International Journal of Refrigeration 144 (2022) 90–98

Contents lists available at ScienceDirect

International Journal of Refrigeration

journal homepage: www.elsevier.com/locate/ijrefrig

Development of supercoolers for ice slurry generators using icephobic coatings.

Mise au point de surrefroidisseurs pour les générateurs de coulis de glace à l...aide de rev.¼tements glaciophobes

Daniel Carbonell [*,1,a], Maike Schubert [a], Jens Røberg Frandsen [b], Joerg Brand [c], Kevin Erb [a], Loris Laib [a], Matteo Munari [d]

[a] SPF Institut für Solartechnik, OST - Ostschweizer Fachhochschule, Oberseestr. 10, CH-8640 Rapperswil, Switzerland
[b] DTI Danish Technological Institute, Kongsvang Allé 29, 8000 Aarhus C, Denmark
[c] ILAG Industrielack AG, Hämmerli 1, Wangen, CH-8855, Switzerland
[d] ALFA LAVAL, Via Ritonda 80/E - IT-370 44 San Bonifacio (VR) - Italy Italy

ARTICLE INFO

Keywords:
Supercoolers
Ice slurry
Icephobicity
Ice storage
Mots clés:
Surrefroidisseurs
Coulis de glace
Glaciophobie
Stockage de glace

ABSTRACT

A supercooler is a heat exchanger that allows to supercool water avoiding ice nucleation on the heat exchanger surface. In this paper, six supercoolers with icephobic coatings were tested for supercooling ice slurry generators. As reference, a supercooler without any coating was used. For coating comparison, three different chemical families were tested at different mass flow rates. Experiments of coated heat exchangers show average supercooling degrees in the range of 3K to 4K. All icephobic coatings improved the supercooling degree respect to the reference non coated case by 7% to 44% at 1000kgh^{-1} mass flow rate with supercooling powers up to 5 kW. For a mass flow rate of 2000kgh^{-1} a supercooling power of about 6kW has been reached for five coatings at a temperature of $-2.5°C$ and hold constant for a time span of 3h. Some coatings could reach lower temperatures at this mass flow, but the experimental setup was limited to this supercooling power. The two coatings performing best in the heat exchanger tests were both from the family class hybrid organic-inorganic silane sol-gel with improvements in the degree of supercooling respect to the reference uncoated heat exchanger of 30% to 40%. The supercooling degrees achieved in the present work are up to two times larger compared to results published in scientific journals until this date using industrially relevant heat exchangers.

1. Introduction

Water is the most used thermal storage medium for temperatures in the range of 5°C to 100°C due to its availability, environmental impact, price and excellent thermal and transport properties. Water is also the perfect phase change material with an infinite number of cycles of solidification and melting. The latent heat of fusion of water is 333kJ kg^{-1}, which corresponds approximately to the sensible heat stored in water with a temperature difference of around 80K. This heat of fusion has not been achieved by any other PCM material with melting points below 20°C(Oró et al. (2012)). All these benefits lead to the fact that an ice storage can be used for multiple applications, e.g. residential, industrial and commercial refrigeration (Kauffeld et al., 2010).

Several heat exchanger concepts for extracting the latent heat from water can be used. The most common one is based on growing ice on the heat exchanger surface. This is the most established concept in ice storages for refrigeration as well as for the solar-ice heating market. Specifically, most of ice storages installed in Europe are based on coil heat exchangers and thus the concept is typically known as "ice-on-coil" (Nelson et al., 1996). Other heat exchanger types, such as capillary mats (Carbonell et al., 2018) and flat plates (Carbonell et al., 2017; 2016; 2015; Ismail et al., 1999) can be used. In those concepts with different type of heat exchangers, a mixture of water and anti-freeze solution is

* Corresponding author.
E-mail address: dani.carbonell@ost.ch (D. Carbonell).
[1] +41 58 257 4143

https://doi.org/10.1016/j.ijrefrig.2022.07.011
Received 14 October 2021; Received in revised form 29 June 2022; Accepted 14 July 2022
Available online 16 July 2022
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used as Heat Transfer Fluid (HTF), which is circulated at temperatures below 0°C inside the heat exchangers that are immersed in a water bath. The latent heat is extracted from the water in contact with the heat exchanger and ice is formed. As long as energy is extracted by the HTF ice will grow continuously increasing the ice thickness and the heat resistance between the HTF and the water (ice has a low thermal conductivity). The transient thermal resistance of the ice layer creates a temperature glide that reduces the efficiency of the storage system. Typically, large heat exchanger areas homogeneously distributed throughout the whole storage volume are necessary. Depending on the extraction power of the refrigeration cycle and on the specific characteristics of the heat exchanger, a maximum ice layer thickness ranging from several centimeters to few decimeters are typical. This maximum ice thickness determines the distribution of the heat exchanger in the storage volume. This approach has the advantage of relative simplicity, with no moving parts. However, the large heat exchanger area represents a significant cost that reduces the storage competitiveness.

In order to reduce the heat transfer area a free-of-ice heat exchanger approach can be used. Here, two main concepts can be used, an ice slurry concept and a thermal de-icing approach (Carbonell et al., 2015; Philippen et al., 2012). The thermal de-icing concept reduces the number of heat exchangers in the ice storage, but it does not eliminate them completely. On the other hand, an ice slurry concept allows to decouple ice generation and storage, which means that no heat exchangers are necessary in the ice storage. This reduces the ice storage cost significantly and in principle it allows to use any storage casing shape. In these technologies ice is created in the form of small particles, typically less than 2 mm in diameter, that remain suspended in a liquid phase. As carrier fluid water or a mixture of water and antifreeze can be used. Even at ice mass fractions up to 40%, such slurries can still be pumped like a liquid through pipes and heat exchangers, enabling extremely compact heat transfer equipment due to the high energy density of the heat transfer fluid (Kauffeld et al., 2005). All ice slurry generators are avoiding the continuous ice growth on the surface of the heat exchanger, either by a method that avoids that ice forms on the surface, e.g. supercooling (Tanino and Kozawa, 2001), direct contact evaporation with a refrigerant (Wijeysundera et al., 2004), water vacuum freezing (Honke et al., 2015) or by actively removing the ice from the heat exchanger surface, e.g by using scrapers (Stamatiou et al., 2005), fluidized beds (Pronk et al., 2003), supercooled water jets (Mouneer et al., 2010) or by blowing compressed air (Zhang et al., 2008). From all these methods the most well know and established technology is the scraper type.

Today, nearly all ice slurry generators are mechanically scraped heat exchangers, where ice is formed on a cold surface, then removed by a rotating auger in a continuous manner. This process is commercially available for conventional refrigerants. However, it has several disadvantages such as the mechanical complexity of the scraping system that adds capital, operation and maintenance costs and has a negative impact on system reliability. The physical size of the scraper type is limited due to mechanical constraints, forcing to use parallel units for large capacity ranges, which increases cost, complexity and penalizes scalability. To overcome these limitations one can think on a passive concept for ice slurry production that does not rely on moving parts. One concept is to supercool water with the heat exchanger, the so-called supercooler, which allows one to supercool a liquid to a metastable state. This supercooled liquid is then pumped to the crystallizer where it undergoes nucleation resulting in an ice slurry which is then pumped to the ice slurry tank. An important variable here is the degree of supercooling, defined as the freezing temperature minus the supercooled liquid temperature. However, achieving a large degree of water supercooling in stable operation, without ice nucleating on the supercooling surface, is a major challenge. In this paper we present experimental results of seven supercoolers based on brazed heat exchangers typically used in residential heat pumps. The supercoolers are sized for a heat pump with 10 kW of nominal thermal power. From those, one is a non-treated version used as reference and the other six were developed using icephobic coatings from three different chemical family types.

1.1. State of the art in supercooling technology

The most advanced state of the art of supercooling technology was established around twenty years ago by researchers from Japanese companies. The status in the rest of the world is by far less advanced in this field. There are several publications from the research group of the Japanese company Takasago Thermal Engineering. Researchers from this company presented ice slurry generators with capacities in the range of 13kW to 250kW that achieved a degree of supercooling of 2 K (Kozawa et al., 2005; Mito et al., 2002; Tanino and Kozawa, 2001). In these publications several ways to release the supercooling state of the flow, i.e. an ice crystallizer unit, were proposed. Kurihara and Kawashima (2001) from Shimizu Corporation presented a system targeting a cooling power of 113kW. It was estimated that the supercooling ice slurry generator would have a 20% higher efficiency compared to ice-on-coil system. A twin-plate supercooler made of stainless steel was used achieving a degree of supercooling of 1.8 K. Nagato (2001) from Shinryo Corporation presented a closed ice slurry system without exposure to atmosphere. They presented results for a continuous operation for 14 h with a degree of supercooling of 2 K. In principle the system was prepared to deliver up to 1.8 MW of cooling power. Unfortunately, in none of these papers from Japanese companies the development of the supercooler itself was a topic and thus no information was given on the supercooler type or surface treatments used (if any). An exception is the work of Wakamoto et al. (1996) where a 6.6 meters long deoxidized copper straight tube-in-tube was used. This long heat exchanger was able to supercool water up to 4 K after four etching processes necessary to obtain a roughness around 2 μm. However, this long polished supercooler can not be considered as industrially relevant since it was only able to provide cooling powers below 1 kW under these conditions.

The state-of-the-art everywhere else except in Japan, is far below in the technology readiness level chain and the literature is not very extensive. Castaing-Lasvignottes et al. (2006) and Bédécarrats et al. (2010) investigated numerically and experimentally a supercooler heat exchanger, where stable operation was achieved with 1.2 K degree of supercooling, leading to slow ice production and only 1.3 kW cooling power. These experiments showed that achieving stable operation with a decent degree of water supercooling is challenging. Faucheux et al. (2006) analyzed the influence of aluminum roughness on the supercooling degree under static conditions concluding that it increases when surface roughness decreases. Analyses of the roughness of a coaxial copper tube with supercooled flows was provided by Ernst and Kauffeld (2016). Roughness was varied between 2.1μm to 0.4 μm obtaining degrees of supercooling around 2.3 K and 3 K respectively. Tap water with a velocity of 0.36ms^{-1} was used. While the frequency of ice blockages as a function of the maximum supercooling degree that was achieved was not stated in the paper, the authors reported by personal communication that the supercooling degree was stable over several hours. However, these results were obtained using a polished long tube (around 5 m) with gentle bends and only 1 kW of cooling capacity. As in the case of Wakamoto et al. (1996), this kind of heat exchanger is not suitable for any practical application. In Wang et al. (2012), the authors coated a coaxial tube heat exchanger (12 mm internal diameter) with a polymer that contained a fluoric binder and an organic solvent. They observed an increase in the maximum supercooling degree from 0.9 K to 1.7 K at a velocity of 2ms^{-1} thanks to the fluorocarbon coating. However, even with the coated surface, this highest supercooling degree only lasted 9 minutes. Increasing the velocity to 2.5ms^{-1} lead to frequent blockage by the ice growth. To address the problem of not achieving continuous ice production due to ice blockage, the same authors proposed a twin supercooler concept in Wang et al. (2016), such that once one

supercooler was ice-clogged, the second one would operate. In this paper a corrugated plate was used with a degree of supercooling in the range of 0.5K to 1K with fluid velocities of 0.1m s^{-1} to 0.45m s^{-1}. Qu and Jiang (2000) analyzed an untreated heat exchanger with stainless steel tubes and a carbon steel shell. Supercooling degrees of 0.5K were experimentally evaluated and no continuous operation for several hours was possible.

In summary, from the literature above one can see that Japanese companies were very advanced two decades ago with ice slurry generators achieving a degree of supercooling in the order of 2 K or below. Everywhere else but in Japan the stable supercooling degree achieved decreases from 2 K to 0.5 K when industrially relevant heat exchangers are used. In this paper we present experiments that show average supercooling degrees in the range of 4 K, which is a significant step beyond the state-of-the-art.

2. Methodology

We have developed and experimentally evaluated a large set of coatings where different testing methods were used. Many coatings were assessed only at sample level at area ranges of 150cm^2*to*180cm^2 without water flows. From these, six coatings were selected and used in the present work to coat brazed heat exchangers and use them as supercoolers. The selected six icephobic coatings make use of three main chemical compositions. As a reference, the same brazed heat exchanger without any coating (Ref) was tested. The evaporator for the foreseen system should provide about 5kW to 7.5kW supercooling power with a temperature glide on the water side of about 0°C to −3°C without freezing. Thus, the final goal is to achieve a 3 K supercooling degree with nominal flow conditions.

2.1. Coating of supercoolers

The coatings developed are characterized by being smooth and hydrophobic to increase long term durability on supercooling flows in comparison to superhydrophobic coatings that are prone to degrade over time (Sojoudi et al., 2016). Hydrophobicity is the ability to repel water which is provided by surfaces having a significant lower surface energy than the surface tension of water and are often characterized by water contact angle measurements (typically above 90°). The hydrophobicity is provided as:

a) bulk property, this is the case of hydrophobic coatings based on silicon-rubber for example. The precursors of those coatings are organo-polysiloxanes that provide hydrophobicity as a bulk property. This coatings are expected to be more durable since when a mechanical damage occurs and some material is removed from the surface, the resulting surface remains hydrophobic too.
b) by adding hydrophobic additives. Polydimethylsiloxane and fluoropolymers can be used as additives, which via reactive terminal functional groups, cross-link chemically with the coating matrix becoming a constituent part of the coating network. Thus, the additive is not leached out when the coatings are in use. Driven by the low surface energy, a part of the additive merges during curing to the surface to form an ultrathin hydrophobic layer. After curing, this surface layer is basically fixed and does not merge away when the surface is in contact with water. When the ultrathin surface layer is damaged, the hydrophobic properties decrease. Despite this disadvantage compared to coatings consisting predominately of hydrophobic material, coatings with a hydrophobic additive are widely applied in the industry as their stability is often sufficient and this concept allows a great freedom in selecting a suitable coating material.

2.1.1. Icephobic coating development

One investigated path is the use of hybrid organic-inorganic coatings (HOIS). They were selected due to previously demonstrated durability in water-like environments, low film thickness and some of them have been previously applied for different anti-fouling purposes and against frost spreading. The HOIS were prepared either by sol-gel processing (Sepeur, 2008) or via moisture-curing route (Holberg, 2017). The precursor solutions were prepared from organosilanes and additional organic precursors, for example, isocyanate resins. After curing, the organosilanes form an inorganic siloxane network (Si-O), which is connected chemically to organic groups or an organic network.

Another strategy is based on the fabrication of isocyanate free hybrid coatings (IFHOIS), these coatings use hybrid silicone-epoxy resins as main coating constituent. The silicone-epoxy resins possess an organic-inorganic siloxane hybrid binder with the siloxane as the matrix and epoxy and alkoxy functionality in the side chains. The epoxy functionality allows for rapid cross linking with standard amine curing agents. Those coatings combine the properties of traditional silicones and epoxy systems. Epoxies are hard and strong due to the high cross-linking and silicones have high elongation and flexibility. They are expected to yield strong and flexible coatings with higher or equal resistance to the HOIS coatings without isocyanates.

Another method is to use hydrophobic coatings which have shown ice formation delay properties with an optimized dry film thickness to enhance mechanical resistance, while still having good thermal conductance. Strategies used for these coatings are Polysiloxane and Fluoroethylenevinylether containing coatings. Fluoroethylenevinylether (FEVE) containing polymers have curing temperature of 200°C to prevent copper oxidation. No copper bonding agent is used, and hydrophobic additives are added to the matrix. The dry film thickness target is approx. 10μm to 15μm to achieve a good heat transfer. Polysiloxane (PS) based coatings are cured at room temperature by humidity, to facilitate the coating process and prevent copper oxidation. No copper bonding agent is used due to the lower curing temperature, but hydrophobic additives have been added to the matrix.

2.1.2. Icephobic coatings selected

Around 29 icephobic coatings were investigated using ice depression tests at atmospheric conditions with samples of 150 cm^2. From those, the six coatings described in Table 1 were selected to be applied in the supercoolers presented in the current paper. These coatings are applied to the water side of brazed plate heat exchangers. These heat exchangers have an overall area of 2.04m^2 with 40 plates of 111 x 526 mm^2 each. The water velocity is in the range of 0.08 ms^{-1} for 1000kgh^{-1}.

As a reference, a heat exchanger without any coating was used. For each icephobic coating two heat exchangers were coated. One was used for the experiments and the second one was cut to analyse the coating application method. The second heat exchanger was crosscut at the middle and at each end to evaluate the coating throughout the heat exchanger. At each crosscut, the coated parts showed good repellent

Table 1
Overview of coatings used in the supercoolers tested.

Coating	Chemistry & others
HOIS-03	Hybrid organic inorganic siloxane prepared by sol-gel method. Transparent smooth surface. Added repellent additive to create hydrophobic and oliophobic surface. Curing temperature of 185°.
HOIS-04	Different backbone matrix and repellent additive compared to HOIS-03. Curing temperature of 200°C.
IFHOIS-28	Isocyanate free variation of HOIS-04 using a silicone-epoxy resin as the main constituent of the coating matrix. Curing temperature of *I*185°C.
PS-04	Methyl polysiloxane resin. Contains silicon oil. Ambient temperature moisture curing for seven days.
FEVE-06	Fluoroethylenevinylether containing polymer. Contains hydrophobic additives. Curing temperature of 200°C for 60 min.
FEVE-11	Same as FEVE-06, but different supplier of the base material.

properties and no sign of cracks or defects. There were no signs of blockage of the channels either. (examples are shown in Fig. 1).

In the water inlet and outlet headers, the heat exchanger has a small hollow in which the coating accumulates and has a higher thickness. Some coatings are more sensitive to thickness and may crack or delaminate if a certain thickness is reached, which can be observed at the inlet/outlet region. The reference and most of the coated heat exchanger show surface irregularities at inlet and outlet.

Examples of pictures of those regions are shown in Fig. 2. The coatings HOIS-04 and PS-04 were not applied perfectly. Despite the visual conspicuities, no incidence was observed regarding anti freezing properties or degradation over time. For HOIS-04, several coating particles originating from the edge sections in the heat exchanger, where the coating had accumulated during curing process, were observed in the storage tank. PS-04 showed particles in the inlet and outlet region of the heat exchanger. To avoid the systems being influenced by these particles both heat exchangers were flushed with a water mass flow rate of 2500kgh^{-1} before starting the test. Several particles were collected and removed from the system before the test.

2.2. Experimental test setup

The test setup is shown in Fig. 3. The chiller is cooling down the brine cycle (left hand side of supercooler) with defined chiller temperatures (TI 1) and at a mass flow rate of about 2000kgh^{-1}. The temperature of the brine is measured at the inlet of the heat exchanger via the sensor TI 2 ($T_{brine,in}$) and at the outlet of the heat exchanger with sensor TI 3 ($T_{brine,out}$).

The water cycle (right hand side of supercooler) has two heating units. Heater 2 (H2) heats the supercooled water after the outlet of the heat exchanger (supercooler) to ensure no ice is present in the system. Heater 1 (H1) is heating up the water to 0.3°C in order to ensure a constant water inlet temperature at the heat exchanger ($T_{wat,in}$) adding a safety factor to ensure no ice particles exist. The water temperature is measured in the tank close to the outlet (TI 7) and after heater 2 (TI 6) within the flow directly. The outlet temperature of the heat exchanger ($T_{wat,out}$) is measured indirectly by a surface sensor (TI 4) at the outside of the pipe in order to do not influence the measurements by inserting an element that could trigger nucleation. Ice formation was prevented in the setup as the presence of ice crystals in the system add uncertainties on the measurement of supercooling capabilities of different heat exchangers.

2.3. Measurement methods

All experimental results used in this article are available in the supplementary material data provided. Experimental values of mass flow rates and temperatures for the brine and water loops are reported on a time step of one minute for all coatings and experiments conducted.

2.3.1. Calculation of the water outlet temperature

For measuring the outflow temperature of the supercooled water $T_{wat,out}$ necessary to calculate supercooling degree (SD), a surface sensor was glued to the pipe without being in contact with the supercooled water. The SD is calculated as the freezing temperature of 0∘C minus $T_{wat,out}$, i.e. $SD = -T_{wat,out}$ K. In a pre-test of the first heat exchanger, a temperature sensor was also placed into the flow of the pipe, directly measuring the outflow temperature. A linear model was fitted for calculating the outflow temperature for several temperatures and mass flows (500kg h^{-1}, 1000kg h^{-1}*and*2000kg h^{-1}) based on the surface sensor on the pipe. The linear fit was very good with the coefficient of the regression above 0.999 for each mass flow on a temperature range of $0.3°C \geq T_{wat,out} \geq -0.95°C$. Reaching temperatures of −1°C or below was not always possible with a temperature sensor on the flow and the supercooler used in this test, which had a low supercooling capacity at that time. This means that potential non-linearities on the $T_{wat,out}$ from −1°C to −4°C are neglected. However, due to the very good linear behavior on the fitted region it is not expected that non-linearities would be relevant. Additional experiments with other heat exchangers able to supercool well below −2°C with a sensor on the flow showed that linear behavior persists for this temperature range. As can be observed in Eq. 2 and Eq. 3 there is no significant difference on relation between $T_{wat,out}$ and $T_{surf,pipe}$ when the water mass flows rates change from 1000kgh^{-1} to 2000kgh^{-1}. The equations used to convert the $T_{surf,pipe}$ from the sensor TI-4 to the $T_{wat,out}$ reported along the paper are:

$$T_{wat,out} = 1.013 \cdot T_{surf,pipe} - 0.3936 \text{ for } 500\ kg\ h^{-1} \quad (1)$$

$$T_{wat,out} = 1.0218 \cdot T_{surf,pipe} - 0.3713 \text{ for } 1000\ kg\ h^{-1} \quad (2)$$

$$T_{wat,out} = 1.0211 \cdot T_{surf,pipe} - 0.3667 \text{ for } 2000\ kg\ h^{-1} \quad (3)$$

2.3.2. Testing sequence

For comparing the coatings applied to the heat exchangers regarding the icephobic potential, the lowest ice free water temperature was determined for water mass flow rates of 500kgh^{-1} and 1000kgh^{-1} (also called supercooling temperature in the following). Starting with a chiller temperature of −1.4°C, the brine was cooled down in steps of 0.2K and each step was hold constant for one hour. This step-wise cooling process was ongoing until ice was built. Seven cycles were performed for every experiment in order to account for statistical effects in the freezing of water. For each cycle the average water outlet temperature of the last stable step before freezing occurred was used for determining the results. Fig. 4 shows an example of the experimental results for the heat exchanger coated with IFHOIS-28 and a mass flow rate of 1000kgh^{-1}. The upper graphs show the results of temperatures (left) and mass flow rates (right) for all the seven cycles. The bottom left graph shows the same values for the first cycle that lasts approximately from hour 17 to hour 32. The bottom right plot of Fig 4 zooms into the freezing of the second cycle where it can be seen that the pump power increases while mass flow rates decreases due to ice generation. This is recognized by the control as freeze alarm and a heating program is initiated to start the next cycle. The average, minimum and maximum supercooling temperatures of all cycles are used to present the results in Fig. 6 and Fig. 7.

2.3.3. Supercooling stability tests

In the evaporator of the heat pump designed for our purpose the



(a) HOIS-03 (b) HOIS-04 (c) PS-04

Fig. 1. Examples for coated and uncoated channels in a heat exchanger cut. Red circle: coated channels (water-side), blue circle: uncoated channels (brine-side).

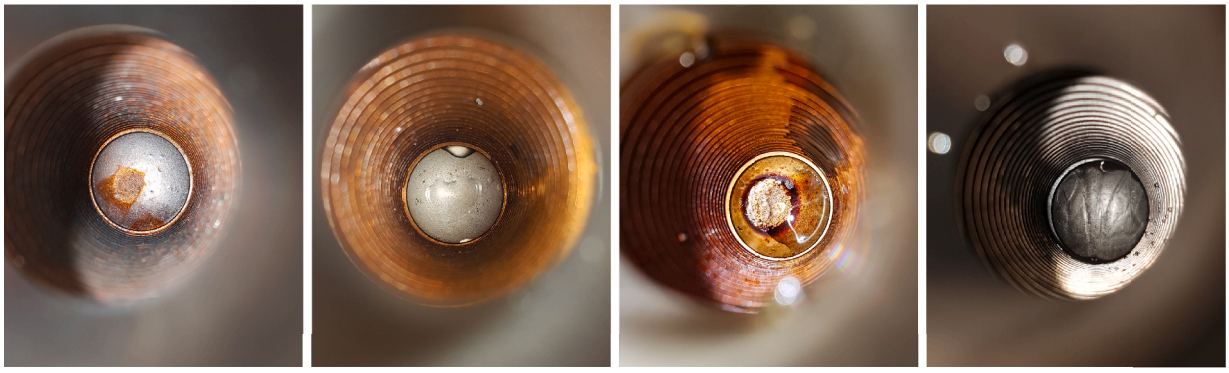


Fig. 2. Examples of coated inlet or outlet after testing.

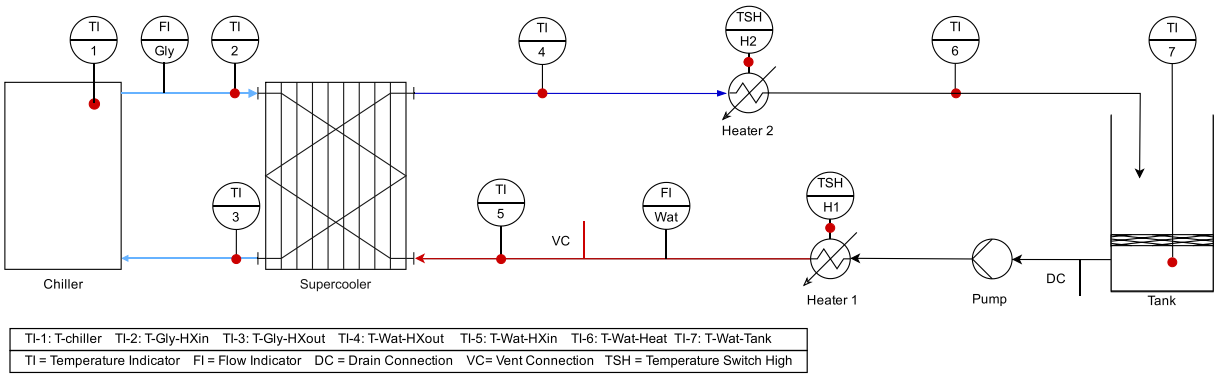


Fig. 3. Setup of the coated heat exchanger tests with temperature sensors.

supercooling has to be held for a long period at a supercooling power range of 5kW to 7.5kW. For a mass flow of 2000kgh^{-1} the stability of the supercooling over a time span of three hours was tested. For every heat exchanger three steps were measured for three hours each consecutively. The targeted water outlet temperatures $T_{wat.out}$ were − 1.5°C, − 2.0°C and − 2.5°C. This means that a coating that reached the last target of −2.5°C for three hours was more than 9 hours with supercooling degrees above 1.5K, i.e. 3 h at SC of 1.5 K, 3 h at SC of 2 K and 3 h at SC of 3 K. The resulting supercooling power $P_{supercool}$ is about 3.4kW, 4.7kW and 5.8kW respectively (see example in Fig. 5). Lower supercooling temperatures or higher water mass flow rates were not addressed because the chiller used in the experimental setup was reaching its cooling power capacity limit of around 6kW at −2.5°C and a mass flow of 2000kgh^{-1}. The stability tests were done only once and thus were not meant to rank the coatings regarding their icephobicity, but rather to proof that we could achieve stable conditions at large supercooling degrees and mass flow rates.

3. Results

The supercooling results of the step experiments for coated heat exchanger are shown in Fig. 6 and Fig. 7.

The bars indicate average values while the points indicate the test results for the different cycles within each experiment and are ordered by time (first cycle result on the left and last cycle result on the right within each experiment). The uncoated reference heat exchanger (Ref) shows an average SD of 3K for the mass flow rate of 500kgh^{-1} and 2.7K for the 1000kgh^{-1} case. All coatings analysed improve the average supercooling compared to the Ref case by 7% to 40%. Lowest supercooling temperatures with improvements in the range of 30% to 40% respect to the Ref case for the two tested mass flows were reached with coatings HOIS-03 and HOIS-04. The best results for 500kgh^{-1} were achieved by the HOIS-03 reaching an average SD of 3.9K, 30% higher than the Ref case, with a maximum SD of 4.5K. The best results for 1000 kgh^{-1} were achieved by the HOIS-04 reaching an average SD of 3.9K, 40% higher than the Ref case, with a maximum SD of 4.6K.

The maximum spread of supercooling temperatures measured in different cycles for one supercooler and fixed mass flow rate is more than 1K for most of the coatings. The measurement uncertainty of the temperature sensor is around 0.03K. Thus, the spread of the supercooling temperature is caused by the stochastic nature of the freezing process of water. The spreading of the freezing temperatures is very different for the FEVE-11 case between the 500kgh^{-1} to the 1000kgh^{-1} test. The test at the mass flow rate of 500kgh^{-1} were always carried out before the 1000kgh^{-1} tests for each supercooler. Thus, one possibility is that the coating degraded showing a higher spread for the 1000kgh^{-1} experiments. However, an analysis of the several cycles freezing of FEVE-11 for 1000kgh^{-1} shows no clear tendency. If degradation would have been the cause, the freezing temperature would have increased in each freezing cycle, i.e. from left dot to right dot within the FEVE-11 bar. That was not the case and we could not say more than the large spread of FEVE-11 at 1000kgh^{-1} might be due to the statistical effects. Similarly, the supercooler using the PS-04 coating shows a maximum spread of only 0.2K for a mass flow rate of 1000kgh^{-1}, but a maximum spread of 1.2K for 500kgh^{-1}. The fact that the PS-04 coating had particles that were flushed before the test and possibly during the 500kgh^{-1} test could explain the lower spread for 1000kgh^{-1}. However, in this case we would

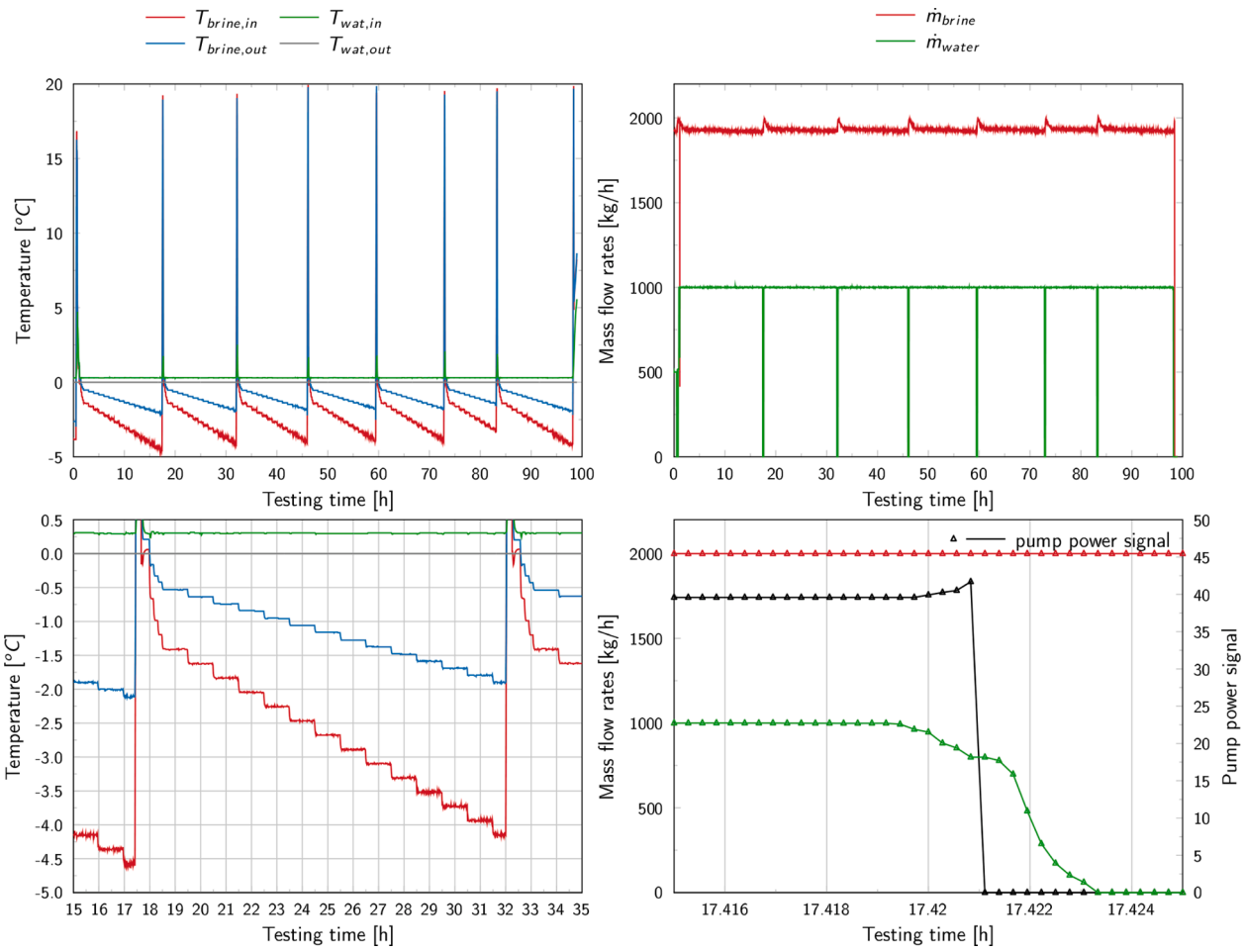


Fig. 4. Example of the step experiment with a heat exchanger coated with IFHOIS-28 and a mass flow rate of 1000kgh^{-1}. Upper graphs show the seven cycles, bottom left shows a zoom into the third cycle and bottom right shows a zoom of the second cycle freezing period. Each cycle starts with a water outlet temperature $T_{wat,out}$ of about −1.2°C.

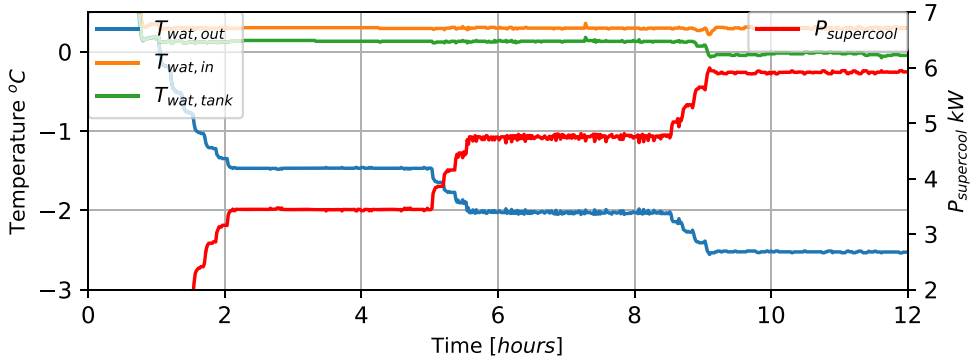


Fig. 5. Example of supercooling stability test experiment for a heat exchanger coated with IFHOIS-28. Results show the inlet and outlet temperature of the supercooler and the temperature in the storage tank.

expect a better performance of PS-04 at 1000kgh^{-1} and this does not seem to be the case. Thus, the very low spread of PS-04 at 1000kgh^{-1} might be a coincidence. Notice that the number of seven cycles is not high enough to cover completely statistical effects of the freezing process. A way larger number of testing cycles would be necessary to clarify these uncertainties. However, this is not possible due to the long duration of these tests, e.g. about five days for one mass flow and supercooler. Faster test methods with small samples would be necessary to assess the stochastic nature of icing. However, it is a big challenge to reproduce the phenomenology observed in a supercooler using small samples. For example, it is not possible to supercool water at this large degrees using small surfaces since an extremely large cooling rate would be necessary modifying the heat transfer rates that will influence the icing process.

The heat exchanger coated with HOIS-04 was the only one achieving higher SD for a mass flow rate of 1000kgh^{-1} compared to the one ach-

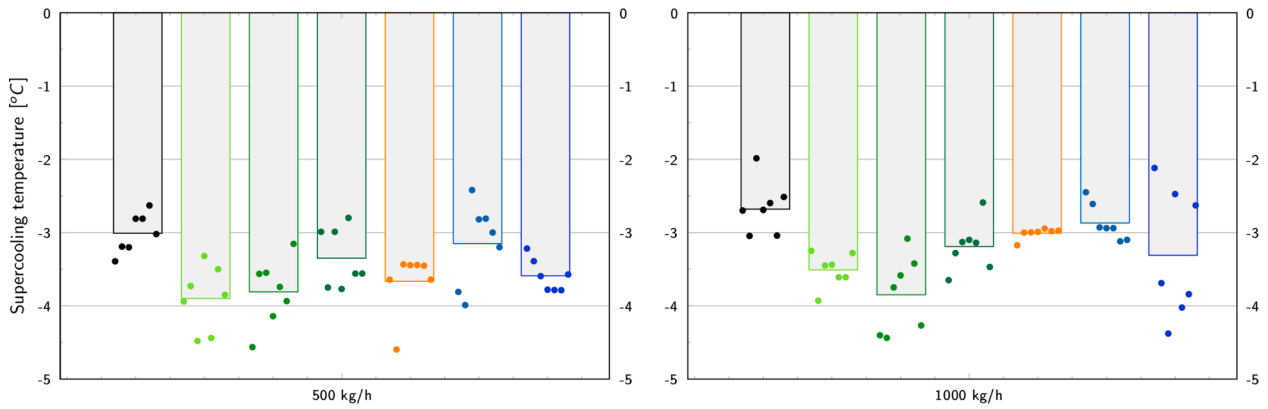


Fig. 6. Supercooling temperature for all heat exchanger from step experiments with mass flow rates of 500kgh^{-1} and 1000kgh^{-1}. The dots indicate results for the different cycles within each experiment and are ordered by time (left: first cycle, right: last cycle). Colors on the coatings are used to differentiate among chemical families.

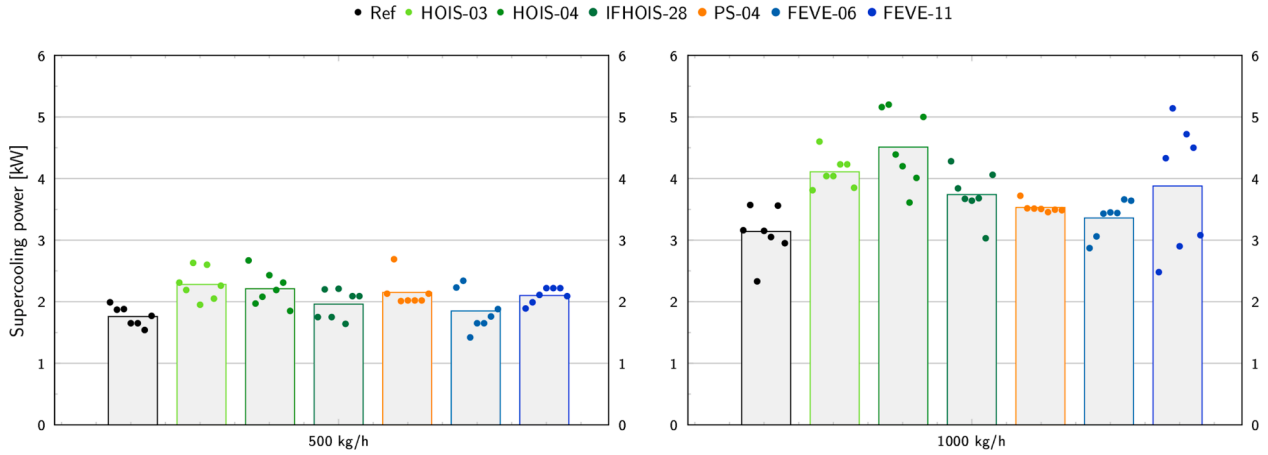


Fig. 7. Supercooling power for all heat exchanger from step experiments with mass flow rates 500kgh^{-1} and 1000kgh^{-1}. The dots indicate results for the different cycles within each experiment and are ordered by time (left: first cycle, right: last cycle).

ieved for 500kgh^{-1}. The water side of this heat exchanger was flushed with water at high mass flow rate before the test to remove particles from inside the heat exchanger. Nevertheless, particles were flushed out during the first cycles of the test. As the test with a mass flow rate of 500kgh^{-1} was performed first, this might be the reason for higher SD achieved at a mass flow rate of 1000kgh^{-1}. The heat exchangers coated with HOIS-04 and PS-04 were the only heat exchangers where particles were observed in the system during the test.

The supercooling power, which is the power calculated for the temperature difference between $T_{water,out}$ and the theoretical freezing temperature of 0°C, is shown for all experiments in Fig. 7. For a mass flow of 1000kgh^{-1}, the highest average supercooling power of 4.5kW was reached with the coating HOIS-04. The measurement uncertainty of the supercooling power is about 3%.

3.1. Supercooling stability tests

The results of the supercooling stability tests are summarized in Table 2. All coatings were used to reach different outlet temperatures for 3 h. The coldest temperature achieved is presented in Table 2. five coatings out of six, i.e. all HOIS coatings, the PS-04 and the FEVE-11 reached a SD of 2.5K for 3h. The reference heat exchanger and the heat exchanger with coating FEVE-06 reached a SD of 2.0K for 3h, but failed to maintain for 3 h the SD of 2.5K. As an order of magnitude, all coatings that reached the SD target of 2.5K for 3h were operated below 0°C for more than 9 h. Temperatures lower than −2.5°C were not possible at this mass flow due to cooling capacity limitations of the experimental set-up, not due to supercoolers capabilities.

Table 2
Results of the stability tests for coated and reference heat exchanger. The goal was to achieve a specific supercooling temperature for three hours. The tests not fulfilling this criterion have been mark red.

Coating	Supercooling degree (SD) [K] ±0.1	Supercooling Power [kW] ±0.2	Time [h]
Ref	2.0	4.7	3.0
	2.5	5.8	2.5
HOIS-03	2.5	5.8	3.0
HOIS-04	2.5	5.8	3.0
IFHOIS-28	2.5	5.8	3.0
PS-04	2.5	5.8	3.0
FEVE-06	2.0	4.7	3.0
	2.5	5.8	1.0
FEVE-11	2.5	5.8	3.0

4. Discussions of current results respect to previous published research

Results shown in this paper show supercooling degrees well beyond previous works and it is of interest to discuss the main reasons for it. Scientific papers published at the beginning of 21st century from Japa-

nese researchers always mention supercooling degrees in the range of 2K using industrially relevant heat exchangers (Kozawa et al., 2005; Kurihara and Kawashima, 2001; Mito et al., 2000; 2002; Nagato, 2001; Tanino and Kozawa, 2001).

All of the works above combine the supercoolers with an ice crystallizer and close the cycle, which is a way more challenging task than working only on the supercooling phenomena as reported in the current paper. Producing ice slurries on the system has a massive implication on the supercooling degree one can achieve in stable form, since it does not only depend on the supercooler itself, but equally important, on the ice crystallizer. It is particularly challenging to control ice formation and clogging once the first ice particle is formed, since the supercooling flow tends naturally to freeze. Thus, methods to prevent upstream ice propagation from the ice crystallizer to the supercooler (Mito et al., 2002) as well as downstream clogging due to either imperfect supercooling release (Mito et al., 2000), and thus nucleation somewhere else, or ice slurry particles agglomeration on non-smooth geometries, are key aspects that limit the stable supercooling degree. Moreover, one also needs to consider the elimination of possible ice particles pumped to the supercooler, which is typically prevented by a good ice slurry storage design and by preheating the water before entering the supercooler. Thus, as soon as ice particles are present in the system the supercooling degree achieved depends on many factors.

In the present paper we separated the phenomena of water supercooling from the ice nucleation and ice slurry management by using a simple and efficient method to completely avoid ice particles formation. This is achieved by reheating water after the supercooler to the melting temperature. This is an important factor on our testing method that allows to isolate the supercooling phenomena,i.e.independent on the uncertainties of improper ice slurry management.

Results from Fig. (left) show supercooling degrees for an untreated heat exchanger ranging from 2.6 K to 3.4 K for 500kgh^{-1} and from 2 K to 3 K for 1000kgh^{-1}, where six out of seven cases froze at temperatures below -2.5°C. The heat exchanger tested should operate in design conditions at around 2000kgh^{-1}. Thus, a lower supercooling degrees could be expected on real operation. In the stability test at 2000kgh^{-1}, 3 hours were stable at a supercooling degree of 2 K and up to 2.5 h were stable at a supercooling degree of 2.5 K. However, as mention before we can not say these results are statistically relevant since we performed only one experiment at these conditions. Nevertheless, these results show stable conditions (supercooling degree between 2 K to 2.5 K) close to the work published before using relevant heat exchangers. Also worth to mention that a safe margin needs to be added to reduce freezing. Thus, results of the untreated heat exchangers presented in this work are in alignment with the supercooling degrees achieved by Japanese researchers. Nothing is mentioned in the works cited above about surface treatments of supercoolers, but looking at the current results, it is very likely that all the previous work from Japanese researchers achieving 2 K supercooling degree were conducted without any special treatment into the heat exchangers.

5. Conclusions

In the present paper we analyzed the effect on supercooling degree achieved by applying several icephobic coatings in brazed heat exchangers designed for a heat pump of 10 kW of heating capacity. Typical mass flow rates in the evaporator of this heat pump are about 2500kgh^{-1} with supercooling needs in the range of 5kW to 7.5kW. Capacities experimentally evaluated were not fully targeting the whole range due to limitations of the experimental setup where a chiller of around 6 kW was installed.

Two main experiments were carried out. In the first one each supercooler was submitted to a sequence of seven cycles of icing for two mass flow rates. In each cycle the chiller temperature was set to −1.4°C and the brine was cooled down by 0.2 K and kept constant for an hour. This step-wise cooling process was running until icing occurred. After that, a melting cycle was used to conduct the following icing cycle. In total seven cycles were carried out for each supercooler test, i.e. seven cycles per coating and mass flow rate.

Experiments with icephobic coated heat exchanger showed that supercooling degrees up to 4.4K are possible with supercooling powers up to 5.2kW for a mass flow rate of 1000kgh^{-1}. All evaluated coatings improved the performance compared to a non treated unit with supercooling degrees between 7% to 40% higher. The best performing coatings were from the family of hybrid organic-inorganic silane sol-gel coatings (HOIS) with improvements in the range of 30% to 40% respect to the non coated version. The reference heat exchanger without any coating showed good supercooling results reaching an average SD of 3K for a mass flow rate of 1000kgh^{-1}.

Supercooling degrees of 2.5K were achieved and kept constantly over 3h with a supercooling power of about 6kW at a mass flow rate of 2000kgh^{-1} with different icephobic coatings. The idea of this test was not to select or compare coatings among each other, but rather to prove a long term and stable operation in supercooling conditions with mass flow rates expected in real operation. The coatings that were stable for all conditions (five out of six) were operated in supercooling conditions for more than 9 h, i.e. 3 h at 1.5 K, 3 h at 2 K and 3 h at 2.5 K supercooling degrees. Some coatings could reach lower temperatures at this mass flow rate, but as mentioned above, the experimental setup was limited to this cooling capacity, i.e. not allowing lower supercooling temperatures or higher mass flow rates. In the supercooling stability test, the reference heat exchanger delivered supercooled water at −2°C, but it was only stable for 2.5h at −2.5°C. Notice that only one experiment per coating was carried out in the supercooling stability test and thus, we can not really assess coatings performance differences using this method due to the stochastic nature of icing.

In general, no clear indications for coatings degradation were observed during the supercooling tests. Nevertheless, long term experiments addressing the durability of the coatings are still missing and will need to be investigated in future works.

In this paper an average degree of supercooling around 4 K has been achieved, which is twice what was achieved by the most performing Japanese systems. Thus, the current work proves a very significant progress beyond the state-of-the-art in supercooling technology that is expected to help to overcome the barriers of ice slurry technology in Europe. However, it is expected that by increasing the mass flow rates the supercooling degree will be reduced. Moreover, a safe margin needs to be used and therefore the average supercooling degree is not likely to be used in real operation, but rather the higher freezing temperature to ensure stability. In near future these results will be reproduced on real, dynamic operation environment with the supercoolers coupled with an ice crystallizer and slurry tank. The development of an ice crystallizer is a key to develop a stable system since supercooled water is likely to produce pipe clogging unless all the supercooling generated in the supercooler is released completely. This is expected to be a challenging task that will affect the stability of the system, which also depends on the ice slurry design and piping system downstream the slurry tank to the supercooler. Moreover, research is still needed to scale up those supercoolers and test the long term stability of the icephobic coatings.

CRediT authorship contribution statement

Daniel Carbonell: Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Maike Schubert:** Validation, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Jens Røberg Frandsen:** Methodology, Validation, Formal analysis, Investigation, Data curation, Visualization, Writing – original draft. **Joerg Brand:** Methodology, Validation, Investigation, Data curation. **Kevin Erb:** Methodology, Validation,

Investigation, Data curation. **Loris Laib:** Methodology, Validation, Investigation. **Matteo Munari:** Resources.

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.

Acknowledgments

The authors thank the European Union's Horizon 2020 research and innovation programme for the financial support received within the TRI-HP project (www.tri-hp.eu) with grant agreement N. 814888.

Supplementary material

Supplementary material associated with this article can be found, in the online version, at 10.1016/j.ijrefrig.2022.07.011

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