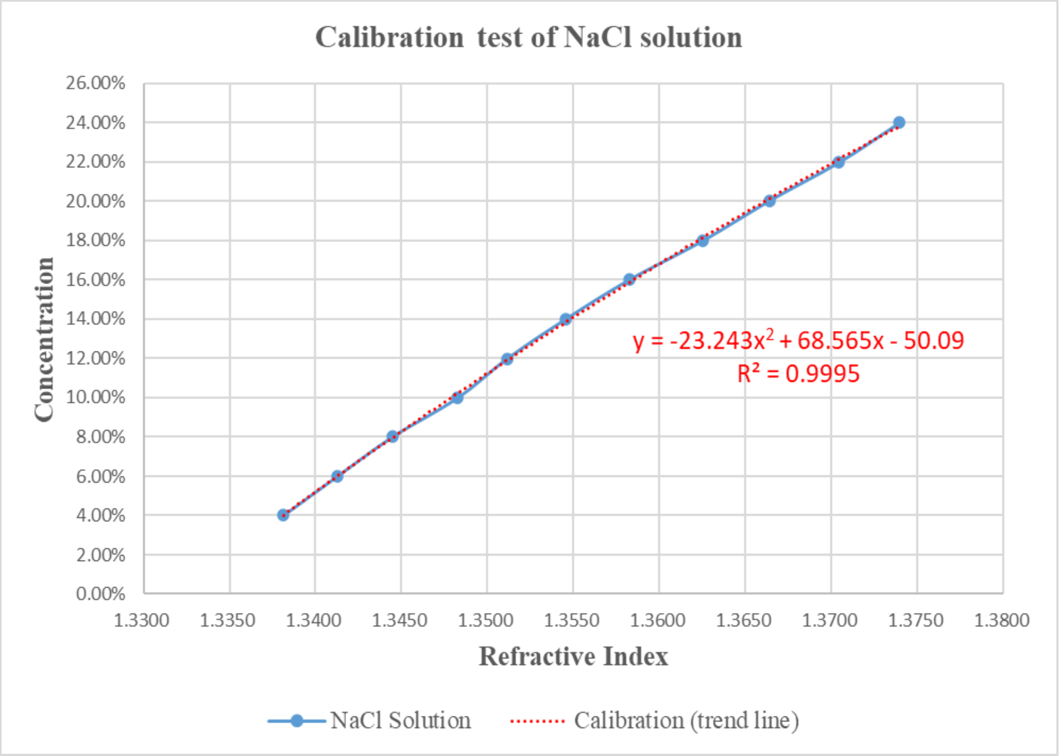


Figure 20 Relationship between the concentrations of NaCl solution and RI values

6.1.2. Calibration for $MgCl_2$ solution

Table 2 shows the results of calibration test for $MgCl_2$ solution. 11 $MgCl_2$ solutions of different concentrations ranging from 3% - 33% are prepared and their corresponding RI values are obtained.

Figure 21 illustrates the relationship between the concentrations of $MgCl_2$ solution and their corresponding RI values. The bule curve shows the real data of concentration and RI value measured by the refractometer. The red curve shows the trendline of the data, which could be regarded as the calibration curve of $MgCl_2$ solution. The quadratic polynomial regression is applied and the coefficient of determination R^2 is 0.9999. The relationship between the concentration and the RI values can be expressed as

$$Y = -4.186X^2 + 15.052X - 12.615 \tag{15}$$

Where Y is the concentration and X is the RI value.

Through Formula (15), it is possible to determine the concentrations of $MgCl_2$ solution with the RI values obtained from refractometer.

Table 2 Results of calibration test for $MgCl_2$ solution

Bottle	Designed Concentration	$MgCl_2*6H_2O$ (g)	Water (g)	Real Concentration	RI
A12	3	6.41	93.59	3.00%	1.3380
A11	6	12.81	87.19	6.04%	1.3458
A9	9	19.22	80.78	9.03%	1.3535
A8	12	25.63	74.37	12.02%	1.3618
H3	15	32.03	67.97	15.77%	1.3723
H4	18	38.44	61.56	18.02%	1.3793
H5	21	44.85	55.15	21.00%	1.3871
H6	24	51.25	48.75	23.78%	1.3953
H7	27	57.66	42.34	25.49%	1.4004
H8	30	64.07	35.93	30.01%	1.4143
H9	33	70.47	29.53	32.46%	1.4221

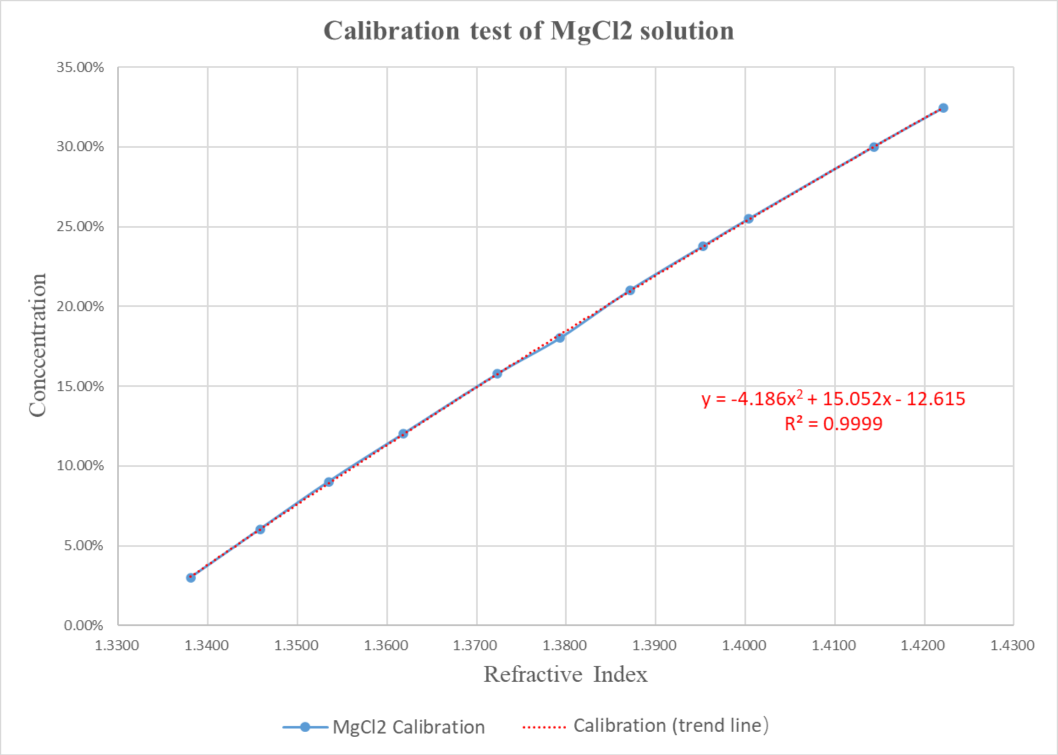


Figure 21 Relationship between the concentrations of $MgCl_2$ solution and the RI values

6.2. Exploring the law of salt concentration changing during the melting process

As mentioned above, during the melting process, the lower limit of the concentration of meltwater (salt solution) is the freezing point concentration and the upper limit is the solubility concentration. On the other hand, both freezing point concentration and solubility concentration are temperature dependent. So, the concentration of meltwater during the melting process would also be effected by the temperature.

Excluding the influence of temperature, in order to determine the specific location of the concentration data between the freezing point concentration and solubility concentration at a given temperature, a new parameter called **Percentage Value** is defined in this study. **Percentage Value** illustrates how close the solution concentration data is to the freezing point cocentration. It is defined as

$$Percentage = \frac{W_{solution} - W_{freezing}}{W_{solubility} - W_{freezing}} \times 100\% \tag{16}$$

Where $W_{solution}$ is the concentration of salt solution; $W_{freezing}$ is the freezing point concentration; $W_{solubility}$ is the solubility concentration.

For example, as shown in Figure 22, the orange point is the concentration data, where the solution concentration is 15% and the temperature is -5°C. While, the freezing point concentration at -5°C is 8.5% and the solubility concentration is 25.52%. Hence, the Percentage can be calculated as

$$Percentage = \frac{15\% - 8.5\%}{25.52\% - 8.5\%} \times 100\% = 38.2\% \tag{17}$$

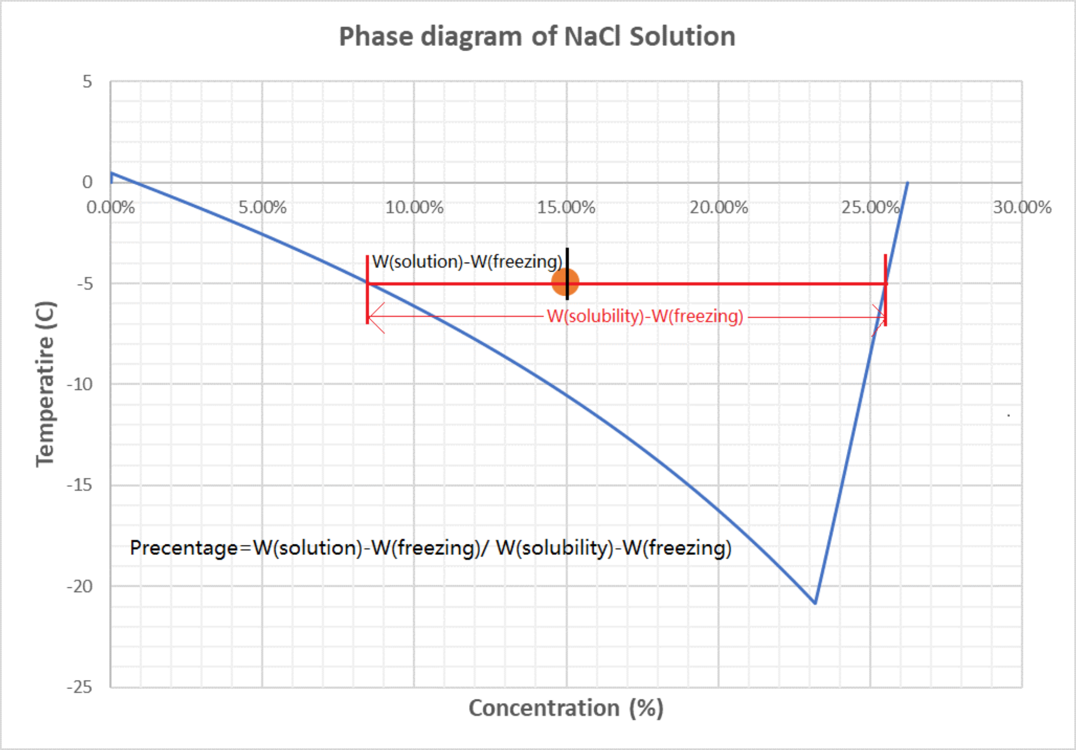


Figure 22 Illustration of the parameter Percentage Value

6.2.1. NaCl tests at -5℃

The results of NaCl tests at -5°C are summarized in Table 3 and Table 4. Both two tests are measured from 3 minutes to 120 minutes. It is noteworthy that the time when the salt particles are most likely to have disappeared is also recorded. The time of salt disppeared for Test 1 is about 38 minutes and for Test 2 is about 30 minutes, which are marked in green in the tables. For test 1, at the time of "disappeared", the concentration is about 11.18% and the Percentage Value is 3.30%. While, for test two, the concentration is 9.75% and Percentage Value is 2.00%.

Table 3 Results of NaCl Test 1 (-5°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
3	-5.7	1.3611	9.43%	25.42%	17.39%	49.78%
4	-7.3	1.3585	11.43%	25.19%	16.02%	33.35%
5	-7.7	1.3576	11.91%	25.13%	15.54%	27.46%
6	-8.8	1.3573	13.16%	24.97%	15.35%	18.58%
8	-8.9	1.3585	13.27%	24.96%	16.00%	23.37%
12	-8.6	1.3564	12.93%	25%	14.87%	16.09%
14	-7.7	1.3568	11.91%	25.13%	15.07%	23.88%
16	-7.6	1.3545	11.79%	25.14%	13.83%	15.26%
20	-6.5	1.3506	10.46%	25.30%	11.60%	7.68%
30	-6.7	1.3521	10.70%	25.27%	12.43%	11.90%
38	-6.7	1.3499	10.70%	25.27%	11.18%	3.30%
45	-5.1	1.3461	8.63%	25.50%	8.96%	1.96%
60	-5.3	1.3458	8.90%	25.47%	8.78%	-0.72%
90	-4.7	1.3434	8.09%	25.56%	7.29%	-4.59%
120	-4.7	1.3436	8.09%	25.56%	7.40%	-3.94%

Table 4 Results of NaCl Test 2 (-5°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
3	-6.6	1.3578	10.58%	25.29%	15.61%	34.17%
4	-8.5	1.3563	12.82%	25.01%	14.81%	16.29%
6	-9.1	1.3593	13.49%	24.93%	16.44%	25.78%
8	-8	1.3566	12.26%	25.09%	14.98%	21.21%
10	-7	1.3555	11.07%	25.23%	14.36%	23.25%
12	-7.6	1.3570	11.79%	25%	15.19%	25.47%
14	-8.4	1.3585	12.71%	25.03%	16.01%	26.82%
16	-7.3	1.3565	11.43%	25.19%	14.89%	25.17%
20	-7.1	1.3537	11.19%	25.22%	13.33%	15.28%
25	-5.9	1.3485	9.69%	25.39%	10.37%	4.33%
30	-5.7	1.3475	9.43%	25.42%	9.75%	2.00%
40	-5.2	1.3453	8.77%	25.49%	8.43%	-2.03%
60	-4.9	1.3448	8.36%	25.53%	8.17%	-1.12%
90	-4.8	1.3440	8.23%	25.55%	7.67%	-3.24%
120	-4.6	1.3430	7.95%	25.57%	7.07%	-4.99%

Figure 23 shows the concentraion development for NaCl tests at -5°C. The results of two groups of tests have shown good similarity. In general, the concentration of salt solution would decrease over time. The rate of decreasing would decrease with time and the concentration tends to be stable after the melting process finished. The final value of concentration is about 7.5%. Theoretically, the stable concentration is the freezing point concentration at the environment temperature. As mentioned above, the "disappeared time" are recorded, which are marked with red circles. It is possible to find that after the "disappeared time", the rates of concentration declining would be lower than the rates before the "disappeared time" (Test 1 is 38 minutes and Test 2 is 30 minutes). Especially for test 2, the "disappeared time" data splits the line chart into parts, where the concentration changes rapidly in the first part and is relatively stable in the second part.

It is also possible to find that there are some fluctuations between 4 minutes and 8 minutes. This would mainly be because all the data at different time points are collected from the different samples. As introduced in Section 5.2.1, it is impossible to trace the concentration on the same sample. So, every data point is from an individual sample. There would be some differences between each sample, including the shape and size of salt particle, the direction of penetrating, the fluctuation of room temperature and so on, which all might influence the melting process. On the other hand, the time interval of data points is very small in this part, only 2 minutes and the variation of concentration is less than 2%. Hence, the fluctuation would be acceptable. More discussions about the fluctuation are performed in Section 7.2.1.

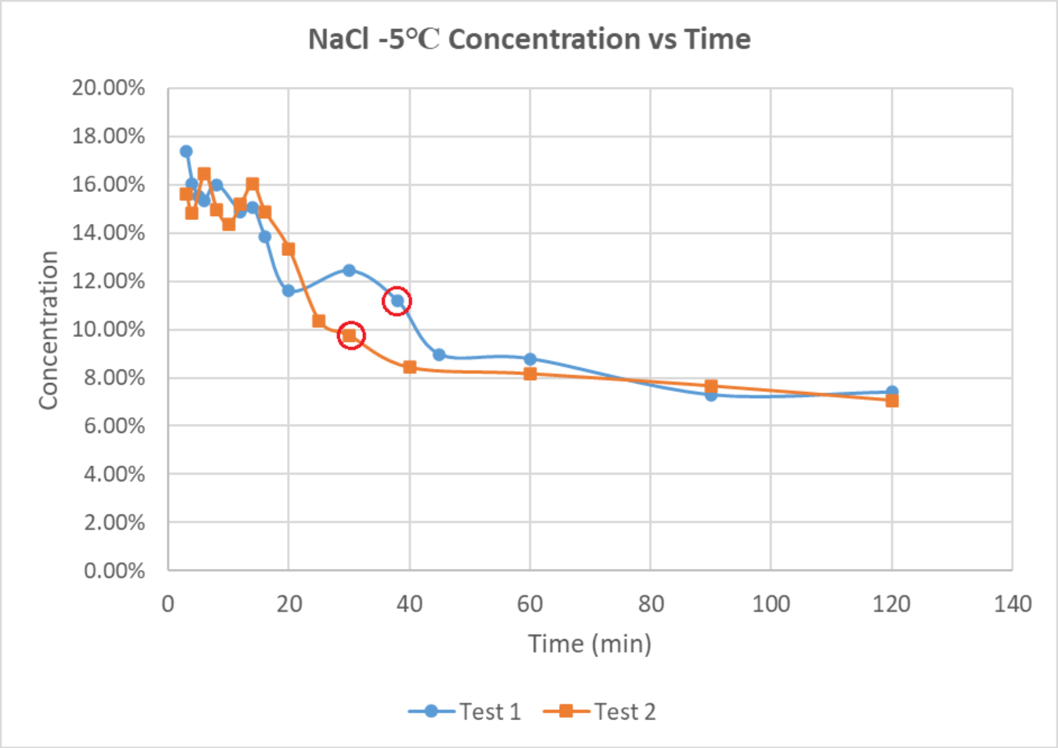


Figure 23 Concentration development of NaCl test at -5°C

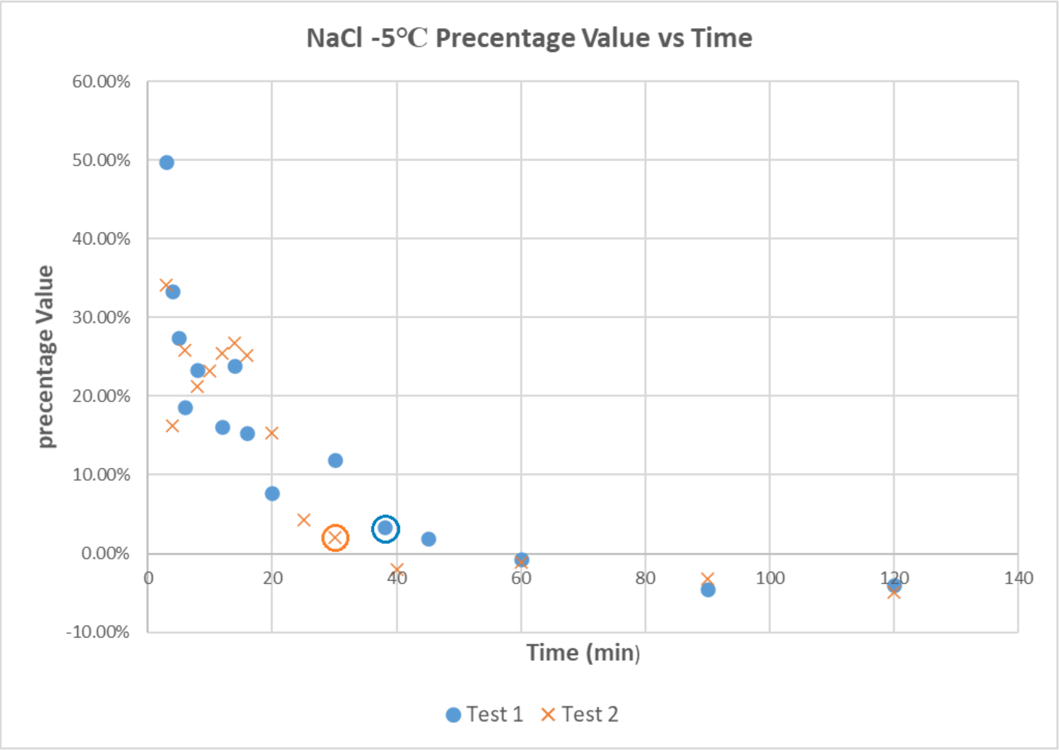


Figure 24 Percentage Value over time for NaCl test at -5°C

Figure 24 shows the results of Percentage Value over time for NaCl test at -5°C. The data on the "disappeared time" of two tests are also marked with circles in the chart. Basically, the results of two repetition tests have relatively good similarity. The trend of Percentage is to decrease with time and eventually be stable. The rate of declining slows down gradually. The stage before "disappeared time" shows some fluctuations, especially for test 2. Between 6 minutes and 16 minutes, the Percentage Value fluctuates between 21% and 26% in test 2. The main reason of that would be same with the concentration data fluctuation. The differences between the individual samples cause the melting processing differently. And in this stage, the time interval is very small, which would make these differences stand out. But generally, the Percentage Value still declines over time in the stage before the "disappeared time" and the decline rate is much higher than the stage after the "disappeared time".

6.2.2. MgCl2 tests at -5℃

The results of $MgCl_2$ tests at -5℃ are summarized in Table 3 and Table 4. Test 1 is measured from 1.5 minutes to 40 minutes, while test 2 is measured until 60 minutes. As for test 1, the salt is most likely to be disappeared from the sample at 10 minutes. For test 2, the "disappeared time" is 7 minutes. At the "disappeared time", the concentration of test 1 is about 11.65% and the Percentage is 11.88%. While, for test two, the concentration is 11.13% and Percentage is 10.52%.

Table 5 Results of $MgCl_2$ Test 1 (-5℃)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
1.5	-5.6	1.3757	8.45%	33.95%	16.97%	33.43%
2	-6.1	1.3766	8.92%	33.84%	17.31%	33.66%
3	-5.8	1.3722	8.65%	33.91%	15.75%	28.10%
4	-6.3	1.3715	9.10%	33.79%	15.49%	25.90%
5	-5.9	1.3679	8.73%	33.88%	14.21%	21.78%
6	-6	1.3676	8.83%	34%	14.08%	20.99%
7	-6.3	1.3663	9.10%	33.79%	13.63%	18.35%
8	-5.9	1.3631	8.73%	33.88%	12.47%	14.87%
10	-5.8	1.3609	8.65%	33.91%	11.65%	11.88%
12	-5.5	1.3573	8.36%	33.98%	10.33%	7.70%
15	-5.1	1.3522	7.97%	34.07%	8.45%	1.85%
20	-4.9	1.3511	7.76%	34.12%	8.04%	1.06%
30	-4.8	1.3503	7.66%	34.14%	7.74%	0.31%
40	-4.7	1.3495	7.55%	34.16%	7.42%	-0.49%

Table 6 Results of $MgCl_2$ Test 2 (-5°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
1.5	-5.6	1.3767	8.45%	33.95%	17.32%	34.79%
2	-5.7	1.3722	8.55%	33.93%	15.74%	28.33%
3	-6	1.3713	8.83%	33.86%	15.42%	26.32%
4	-6.3	1.3694	9.10%	33.79%	14.75%	22.90%
5	-6	1.3651	8.83%	33.86%	13.20%	17.47%
6	-6	1.3627	8.83%	34%	12.32%	13.93%
7	-5.6	1.3595	8.45%	33.95%	11.13%	10.52%
10	-5.4	1.3574	8.26%	34.00%	10.38%	8.24%
12	-5.6	1.3570	8.45%	33.95%	10.23%	6.99%
15	-5.1	1.3538	7.97%	34.07%	9.05%	4.13%
20	-5	1.3535	7.86%	34.09%	8.93%	4.07%
30	-4.8	1.3504	7.66%	34.14%	7.78%	0.45%
40	-4.6	1.3486	7.45%	34.19%	7.09%	-1.35%
60	-4.7	1.3489	7.55%	34.16%	7.21%	-1.28%

Figure 25 shows the concentration development of $MgCl_2$ at -5°C. The results of two groups have good similarity. The concentration keeps falling over time and tend to be stable at approximately 7.4%. Considering the “disappeared time”, the stage before it is named stage 1 and the latter part is called stage 2. The decline rate of test 2 in stage 1 is larger than test 1 and the “disappeared time” is also earlier than test 1. So, the melting process of test 2 would be likely to be a bit faster than test 1. In addition, in test 2, the “disappeared time” data clearly splits the line chart into two different parts. The rate of falling in stage 1 is much larger than it in stage 2. While, for test 1, in general the decline rate in stage 2 is lower than it in stage 1. But within the 5 five minutes after the “disappeared time”, the decline rate still seems to keep relatively large.

Figure 26 shows the results of Percentage Value over time for $MgCl_2$ test at -5°C. The Percentage Value declines gradually and would be stable eventually. Decline rate in stage 1 is larger than it in stage 2. Especially for test 2, the difference between two stages is obvious. In addition, the Percentage Value in part 1 looks probably linearly related with time.

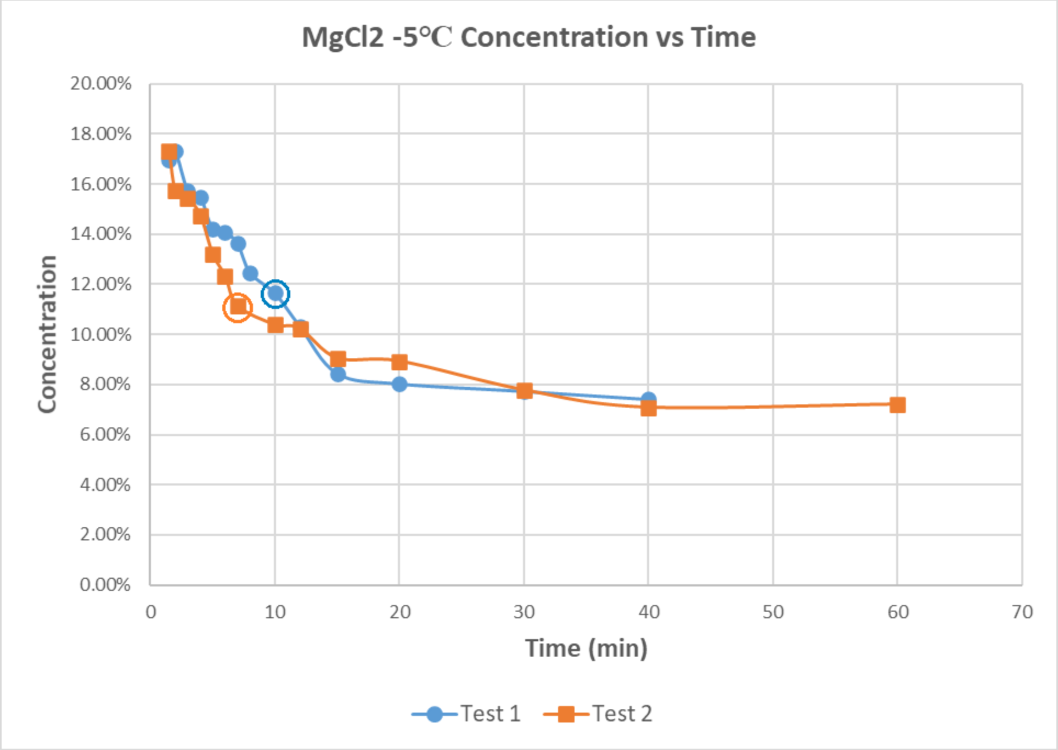


Figure 25 Concentration development of $MgCl_2$ test at -5°C

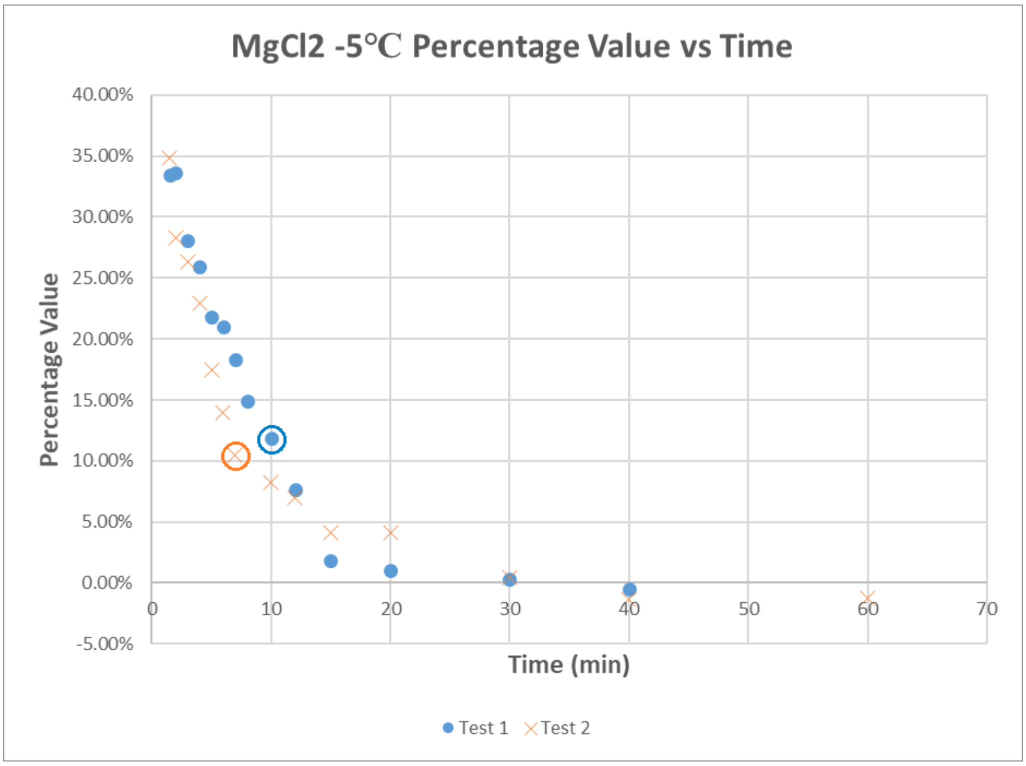


Figure 26 Percentage Value over time for $MgCl_2$ test at -5°C

6.2.3. NaCl tests at -10℃

Table 7 and Table 8 summarized the results of NaCl tests at -10°C. In test 1, the salt is likely to be disappeared at 60 minutes, while for test 2, is about 80 minutes. At the “disappeared time”, the concentration of test 1 is 14.24% and the Percentage Value is about 0.1%. Regarding test 2, the concentration is 14.03% and the Percentage is about -1.90%. Figure 27 shows the concentration changing of NaCl test at the temperature of -10°C. Results show good similarity, where the concentration declines over time. The declining rate in stage 1 (before “disappeared time”) is obviously larger than it in stage 2. As shown, the line of test 2 keeps a bit higher than the line of test 1 and the “disappeared time” is later than test 1. In addition, the final concentration of test 2 is a bit larger than test 1. So, it is reasonable to expect that the real test temperature of test 2 would be a bit lower than test 1.

Figure 28 shows the results of Percentage Value development of NaCl test at -10°C. The trend of Percentage is falling over time and the rate of falling in part 1 is higher than part 2. In test 1, the Percentage seems to be stable from 35 minutes to 60 minutes and after “disappeared time” (60 minutes), it declines again. While, in test 2, the Percentage seems to keep decreasing. The reason of this might be the data fluctuation as explained. Also, from observation, it is possible to find that the declining rate would be very large at the very beginning of test, but seems to getting smaller over time. So, between 35 minutes and 60 minutes the rate of decreasing might be relatively small.

Table 7 Results of NaCl Test 1 (-10°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
5	-11.7	1.3636	16.13%	24.55%	18.73%	44.71%
10	-10.6	1.3605	15.06%	24.71%	17.08%	26.50%
15	-11.7	1.3626	16.13%	24.55%	18.18%	32.14%
20	-11.4	1.3602	15.84%	24.60%	16.93%	14.25%
25	-11.8	1.3600	16.22%	24.54%	16.79%	7.40%
30	-11.1	1.3591	15.55%	25%	16.35%	9.70%
35	-10.5	1.3567	14.95%	24.73%	15.04%	0.90%
40	-10.5	1.3566	14.95%	24.73%	14.99%	0.44%
45	-10.5	1.3567	14.95%	24.73%	15.01%	0.67%
55	-10.4	1.3563	14.85%	24.74%	14.82%	-0.34%
60	-9.8	1.3553	14.23%	24.83%	14.24%	0.10%
70	-9.7	1.3542	14.13%	24.84%	13.65%	-4.30%
80	-9.6	1.3535	14.02%	24.86%	13.23%	-6.80%
120	-9.6	1.3537	14.02%	24.86%	13.38%	-5.59%
150	-9.6	1.3535	14.02%	24.86%	13.25%	-6.60%

Table 8 Results of NaCl Test 2 (-10°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
3	-11.3	1.3661	15.75%	24.61%	20.01%	48.06%
5	-12.7	1.3641	17.06%	24.41%	18.98%	26.08%
10	-12.3	1.3625	16.69%	24.47%	18.12%	18.33%
15	-11.7	1.3619	16.13%	24.55%	17.84%	20.34%
20	-11	1.3609	15.45%	24.65%	17.28%	19.93%
40	-11	1.3594	15.45%	25%	16.47%	11.11%
50	-10.5	1.3577	14.95%	24.73%	15.55%	6.15%
60	-10.6	1.3564	15.06%	24.71%	14.87%	-1.95%
70	-10	1.3554	14.44%	24.80%	14.30%	-1.39%
80	-9.8	1.3549	14.23%	24.83%	14.03%	-1.90%
90	-9.7	1.3549	14.23%	24.84%	14.05%	-1.69%
110	-9.6	1.3542	14.02%	24.86%	13.63%	-3.64%
130	-9.7	1.3546	14.13%	24.84%	13.84%	-2.72%
150	-9.7	1.3548	14.13%	24.84%	13.96%	-1.57%

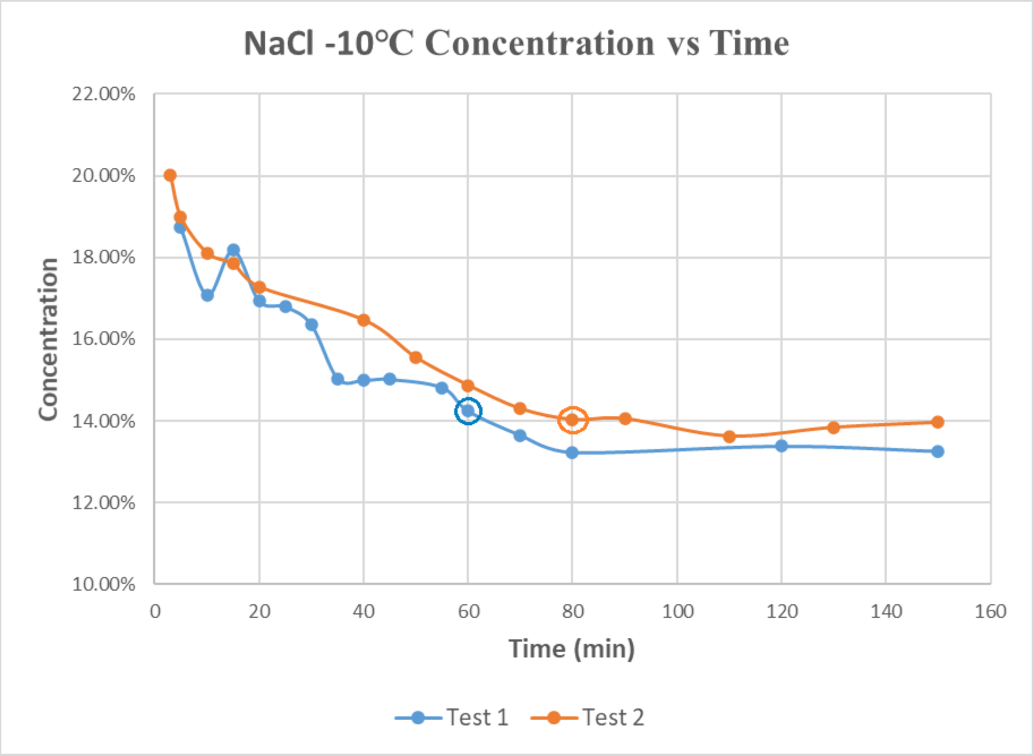


Figure 27 Concentration development of NaCl test at -10°C

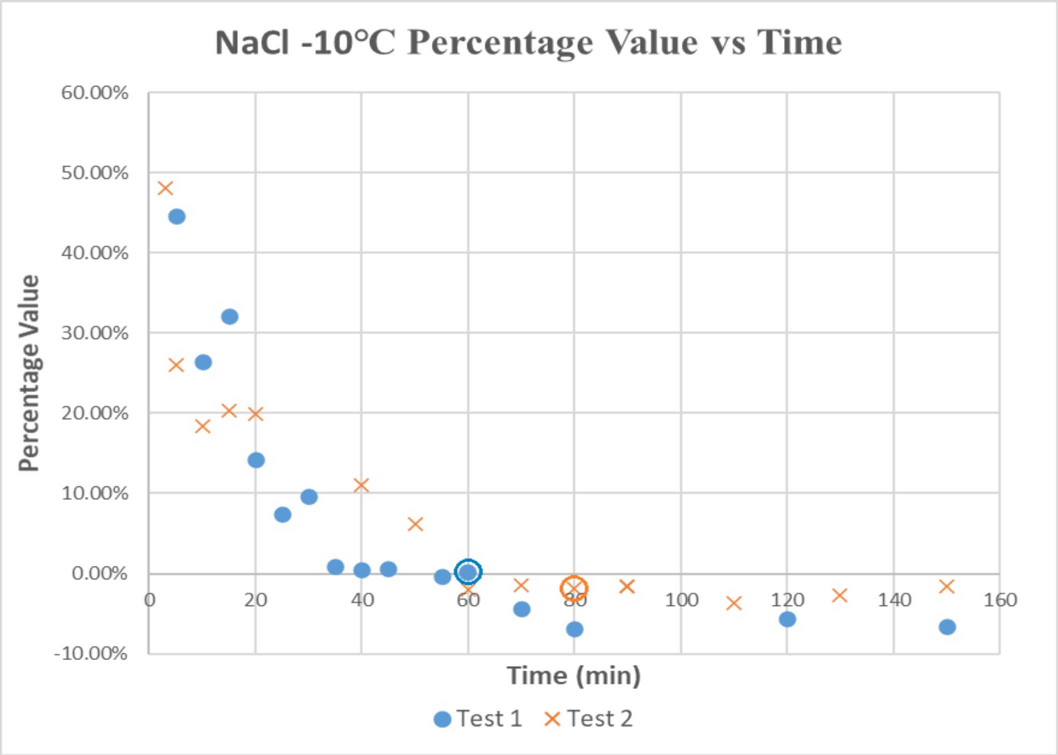


Figure 28 Percentage Value over time for NaCl test at -10°C

6.2.4. MgCl2 tests at -10℃

Table 9 and Table 10 shows the results of $MgCl_2$ tests at -10°C. The "disappeared time" are recorded, which are 14 minutes in both test 1 and test 2. For test 1, the corresponding concentration is 13.49% and the Percentage is 7.88%. For test 2, the concentration is 13.59% and the Percentage is 7.39%.

Figure 29 shows the results of concentration development of MgCl2 at -10°C. Results of two tests have very good similarity. Same as other tests, the concentration keeps falling during the melting process. The rate of decreasing obviously slows down after the "disappeared time". The lines in stage 1 might close to linearly related. The reason why there is a relatively large difference between 20 minutes and 45 minutes is that one data point in test 1 at 30 minutes was missed. So, the points at 20 minutes and 45 minutes are directly connected when data processing is conducted by Excel.

Figure 30 shows the results of Percentage Value development for the $MgCl_2$ tests at -10°C. Two repetition tests have very high similarity and the "disappeared time" point are almost coincident in the figure. The Percentage Values keeps decreasing during the melting process. The "disappeared time" point splits the line into two different stages, where the decline rate in stage 1 is much larger than it in stage 2. Also, in stage 1 the Percentage seems to be linearly related with time.

Table 9 Results of $MgCl_2$ Test 1 (-10°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
2	-10.2	1.3845	12.10%	32.94%	20.07%	38.26%
3	-10.5	1.3858	12.30%	32.88%	20.50%	39.82%
4	-10.6	1.3803	12.37%	32.86%	18.61%	30.43%
5	-10.5	1.3789	12.30%	32.88%	18.09%	28.16%
6	-10.5	1.3765	12.30%	32.88%	17.27%	24.16%
7	-10.6	1.3790	12.37%	33%	18.13%	28.11%
8	-10.2	1.3742	12.10%	32.94%	16.45%	20.88%
10	-10.3	1.3693	12.17%	32.92%	14.70%	12.17%
12	-9.7	1.3658	11.77%	33.05%	13.44%	7.88%
14	-9.9	1.3659	11.90%	33.01%	13.49%	7.54%
20	-9.8	1.3643	11.84%	33.03%	12.91%	5.06%
45	-9.5	1.3604	11.63%	33.09%	11.48%	-0.68%
60	-9.6	1.3599	11.69%	33.07%	11.28%	-1.93%
90	-9.6	1.3600	11.69%	33.07%	11.31%	-1.76%

Table 10 Results of $MgCl_2$ Test 2 (-10°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
2	-10.5	1.3841	12.30%	32.88%	19.92%	37.03%
3	-10.2	1.3825	12.10%	32.94%	19.37%	34.87%
4	-10.6	1.3804	12.37%	32.86%	18.63%	30.54%
5	-10.6	1.3795	12.37%	32.86%	18.33%	29.10%
6	-10.4	1.3766	12.23%	32.90%	17.29%	24.46%
7	-10.5	1.3762	12.30%	33%	17.14%	23.54%
8	-10.3	1.3731	12.17%	32.92%	16.06%	18.75%
10	-10.5	1.3738	12.30%	32.88%	16.29%	19.41%
12	-10.3	1.3713	12.17%	32.92%	15.41%	15.62%
14	-10.1	1.3662	12.04%	32.97%	13.59%	7.39%
20	-9.8	1.3627	11.84%	33.03%	12.33%	2.32%
25	-9.7	1.3616	11.77%	33.05%	11.91%	0.67%
30	-9.6	1.3602	11.69%	33.07%	11.39%	-1.39%
45	-9.6	1.3605	11.69%	33.07%	11.50%	-0.90%
60	-9.6	1.36042	0.1169	33.07%	11.48%	-0.97%

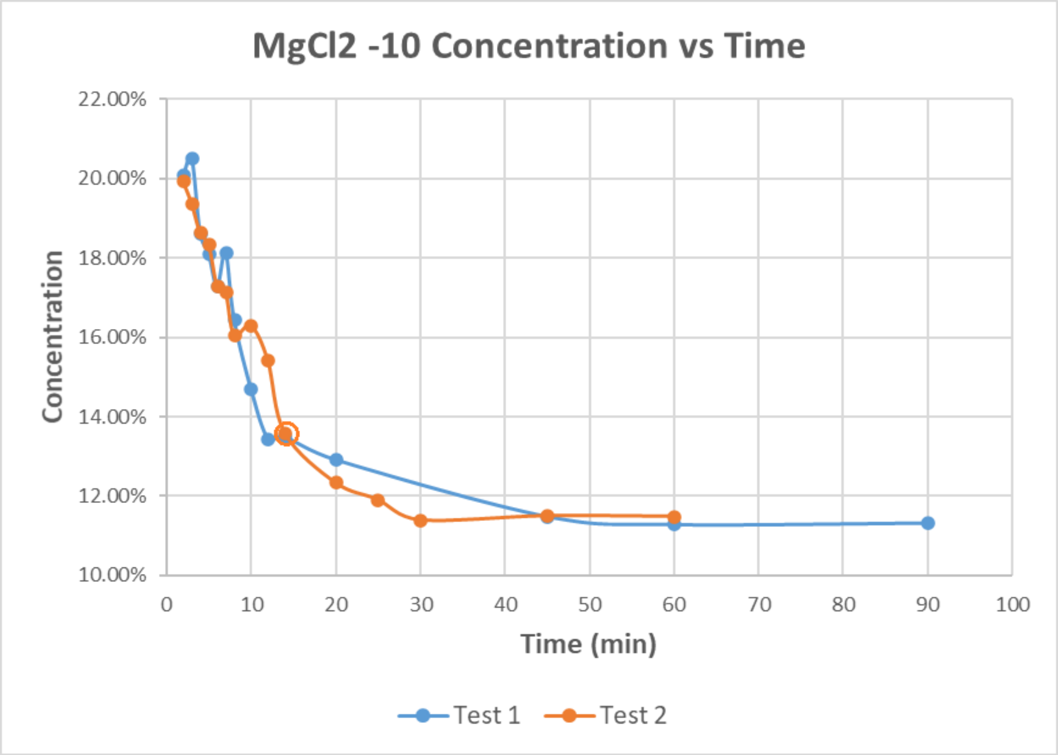


Figure 29 Concentration development of $MgCl_2$ test at -10℃

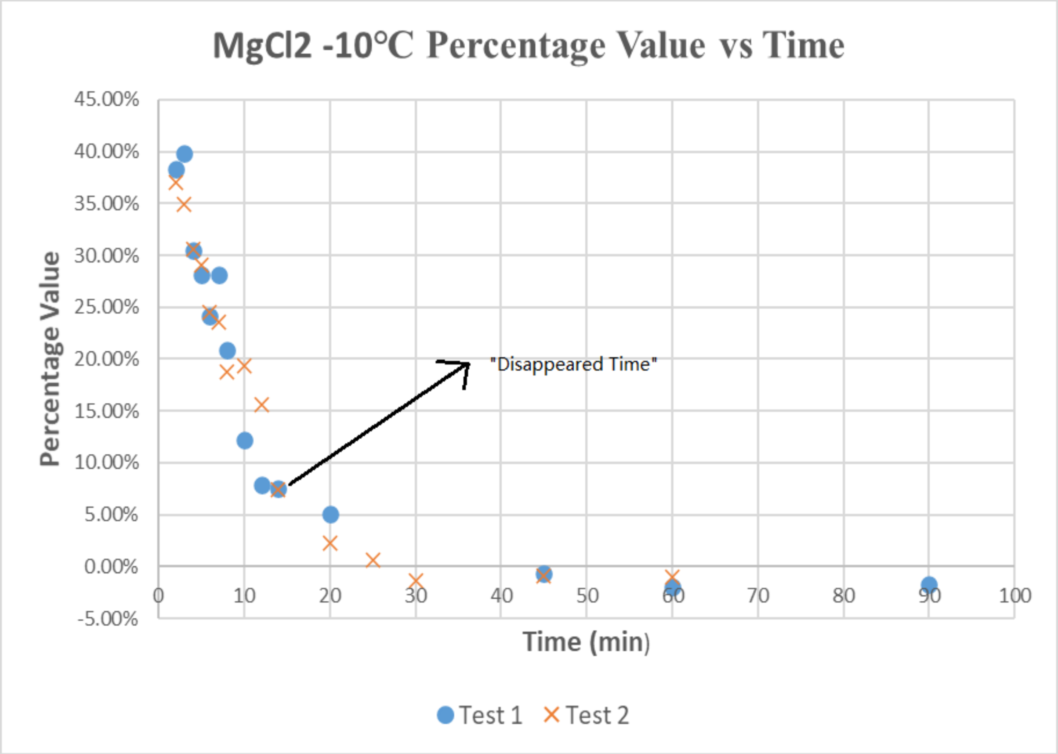


Figure 30 Percentage Value over time for $MgCl_2$ test at -10℃

6.2.5. NaCl tests at -15℃

The results of NaCl test at -15°C are summarized in Table 11 and Table 12. Melting process is very slow under these conditions and the first sampling is conducted at 20 minutes. The "disappeared time" in test 1 is 160 minutes and 180 minutes in test 2. The corresponding concentration is 18.41% and the Percentage Value is -8.64% in test 1. In test 2, they are 18.29% and -7.50% respectively.

Figure 31 shows the concentration development. The fluctuation in two tests are relatively large, but the trend of concentration is still decreasing over time. The starting points and "disappeared time" points in two lines are not much different with each other.

Figure 32 shows the results of Percentage Value development for NaCl test at -15°C. Both two tests have relatively scattered results, especially for the stage 1 in test 2. But it is still possible to find that the Percentage is very large and ends with low values. In test 1, the trend of declining is still obvious. While, in test 2, the data points are quite scattered. At the "disappeared time", the concentration of test 1 is about 16.07% and the Percentage is 7.67%. While, for test two, the concentration is 15.40% and Percentage is 3.47%.

Table 11 Results of NaCl Test 1 (-15°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
20	-14.9	1.3683	18.94%	24.09%	21.07%	41.37%
30	-15.6	1.3652	19.50%	23.98%	19.52%	0.46%
40	-15.4	1.3676	19.35%	24.01%	20.73%	29.73%
50	-15.1	1.3658	19.11%	24.06%	19.86%	15.08%
60	-15.8	1.3674	19.66%	23.96%	20.66%	23.33%
80	-14.9	1.3656	18.94%	24%	19.75%	15.82%
100	-15.3	1.3662	19.27%	24.03%	20.02%	15.72%
120	-14.9	1.3646	18.94%	24.09%	19.20%	5.11%
140	-15.6	1.3660	19.50%	23.98%	19.96%	10.22%
160	-14.8	1.3630	18.86%	24.10%	18.41%	-8.64%
185	-14.7	1.3639	18.78%	24.12%	18.84%	1.18%
220	-15.1	1.3642	19.11%	24.06%	19.04%	-1.51%
240	-14.6	1.3622	18.70%	24.13%	18.00%	-12.89%

Table 12 Results of NaCl Test 2 (-15°C)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
20	-15.5	1.3689	19.42%	24.00%	21.39%	42.94%
31	-14.9	1.3661	18.94%	24.09%	19.99%	20.35%
40	-15.6	1.3649	19.50%	23.98%	19.37%	-2.96%
50	-15.3	1.3648	19.27%	24.03%	19.31%	0.75%
60	-15.1	1.3649	19.11%	24.06%	19.38%	5.40%
70	-15.4	1.3649	19.35%	24%	19.38%	0.70%
80	-15	1.3647	19.02%	24.07%	19.25%	4.64%
100	-15.5	1.3651	19.42%	24.00%	19.50%	1.75%
120	-14.8	1.3646	18.86%	24.10%	19.23%	7.14%
140	-14.8	1.3638	18.86%	24.10%	18.81%	-0.92%
160	-14.7	1.3651	18.78%	24.12%	19.48%	13.10%
180	-14.6	1.3628	18.70%	24.13%	18.29%	-7.50%
200	-14.6	1.3635	18.70%	24.13%	18.67%	-0.61%
240	-14.6	1.3627	18.70%	24.13%	18.24%	-8.46%

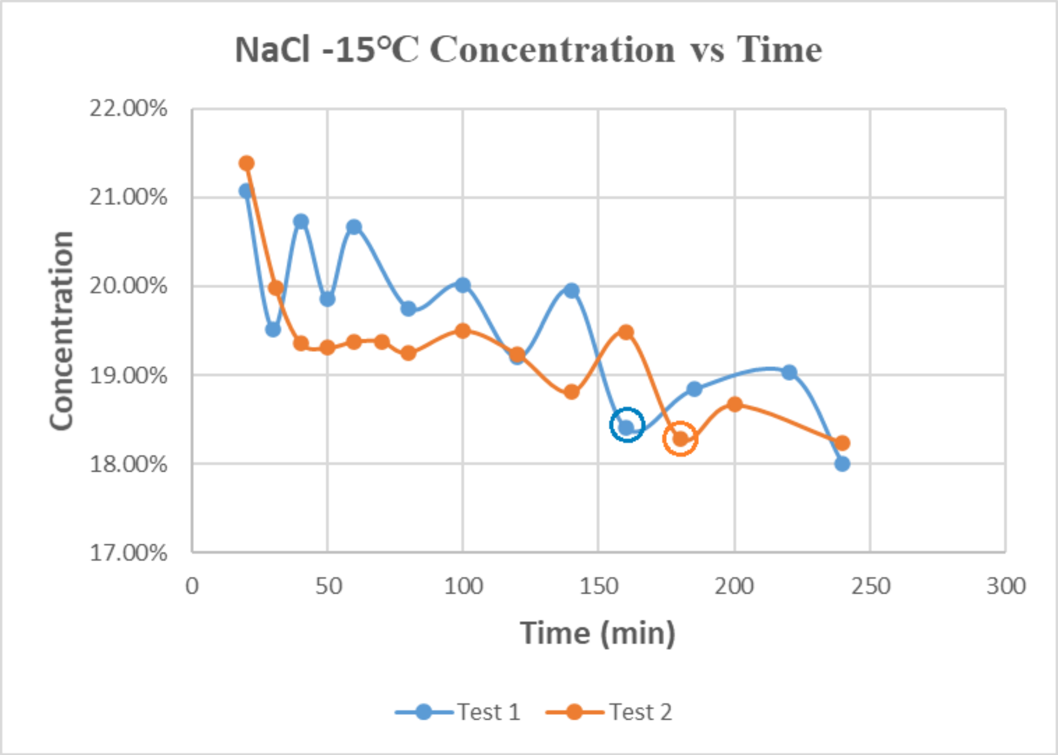


Figure 31 Concentration development of NaCl test (-15℃)

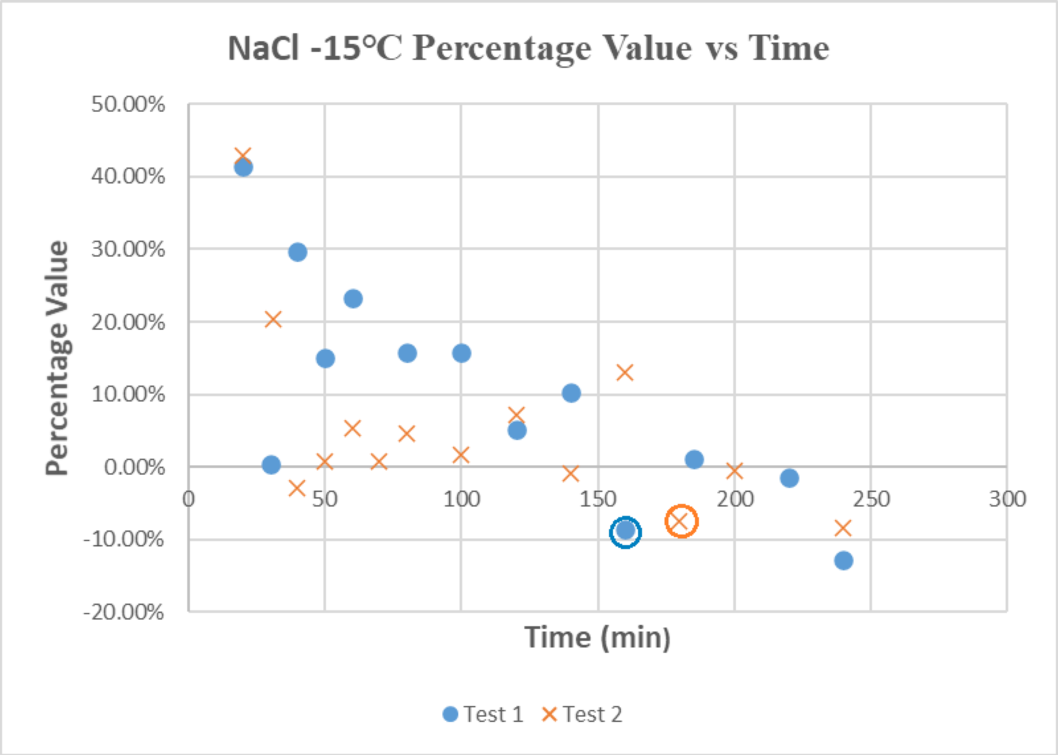


Figure 32 Percentage Value over time for NaCl test at -15℃

6.2.6. MgCl2 tests at -15℃

Table 13 and Table 14 summarized the results of MgCl2 tests at -15°C. Both tests are measured between 2 minutes and 60 minutes. The “disappeared time” is 20 minutes in test 1 and 30 minutes in test 2. At the “disappeared time”, the concentration of test 1 is about 16.07% and the Percentage is 7.67%. While, for test two, the concentration is 15.40% and Percentage is 3.47%.

As shown in Figure 33, the results of two repetition tests have good similarity. The concentration keeps falling and the “disappeared time” points split the lines obviously, where the falling rates in stage 1 are much higher than stage 2.

Figure 34 shows the results of Percentage Value. Same as the result under other conditions, the Percentage keeps falling over time. In stage 1(before “disappeared time”), both two tests show the results, where the Percentage looks to be linearly related with time. The declining in stage 2 is much slower than it in stage 1.

Table 13 Results of $MgCl_2$ Test 1 (-15℃)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
2	-15.2	1.3939	14.95%	31.93%	23.29%	49.12%
3	-15.2	1.3905	14.95%	31.93%	22.11%	42.19%
4	-15.1	1.3919	14.90%	31.95%	22.60%	45.15%
5	-15	1.3924	14.85%	31.97%	22.76%	46.18%
6	-14.9	1.3881	14.80%	31.99%	21.29%	37.74%
7	-14.9	1.3884	14.80%	32%	21.39%	38.33%
8	-15.2	1.3844	14.95%	31.93%	20.02%	29.86%
10	-15.1	1.3822	14.90%	31.95%	19.24%	25.48%
12	-15	1.3858	14.85%	31.97%	20.51%	33.06%
15	-14.9	1.3787	14.80%	31.99%	18.05%	18.88%
20	-14.8	1.3731	14.75%	32.01%	16.07%	7.67%
30	-14.4	1.3723	14.55%	32.09%	15.76%	6.90%
40	-14.6	1.3712	14.65%	32.05%	15.37%	4.16%
50	-14.7	1.3690	14.70%	32.03%	14.58%	-0.71%
60	-14.6	1.3689	14.65%	32.05%	14.54%	-0.60%

Table 14 Results of MgCl2 Test 2 (-15℃)

Time (min)	Tem (℃)	RI	$W_{freezing}$	$W_{solubility}$	$W_{solution}$	Percentage
2	-14.8	1.3938	14.75%	32.01%	23.25%	49.24%
3	-14.8	1.3929	14.75%	32.01%	22.94%	47.44%
4	-15.1	1.3921	14.90%	31.95%	22.67%	45.55%
5	-15	1.3880	14.85%	31.97%	21.27%	37.52%
6	-15.2	1.3883	14.95%	31.93%	21.38%	37.84%
7	-15	1.3877	14.85%	32%	21.16%	36.88%
10	-15.3	1.3827	15.00%	31.91%	19.45%	26.31%
13	-15.3	1.3828	15.00%	31.91%	19.46%	26.35%
15	-15.3	1.3816	15.00%	31.91%	19.05%	23.93%
20	-15.2	1.3774	14.95%	31.93%	17.58%	15.50%
30	-14.9	1.3712	14.80%	31.99%	15.40%	3.47%
40	-14.7	1.3692	14.70%	32.03%	14.67%	-0.19%
50	-14.7	1.3680	14.70%	32.03%	14.24%	-2.68%
60	-14.7	1.3683	14.70%	32.03%	14.34%	-2.10%

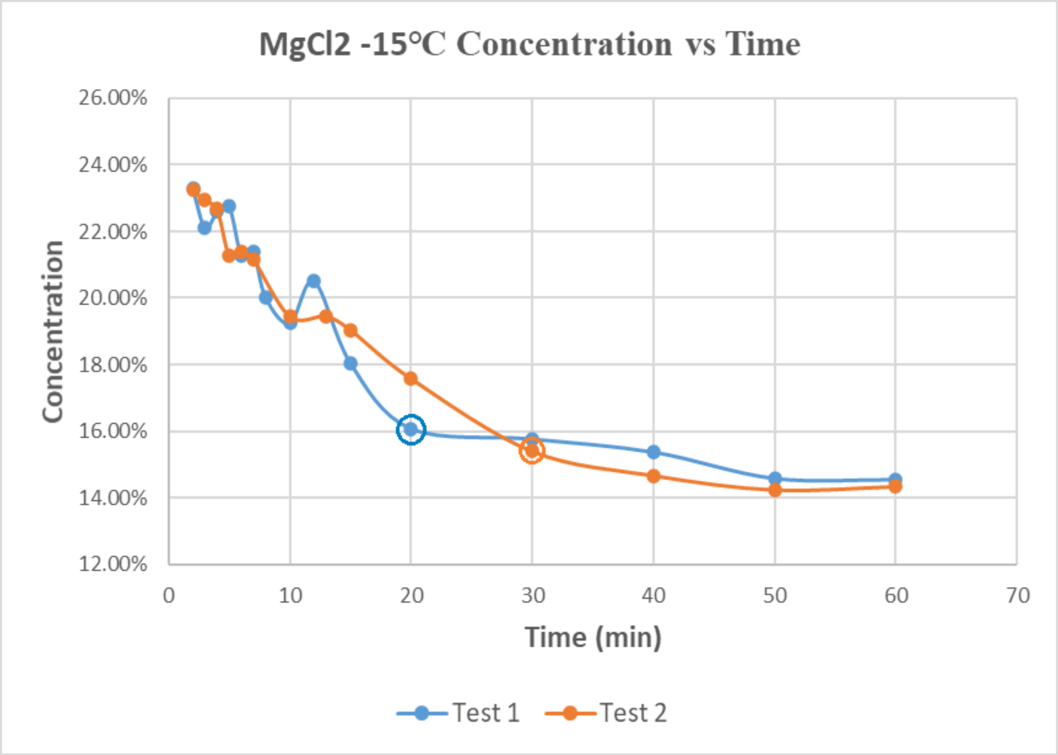


Figure 33 Concentration development of $MgCl_2$ test at -15°C

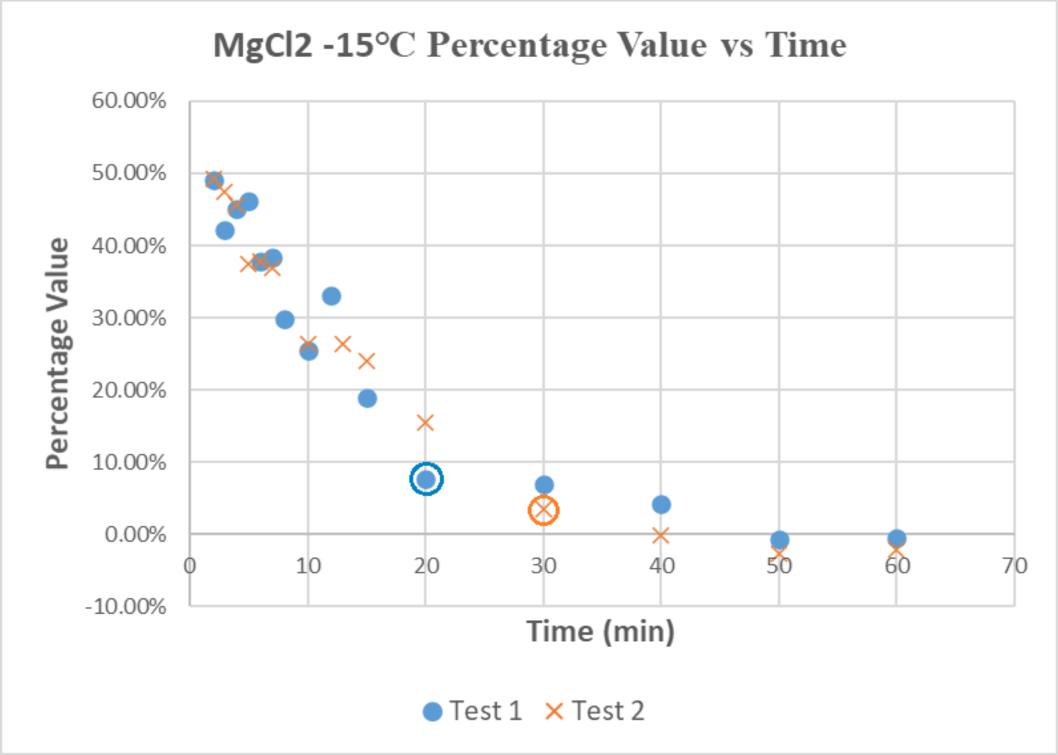


Figure 34 Percentage Value over time for $MgCl_2$ test at -15°C

7. Discussion

7.1. $MgCl_2$ tests

7.1.1. Law of Percentage Value development

According to the results in Chapter 6, it is possible to find that the data fluctuation of $MgCl_2$ tests are much smaller than the NaCl tests. Hence, to explore the law of Percentage Value development, the $MgCl_2$ tests data are discussed firstly.

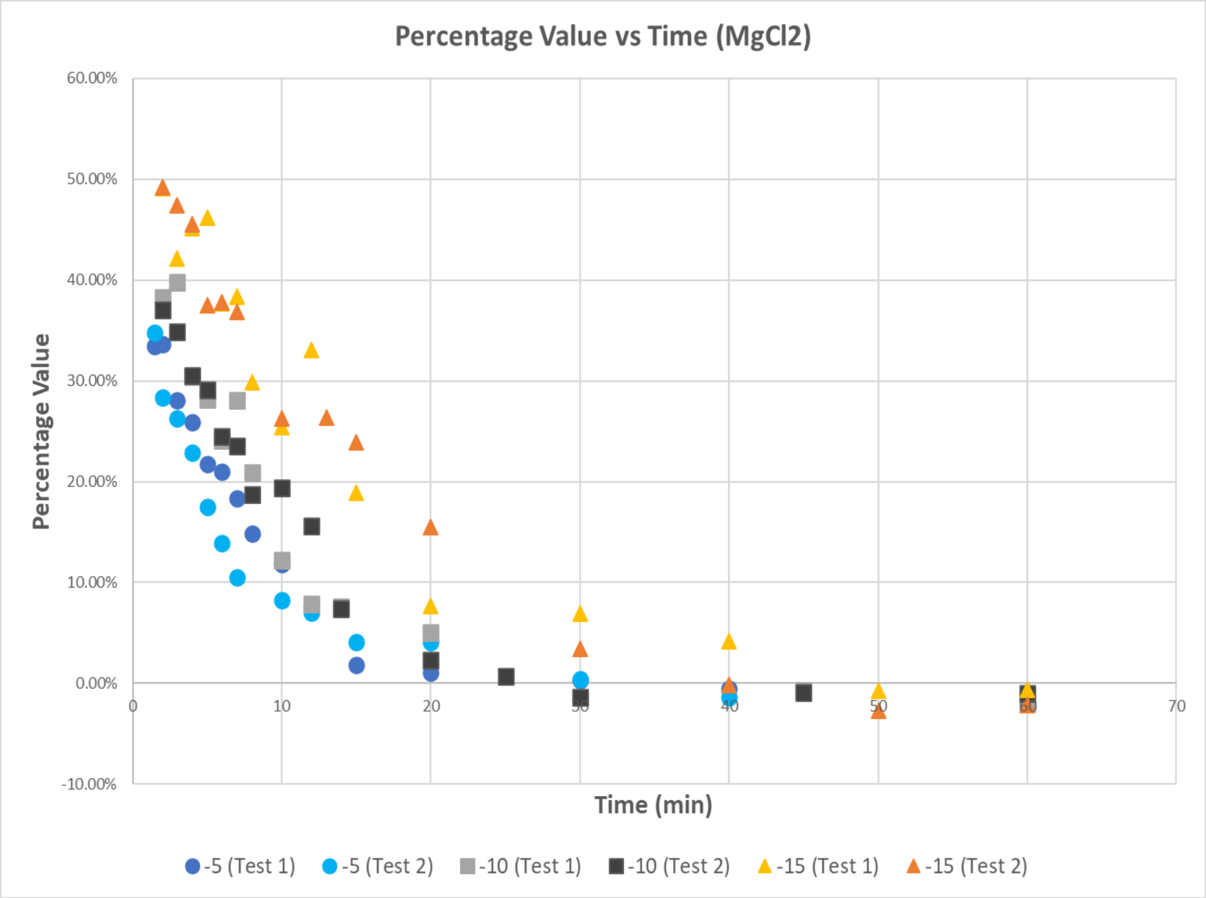


Figure 35 Percentage Value vs Time ($MgCl_2$)

Figure 35 shows the summary of Percentage Value development over time for $MgCl_2$ at 3 different temperatures. In all the tests, the Percentage Values decline gradually over time and theoretically until 0. It is also possible to find that the results of tests at different temperatures are obviously different. As shown in the figure, the plots of tests at -15°C are at the top of three temperatures. While, the plots of tests at -5°C are at bottom. So, it is reasonable to believe that the environment temperature would affect the Percentage Value development during the melting process. Under a higher temperature, which is -5°C in this study, the Percentage would reach zero faster. Also, from the MgCl2 results, it seems that Percentage Value in a high temperature test might start with a relatively lower value compared with it in a low temperature test.

Besides the Percentage Value, another parameter defined in this study is the "disappeared time". The "disappeared time" shows the first sampling time when the salt in the sample looks to be almost disappeared. It is not the accurate time that the deicers are completely dissolved. Because the sampling could be conducted continuously and the "disappearance" is judged from naked eyes. But it could reflect the approximate time when the mechanism of melting might change. When the salt is still present, the solid salt could be dissolved continuously to maintain the melting processing. While, when the solid salt is completely dissolved, the meltwater would only be diluted until the freezing point concentration and melting would stop. In addition, the thermodynamic calculation in these two stages are different. Before the "disappeared time", the heat due to dissolved of salt would be considered. But after that, there would be no dissolved heat. Hence, the "disappeared time" is defined and very interested in this study.

For the purpose of improving the tests that measuring the ice melting rate with calorimetry, as mentioned in Section 4.3.2, improved assumptions about salt concentration during the melting rate is needed. According to the Equation (12), the concentration assumption is needed before all the salt has been dissolved. Hence, the stage where the salt is still present, which is actually the stage before "disappeared time", is more interested.

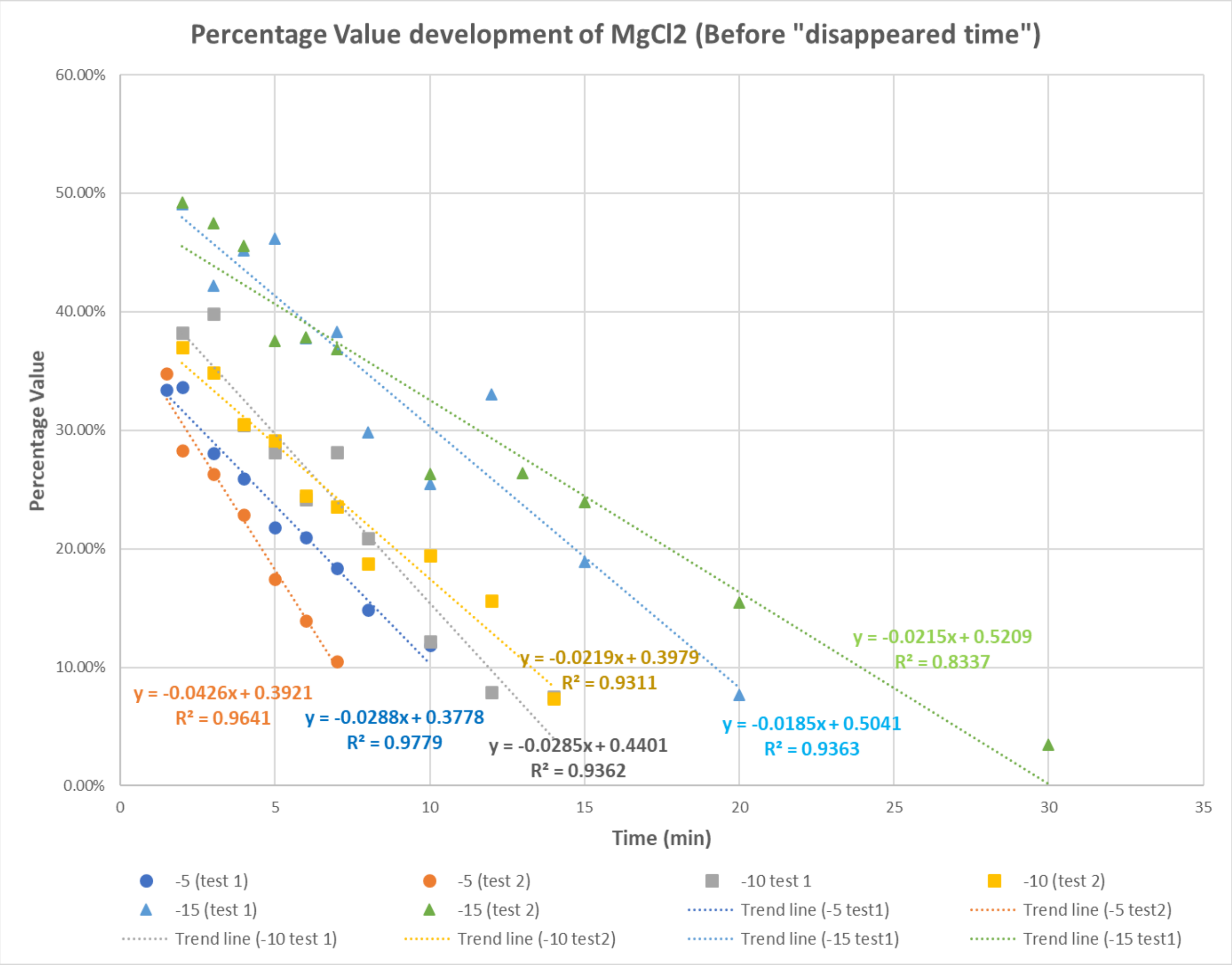


Figure 36 Percentage Value development of MgCl$_2$ tests (Before “disappeared time”)

Figure 36 summarized the Percentage Value development over time of MgCl$_2$ before all the salt has been disappeared. Trendlines are founded by Excel and the linear related is applied. It is possible to find that all the R^2 values of trendlines are relatively high. Table 15 summarized the parameters of these trendlines, where only the R^2 value of test 2 (-15℃) is less than 0.93. So, it is reasonable to think that the relationship between Percentage Value and time would be close to **linear correlation** when the salt is still present in the melting process.

Table 15 Parameters of trendlines of MgCl2 tests

Test	-5°C test1	-5°C test2	-10°C test1	-10°C test2	-15°C test1	-15°C test2
R^2	0.9779	0.9641	0.9362	0.9311	0.9363	0.8337
a	-0.0288	-0.0426	-0.0285	-0.0219	-0.0185	-0.0215
b	0.3778	0.3921	0.4401	0.3979	0.5041	0.5209

(R^2 is the coefficient of determination; a is the slope; b is the y-intercept.)

In addition, the **slope** of -5°C tests has the largest absolute value, which means that it has the largest decline rate of Percentage Value. So, it is reasonable to believe that under a higher temperature, the melting rate would be relatively larger and the rate of Percentage Value declining would also be larger. Regarding the results of **y-intercept** b, the tests at -15°C have the largest values, while the -5°C tests have the lowest values. Therefore, the test under a lower temperature would start with a relatively higher Percentage Value.

Table 16 Percentage Value of $MgCl_2$ tests at different time points

	-5°C		-10°C		-15°C	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
First sampling	33.43%	34.79%	38.26%	37.03%	49.12%	49.24%
“Disappeared point”	11.88%	10.52%	7.54%	7.39%	7.67%	3.47%
T=0 (Y-intercept)	37.78%	39.21%	44.01%	39.79%	50.41%	52.09%
“disappeared time” (min)	10	7	14	14	20	30

Table 16 summarized the Percentage values of $MgCl_2$ tests at different time points. It is possible to find that for the two repetition tests at the same temperature, their **Percentage values** at first sampling (close to the start of melting process) and at “disappeared time” are quite close to each other, although the “disappeared time” are not very close. For example, at -5°C, the “disappeared time” of test 1 and test 2 is 10 minutes and 7 minutes respectively. And at -15°C, they are 20 minutes and 30 minutes respectively.

Since before the first sampling time, the liquid is not enough to have a concentration measurement, there is no available data before it. Therefore, the Percentage Values at t=0 is assumed to be equal to the y-intercept of trendlines. Results shows that they are also relatively close to each other, although the calculations are based on the assumption of trendlines.

Hence, it is possible to say that in the melting process with $MgCl_2$ at a certain temperature, the Percentage Value might start around a certain value and also end around a certain value when the solid salt is completely dissolved. From the results in this study, the start Percentage Values might be about 38.5%, 42% and 51% for -5°C, -10°C and -15°C respectively. The "disappeared time" Percentage Values might be about 11.2%, 7.5% and 5.5% for -5°C, -10°C and -15°C respectively. (Average values of two repetition tests).

7.1.2. New assumption of MgCl2 solution concentration during the melting process

Based on the discussion above, the new assumption of $MgCl_2$ concentration during the melting process could be proposed. According to the Equation (16), the real concentration of $MgCl_2$ can be expressed as

$$W_{MgCl_2} = (1 - P)W_f + PW_S \qquad (18)$$

Where W_{MgCl_2} is the concentration of MgCl2 solution during the melting process; P is the Percentage Value; W_f is the freezing point concentration; W_S is the solubility concentration.

Overall, during the melting process, Percentage Value P would decrease gradually until zero. In other words, the concentration would gradually reach the freezing point concentration. At the stage where the salt is still present, P might be linear related with time. Under a higher reaction temperature, the declining rate of P would be larger. In addition, at a certain temperature, the Percentage Value might start around a certain value and also end around a certain value. During the melting process, the Percentage Values would be highly likely to be less than 50%, which means actually the salt concentration would be closer to the freezing curve rather than solubility curve.

7.2. NaCl tests

7.2.1. Data fluctuation analysis

The results of NaCl tests are much more fluctuant than $MgCl_2$ test. As explained in Chapter 6, the main reason is that different data points are from the individual samples. There would be some differences between each sample, including the shape and size of salt particle, the direction of penetrating and so on, which all would influence the melting process. For NaCl test, the melting rate is much slower than $MgCl_2$, especially at low temperatures. In this study, at -15°C, it takes only about 30 minutes for the $MgCl_2$ to finish the melting. While, for the NaCl, it takes more than 3 hours. Hence, during the NaCl tests, the NaCl chemical itself might not contribute a lot on the difference between each data point. Therefore, other influence factors which are not controlled in the tests, would be relatively large. Hence, that could one of the reasons that the NaCl tests at -15°C has the largest data fluctuation.

It is important to know that the NaCl coarse particles are applied in tests. These particles are not perfect spherical. On the contrary, they have many edges and corners and the shapes are different from each other. While, for the $MgCl_2$ tests, the flakes are applied, which have very similar shapes. So, the contact between salt and ice in the NaCl tests are relatively different for different samples, while in the $MgCl_2$ tests, they are quite similar. Different contact So, this could also be one of the reasons that results of NaCl tests have large fluctuation.

Another factor is the temperature measurement. In NaCl tests, since the melting capacity is relatively large, particle could penetrate deeply into the ice cylinder. So, there would be thin, deep and rugged holes formed in the samples. Such long holes would have large temperature difference at different parts, which leads a large uncertainty on temperature measurements. In the actual operation, the thermal sensor was tried as close to the melt front (the contact area between salt and ice) as possible, and liquid was also collected as deep as possible. However, sometimes the melt front could not reach when the hole is very deep and curved. And from the experience of operation, sometimes it is very hard to have a stable result shown on the thermal sensor during the temperature measurements on NaCl tests. So, there would also be an uncertainty on the temperature results. In addition, melting holes have different directions and shapes due to the different shapes of the salt particles. Hence, in different samples, since the salt are located in different positions, the heating from surroundings are also different. Those could also be the reasons of data fluctuation.

Regarding the concentration measurement, basically it is relatively accurate in the tests. It is conducted by measuring the refractive index and converted to the concentration through the calibration curves shown in Figure 20 and Figure 21. Therefore, there would be some little errors in the conversion. In addition, there would be variations to conduct such quick measurements with refractometer. Hence, it could be possible to have some errors. If this variation is about 0.3%, it would not affect much on the most results in this study. However, as for the Percentage Values for the NaCl tests at -15°C, it could have a relatively large influence. For example, at -15°C, the freezing point concentration is 19.02% and the solubility concentration is 24.07%. So, the impact of the variation of 0.3% would be $0.3/(24.07-19.02)\times 100\% = 5.94\%$, which is very larger and could cause the data fluctuation.

It is important to find that in the results of Percentage Values, there are negative values present. Theoretically, the Percentage Value could only decrease until 0. The reason of this could be both the error of temperature measurements and the variation of concentration measurements as mentioned above. In addition, the room temperature changes periodically. For instance, through observation when the set temperature is -15℃, the real air temperature could change from -14.2℃ to -15.2 ℃ and period is only about 6 minutes. So, although the average temperature is -14.7℃, the real air temperature just above the ice surface could drop to -14.2℃ in a very short time. Hence, when the solution concentration is just below the freezing point concentration at -14.7℃, it might not be frozen in the tests.

7.2.2. Law of Percentage Value development

Since the results of NaCl tests are relatively scattered, it would be meaningless to find their trendlines as conducted in $MgCl_2$ tests. But, same as $MgCl_2$, the Percentage Value keeps the trend of declining during the melting process. Table 17 shows the Percentage Values at first sampling points and “disappeared point”, it is possible to find that these values of the two tests at the same temperature are relatively close to each other, especially for the data at “disappeared point”. Compared with the law of Percentage Value development in $MgCl_2$ tests, it would be possible to have a speculation that during the melting process with NaCl, at a certain temperature, the Percentage value might start around a certain value and end around a certain value when all the salt is completely disappeared. In addition, the Percentage Value would be highly likely to be less than 50% during the melting process, which means that actually the concentration of NaCl would be closer to the freezing curve rather than the solubility curve.

Table 17 Percentage Value of NaCl tests at different temperatures

	-5℃		-10℃		-15℃	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
First sampling point	49.78%	34.17%	44.71%	37.03%	41.37%	42.84%
"Disappeared point"	3.30%	2.00%	0.10%	-1.90%	-8.64%	-7.50%

7.3. Improved assumption applied on the calculation model of calorimeter

As mentioned in Section 4.3.2, in Kulyakthin and Klein-Paste's study (2020), the salt concentration is assumed either to be freezing point concentration or solubility concentration during the melting process. In the real calculation model, the concentration is determined by looking for the corresponding concentration data to a specific temperature either in the freezing curve or solubility curve, where the temperature is monitored and recorded in the data log. Hence, with the log of temperature, the salt concentration during the melting process could be obtained.
Since, the thermodynamics balances are different before and after the salt is completely dissolved. If the salt has completely been dissolved needs to be determined first. With Equation (12), it is possible to calculated the amount of meltwater Δm_w for each time step when the concentration is known. Then, through Equation (7) and Equation (19), the accumulated mass of dissolved salt at each time point can be obtained. Therefore, only if accumulated mass of dissolved salt $m_{salt\_diss}^{t}$ is smaller than the initial mass m_{salt}^{0}, the heat of salt dissolution would be considered.

$$m_{salt}^{t} = m_{salt}^{t-1} + \Delta m_{salt} \tag{19}$$

Where Δm_{salt} is the mass of salt dissolved at each time step.

In other words, **only when the concentration could be determined first, the judgment of whether the salt is completely dissolved could be conducted and then the subsequent calculations on the melting rate could be applied.** So, based on this model, it would be **impossible** to calculate with the assumption that the Percentage Value is linear related with time as discussed in the Section 7.1. Because, as the shown in the Equation (20), the Percentage value when the melting start, b could be determined, but the slope, a could be determined since the "disappeared time" could not be determined. That means the concentration could not be determined firstly and calculation could not continue.

$$P = at + b \tag{20}$$

Hence, a new improved assumption would be proposed which could be applied in the calculating model. Since the Percentage Value would keep decreasing during the melting and might start and end with a certain value, a possible solution is that **applying the average of start value and end value to the whole melting process.** In this study, the start value could be assumed as the value at the first sampling and the end point could be the value at the "disappeared point". In other words, the Percentage Value would be assumed as

$$P = \frac{P_{first\ sampling} + P_{disappeared\ point}}{2} \tag{21}$$

Where $P_{first\ sampling}$ is the Percentage value at the first sampling; $P_{disappeared\ point}$ is the Percentage Value at the "disappeared point". Both values can be calculated and summarized based on the tests results in this study, which are shown in Table 18 and Table 19 .Since the Percentage Value could not be less than zero in theory, all the values less than 0 in NaCl tests are assumed as 0. In conclusion, during the melting process with solid $MgCl_2$, before all the salt is dissolved, the concentration of $MgCl_2$ solution would be $0.77W_f + 0.23W_S$, $0.77W_f + 0.23W_S$ and $0.73W_f + 0.27W_S$ for the environment temperature at -5°C, -10°C and -15°C respectively. Where, W_f is freezing point concentration and W_S is solubility concentration. Regarding melting with Solid NaCl, the concentration of NaCl solution would be $0.78W_f + 0.23W_S$, $0.8W_f + 0.2W_S$ and $0.79W_f + 0.21W_S$ for the environment temperature at -5°C, -10°C and -15°C respectively.

Table 18 Percentage Value of $MgCl_2$ tests in the new assumption

	-5°C		-10°C		-15°C	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
First sampling	33.43%	34.79%	38.26%	37.03%	49.12%	49.24%
"Disappeared point"	11.88%	10.52%	7.54%	7.39%	7.67%	3.47%
P first sampling	34.11%		37.65%		49.18%	
P disappeared point	11.20%		7.47%		5.57%	
P	22.66%		22.56%		27.38%	
W_{MgCl_2}	$0.77W_f + 0.23W_S$		$0.77W_f + 0.23W_S$		$0.73W_f + 0.27W_S$	

Table 19 Percentage Value of NaCl tests in the new assumption

	-5°C		-10°C		-15°C	
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
First sampling point	49.78%	34.17%	44.71%	37.03%	41.37%	42.84%
"Disappeared point"	3.30%	2.00%	0.10%	0.00%	0.00%	0.00%
P first sampling	41.98%		40.87%		42.11%	
P disappeared point	2.65%		0.05%		0.00%	
P	22.31%		20.46%		21.05%	
W_{NaCl}	$0.78W_f + 0.23W_S$		$0.8W_f + 0.2W_S$		$0.79W_f + 0.21W_S$	

7.4. Attempt to Apply the improved assumption

Since the time of this Master's thesis is very limited, melting test in calorimeter is not conducted in this study. Hence, an attempt to apply the improved assumption is performed based on the test data from Kulyakthin and Klein-Paste's study (2020). Python script is modified to apply the new assumption in this study. Since only tests at -15°C were performed in their study, the new assumption for -15°C is applied. The results of melted mass calculations are summarized in Table 20.

The theoretical melted mass can be calculated by the freezing point concentration and the mass of salt applied, because when the melting process finishes, the solution concentration would equal to the freezing point concentration. The equation is shown as

$$m_{total\ melted\ ice} = \frac{1 - W_f}{W_f} m_{total\ salt} \tag{22}$$

Table 20 Results of melted mass calculations (-15°C)

	Used assumption	NaCl	MgCl2 · 6H2O
Total melted mass (g)	New assumption	10.01 ± 0.41	10.10 ± 0.34
Theoretical melted mass (g)	New assumption	10.08	10.08
Total melted mass in Kulyakthin’s study	Freezing	9.92 ± 0.50	9.87 ± 0.50
	Solubility	9.92 ± 0.50	10.00 ± 0.45

It is possible to find that under the conditions of new assumption in this study, for both two types of salt, the mean values of total melted mass are very close to the theoretical melted mass. Compared with the results in Kulyakthin’s study, the mean values are closer to the theoretical values and the variations are smaller. Hence, it is reasonable to believe that the new assumptions have improvements on the tests of measuring ice melting rate with colorimetry. As at the higher temperatures, the range between the freezing point temperature and solubility concentration would be relatively larger, the inaccuracy of the old assumptions would be much larger. So, the new assumption in this study might have more improvements, but it is still needed to be tested in the future.

8. Conclusion

In order to improve the tests of measuring ice melting rate of de-icing chemicals with calorimetry, some tests on exploring the law of salt concentration development during the melting process are performed in this thesis. Based on the results the main findings are:

- A parameter called **Percentage Value** is defined in this thesis, which illustrates how close the salt concentration is to the freezing point concentration in the range between freezing point concentration and solubility concentration. During the melting process, the trend of Percentage Value is decreasing gradually until it reaches zero. In other words, as the melting processing, the salt concentration would get closer to the freezing point concentration gradually and away from the solubility concentration. Eventually, it would equal to the freezing point concentration.

- Two different stages could be found in the melting process. The declining rate of Percentage Value at the stage that the salt is still present would be higher than the rate when all the salt is completely dissolved.

- As for melting with $MgCl_2$, the relationship between Percentage Values and time would be close to a linear correlation when the salt is still present. In addition, at a certain temperature, the Percentage Value might start around a certain value and also end around a certain value. Also, the Percentage Values would be highly likely to be less than 50% throughout the melting process, which means actually the salt concentration would be closer to the freezing curve rather than solubility curve.

- As for the melting with NaCl, a specific relationship between Percentage Value and time could not be found. It might have the same regular with $MgCl_2$ that the Percentage Value might start around a certain value and also end around a certain value when the environment is at a certain temperature.

- A new assumption applied on the calculation model of measuring ice melting rate with calorimetry is proposed. The new improved assumption is that throughout the melting process, the percentage value is assumed to be equal to the average of the start value and end value, which both could be measured from tests.

- Compared with the old assumptions in Kulyakthin and Klein-Paste's study (2020), the new assumption in this study makes some improvements on the tests at -15°C.

9. Future work

To improve the accuracy of data and decrease the variation, stricter test conditions could be applied in the future, which includes tighter controlling the shape and size of salt particles. Especially, for the NaCl, more regularly shaped particles should be used. In addition, the test environment should avoid large temperature fluctuations. Rather the large cold room in this study, a smaller room or a large freezer which could provide stable temperature and is convenient to perform the tests.

More repetition tests should be conducted in the future to verify the results and laws found in this study. Also, more results from repetition tests could be helpful to propose better assumption.

Tests for tracing the concentration directly in the calorimeter, which did not perform successfully in this study, should be conducted in the future. The data from the melting process conducted in the calorimeter would be better suited for the calculation models. A new smaller customized calorimeter could be developed for the measuring the ice melting rate, which might be easier to collect salt solution direct from the calorimeter.

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Appendix 1: Results of the application of new improved assumption

Table and table are the results of the application of new improved assumption. Original test data are from Kulyakthin and Klein-Paste's study (2020).

Table A. 1 Application of new improved assumption ($MgCl_2$)

Test name	MgCl2_std_e_10g	MgCl2_std_g_10g	MgCl2_std_h_10g
Ice melted (New assumption)	10.44	9.78	9.76
Ice melted (Theory)	10.08	10.08	10.08

Table A. 2 Application of new improved assumption (NaCl)

Test name	NaCl_std_a_10g	NaCl_std_b_10g	NaCl_std_c_10g
Ice melted (New assumption)	9.75	9.59	10.42
Ice melted (Theory)	10.09	10	10.03

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