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Can calorimetry be used to measure the melting rate of deicers?

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ABSTRACT

Chemical deicers are used in winter maintenance of roads and runways to melt ice and restore a bare pavement. The melting rate of these deicers is a fundamental performance factor, but good test methods to quantify the melting rate are still lacking. In this study, we present a method to measure the melting rate with calorimetry. The method provides a good control over heat fluxes and mixing which are crucial factors for the melting. In addition, it has an advantage of testing a deicer 'as received' without any sample handling prior to the test. The results showed that the melting rate of $CaCl_2$ and $MgCl_2$ can be clearly distinguished from NaCl. Solving the heat balance for solid deicers requires the deicer concentration in the meltwater to account for the enthalpy of dissolution. The freeze point and solubility concentrations set the physical limits on concentration and were used to assess the uncertainty due to unknown concentration. The extent of the uncertainty did not allow for a distinction between $CaCl_2$ and $MgCl_2$. This showed the need for an improved assumption scheme based on direct measurements. To represent a non-linear melting rate, different single-number metrics were investigated. The time it takes to reach 75% of the melting capacity gave the best characterization of the melting performance.

1. Introduction

Snow and ice on roads pose a danger for road users as it causes slippery driving conditions. The main strategy is to prevent such slippery conditions by applying anti-icing chemicals. These chemicals (typically salts), can prevent water on the road from freezing or from compacting snow into a hard layer that is difficult to remove (Klein-Paste and Dalen, 2018). Similar chemicals are also used to melt ice layers and regain a bare pavement (dry or wet). In such de-icing operations the goal is to restore the bare state of the pavement as quickly as possible.

There is a large range of commercial de-icing products available and new products and brands are being launched regularly. Most of these products contain chloride salts (sodium chloride (NaCl), magnesium chloride ($MgCl_2$) or calcium chloride ($CaCl_2$)), but also non-chloride alternatives such as Calcium Magnesium Acetate (CMA), or Potassium formate (KCOOH) are being used. Some products contain additives, such as beet juice, corn syrup or other so-called agricultural by-products (ABP's) and the physical properties such as the grain size, moisture content and density can be different. This leads to differences in performance and road authorities or private contractors that perform the winter maintenance operations have the challenging task to understand which product works best for their part of the road network.

The word "performance" has several dimensions for anti−/de-icing chemicals. For anti-icing purposes, it is mainly: the ability to depress the freezing point, how uniform the product can be applied (often referred as bouncing and scattering during the application) and how well the product sticks to the road surface (longevity). For de-icing purposes, the main performance factors are the ice melting capacity (in g ice/g product) and how quickly the product melts (known as the melting rate). In addition to these performance characteristics comes other aspects such as environmental effects and corrosion on vehicles, concrete and road side infrastructure.

Comparative field tests can give a very good overall sense of how two or more products perform relative to each other, but it is often challenging to address performance differences to the actual product. The reason is that it very difficult to keep all other factors constant. Differences in traffic, climate, surface conditions, and timing of the applications can skew the results of comparative field tests and cause misleading conclusions. Another often chosen approach is to isolate a certain performance factor and conduct tests under controlled laboratory conditions. For de-icing purposes, this is mainly the ice melting capacity and ice melting rate tests.

A deicer can melt ice until it is so diluted by meltwater that the solution reaches its equilibrium concentration at a given temperature (Nilssen et al., 2016). The ice melting capacity is therefore solely determined by the thermodynamics of the system. As long as the reaction is allowed to reach equilibrium, the ice melting capacity can be

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measured based on measuring concentration (Koefod, 2017), mass (Gerbino-Bevins et al., 2012), or energy (Nilssen et al., 2017; Klein-Paste and Dalen, 2018). Measuring ice melting rate is fundamentally much more challenging because it depends on the kinetics of the reaction. The particle size, degree of mixing (as normally occurs in real life due to traffic) and the availability of heat from the surroundings affect the speed at which a deicer melts ice.

The widely used SHRP H205.1 and SHRP H205.2 tests (Chappelow et al., 1992) have been used to evaluate the ice melting rate, in addition to ice melting capacity, by measuring the melted volume at different time intervals. However, since it is difficult to extract all the melted ice and brine, and the sampling procedure of extracting and re-applying the meltwater provides a poorly controlled mixing and can add undesired heat fluxes to the system (Klein-Paste and Potapova, 2014). Koefod et al. (2012) reports up to 25% coefficient of variation in repetitive SHRP H205.1/SHRP H205.2 tests. More accurate methods exist (Sugawara and Irvine, 2000; Wåhlin and Klein-Paste, 2017) where the ice melting front is traced, but these methods are only applicable to study the liquid deicers. Koefod et al. (2015) investigated the ice melting rate of unmixed solid deicers at low temperatures of deicers with a known chemical composition.

There is still a need for a sound method that can quantify the ice melting rate performance of commercial deicers (when the exact chemical composition is unknown). Such method should ideally evaluate the product in its 'as received' physical state and to some degree be exposed to a standardized/reproducible mixing.

Nilssen et al. (2017) showed that calorimetry can give accurate measurements of the ice melting capacity of liquid deicers, and they applied it to investigate the effect of additives at low temperatures (Nilssen et al., 2018). The benefit of the calorimeter is that it does not require a separation of the liquid and solid phase and provide a reproducible gentle mixing. In this study, we investigated whether calorimetry also can be used to quantify the ice melting rate of different deicers. In contrast to ice melting capacity measurement, this requires that the full energy balance is solved for every time step. The time step refers to the time between consecutive measurements of the temperatures and amount of added heat during a test. In this paper, we start by describing the test set-up, then we present the melted mass calculations from the energy balance equation, and, lastly, we compare the ice melting rate of three different solid deicers: NaCl, $MgCl_2{\cdot}6H_20$ and $CaCl_2{\cdot}2H_20$.

2. Methods

2.1. Calorimeter

Ice melting experiments were performed in the calorimeter earlier described in Nilssen et al. (2017) and shown in Fig. 1. It consists of a 500 ml plastic reactor that is insulated with 150 mm extruded polystyrene. Five PT100 temperature sensors are installed inside the insulation to monitor the temperature gradient and calculate the heat flux through the walls. The reactor is accessed by separating the insulation into two pieces. The reactor houses an immersible 50 W heating element with integrated temperature sensor, and a separate temperature sensor that measures the ice/deicer/meltwater mixture. The heater element is made of stainless steel and has a total mass of 200 g.

A loading chamber allows to add de-icing chemicals in the reactor without the need to remove the insulation or open the reactor which otherwise would introduce an uncontrolled heat flux from the environment. The opening of the loading chamber is closed with a rubber plug which can be pushed inside the reactor by the plunger together with a tested deicer.

The calorimeter is placed on a mixing table consisting of four wheels driven by two stepper motors. The mixing is done by rotating the calorimeter 180° back and forth with the rotation speed of 64 deg. s^{-1}.

The heater is connected to a power supply (Elektro Automatik PS8160-04) and the temperature sensors are connected to PicoTech PT104 data loggers. The readings from the PicoTech PT104 and the power supply are recorded by National Instruments NI-USB-6211. The temperature readings from the heater are used to control the power supply. Proportional-integral-derivative controller was used to keep the heater at a defined temperature. The whole set-up is installed in a walk-in cold room with the temperature control of ± 0.5 °C.

2.2. Procedures and materials

All melting tests and preparations were performed in the lab at −15 °C. Ice was prepared by crushing commercial ice cubes into 3 mm – 10 mm fragments in a manual hand crank operated ice breaker. The calorimeter, crushed ice and deicers were kept in the lab prior to tests for a least 15 h. A 100 g of crushed ice was loaded inside the reactor and the insulation was closed. A tested salt was loaded inside the loading chamber. Before starting a test, it was ensured that the calorimeter and materials are in thermal equilibrium. This took about one hour. The tests were started by pushing the deicer with the plunger inside the reactor, starting the mixing motors, and turning on the heating element. The heating element was kept at the constant temperature of −14 °C. The tests were finished when the temperature of the mixture reached the initial temperature of −15 °C. The temperatures and added heat were recorded every 0.4 s.

Three deicers were tested: NaCl (CAS: 7647-14-5), $MgCl_2{\cdot}6H_2O$ (CAS: 7791-18-6) and $CaCl_2{\cdot}2H_2O$ (CAS: 10035-04-8). NaCl and $CaCl_2{\cdot}2H_2O$ had crystal sizes in the range of 0.125 mm – 0.5 mm. $MgCl_2{\cdot}6H_2O$ crystals were in the range of 0.125 mm – 1 mm. The amount of each salt was chosen to melt 10 g of ice according to their theoretical melting capacities. Melting capacity is defined as the ratio of the total mass of melted ice to the mass of added deicer. For a given temperature, this ratio is constant and given by the freeze-point concentration of a deicer dissolved in water, $x(T)$

$$melt_capacity = \frac{1}{x(T)}\frac{M_{anhyd}}{M_{hydr}} - 1 \tag{1}$$

where the ratio of molar masses of anhydrous salt, M_{anhyd}, and its hydrate form, M_{hydr}, are used to compensate for the presence of crystalline water in hydrates. This is required because $x(T)$ is taken from phase diagrams which report anhydrous forms of salts, whereas commercial deicers typically are hydrates. The phase diagrams of NaCl, $MgCl_2$ and $CaCl_2$ were taken from Li et al. (2016) who gives numerical values in supplementary material. According to the phase diagrams and Eq. (1), the melting capacities at −15 °C of NaCl, $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}2H_2O$ are equal to 4.3, 2.1 and 3.2 g/g respectively. Therefore, 2.35 g of NaCl, 4.68 g of $MgCl_2{\cdot}6H_2O$ and 3.14 g of $CaCl_2{\cdot}2H_2O$ are needed to melt 10 g of ice.

2.3. Melting rate calculations

To quantify the rate of melting, the mass of melted ice, $m_w[t]$, should be evaluated as a function of time. This mass is equal to the mass of water in the reactor since the liquid water is not present at the beginning of tests. This section describes how the increase of water mass, Δm_w, was computed for every time increment.

The water mass increment is calculated from the energy balance. It consists of the heat due to mixing ΔQ_{mix}, the heat added into the reactor, ΔQ_{add}, the heat through the calorimeter walls, ΔQ_{walls}, the heat of melting, ΔQ_{melt}, the heat of dissolution, ΔQ_{diss}, the heat due to capacities of ice, ΔQ_{ice}, salt, ΔQ_{salt}, water, ΔQ_{water}, and the heating element, ΔQ_{heat}.

$$\Delta Q_{mix} + \Delta Q_{add} + \Delta Q_{walls} + \Delta Q_{melt} + \Delta Q_{diss} + \Delta Q_{ice} + \Delta Q_{salt} + \Delta Q_{water} + \Delta Q_{heat} = 0 \tag{2}$$

By convention, a heat increment is considered positive if it increases the energy inside the reactor.

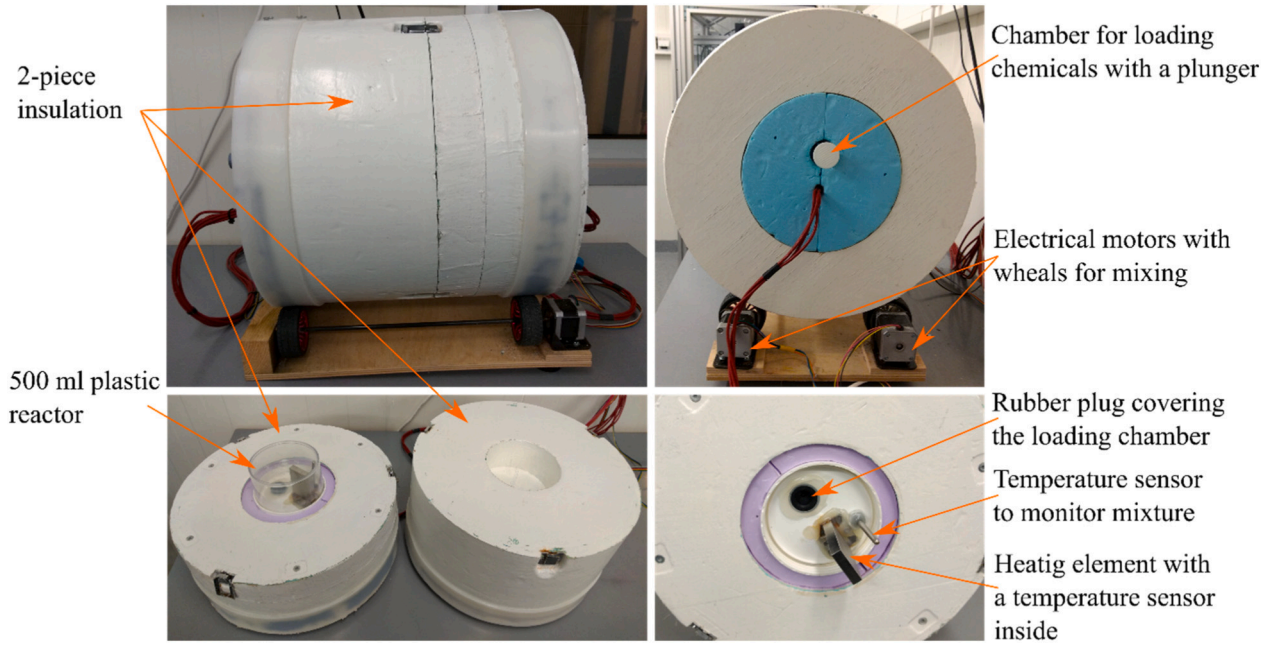

Fig. 1. Calorimeter overview.

The heat due to the friction of mixing was assessed by mixing ice cubes for 12 h at −15 °C without heating. During this process, the temperature inside the reactor changes by less than 0.1 °C. Therefore, the heat due to mixing is negligible in comparison with the heat loss through the walls.

The added heat, ΔQ_{add}, is calculated by integrating the electrical power supplied to the heating element

$$\Delta Q_{add} = \int_{t}^{t+\Delta t} IU\,dt \tag{3}$$

where I and U are the current and voltage recorded from the power supply.

The flux through the calorimeter walls is calculated from the heat transfer equation

$$\Delta Q_{walls} = -h(T_{reac} - T_{out})\Delta t \tag{4}$$

where h [W/°C] is the heat transfer coefficient for the total area of the calorimeter; T_{reac} and T_{out} are the temperatures inside the reactor and on the outside surface of the insulation; and Δt is the time increment, 0.4 [s]. In the above and following equations, symbol Δ denotes the difference of a physical quantity between a given time, [t], and its previous time increment [$t - 1$].

The heat of melting is calculated from the enthalpy of melting, H_{melt}, and the increase of water mass, Δm_w

$$\Delta Q_{melt} = -H_{melt}\Delta m_w \tag{5}$$

The heat of dissolution is calculated from the enthalpy of dissolution, H_{diss}, and the increase of dissolved mass of a salt, Δm_{salt}

$$\Delta Q_{diss} = -H_{diss}\Delta m_{salt} \tag{6}$$

The increase of dissolved salt is calculated from the mass concentration of a salt, x, and the increase of water mass, Δm_w

$$\Delta m_{salt} = \frac{x}{1-x}\Delta m_w \tag{7}$$

The salt concentration was not measured during the tests, but the physical limits can be set on its value. For a given temperature, the salt concentration cannot be lower than the freezing point concentration, and it cannot be higher than the solubility concentration. These concentrations are used as long as crystalline salt is present. When all crystalline salt is dissolved, the contribution of the heat of solution, ΔQ_{diss}, is taken as zero. For hydrates, Eq. (7) should include a correction factor since the concentration of a pure salt is given in phase diagrams

$$\Delta m_{salt}^{hyd} = \frac{M_{hyd}}{M_{anhyd}}\Delta m_{salt}^{anhyd} \tag{8}$$

where M_{anhyd} and M_{hydr} are molar masses of a anhydrous salt and its hydrate.

The heat conducted into the ice is given by the specific heat capacity of ice, ${c_p}^{ice}$, the mass of ice, m_{ice}, and the temperature change inside the reactor, ΔT_{reac}

$$\Delta Q_{ice}^{cond} = -c_p^{ice}(m_{ice}^0 - m_w[t-1] - \Delta m_w)\Delta T_{reac} \tag{9}$$

The mass of ice at a given time increment is equal to the initial ice mass, $m_{ice,}^0$ minus the mass of water from the previous time increment, $m_w[t - 1]$ and current increase of water mass, Δm_w.

The heat conducted into the salt is given by the specific heat capacity of salt, ${c_p}^{salt}$, the mass of salt, m_{salt}^0, and the temperature change inside the reactor, ΔT_{reac}

$$\Delta Q_{salt} = -c_p^{salt} m_{salt}^0 \Delta T_{reac} \tag{10}$$

The heat capacity of salt in solid and dissolved forms are different. But this can be neglected due to small masses of a salts which were used.

The heat conducted into the water is given by the specific heat capacity of water, ${c_p}^{w}$, the mass of water, m_w, and the temperature change inside the reactor, ΔT_{reac}

$$\Delta Q_{water} = -c_p^{w}(m_w[t-1] + \Delta m_w)\Delta T_{reac} \tag{11}$$

The heat conducted into the heating element is given by the specific heat capacity of stainless steel, ${c_p}^{steel}$, the mass of the heater, m_{heat}, and the temperature change of the heating element, ΔT_{heat}

$$\Delta Q_{heat} = -c_p^{steel} m_{heat}\Delta T_{heat} \tag{12}$$

Substituting Eqs. (3)–(12) into Eq. (2), the increase of water mass can be calculated

Table 1
Constants for melted mass calculations.

Constant			Value
Water/ice constants			
H_{melt} (J/g)			333.6[1]
c_p^{ice} (J/g/°C) average of −10 and − 20 °C values			2.0[1]
c_p^{w} (J/g/°C) at 0 °C and 1 bar			4.22[1]
Salt constants	**NaCl**	**$CaCl_2 \cdot 2H_2O$**	**$MgCl_2 \cdot 6H_2O$**
H_{diss} (J/g)	66.39[1]	−304.60[*,2]	−77.07[*,3]
c_p^{salt} (J/g/°C)	0.84[1]	1.17[2]	1.83[4]
M_{anhyd} [g/mol]	58.44	95.21	110.98
M_{hyd} [g/mol]	–	203.33	147.02
Calorimeter constants			
h (W/°C)	0.05[5]		
c_p^{steel} (J/g/°C) for composition 58% Fe, 27% Ni, 15% Cr	0.45[1]		

[1] Haynes et al. (2017).
[2] Occidental Petroleum (OXY), n.d.
[3] Jahn and Wolf (1993).
[4] Höhlein et al. (2017).
[5] Experimentally determined: the calorimeter was loaded with 100 g of ice, the heater temperature was set to 0 °C, and the lab temperature was set to −20 °C; after, approximately, 6 h the system came to a steady state; the steady state was observed for 3 h and gave an average temperature in the reactor of −4.1 °C and average heat flux from the heater of 0.8 W.
[*] By convention, exothermic dissolution enthalpies are negative.

$$\Delta m_w = -\frac{\Delta Q_{add} + \Delta Q_{walls} + \Delta Q_{heat} - (c_p^{ice}(m_{ice}^0 - m_w[t-1]) + c_p^{salt} m_{salt} + c_p^w m_w[t-1])\Delta T}{H_{melt} + H_{diss}\frac{x}{1-x}\frac{M_{hyd}}{M_{anhyd}} + (c_p^w - c_p^{ice})\Delta T} \tag{13}$$

By adding the results of the above equation, the mass of water for every time step is determined

$$m_w[t] = m_w[t-1] + \Delta m_w \tag{14}$$

where $m_w[t = 1] = 0$. The melting rate is calculated by taking the time derivative of the melted mass.

The constants needed for the calculation are given in Table 1. The temperature dependence of specific heat capacities and enthalpies of solution is ignored. For the enthalpies of solution, the values for the infinite dilution are used at standard conditions, a temperature of 20 °C and pressure of 1 atm.

3. Results

Each salt was tested with three replicates, leading to a total of nine tests. Fig. 2 shows the temperature of the mixture for the repetitive tests of each salt. In all tests, the temperature dropped to a lower temperature, but this drop was faster and lower for $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}2H_2O$ compared to NaCl. The NaCl mixture reached the minimum temperature of −18 °C after 400 s–800 s in three tests. $MgCl_2{\cdot}6H_2O$ mixture reached the minimum temperature between −22 °C and − 21 °C after 130 s–300 s. $CaCl_2{\cdot}2H_2O$ mixture reached the minimum temperature between −21 °C and − 20 °C after 120 s–250 s. The measured raw data is available here (Kulyakthin and Klein-Paste, 2020).

The melted mass as a function of time were calculated for all tests using Eqs. (13) and (14). Eq. (13) requires a value for the mass concentration of salt, x, which needs to be assumed. Theoretically, this concentration can range between the freeze point concentration and the solubility. Fig. 3 shows melted mass as function of time for the three deicers, separated for the two used assumptions. The calculated melted mass data is available here (Kulyakthin and Klein-Paste, 2020). The time where the deicers reached 75% of their melting capacity (7.5 g) is marked and the key parameters are tabulated in Table 2.

In general, the chosen assumption did not have a big impact on the development of the melted mass over time. NaCl melted ice at a gradually reducing rate while $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}2H_2O$ had a much faster melting in the early stage of the melting process (up to about 200 s) followed by a more distinct reduction in melting rate. Independently of the chosen assumption, NaCl reached 75% of its melting capacity after about 1600 s while $MgCl_2{\cdot}6H_2O$ reached this after about 500 s, irrespective of the used assumption. However, the chosen assumption had an influence on the time $CaCl_2{\cdot}2H_2O$ reached 75% of its melting capacity; about 450 s when the freezing concentration was used, contrastingly about 250 s when the solubility concentration was used.

Fig. 4 shows the melting rates which were calculated from the results in Fig. 3 by taking the gradient (second order accurate central difference) and averaging it over 5 s. The figure focuses on the first 200 s of test where the main changes in rates are occurring. After that, the rates slowly decrease towards zero. The data is plotted from 15 s after start. Before 15 s the heater temperature increased rapidly from −15 °C to −14 °C (according to the set temperature on the heater) which caused a peak in the calculated melting rate. This peak is not related to the ice melting, but to the heat which went into the heating element which has much higher thermal conductivity than ice mixture and sufficiently high heat capacity to affect the calculations. For NaCl, the maximum melting rate reached 0.020 g/s for both assumptions. For $MgCl_2{\cdot}6H_2O$, the maximum melting is 0.075 g/s for the freeze curve assumption and 0.086 g/s for the solubility curve assumption. For $CaCl_2{\cdot}2H_2O$, the maximum melting rate is 0.085 g/s for the freeze curve assumption and 0.175 g/s for the solubility curve assumption. Table 2 also shows the average melting rates over 100% and 75% of melting capacity. It shows similar trends as the corresponding melting times.

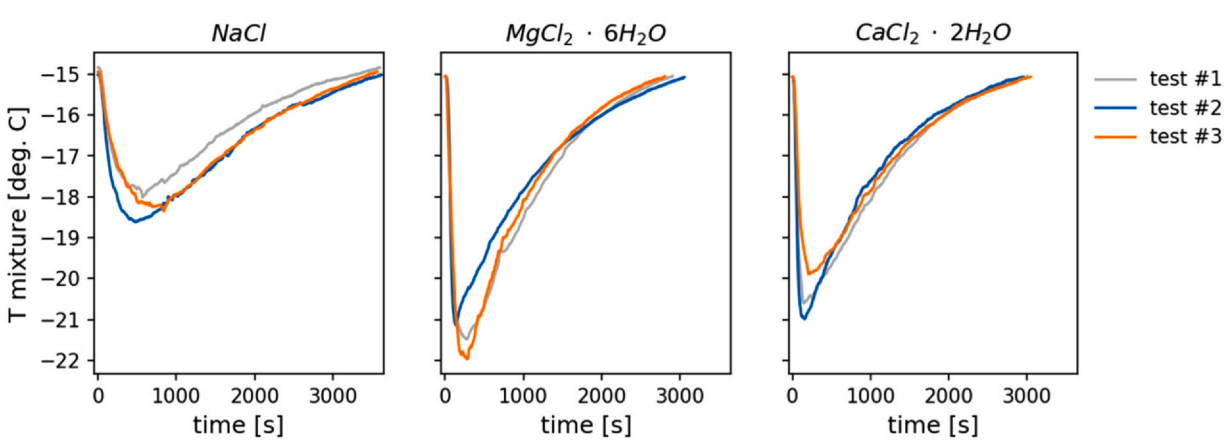

Fig. 2. Temperature of the mixture during triplicated tests.

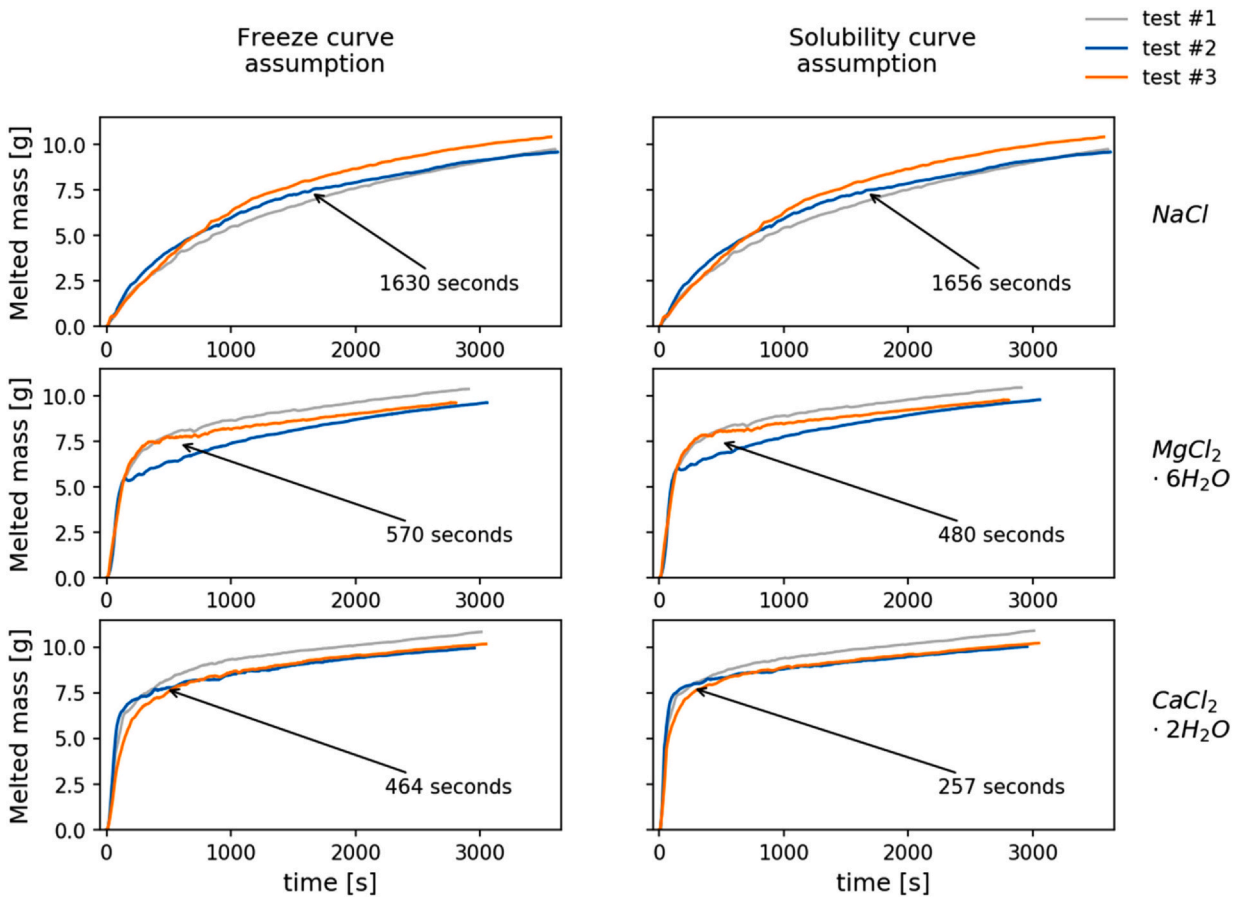

Fig. 3. Calculated melted mass as a function of time.

Table 2
Summary of melted mass calculations; the average of three replicates is given ± their maximum deviation from the average.

Melting rate metric	Used assumption*	NaCl	$MgCl_2 \cdot 6H_2O$	$CaCl_2 \cdot 2H_2O$
Total melted mass [g]	F	9.92 ± 0.50	9.87 ± 0.50	10.33 ± 0.51
	S	9.92 ± 0.50	10.00 ± 0.45	10.39 ± 0.52=
Time to reach 100% of melting capacity [s]	–	3598 ± 29	2922 ± 132	3003 ± 49
Time to reach 75% of melting capacity [s]	F	1630 ± 278	570 ± 435	464 ± 82
	S	1656 ± 279	480 ± 364	257 ± 49
Average melting rate over 100% of melting capacity [g/s]	F	0.0028 ± 0.0002	0.0034 ± 0.0002	0.0034 ± 0.0002
	S	0.0028 ± 0.0002	0.0034 ± 0.0002	0.0035 ± 0.0002
Average melting rate over 75% of melting capacity [g/s]	F	0.0046 ± 0.0008	0.0145 ± 0.0075	0.0198 ± 0.0042
	S	0.0045 ± 0.0008	0.0199 ± 0.0110	0.0420 ± 0.0146
Maximum melting rate [g/s]	F	0.021 ± 0.003	0.075 ± 0.013	0.085 ± 0.025
	S	0.020 ± 0.003	0.086 ± 0.013	0.175 ± 0.052

* F means assuming freezing point concentration, S means assuming solubility concentration.

4. Discussion

The deicer's melting rate is a kinetic characteristic. Unlike ice melting capacity, the melting rate is not an equilibrium state property but the result of the kinetic process and will therefore depend on various factors that are not influencing the total ice melting capacity. This sets higher demands to the test procedure, compared to an ice melting capacity measurement. We believe that there are three main factors that one needs to control when attempting to measure the melting rate of deicers: 1) the deicer's physical properties, 2) the degree of mixing and 3) the flow of heat.

The physical properties of a deicer (e.g. whether it is solid or liquid, its grain size distribution, density, moisture content) will affect the melting rate. Two deicer products may therefore have a different melting rate, even though their chemical composition is the same. It is therefore crucial that a melting rate test does not require any operations that change these physical properties such as dissolving, crushing, drying, sieving, compressing or melting the deicer. The deicer needs to be evaluated “as-delivered”. It is legitimate to prewet the deicer, if this is also done in real-life applications, but it will demand a realistic prewetting ratio. The calorimeter described in this study can handle “as-delivered” solid (dry and prewetted) and liquid deicers.

Mixing the deicer/ice/meltwater will also affect the melting rate. Without any mixing, the melting rate is low and mainly controlled by the diffusion of deicer molecules into the meltwater (Wåhlin and Klein-Paste, 2017). Mixing reduces the concentration gradients in the meltwater and facilitates both the dissolution of the deicer into the solution, and the dissolution of H_2O molecules from the ice into the same solution. Among winter maintenance practitioners it is widely acknowledged that the action of traffic speeds up a de-icing operation. Although

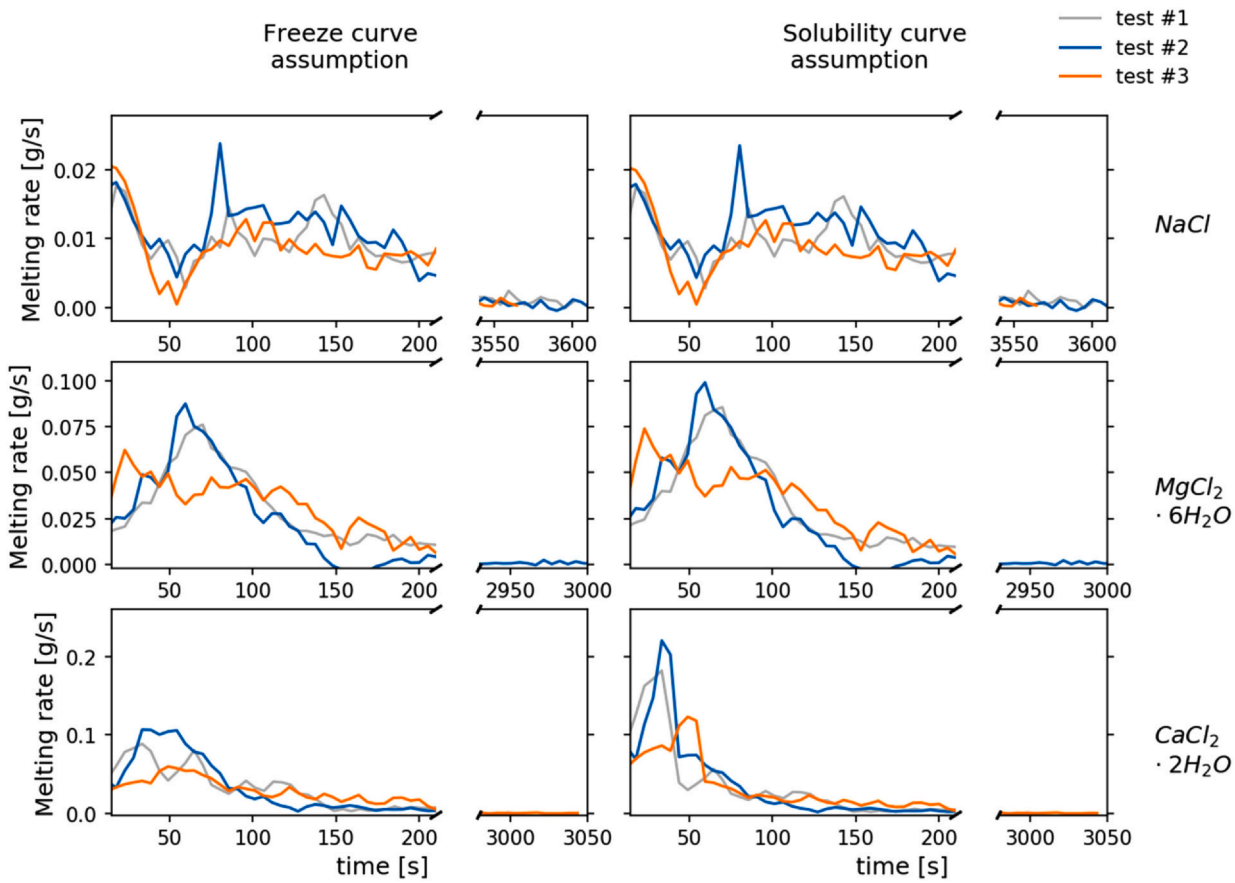

Fig. 4. Calculated melting rate over time.

the contribution of heat from the tires cannot be neglected a priori, it is likely that the traffic also contributes to mixing. Melting rate experiments without any mixing are usually easier to conduct but are likely to underestimate the melting rate for real-life performance. To measure the melting rate with some degree of mixing, it is crucial that the mixing is constant between different tests. Poorly controlled mixing can lead to a large variability in the results, which is likely the case for the SHRP H205.1 ice melting capacity test for solid deicers (Nilssen et al., 2016). In SHRP H205.1 test, the formed meltwater is extracted from ice plates at regular intervals and re-applied after determining the mass. It is not certain that the degree of mixing used in the current study is realistic for real-life conditions. To answer this question, it will require a dedicated study of comparing the melting rates measured by the calorimeter with the real-life deicing speeds. Real-life conditions are likely to be highly variable due to differences in travel speed and traffic composition, so the investigation of these parameters would require multiple field tests. Nevertheless, most important is that the mixing is repeatable and constant within different tests, which is provided by the calorimeter. The chosen mixing settings (180° back and forth at 64 deg. s^{-1}) used in this study provides a gentle tumbling of the ice particles over the heater element without introducing measurable heat.

The third factor influencing the melting rate is the flow of heat towards the melting front. As Fig. 2 shows, the overall temperature inside the reactor dropped for all three tested deicers when the melting process starts. In real-life, this temperature reduction occurs as well and allows a heat flux from the surroundings (convective heat from air, conduction from the underlying pavement, incoming short- and long-wave radiation and possibly frictional heat from tires). The flow of heat reduces the extent of the temperature drop and determines how quickly the ice/deicer solution warms up again to the initial temperature, where ice melting capacity is reached (Klein-Paste and Potapova, 2014). The average melting rate of the total melting process is therefore strongly dependent on the heat fluxes towards the ice/deicer/solution system. Any ice melting rate tests require therefore the control over the magnitude of the heat fluxes or should at least attempt to keep the heat flow constant between different tests at a given test temperature. In our calorimeter, the heater was programmed to keep a constant temperature to mimic surroundings that can give infinite amount of heat, but at a rate which is controlled by the difference between the temperature of system and the surroundings. For practical reasons, it was chosen to keep the surroundings 1 °C warmer than the setpoint to prevent a very slow heat flow at the final stage of the test. The actual magnitude of the heat flow will be dependent on the efficiency of heat transfer between the heater and the ice/deicer/solution mixture. As for the mixing, it is not certain that this approach captures a representative heat flux for real-life deicing operations. But at least it is a way to control the heat flow and mimic the flow of heat from the surroundings in a repeatable manner.

The melting rate dependency on mixing and heat flow implies that the results measured in this study are instrument specific. If an international standardized test is to pursue, it would require a clear specification of the design which describes: the rotation speed; size and amount of ice particles; shape and size of the reactor; area of the heater; thermal conductivity and capacity of the heater material; the thickness and thermal conductivity of the insulation.

A main advantage of calorimetry over other measurement techniques is that the melting process is not disturbed by taking physical samples of the melt water. Once the reactor is filled with ice and the deicer is placed in the loading chamber, it is simply pressing the deicer into the reactor and starting the datalogging. The melting rate is determined solely from the temperature and the power readings and solving the energy balance for each time step (Eqs. (13) and (14)). For

solid deicers however, this approach requires an assumption on the concentration. As explained in the Methods section, the concentration of the deicer in the meltwater is needed to account for the enthalpy of dissolution. If the deicer concentration remains high as meltwater volume increases, it means that the deicer quickly dissolves and quickly released its heat of dissolution in the reactor. In contrary, a low deicer concentration implies that the dissolution takes longer time. Physically, the concentration can range between the freezing point concentration and the solubility temperature at a given temperature. In reality, the concentration is likely to change somewhere between its minimum and maximum values as long as solid deicer is present in the reactor. Nevertheless, these two assumptions provided a good way to assess the importance of dissolution contribution to the total heat balance.

For all tested deicers, the concentration assumptions had little effect on the total melted mass; the variation between the two assumptions was less than the variability between test repetitions. The same holds for the average melting rates for the three deicers. But the assumption did have an impact on the maximum melting rate. For $MgCl_2{\cdot}6H_2O$, the maximum melting rate is 13% higher when the solubility concentration assumption is used, compared to the freeze point concentration assumption. For $CaCl_2{\cdot}2H_2O$, the maximum melting rate is two times higher for the solubility concentration as compared to the freeze-point concentration. For NaCl, however, there was no difference in maximum melting rate for the two assumptions. These differences can be explained by two factors: 1) the enthalpies of dissolution and 2) the difference between the two concentrations. The effect of the chosen assumption increases when the deicer is either highly endothermic (large positive heat of dissolution) or highly exothermic (large negative heat of dissolution). For $CaCl_2{\cdot}2H_2O$, the absolute value of the enthalpy of dissolution is almost five times higher than for NaCl (see Table 1). This makes the term ΔQ_{diss} more important in the total energy balance for $CaCl_2{\cdot}2H_2O$ than for NaCl. In addition, the difference between freeze point and solubility concentrations is also significant for $CaCl_2$; it is 17 wt% for −15 °C. These two factors combined explain why the melting rate of Calcium Chloride is more sensitive to the chosen assumption, compared to NaCl. The enthalpies of dissolution of NaCl and $MgCl_2{\cdot}6H_2O$ are rather similar by absolute values but the difference between the freeze point and solubility concentrations is only 5 wt% for NaCl and 19 wt% for $MgCl_2$. That is why $MgCl_2{\cdot}6H_2O$ shows 13% difference melting rates for the two concentration assumptions, while the melting rate of NaCl is virtually unaffected by the chosen assumption. These considerations also imply that the dependency of the chosen assumption gets larger at higher temperatures because here all deicers have a larger difference between the freeze point and solubility concentrations.

The above shows that the knowledge about the concentration becomes important for the deicers with high enthalpy of dissolution. For such deicers, the current method can be improved by either direct measurement of concentration or a more precise model for the dissolution process. The first option is straight forward, but it will diminish the advantage of non-disturbed measurements. Therefore, it is desired to use direct measurements for a limited number of tests to establish a better dissolution model than just the physical limits which were used in this study. For products of unknown composition, it will be required to determine the heat of dissolution. This can easily be done in the calorimeter by dissolving the deicer in a known mass of water and measure the temperature increase.

Fig. 4 shows that the calorimeter allows one to evaluate the melting rate throughout the whole melting process. But for easy comparison of different deicers, it is desirable to reduce this information to a single number. In this study, we calculated different metrics for the ice melting rate. First metric is the time to reach 100% of melting capacity. The disadvantage of this metric is that it depends strongly on the last part of the melting phase where the temperature rises again to the setpoint. Table 2 shows that the time to reach 100% of melting capacity for NaCl is only about 20% longer than that of $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}2H_2O$, while there is virtually no difference between $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}2H_2O$. Second metric is the time to reach 75% of melting capacity. It shows larger differences between the three deicers. It takes NaCl 285% longer time than $MgCl_2{\cdot}6H_2O$, when the freezing point assumption is used. This metric does also show the effect of the chosen assumption which, as discussed earlier, still contributes to an uncertainty in the melting rate estimate. When the freeze point assumption is used, the difference in melting rate between $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}2H_2O$ would be considered small (570 vs 464 s, respectively). While assuming solubility concentration results in a significant difference (480 vs 257 s, respectively). Obviously, the choice of 75% as criteria is somewhat arbitrary, but it seems to give a good trade-off between the sensitivity for deicer specific differences and representation of a large portion of the total melting process. From a practical point of view, winter maintenance practitioners may not have the time to wait until all the ice melting capacity has been reached, hence the long time to reach the last 10–25% of melting capacity might be not relevant. A third and forth metrics which we considered are the average melting rates over the whole melting process and over the range from 0 to 75% melting capacity. For comparisons between different deicers, this does not differ from the time to reach 100% or 75% of melting capacity, but the benefit is that the unit [g/s] reflects indeed melting rate, rather than time. For practical purposes, however, it may be a less intuitive number, because winter maintenance practitioners rarely know exactly how much ice is needed to be melted. They just want to know how long they should wait before they no longer can expect more melting at a reasonable rate. The last considered metric is the maximum melting rate, averaged over 5 s. This averaging is needed to ensure the number is not dependent on an extreme value that can be a single measurement error. This indicator captures the main differences in melting rate well, since a high maximum melting rate also represents a fast melting overall. However, as can be seen in Fig. 4, the variability in maximum melting rate between different runs is rather large. Based on the evaluation of all these metrics, we believe that the time to reach 75% of melting capacity is the most relevant way to reduce the information of the melting rate as function of time to a single number.

This study shows that it is possible to quantify the melting rate of solid deicers throughout the melting process using calorimetry. Further improvements of the method can be made by improving the estimation of the deicer concentration in the meltwater solution, either by direct measurements (taking the samples of ice melt periodically and measuring its ion concentration) or by an improved assumption. The latter is preferred to ensure the melting rate can be determined without disturbing the process; one of the key advantages of calorimetry. Due to the kinetic nature of the melting process, the experimental setup needs to be well specified as many details can influence the obtained results.

5. Conclusions

A method is presented here to measure the melting rate of deicers based on the principle of calorimetry and solving the heat balance equation at every time step. It allows to measure the melting rate of "as-delivered" deicers throughout the whole melting process without disturbing the melting process. The melting rate of $CaCl_2$ and $MgCl_2$ was clearly faster than NaCl.

Solving the heat balance for solid deicers that release or require heat upon dissolution requires an assumption or measurement of the deicer concentration in the meltwater. Theoretically, the concentration can range between the freezing point and solubility concentrations. Both limits were used to assess the uncertainty of the unknown concentration. The extent of the uncertainty does not currently allow for a distinction between $CaCl_2$ and $MgCl_2$, but this uncertainty can be reduced by improving the assumption scheme based on direct measurements.

In general, the melting rate of deicers depends on the physical characteristics of the product, the degree of mixing and the flow of heat towards the ice/deicer/solution system. The implications of these

factors for the design requirement of a test setup is discussed.

Different metrics to reduce the information of melting rate as function of time are investigated, and the time it takes to reach 75% of the melting capacity does give the best characterization of the melting performance, compared to the other considered metrics.

Authors contribution

Sergey Kulyakthin has contributed to this work by developing and programming the model, conducting the experiments and writing the majority of the manuscript. Alex Klein-Paste has contributed with the research idea, guidance during the study, and commenting/adjusting the manuscript. All authors have reviewed the results and approved the final version of the manuscript.

CRediT authorship contribution statement

Sergey Kulyakthin: Methodology, Software, Validation, Investigation, Data curation, Writing - original draft. **Alex Klein Paste:** Conceptualization, Supervision, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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