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Purification of spent deicing fluid by membrane techniques

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ABSTRACT

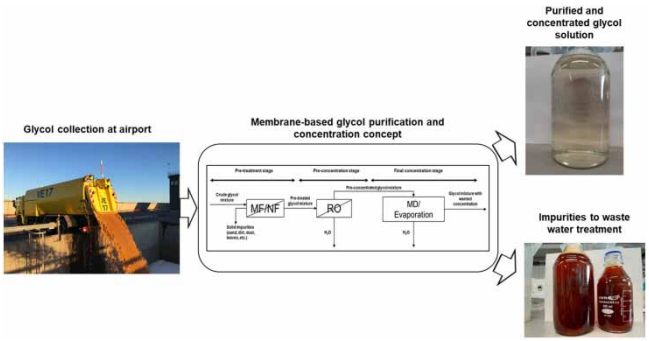
Membrane-based concept comprising microfiltration and nanofiltration pre-treatments, reverse osmosis pre-concentration, and membrane distillation used for final concentration was applied for producing purified and concentrated recycled deicing fluid. Additionally, a techno-economic assessment was conducted to determine the economic viability of the recycling concept. By a straightforward membrane-based concept, ~95% of solid and colloidal impurities together with certain deicing fluid additives such as colorants and surfactants could be efficiently removed (removal efficiencies of ~90% and ~93%, respectively), and resulting purified deicing fluid could be concentrated to ~60 wt% glycol solution, enabling its recycling in deicing operations. Preliminary techno-economic assessment indicated that a membrane-based concept can be used as an economically viable alternative for recycling the spent deicing fluid at airports. The techno-economic case study at an airport consuming 4,000 tonnes of deicing fluid during 6 months annually showed the concept to be economically feasible when the price of purchased propylene glycol is over 1,000 EUR/tonne. In addition to the purchase price of the propylene glycol, the most important cost factors were labor cost and the annual consumption of deicing fluid. Integrating the membrane concept with other operations at airport has potential to decrease the labor cost and further improve the economic feasibility of the concept.

Key words: deicing fluid, membrane distillation, membrane filtration, propylene glycol, reverse osmosis, techno-economic assessment

HIGHLIGHTS

- Membrane concept was successfully utilized for purification and concentration of spent deicing fluid.
- By the applied membrane concept, a glycol solution having ~60 wt% of glycol could be produced.
- Utilized concept was able to remove over 90% of impurities.
- TEA indicated the concept to be economically feasible.
- Integrating the operation of the concept with other operations at airport can potentially decrease the labor cost.

GRAPHICAL ABSTRACT



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INTRODUCTION

Airplane deicing is a vital and integral part of aviation safety, by which formation of frost and ice on airplane surfaces is prevented and safe operation of the airplanes is ensured (Corsi *et al.* 2006a; Marin *et al.* 2010). Deicing operations are primarily conducted by chemical methods by using either ethylene or propylene glycol-based chemicals (Shi *et al.* 2017). If not properly handled, glycol wastewaters might pose an environmental threat to the surrounding environment (Switzenbaum *et al.* 2001; Corsi *et al.* 2006b). For this reason, at modern airports glycol wastes are usually collected and handled appropriately in the wastewater treatment plants (Nitschke *et al.* 1996; Kent *et al.* 1999). However, increased interest has been targeted toward recycling and reusing glycolic wastes. Hence, at international airports, deicing operations are conducted at specific areas from where glycolic wastewaters can be collected and directed to recycling operations (Johnson 2012).

According to their chemical composition, the deicing fluids can be classified in four types (International Organization of Standardization 2007a, 2007b; SAE International 2007). Type I fluids have a low viscosity and they are considered unthickened, providing only short-term protection because they quickly flow off surfaces after use. Type I fluids are typically sprayed heated (55–80 °C) at high pressure to remove snow, ice, and frost adhered to plane surfaces. Usually, they are dyed orange to aid in identification and application. Type II fluids are pseudoplastic fluids containing polymeric thickening agents to prevent their immediate flow off from aircraft surfaces. Type II prevents snow, ice or frost from adhering to the aircraft from the apron to takeoff, and they are generally clear in color. Type III fluids can be considered as a compromise between Type I and Type II fluids. They are intended to be used on slower aircraft and they are generally bright yellow in color. Type IV has the same purpose and meets the same AMS (aerospace material specification) standards as Type II fluids, but it provides longer holdover time. They are typically dyed green to aid in the application of a consistent layer of fluid.

In general, type I and type III fluids are applied on the aircraft surface to remove snow, whereas types II and IV fluids are applied on aircraft surfaces to prevent the formation of ice and snow (Sulej *et al.* 2012; Mohiley *et al.* 2015). The main components of all above-mentioned deicing fluids are ethylene and/or propylene glycol and water, constituting ~99% of the total fluid volume (International Organization of Standardization 2007a, 2007b; SAE International 2007). Depending on the type of spent deicing fluid, an additive package containing corrosion inhibitors (benzotriazole and methyl-substituted benzotriazole, ~0.5% of the total volume), nonionic surfactants (alkylphenols and their ethoxylates, ~0.4%–0.5%), pH buffers (e.g., triethanolamine, ~0.25%), high-molecular-weight nonlinear polymers, and dyes (less than 0.25%) is added to glycol solution (Novak *et al.* 2000; Cancilla *et al.* 2003; Corsi *et al.* 2003, 2006a, 2006b).

Due to tightened environmental regulations, disposal of spent deicing fluid has become an environmental and economic challenge to airports and many major international airports have been forced to implement operating management systems to handle these fluids (Cornell *et al.* 2000; Murphy *et al.* 2015). The environmental effects of deicing fluids are mainly related to the high oxygen demand they exert when released to different water bodies, where they can have detrimental effects on fish and other aquatic organisms needing aerobic environments (Zitomer *et al.* 2001; Freeman *et al.* 2015). It has been estimated that the volume of deicing fluid needed to deice a large jet is about 4,000 L, having a 5-day biological oxygen demand (BOD_5) equivalent to the domestic wastewater generated by 5,000 people in one day (Castro *et al.* 2005). Collection of the spent deicing fluid at the airport is usually performed either at specific deicing areas having drainage systems, or by using ground recovery vehicles, which collect the spent glycol from the runways. From these operations, the collected deicing fluid is either transported to wastewater treatment or purified for recycling and reuse (Switzenbaum *et al.* 2001).

In order to produce reusable and potentially saleable glycol product, it is necessary to reduce the water content as well as to remove the turbidity, color, odor, and various other contaminants, such as heavy metals, from spent deicing fluid. Common methods used for recycling the spent deicing fluid are composed of mechanical processes combined with evaporation and/or distillation (Johnson 2012). At the mechanical stage, particulate impurities (i.e., sand, dust, etc.) are removed prior to a concentration stage performed with evaporation or distillation. However, concentration performed with evaporation or distillation are notoriously energy-consuming methods requiring large infrastructure and facilities. Additionally, they are usually located outside of the airports, creating a need for transporting diluted glycol solution to the treatment facilities. Hence, the aim of this study was to investigate if the spent deicing fluid could be purified and concentrated by using compact and energy-efficient membrane technologies. However, it should be noted that the objective of the experimental section was not to obtain the performances in steady state, but to obtain performances of the laboratory-scale membrane processes depending on the progress of concentration in the feed solution. Additionally, light techno-economic assessment (TEA) was conducted to evaluate the economic performance of the membrane-based purification process.

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METHODS

Characterization of the raw waste glycol sample

Waste glycol (type I deicing fluid) samples were collected from the Helsinki-Vantaa Airport in the beginning of February 2020. Prior to purification and concentration experiments, received raw glycol sample was characterized in terms of elemental composition, chemical oxygen demand (COD), total alkalinity, total organic carbon (TOC), pH, conductivity, color (maximum absorbance at wavelength 490 nm), refractive index, dissolved and total suspended solids (DS and TSS), osmotic pressure, non-ionic surfactants, hardness, phenols, and turbidity.

Elemental composition (i.e., content of Ca, Mg, Na, K, P, S, Fe, Al, Si, Ti, Mn, Ba, Cr, Cu, Ni, Zn, Pb, and V) of the waste glycol was analyzed by using inductively coupled plasma atomic emission spectroscopy (ICP-OES) according to SFS-EN ISO 11,885 standard procedure. Prior to an ICP-OES analysis, sample solutions were diluted and acidified according to standards SFS-EN 13,656 and SFS-EN 15,410.

A Hach DR3900 laboratory spectrophotometer (Hach, USA) was used for the analysis of COD, which was analyzed by LCK (Lange Chemie Küvette) methods 314, 114 or 014 depending on the COD concentration. Additionally, a Hach DR3900 spectrophotometer was used for analyzing total organic carbon (method LCK381), non-ionic surfactants (method LCK333), hardness (method LCK327), alkalinity (method 10,239), phenols (method LCK346), chloride (method LCK311), and phosphorus (method LCK350).

Turbidity was measured using a Hach 2100AN IS Turbidimeter (Hach, USA) and ISO method 7,027, and osmotic pressure by a Wescor Vapro 5600XR osmometer. Conductivity was measured using a VWR conductivity meter CO 3,000 H (VWR, Germany), and pH using a VWR pH1000 pH-meter (VWR, Germany). Color (i.e., maximum absorbance at wavelength 490 nm) was measured with a Hitachi U-2900 UV-Vis spectrophotometer. Glycol concentration was determined by measuring the sample's refractive index (i.e., degree Brix), which is a common method for determining the concentration of ethylene and propyleneglycol-based fluid mixtures (GoGlycolPros 2021). For analysis of refractive index, a Master Series refractometer (Atago Co., Ltd, Japan) was used.

In order to evaluate and monitor the efficiency of each filtration step, the following selected parameters were determined after each process stage: pH, conductivity, COD, color/maximum absorbance at 490 nm, turbidity, nonionic surfactants, and refractive index.

Microfiltration (MF) and nanofiltration (NF) pre-treatments prior to concentration

MF was used for removing large-size particulate impurities, such as sand, dust, and organic debris prior to NF. NF was used for removing especially turbidity-causing colloidal materials, colorants, and surfactants passing the MF stage from the waste glycol prior to concentration experiments conducted with reverse osmosis (RO) and membrane distillation (MD). The MF stage was performed by using a Watman FP3-9 3/4 filter housing (height 310 mm, diam. 120 mm, 8 bar, 50 °C) equipped with a 0.2 μm 9-3/4 K01 absolute polyether sulfone cartridge filter (from Sarlin Oy, Finland). After the MF stage, permeate was forwarded to the NF stage, conducted with a Filmtec™ NF270 membrane (from Dow Chemical Company, USA) placed in a SEPA CF crossflow filtration module (from Sterlitech, USA) having an effective filtration area of 0.014 m^2. The operating filtration pressure was 10 bar.

Concentration stage

The concentration stage was divided into two separate stages. In the pre-concentration stage, permeate from NF270 filtration was pre-concentrated by RO. The chosen membrane for the RO pre-concentration stage was a Filmtec™ SW30XLE RO-membrane from Dow Chemical Company (USA). As during the NF270 filtration, a Sterlitech SEPA CF filtration module having 0.014 m^2 effective filtration area was used. The maximum operating filtration pressure was about 55 bar.

After the pre-concentration stage, the RO concentrate was forwarded to MD for final concentration. During the MD stage, a Sterlitech forward osmosis (FO) module (active membrane area of 0.0042 m^2) equipped with a CF042 laminated hydrophobic polytetrafluoroethylene (PTFE) flat sheet membrane (from Sterlitech, USA) having a pore size of 0.2 μm was used.

To simulate an ordinary distillation method, Büchi R-200 Rotavapor® equipped with a jack and an insulated/heated water bath was used as a reference concentration method, and the efficiency of this method was compared to the RO+MD process. A sample (1,010 g of glycol solution pre-concentrated with RO) was loaded into a flask, heated to 35 °C in a water bath, and evaporated under vacuum until the evaporation of water was no longer taking place.

The experimented membrane process for glycol purification and concentration is presented in Figure 1.

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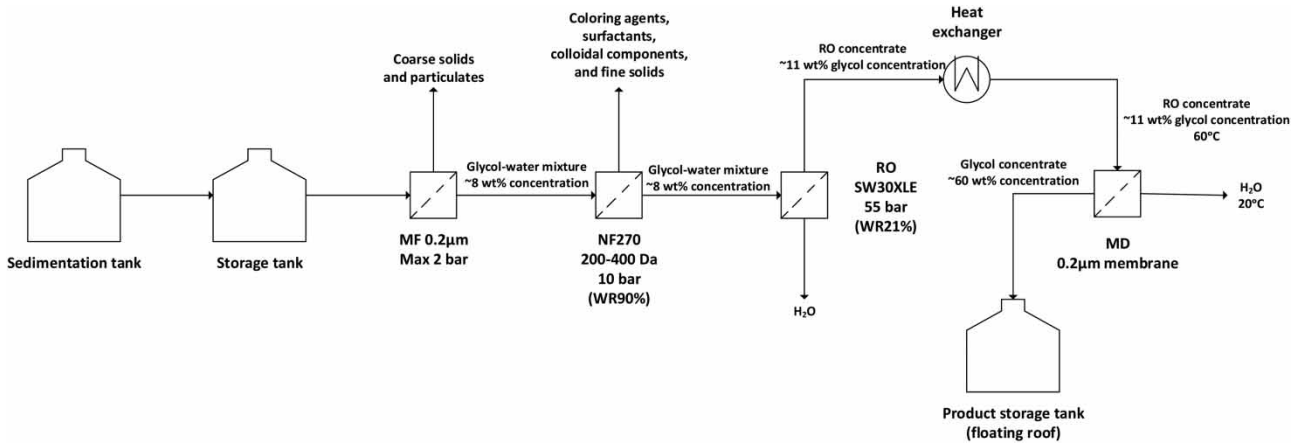

Figure 1 | Experimented membrane process for glycol purification and concentration.

Techno-economic assessment

A conceptual level techno-economic assessment was conducted to evaluate the feasibility of the spent deicing fluid purification and concentration of propylene glycol by membrane concept. Based on the experimental results, the quality of the recycled and purified deicing fluid was assumed sufficient for replacing normally purchased deicing fluid in the feasibility estimation. As propylene glycol is not utilized for deicing during the summer seasons, the membrane process was assumed to be in operation 6 months of the calendar year and the availability was assumed to be 95% during the operation months. The annual consumption of deicing fluid at the airport was assumed to be 4,000 tonnes, of which 30 wt% was propylene glycol (later in the text as glycol). It was assumed that 70% of the spent pure glycol was collected in the spent deicing fluid. The collected spent deicing fluid was assumed to be 10,533 tonnes/a, containing 8 wt% glycol and 0.5 wt% other impurities.

The evaluated and proposed membrane process is described in Figure 1. The first step was sedimentation, by which sand and coarse particulates were removed from the spent deicing fluid. Sedimentation was assumed to take place in two vessels, with the sedimentation time of 1 d and removal efficiency of 96 wt% of these impurities. After sedimentation, the spent deicing fluid continues to a hold tank (storage tank) having a storage capacity of 7 d. This provides flexibility for the start-up and shutdown of the membrane process. From the storage tank, the spent deicing fluid is pumped to MF for separation of fine solids. Permeate from MF is directed to NF to remove colloidal impurities and deicing fluid additives, such as coloring agents, and permeate from NF is then directed to RO to preliminary concentration of glycol. The retentate from RO is heated to 60°C with low pressure steam assuming energy efficiency of 95%. The heated retentate from RO continues to MD for final concentration, providing the retentate from MD as the final product containing 60 wt% glycol. The recycled glycol solution is led to the product tank having a storage capacity of 7 d. In MF, the removal efficiency for fine solids was assumed as 99 wt% and in NF the removal efficiency, for example, coloring agents and other ingredients was set as 100 wt%. In reality, a very small amount of impurities may be present in the final product, but the effect of these impurities is assumed insignificant for the considered application. Electricity consumption in the purification process was estimated based on the fluid pumping requirements in terms of output pressure and volume flow, assuming the pump efficiency of 80% and pump motor efficiency of 90%.

Total capital investment (TCI) was estimated based on the factorial method, by using literature estimates for purchased equipment costs, and by applying the cost factors for direct costs and indirect costs based on Peters *et al.* (2003) for fluid processing plant. The estimation of working capital varies depending on the literature source. As an example, Peters *et al.* (2003) proposes to use 15% of TCI, while Humbird *et al.* (2011) applied the value of 5% of fixed capital investment (FCI), corresponding here to 4.8% of TCI. In this study, a value in between these references, 8% of TCI, was considered suitable for the deicing fluid purification concept and thus applied. The applied cost factors are presented in the Table 1. Purchased equipment costs for pumps and drives, pump motors, heat exchanger and tanks were estimated by purchased equipment cost correlation formulas given by Towler & Sinnott (2008) for the year 2006 in USD currency. Sedimentation and holding tanks were selected to be cone roof tanks and the product storage tank a floating roof tank. Pump and drive were set as single-stage centrifugal and pump motor as explosion-proof. The heat exchanger (HEX) was based on a shell and tube

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Table 1 | Applied ratio factors for estimating TCI based on purchased equipment costs

Purchased equipment	1.00	Engineering and supervision	0.33
Purchased equipment installation	0.47	Construction expenses	0.41
Instrumentation and controls	0.36	Legal expenses	0.04
Piping	0.68	Contractor's fee	0.22
Electrical system	0.11	Contingency	0.44
Buildings	0.18	**Indirect costs**	**1.44**
Land and yard improvements	0.10	**FCI -Direct and indirect costs**	**5.04**
Service facilities	0.70	Working capital	0.44
Direct costs	**3.60**	**TCI**	**5.48**

HEX. RO and MD filtration housings and filters (spiral wound) were estimated based on the surface area costs of 62.5 USD/m^2, which was an average value of the minimum (25 USD/m^2) and maximum (100 USD/m^2) values for the year 2000 reported by Peters *et al.* (2003). MF cartridge bodies' purchased cost estimation of 500 EUR (year 2020) for a capacity of 3 m^3/h was based on the expertise within this study. Currency of the purchased equipment cost were converted to EUR and brought to year 2019 by Chemical Engineering Plant Cost index (CEPCI), where needed. On top of the resulting estimates, 10% was added for the possibly missing equipment.

Fixed operational costs estimation included labor, overheads, maintenance and materials. The labor costs were estimated by assuming two operators per shift, operation in five shifts, and in addition two supervisors (one per shift, but working only in two shifts). The labor was assumed to be required for 6 months of the calendar year, thus in total 6 person-years. It was further assumed that operators can take care of the maintenance work and supervisors can cover the duties of the production engineer. Supervisor's salary was assumed as 125% of operator's salary. Overheads were estimated to be 50% of the labor expenses. Annual maintenance and materials costs were assumed to be 2% of FCI. The membrane-related fixed costs were estimated separately. These included membrane cleaning costs, replacement of MF cartridges, and replacement of NF, RO and MD filter membranes. Cleaning costs, filters and cartridges replacement periods together with surface area-based filter replacement costs are based on the expertise within this study. The applied prices for economic calculations are listed in Table 2.

Mass and energy balances were calculated using Excel spreadsheets. At this stage it should be noted that, for example, the electricity consumption in a real plant may be different from the estimation in this study because the volume flux obtained in these experiments was not equal to the real volume flux in continuous operation in a full size operational plant. Hence, the electricity consumption should be treated as a rough estimate. A sensitivity analysis to illustrate the effects of input parameter distribution on profitability was conducted based on stochastic simulation with the simulation runs of 10,000. The analysis tool @Risk was used (Palisade Corp 2015).

RESULTS AND DISCUSSION

Characterization of the spent deicing fluid

Determined chemical and physical parameters of the received deicing fluid sample are presented in Table 3. Analysis for total carbon (TC) measures both the total organic carbon (TOC) present and the complementing total inorganic carbon (TIC), the latter representing the amount of non-organic carbon, like carbon in carbonate minerals. Subtracting the inorganic carbon from the total carbon yields TOC.

The received deicing fluid sample was orange-colored, which was consistent with the background info received from the airport indicating that the sample was composed of type 1 deicing fluid. The sample contained suspended solids and visible impurities, which made the sample outlook cloudy and of relatively high turbidity. Maximum absorbance was measured at 490 nm, which was used later for monitoring the removal of colored additives. Of the other additives, nonionic surfactants and phenolic compounds were also detected, indicating their utilization as deicing fluid additives. As could be assumed based on the background information and literature, the COD was relatively high already in the untreated sample. When considering the concentration of the solution by RO, already at this point it was evident that due to the high osmotic pressure also

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Table 2 | Applied prices (location Finland)

	Unit	Best	Static	Worst	Reference/additional information
Deicing fluid for recovery −8 wt% glycol	EUR/tonne	0[a]	0[a]	0[a]	Free of charge
Propylene glycol −100 wt% glycol	EUR/tonne	1,700[a]	1,500[a]	851[a]	Virgin glycol to be replaced with the recovered deicing fluid
Wastewater treatment	EUR/m^3	0.5[a]	1.0[a]	1.4	Worst: Local operator in Finland
Solid reject treatment	EUR/tonne	5.0[a]	7.7	10[a]	Static: Local operator in Finland
Fresh water	EUR/m^3	0.1[a]	0.5[a]	1.2	Worst: Local operator in Finland
Heat as low-pressure steam	EUR/GJ	18.6	20.6	21.7	Ulrich & Vasudevan (2006) -based on the natural gas price
Natural gas (HHV)	EUR/GJ	13.9[a]	15.4	16.3	Worst 2018s2[b] and static 2019s2[b]: Eurostat (2020a)
Electricity	EUR/MWh	66.5	69.5	75.6	Best 2017. static 2020 and worst 2011: Eurostat (2020b)
MF cartridge	EUR/pcs	7[a]	10[a]	30[a]	Worst: Based on the capacity of 3 m^3/h. Assumed time of operation: 1 operation month
NF filter replacement	EUR/m^2	20[a]	100[a]	137	Worst: Accepta (1997). Assumed time of operation: 1 year
RO membrane replacement	EUR/m^2	10[a]	25[a]	40[a]	Assumed time of operation: 1 year
MD membrane replacement	EUR/m^2	10[a]	30[a]	100[a]	Assumed time of operation: 1 year
Membrane cleaning cost (NF, RO, MD)	EUR/m^2/year	25[a]	50[a]	75[a]	
Operator	EUR/person-month		3,360[a]		
Supervisor	EUR/person-month		3,500[a]		

[a]Expert estimation within the study.
[b]s2=second semester of the year.

Table 3 | Chemical and physical properties of the received deicing fluid sample

Parameter	Value	Parameter	Value
pH	7.2	Alkalinity (mmol/L)	5.8
Conductivity (μS/cm)	1,300	DS (mg/g)	1.6
COD (mg/L)	133,600	DS (g/L)	1.7
TOC (mg/L)	45,200	TSS (g/L)	0.2
TC (mg/L)	45,800	Nonionic surfactants (mg/L)	28.1
TIC (mg/L)	630	Hardness (°dH)	4.4
Maximum absorbance (nm)	490	Phenols (mg/L)	3.6
Maximum absorbance at 490 nm	1.3	Chloride (mg/L)	20.3
Osmotic pressure (bar)	29	Refractive index (degree Brix)	7.0
Turbidity (NTU)	270		

other concentration methods besides RO were needed to increase the concentration of the glycol solution to a reasonable level. The refractive index of the solution was 7.0, indicating propyleneglycol concentration of ~8 wt%.

In general, amounts of heavy metals were relatively low. High concentrations were determined for potassium and sodium, with 500 and 76 mg/L concentrations, respectively. As sodium and potassium formates are widely utilized at airports as runway deicing substances, they are also incorporated to wastewaters and hence the waste glycol collected from the runways and deicing areas. Results of the metal analyses are presented in supplementary/supporting materials.

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Pre-treatment experiments

Large size impurities, such as sand, dust, and organic debris were removed prior to the NF stage by a cartridge filter having a pore size of 0.2 μm. After MF, an NF270 membrane having MWCO of 400 Da was used for removal of fine solids, turbidity, colloidal impurities, color, and surfactants prior to concentration experiments. In total, 43.44 kg of waste glycol was treated at room temperature with 0.2 μm cartridge filter, from which 42.75 kg (i.e., 98.4%) filtrate was collected. From the cartridge filtrate, 42.5 kg of sample was forwarded to filtration conducted with an NF270 membrane. Operating pressure during NF270 filtration was 10 bar, and 35.8 kg of permeate was recovered. Flux and permeate conductivity of NF270 pre-treatment filtration are presented in Figure 2. An increase in feed total dissolved solids also increased permeate conductivity since the NF will reject a fixed percentage of the salts.

The values of the chosen monitoring parameters after NF270 filtration are presented in Table 4.

Permeate collected during NF270 filtration was practically clear (turbidity 0.3 NTU) and only very slightly colored ($A_{490} = 0.2$), indicating that under these filtration conditions colorants and fine solids were effectively removed. In addition to the removal of turbidity and color, the amount of surfactants was also clearly decreased, indicating also their retention during the NF-stage. NF270 permeate was forwarded to a pre-concentration stage conducted with RO.

Pre-concentration experiments

In total, 35.5 kg of permeate from the NF stage was treated with RO using an SW30XLE membrane. Flux and permeate conductivity of the RO stage are presented in Figure 3.

Due to the high osmotic pressure (i.e., 29.3 bar) of the sample, possibilities for concentrating glycol samples by RO were rather limited. During the RO pre-concentration stage, 7.5 kg of permeate could be recovered, corresponding to water recovery (WR) value of ~19%. After this, the value of the permeate flux was zero; that is, the concentration could not be continued further with RO at 55 bar pressure. During the RO stage, the refractive index of the concentrate was increased from 7 (after NF270) to 9.4, corresponding to ~11 wt% propylene glycol concentration and ~1.3 in terms of concentration factor (CF). The values of the chosen monitoring parameters after the RO stage are presented in Table 5.

After the RO stage, the elemental composition of the pre-concentrated glycol was also determined, especially for determining the content of heavy metals and other detrimental elements, such as sulfur, possibly hindering the catalytical processes by which the purified glycol stream can be further refined.

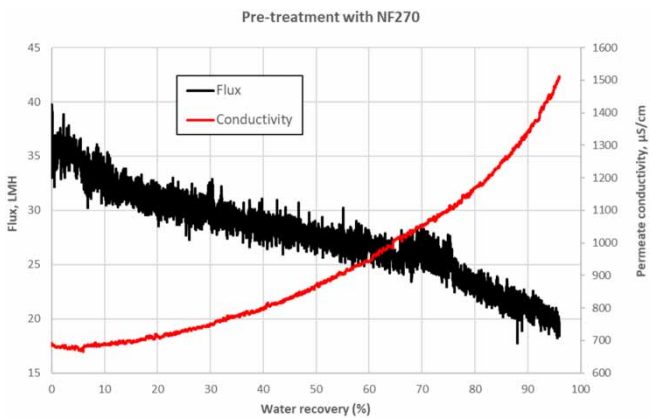

Figure 2 | Flux and permeate conductivity of the NF270 pre-treatment stage.

Table 4 | Monitoring parameters after NF270 filtration

Membrane (MWCO)	pH	Conductivity (μS/cm)	COD (mg/L)	Turbidity (NTU)	Color (A_{490})	Surfactants (mg/L)	Degree Brix
NF270 (400 Da)	7.6	1,005	133,340	0.3	0.2	0.165	7.0

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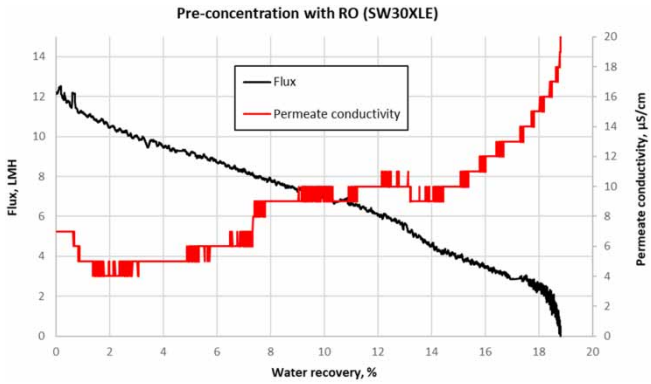

Figure 3 | Flux and permeate conductivity of the RO pre-concentration stage (55 bar, room temperature).

Table 5 | Monitoring parameters after RO pre-concentration stage

Membrane	pH	Conductivity (µS/cm)	COD (mg/L)	Turbidity (NTU)	Color (A_{490})	Surfactants (mg/L)	Degree Brix
SW30XLE	8.1	1,290	180,760	0.6	0.27	0.245	9.4

Generally, the content of heavy metals such as Pb, Cu, Cr, and Ni were very low. However, when considering the possible catalytical conversion of the purified glycol solution, content of sulfur might pose a problem as sulfides and sulfites especially can hinder the catalytical process by acting as catalyst poisons. Results of the metal analyses are presented in supplementary/supporting materials.

Final concentration

Results of the final concentration experiments conducted with MD are presented in Figure 4 (temperature, conductivity, mass of the solutions, and flux) and with Rotavapor in Figure 5. Related monitoring parameters are presented in Table 6. Results of the metal analyses from MD and Rotavapor concentration experiments are presented in supplementary/supporting materials.

The total duration of the MD stage was 50 hours, after which the determined flux was so low that the experiment was halted. With MD, the glycol sample could be concentrated to approximately 41-degree brix, corresponding to 60 wt% glycol concentration. During the MD concentration, values of color, pH, turbidity, and surfactant were slightly increased, indicating that some impurities passed the NF stage and concentrated during the concentration stage. The measured pH is in line with the information found from literature, which reports pH values between 9.0 and 10.7 for 50 wt% propylene

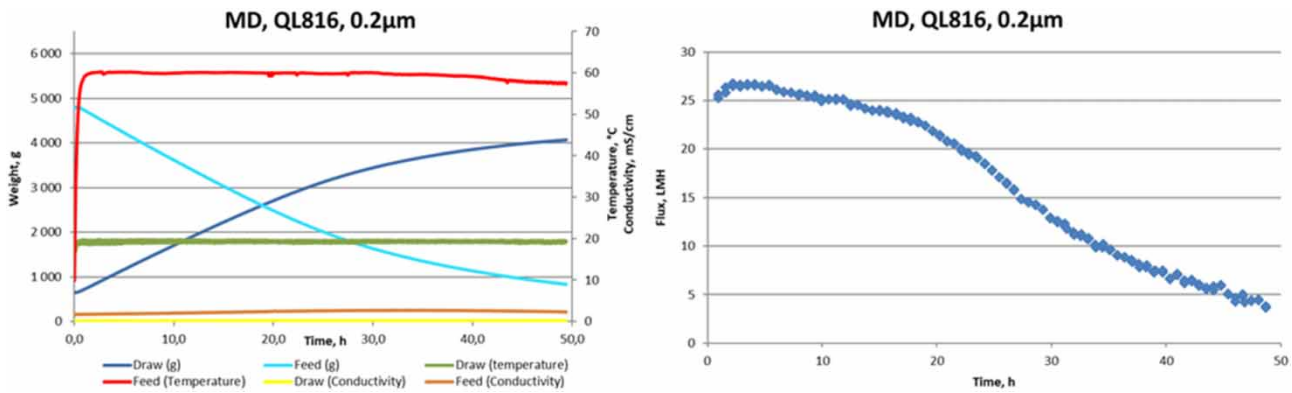

Figure 4 | Temperature, conductivity, mass of the solutions, and flux during MD concentration stage.

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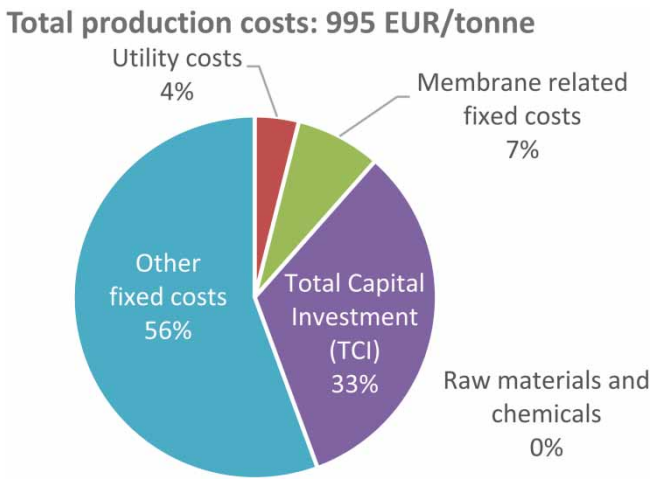

Figure 5 | Total production costs expressed as per tonne of recovered glycol (dry, 100%) in the glycol-water solution.

glycol solutions. Again, the content of heavy metals were relatively low despite the increased concentration of the glycol solution. The only elements showing significant contents were sodium and potassium, most likely originated from runway deicing operations. In addition, increased content of sulfur was detected from the MD concentrate. These compounds may require additional purification and removal operations.

For comparison and as a reference method, conventional evaporation conducted with a rotary evaporator (RE) was also tested for glycol concentration to evaluate and compare the performance of two different concentration systems. The feed for rotary evaporation was the concentrate from the RO pre-concentration experiment. In total, 163 g of residual sample out of the 1,010 g sample loaded into the evaporation flask was recovered after the evaporation, corresponding to ~84% water recovery. The degree Brix of the distillate was 0.2, indicating that only a very small amount of glycol was lost during the evaporation. With rotary evaporation, clearly higher degree Brix of the final product and hence clearly higher final glycol concentration was achieved when the evaporation results were compared to MD. The degree Brix of the evaporated glycol sample reached as high a value as 54, corresponding to a glycol concentration of over 95 wt%. High concentration was also visible in terms of COD, which reached a value over 1 million mg/L.

Techno-economic assessment

The membrane process parameters applied are presented in Table 7, as well as calculation results for mass streams and for glycol content. Overall mass balance of the membrane process is presented in Table 8. Glycol losses in membrane processing were estimated as ca. 18 wt% of the entering glycol in the collected spent deicing fluid. Estimated annual electricity consumption for the membrane process is 22.2 MWh and annual heat demand 1,049 GJ.

Equipment scaling parameters, their sizes and purchased cost estimations are given in Table 9. The resulting TCI of 1.72 M EUR was annualized by assuming a cost of capital of 10% and an investment payback period of 15 years. Some inaccuracy is due to scaling parameters of some equipment being outside the valid range of purchased equipment cost correlation formulas (MIN and MAX in the 15). These equipment include all pump motors except the NF filtration-related pump motor, heat exchanger for RO concentrate and the product tank.

Table 6 | Monitoring parameters after MD and RE concentration experiments

	pH	Conductivity (μS/cm)	COD (mg/L)	Turbidity (NTU)	Color (A_{490})	Surfactants (mg/L)	Degree Brix
MD	9.6	1,129	777,400	12.5	0.142	2.09	41
RE	11.4	668	1,053,200	1.4	0.058	0.82	54

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Table 7 | Applied process parameters (such as flux, water recovery rate and glycol recovery rate) based on the experimental work, and resulted mass streams and glycol contents for feed, permeate and retentate at each filtration stage

	FLUX[a] L/m²/h	Pressure[a] bar	Water recovery, permeate[a] wt%	Glycol recovery, permeate[a] wt%	Feed L/h	Permeate L/h	Retentate L/h	Glycol content after the treatment stage wt%
MF		2	98	98	2,504	2,464	40	8
NF	30	10	84	84	2,464	2,070	394	8
RO	5	50	21	0	2,070	439	1,631	10
MD	15	1.2	83	0	1,631	1,360	271	60

[a]Process parameters based on experimental results.

Total production costs were estimated as 687 k EUR per year, corresponding 995 EUR/tonne of recovered glycol, concentrated to 60 wt% glycol-water solution. Recovered glycol here refers to 100 wt% glycol component in the glycol-water solution, although the product also contains 40 wt% water. This simplifies the cost comparison between the recycled product and the pure glycol purchase price. 60 wt% glycol concentration in the product is enough for diluting it further to 30 wt% deicing fluid concentration. Cost distribution is presented in Figure 5. The highest share of production cost was composed of other fixed costs, in which the labor cost (37%) was the most significant cost factor. Annualized total capital investment cost was the other significant cost factor with the share of 33% of total production cost.

Annual saving due to re-using the glycol for deicing fluid and avoiding glycol purchase was 1,036 k EUR, based on assumed glycol (100%) purchase price of 1,500 EUR/tonne. Additional saving of approximately 4 k EUR/a (5 EUR/tonne of recovered glycol) can be achieved by using the RO and MD permeates (water) instead of fresh water. By accounting these savings, the profitability of the membrane system is a promising 353 k EUR/a (511 EUR/tonne of recovered glycol), providing 21% return of investment (ROI).

A sensitivity analysis was performed for the profitability using the Monte Carlo simulation method. The selected input parameters as key cost factors are listed in Table 10 with the range for each input parameter. A triangle for distribution was applied to the input parameters. The sensitivity of profitability to key cost factors is illustrated in Figure 6. The baseline value in Figure 6 is based on the assumed distributions and not on the static values directly. The baseline value is thus different

Table 8 | Overall mass balance of the spent deicing fluid purification process

Stream		Tonne/annually	Tonne/tonne glycol in feed
Feed total		**10,553**	**12.56**
Waste glycol		10,553	12.56
	Of which pure glycol	*840*	*1.00*
Output total		**10,553**	**12.56**
Product: Glycol-water solution		1,151	1.37
	Of which pure glycol	*691*	*0.82*
Reject sedimentation tank		101	0.12
	Of which pure glycol	*4*	*0.00*
Retentate MF		169	0.20
	Of which pure glycol	*13*	*0.02*
Retentate NF		1,645	1.96
	Of which pure glycol	*132*	*0.16*
Permeate RO (water)		1,825	2.17
Permeate MD (water)		5,661	6.74

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Table 9 | Equipment scaling parameters, their designed sizes and estimated purchased costs

Equipment	Scaling parameter	Unit	Size	Valid MIN	Valid MAX	No of equipment	Purchased eq. cost EUR 2019	Share
SEDIMENTATION TANK								
Sedimentation tank	Volume	m^3	75.5	10	4,000	2	40,426	12.9%
Pump and drive	Speed	L/s	1.20	0.2	500	1	3,371	1.1%
Pump motor	Power	kW	0.12	1.0	1,500	1	1,056	0.3%
HOLDING TANK								
Hold tank	Volume	m^3	526	10	4,000	1	62,117	19.8%
FILTRATION								
Pump and drive to MF	Speed	L/s	1.20	0.2	500	1	3,371	1.1%
Pump motor (MF)	Power	kW	0.19	1	1,500	1	1,114	0.4%
MF cartridge housing	Flow	m^3/h				2	1,000	0.3%
Pump and drive to NF	Speed	L/s	1.18	0.2	500	1	3,371	1.1%
Pump motor (NF)	Power	kW	0.95	1	1,500	1	1,504	0.5%
NF filtration housing and filters	Area	m^2	82				8,567	2.7%
Pump and drive to RO	Speed	L/s	1.07	0.2	500	1	3,364	1.1%
Pump motor (RO)	Power	kW	3.99	1	1,500	1	2,510	0.8%
RO filtration housing and membranes	Area	m^2	414				43,179	13.8%
Pump and drive to MD	Speed	L/s	0.95	0.2	500	1	3,357	1.1%
Pump motor (MD)	Power	kW	0.08	1	1,500	1	1,022	0.3%
Heater for RO concentrate	Area	m^2	0.22	10	1,000	1	10,055	3.2%
MD filtration housing and membranes	Area	m^2	109				11,344	3.6%
PRODUCT TANK								
Product tank	Volume	m^3	57	100	10,000	1	80,399	25.6%
Product pump and drive	Speed	L/s	0.58	0.2	500	1	3,336	1.1%
Pump motor	Power	kW	0.01	1	1,500	1	951	0.3%
Missing equipment +10% added							28,542	9.1%
Total purchased equipment cost							313,960	100%
Direct costs							1,130,000	360%
FCI							1,582,000	504%
TCI							1,720,000	548%

from the previously estimated profitability value. The glycol (as 100%) purchase price is the most predominant factor. Other notable factors are labor required, annual consumption of deicing fluid containing glycol, spent deicing fluid collection rate, and glycol concentration of the collected spent deicing fluid. In addition, TCI of 1.72 M EUR was varied separately between 75 and 150%, resulting the profitability range of 429 to 674 EUR/tonne of recovered glycol.

Based on the assumptions used in the techno-economic assessment, the concept is economically feasible if the purchase price of propylene glycol (100%) is at least 1,000 EUR/tonne. A realistic option to decrease the production cost and improve profitability further would be to integrate the operation with other airport processes, thus decreasing the labor cost. As the sensitivity analysis showed, it has a significant effect on the profitability.

The airport itself affects strongly the economic feasibility: the size of the airport and the annual average duration of the deicing period together define the annual consumption of deicing fluid, which is the third significant cost factor based on the sensitivity analysis. However, even high consumption of deicing fluid at a very large airport with short seasonal need for deicing may lead to economically unfeasible investment cost.

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Table 10 | Varied input parameters for the sensitivity analysis

Parameter varied	BEST	STATIC	WORST	UNIT
Propylene glycol (100%) purchase price	1,700	1,500	851	EUR/tonne
Annual person-years	4	6	10	a
Annual consumption of deicing fluid (glycol content 30 wt%)	5,000	4,000	3,000	tonne/a
Spent deicing fluid glycol collection rate	80	70	60	%
Propylene glycol concentration in the collected spent deicing fluid	10	8	3	wt%
RO membrane replacement	10	25	40	EUR/m^2
NF filter replacement	20	100	137	EUR/m^2
MD membrane replacement	10	30	100	EUR/m^2
MF cartridge	7	10	30	EUR/pcs
Holding and storage tank	4	7	14	d

Triangle distribution for input parameters was assumed. The @Risk tool was applied for the sensitivity analysis.

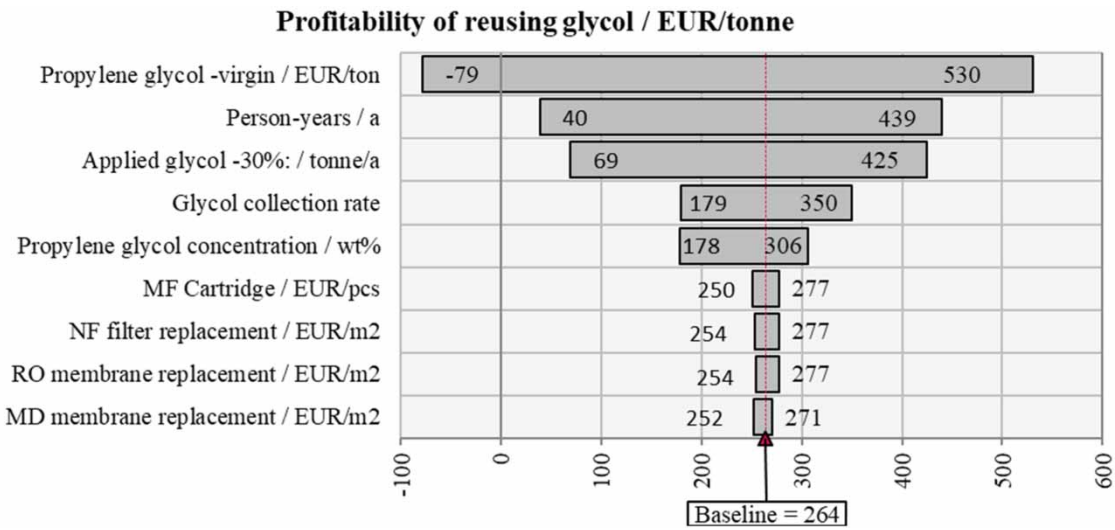

Figure 6 | The sensitivity of profitability to the selected cost factors in membrane processing. Inputs ranked by effect of output mean. Expressed as per tonne of recovered glycol in the glycol-water solution.

CONCLUSIONS

Membrane-based concept was applied for purification and concentration of spent deicing fluid collected from an airport wastewater treatment system. The main aim of the process was to remove various impurities, such as particulates, colloidal components, and deicing fluid additives, and to concentrate the purified glycol solution to the highest maximum concentration, allowing its recycling either again as a deicing fluid or in other purposes. The applied purification concept comprising MF, NF, RO, and MD stages was able to remove ~95% of the components causing turbidity, ~90% of the colorants, and ~93% of non-ionic surfactants. As a final product, a solution having 60 wt% of glycol was produced, enabling its recycling in deicing operations.

Techno-economic assessment indicated the concept to be economically feasible with used assumptions at an airport consuming 4,000 tonne deicing fluid with 30 wt% glycol concentration during 6 months annually. The total production cost was 995 EUR/tonne recycled propylene glycol (100%) in water solution. The profitability of the concept was 511 EUR/tonne recycled propylene glycol (100%) in water solution, when assuming a propylene glycol (100%) purchase price of 1,500

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EUR/tonne. The break-even purchase cost of glycol (100%) was 1,000 EUR/tonne. The sensitivity analysis showed that the most important cost factors were propylene glycol (100%) purchase price, labor cost, annual consumption of deicing fluid, and investment costs. There is potential to decrease the labor cost (currently 37% of total production costs) by integrating the operation of the process with other operations at the airport.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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