Direct Contact Membrane Distillation with Crystallization Applied to NaCl Solutions*

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Preparation of NaCl supersaturated solutions by direct contact membrane distillation (DCMD) integrated with salt crystallization has been studied. For the purpose of this study a module assembled from macroporous polypropylene capillaries was used. The feed temperature was kept at 353 K or 358 K, and the temperature of distillate stream was changed from 293 K to 328 K. Salt crystallization on the membrane surfaces has been observed during the process when the distillate temperature was kept below 308 K. As a consequence of that phenomenon an increase of membrane wettability and reduction of the distillate flux were observed. When distillate temperature was raised to 328 K, salt crystallization on the membrane surfaces was eliminated, and permeate flux was stabilized during the process runs. After 138 h of the process operation, the permeate flux decrease of about 40 % was observed. Additionally, the DCMD process integrated with crystallization yielded average NaCl production of 55 kg m^{-2} d^{-1}.

Membrane distillation (MD) is a mass transport process of volatile components that takes place across the pores of nonwetted membranes. Among different modes of the MD process [1] for the preparation of salt-concentrated solutions, the direct contact membrane distillation (DCMD) mode is frequently used [1—9]. In this process, a hydrophobic porous membrane is in direct contact with a hot feed and a cold distillate. A thin air layer entrapped within the pores of a membrane comprises the gas membrane. Volatile components of the feed evaporate at the feed/membrane interface, diffuse through the air inside the membrane pores and condense in the cold distillate stream. The driving force for the mass transfer is the vapour partial pressure difference related to the temperature gradient and the solution composition on both sides of the membrane. In the case of nonvolatile solutes, e.g. NaCl, only water vapour flows through the membrane. Therefore, the retention degree of the salts in MD is close to 100 %, and the obtained distillate constitutes pure water with the electrical conductivity within the range of 0.5—10 μS cm^{-1} [1, 5, 6, 9].

A decrease of permeate flux along with the increase of the salts concentration in the feed during MD process is observed [1—9]. This results from the decrease of the vapour partial pressure being in equilibrium with the feed solution (Raoult's law). Additionally, a rapid decrease of the temperature polarization coefficient with an increase of the solute content in the feed was found [10]. However, such decrease of the permeate flux in MD process is significantly smaller than that in the pressure-driven membrane processes, e.g. reverse osmosis (RO) [11—13]. Therefore, the membrane distillation can be used for treatment of saline wastewater to obtain pure water and a salt concentrate. Many times, the preparation of concentrate does not solve the problem and isolation of solid salt becomes the crucial issue. On the other hand, MD process allows raising the salt concentration up to the supersaturated state followed by the salt crystallization [2—4]. Processed solution flows through the MD module, there it is simultaneously concentrated and cooled. This may lead to the formation of salt crystals on the membrane surface or/and within the membrane pores [5, 8]. These processes take place particularly in the region of the module outlet. The phenomena of temperature and concentration polarization facilitate significantly the salt nucleation on/in membrane. A fundamental condition required to carry out the MD process is the maintenance of the gas phase in the membrane pores. However, the salt crystallization on the membrane surface induces wettability of the membrane pores [14, 15]. An essential inconvenience asso-

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ciated with the concentration of NaCl is the solubility of this salt, which only slightly depends on the temperature (between 35—40 mass %) [16, 17]. Therefore, the prevention of the salt crystallization inside the MD module using temperature program is quite difficult.

During the initial period of MD process with a new MD module, a slight increase of the yield is sometimes observed [15, 18]. The pores structure in polymeric membrane may be modified at elevated temperatures (333—363 K). Thus, a slight increase of the membrane permeability was observed. Unfortunately, during the subsequent module operation a successive pore filling by the feed proceeded and a slow decrease of the module efficiency was found. The MD studies performed for a period exceeding 1000 h demonstrated that the highest decline of the permeate flux took place during the initial 300—500 h of the process [15, 19]. Fouling was indicated as one of the major reasons of the membrane wettability.

The selection of appropriate process parameters to run the membrane hybrid process – distillation connected with salt crystallization – was the major aim of this work. Such arrangement served to reduce deterioration of membrane performance by deposited salt crystals.

EXPERIMENTAL

The experimental set-up of the studied hybrid process is shown in Fig. 1. The MD module was assembled from the polypropylene membranes with outside/inside diameter equal to 2.6 mm/1.8 mm (Accurel PP S6/2 membrane, Akzo Nobel). These membranes have pores with the maximum and nominal diameters of 0.55 μm and 0.22 μm, respectively [9]. The porosity was estimated to be 75 %. The nine membranes, each of 0.52 m length, were assembled in a 12 mm inner diameter tubular housing. The module was placed in MD installation in a vertical position. The streams on both sides of membrane were set co-currently, and the salt and stripping solutions were pumped by peristaltic pumps from the bottom part of MD module with the speed of 7 cm^3 s^{-1}. The streams did not wet the membrane pores, and the vapour inside the pores separated the liquids adjacent to the membrane surfaces. The feed was circulated inside the capillary membranes and its temperature at the module inlet was kept at 353 K (one-stage crystallization) or 358 K (three-stage crystallization). The temperature of the distillate stream was changed from 293 K to 328 K. Individual measurements lasted 2 h and the distillate flux was calculated as an average value obtained during this period. In one set of experiments the system for crystallization was composed of a single tank (3 dm^3 volume), in which the temperature was kept at 303 K. The solution residence time of about 7 min was achieved for this tank. At the beginning of crystallization experiments, the feed
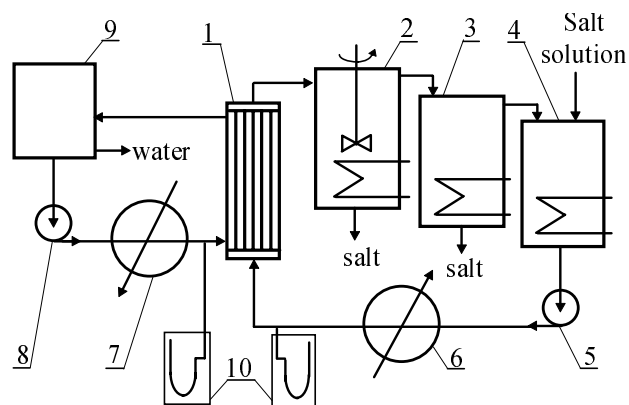

Fig. 1. Diagram of the DCMD experimental set-up integrated with crystallizer. *1.* Capillary module, *2, 3, 4.* crystallization system, *5, 8.* pump, *6.* heating system, *7.* cooling system, *9.* distillate reservoir, *10.* manometer.

side was filled with NaCl solution (ρ(NaCl) = 306 g dm^{-3}).

In the other runs, the crystallization was carried out in three tanks (3 dm^3 each) connected in line. The temperatures in these tanks were 310 K, 290 K, and 353 K, respectively. A salt solution (ρ(NaCl) = 306 g dm^{-3}) was supplied into the third tank in a continuous mode. The residence time of salt solution flowing through the first two tanks was 14 min. In the case of salt crystallization inside MD module, the membranes were cleaned by rinsing with distilled water (323 K) for at least 10 min.

During the experiments, a part of the membrane pores was filled by liquid, thus the working membrane area for vapour transport decreased. As a consequence of partial membranes wettability, a decline of permeate flux was observed. Distilled water as a feed was used for investigation of the membranes permeability variation (maximum permeate flux – MPF) during the module exploitation. In this case, the distillate and feed temperatures were set at 293 K and 353 K, respectively. MPF was determined after each series of NaCl concentration.
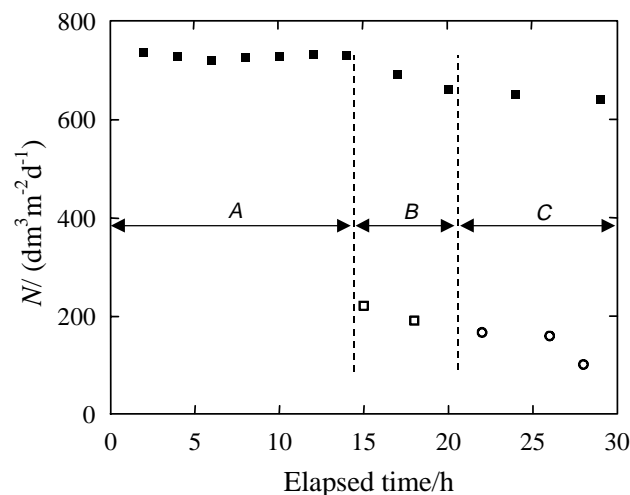
The removal of liquid from the partly wetted membranes permits to recover the initial yield of the module. One of the methods used for the liquid removal is the membrane drying. This procedure involved a preliminary module rinsing with distilled water for 1 h (minimum), followed by module disconnection from the installation, and final drying under ambient conditions for two weeks.

The electrical conductivity and the TDS (total dissolved solids) parameter of the solutions examined were measured by a 6P Ultrameter (Myron L Company). Both the membrane surfaces and cross-sections were investigated by scanning electron microscopy (SEM). SEM observations were performed with brand-new membranes as well as those removed from MD module after completing the studies.
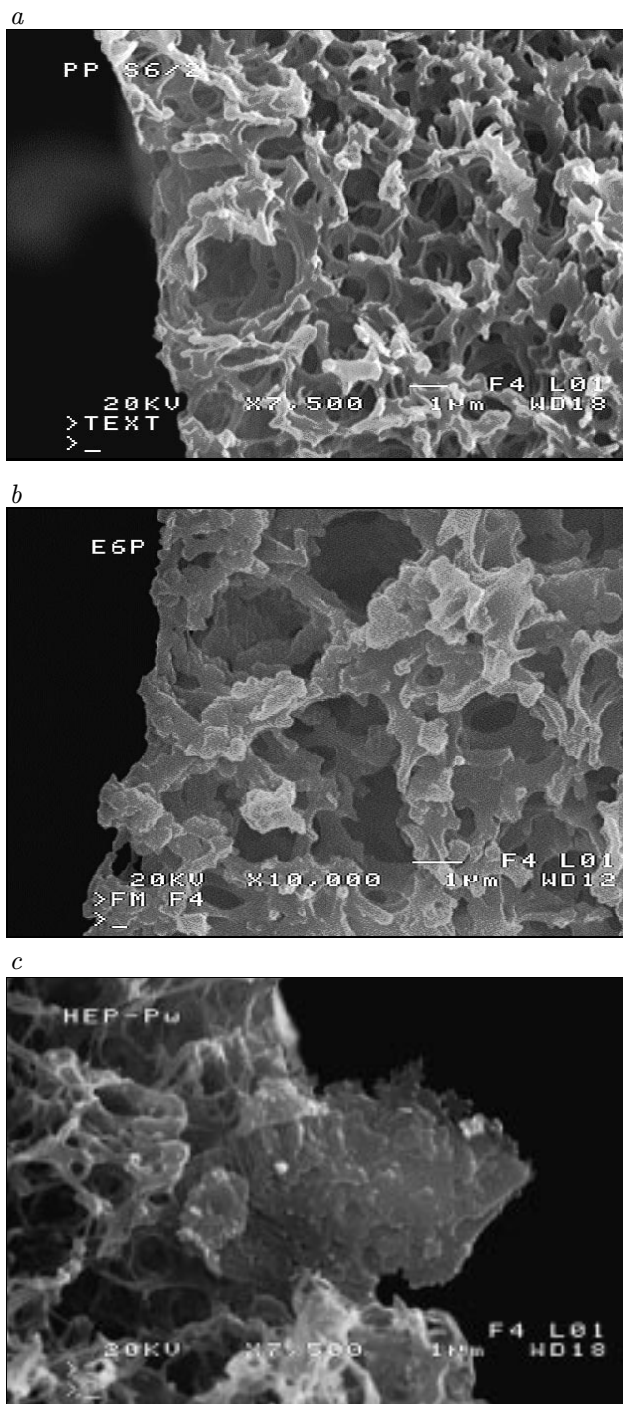
RESULTS AND DISCUSSION

The thermal stability of the membrane was evaluated using the distilled water as a feed during the first 14 h of the experiments. Achieved permeate flux was stable and amounted to about 728 dm^3 m^{-2} d^{-1} (period A in Fig. 2). The cross-section of a brand-new Accurel PP S6/2 membrane is presented in Fig. 3a. The SEM observation revealed that the membrane morphology was not significantly changed after 138 h of process operation (Figs. 3b and c). The long-term investigations of other MD modules assembled with the Accurel PP S6/2 membranes [19] also demonstrated that the membranes used at temperatures of 333 K —358 K were thermally stable.

The permeate flux decreased to a level of 250 dm^3 m^{-2} d^{-1} (Fig. 2) when the feed (distilled water) was replaced with a NaCl solution (ρ(NaCl) = 306 g dm^{-3}). The salt crystallization in a single tank crystallizer was initiated when the concentration of NaCl in the feed reached the value of about 320 g dm^{-3}. Moreover, a rapid pressure increase was observed at the inlet on the feed side of MD module, due to the salt crystallization inside the capillary membranes. The salt crystals precipitated not only onto the membrane surface, but also inside the membrane pores (Fig. 3c). The presence of salt crystal at the pore inlet caused the pore wetting by the feed [14]. The complete filling of the pores by feed made impossible the water vapour to flow through them, hence a decline of the flux was observed. The MPF measurements demonstrated that the permeate flux was reduced to a level of 660 dm^3 m^{-2} d^{-1} due to the repeated salt crystallization inside the module (Fig. 2 – period B). The distillate produced by MD had the


a

b

c

Fig. 3. SEM micrographs of a cross-section of Accurel PP S6/2 membrane showing the pores on the feed side (inside the membrane capillary). a) Brand-new membrane, b) after 138 h of MD connected with salt crystallization, c) membrane with salt crystals grown inside the membrane pore.

Fig. 2. Permeate flux as a function of the elapsed time for MD process integrated with one-stage crystallization. Feed: ■ distilled water; □ solution saturated with NaCl and T_D = 293 K; ○ solution saturated with NaCl and T_D = 323 K.

electrical conductivity in the range of 5—10 μS cm^{-1}. The distillate electrical conductivity was not increasing during these experiments.

In order to prevent the salt crystallization inside the MD module, the temperature of the membrane

surface was elevated by increasing the inlet temperature of distillate from 293 K to 323 K. This allowed to run the MD process integrated with the salt crystallization in the single tank crystallizer. However, an increase of the pressure by 20 %—30 % was observed on the feed side after 2 h of measurement. This increase was associated with the formation of a minor amount of salt deposit on the membrane surfaces. Therefore, a further decline of the module efficiency was observed. The measurements carried out with distilled water demonstrated that the permeate flux during 8 h of measurements was reduced from 660 to 640 dm^3 m^{-2} d^{-1} (Fig. 2 – period C).

The experimental results confirmed that the one-stage crystallization system did not prevent the salt crystallization in the module. The same conclusion was observed by *Wu et al.* [3]. Thereby, the three-stage system was used in further experiments (Fig. 1). In the first tank, the bulk crystallization with the secondary nucleation took place. In the second stage, crystallization proceeded without mixing, which allowed to retain the salt crystals in the tank. Heating and dosage of fresh batch of feeding solution destroyed the crystal nuclei that passed to the third tank. An unsaturated solution obtained in the third stage was subsequently supplied to the MD module. This system design allowed preventing the salt to crystallize and deposit in the module. The hybrid process of membrane distillation and salt crystallization was carried out for over 20 h. A slow decline of the module efficiency was observed during this time (Fig. 4 – period A). After completing these measurements, the test-evaluation with distilled water demonstrated that the MPF decreased to 470 dm^3 m^{-2} d^{-1}. The distillate flux decline was associated with the decrease of separated salt amount in crystallizer which dropped from 70 to 53 kg NaCl
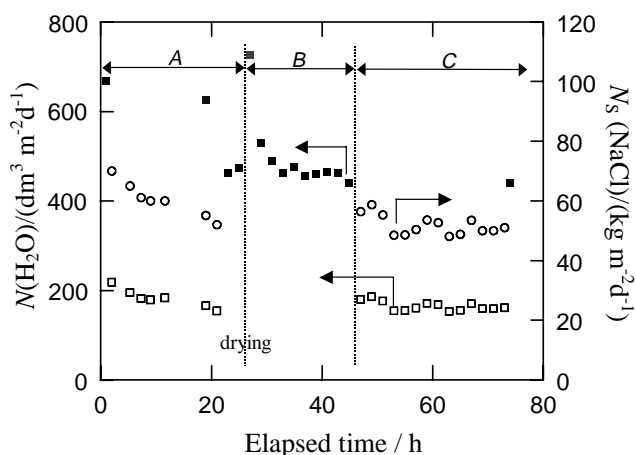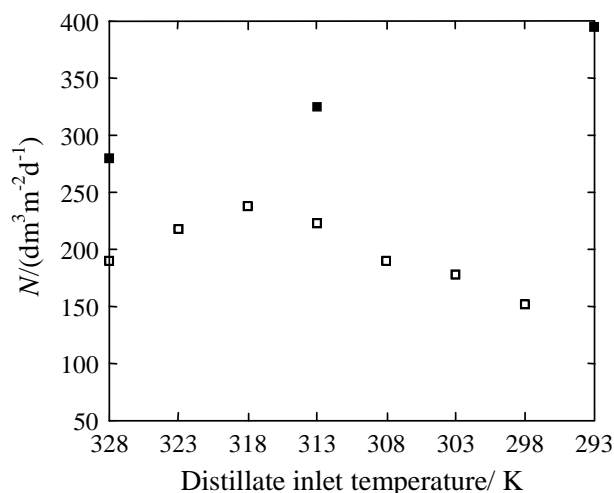

Fig. 4. Permeate flux *vs.* time for MD process integrated with three-stage crystallizer. Distillate flux for different feeds: ■ distilled water, □ solution saturated with NaCl. N_S, ○ flux of crystallized salt.

m^{-2} d^{-1}. Moreover, the quality of distillate was deteriorated and the electrical conductivity reached the value of 30 μS cm^{-1}. These data demonstrated that the membrane pores wetting initiated in the previous experiments (with one-stage crystallization) still took place.

The membrane wettability phenomenon during the MD is the major disadvantage of this process. Hence, the development of membrane regeneration methods to recover their initial nonwettability state is of prime importance. Drying of the membranes allows to remove liquid from their pores and to restore their hydrophobic properties [20]. During the first measurement with distilled water (Fig. 4 – period B), the MPF of 727 dm^3 m^{-2} d^{-1} was achieved, indicating that the module drying permitted to recover the initial flux. However, during the consecutive hours of measurements a rapid flux decline was observed to the same level as before module drying. A possible explanation for this phenomenon is the re-dissolution of salt deposit inside the membrane pores and their subsequent wetting. The results demonstrated that the accurate removal of solute from wetted pores was not achieved, even after rinsing the module with distilled water for several hours. The amount of salt deposit inside the pores was very small, thus its presence was not detected by SEM observation (Fig. 3*b*).

The stabilization of module permeate fluxes during further measurements, with both distilled water and a saturated salt solution, was found (Fig. 4 – periods B and C). Although the process conditions during the run periods A and C were the same, the flux decline (associated with the membrane wetting) was observed only for the period A (Fig. 4). This confirmed that the membranes partial wetting was caused by the salt crystallization on the membrane surface during the one-stage crystallization study. The precipitation of salt crystals at the pore inlet (Fig. 3*c*) does not imply an immediate filling of the membrane pores by the feed. A salt deposit can only cause the pore filling by feed to a depth of *e.g.* 10 μm, whereas the thickness of the membrane wall used in this study was 400 μm. However, this phenomenon initiated the wetting process of the pores. The feed evaporation inside the pores resulted in the increase of solute concentration at the feed/vapour interface. A super-saturation state was achieved due to the increased resistance of the back diffusive flow of the salt inside the pores. Under these conditions, the salt crystals were formed at the feed/vapour interface and a further part of the pores occupied by crystals was filled by feed (water-logging [14]). As a consequence of the above-mentioned phenomena, the total pore volume became filled by the feed after a certain time.

It is predictable that the distillate temperature lowering results in the increase of the driving force for MD process, and finally it enlarges the distillate flux. The fluxes for various distillate temperatures are

Fig. 5. Permeate flux *vs.* distillate temperature. MD process integrated with the three-stage crystallizer. Distillate flux for different feeds: ■ distilled water, □ solution saturated with NaCl.

Fig. 6. Changes of maximum permeate flux (MPF) estimated for MD module during the investigation of MD process integrated with salt crystallization. Periods: *A* – one-stage crystallization, *B* – three-stage crystallization, *C* – three-stage crystallization with different distillate inlet temperature.

presented in Fig. 5. The results were plotted according to the measurement sequence. A decrease of the permeate flux was observed for the saturated NaCl solution at distillate temperatures below 318 K. A slow increase of hydraulic pressure at the inlet of MD module on the feed side was also observed at temperatures lower than 318 K due to the salt crystallization inside the capillary membranes. A gradual increase of the electrical conductivity of distillate (up to 50 μS cm^{-1}) confirmed that a progressive wetting of the membranes took place during these series of experiments. Based on these results, it can be concluded that the MD integrated with crystallization should be carried out at distillate temperature above 318 K.

The total time of membrane distillation integrated with the salt crystallization lasted 138 h. Changes of the maximum permeate flux during this period are presented in Fig. 6. The MPF determined after 138 h reached the value of 450 dm^3 m^{-2} d^{-1}, whereas the initial flux was equal to 725 dm^3 m^{-2} d^{-1}. Thereby, almost 40 % decline of the flux was observed. The MD module lost its efficiency at the initial period of studies. This decline was not only due to the crystallization of salt on the membrane surface, but it is also related to the membrane pore size distribution. Majority of the membrane pores have the diameter close to the average value (0.22 μm), however, the SEM observation revealed that the membranes used in this study have also large pores with diameter exceeding 10 μm (Fig. 7). These largest pores are readily wetted at the initial period of MD module exploitation [19, 20]. The feed hydraulic pressure is sufficient to fill up these pores. Thus, the pores wetting induced by the water-logging phenomena was observed.

The second drying operation (Fig. 6) confirmed previous results (Fig. 4) that the regeneration of mem-
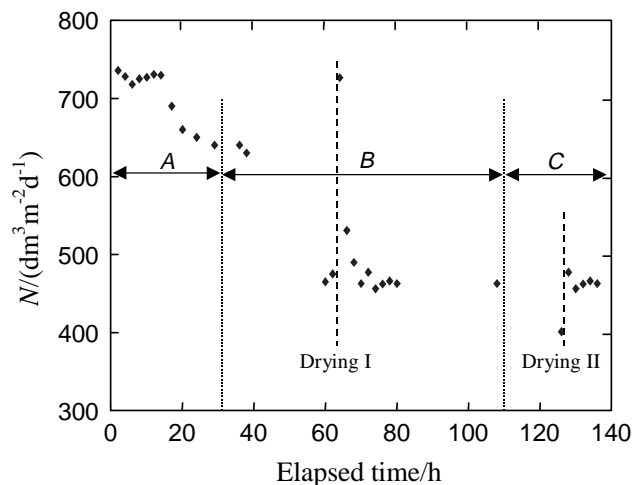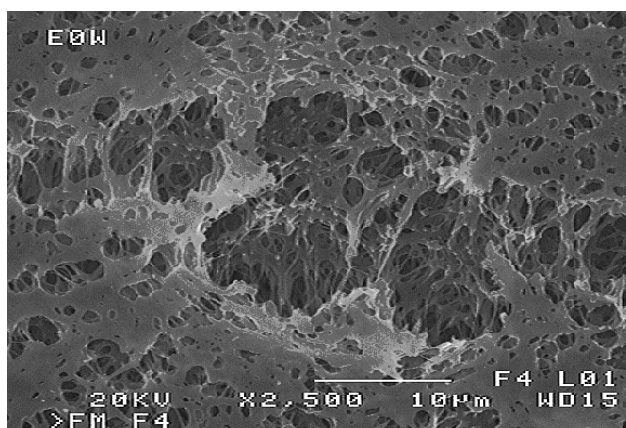
Fig. 7. SEM micrograph of the surface of brand-new Accurel PP S6/2 membrane on the feed side.

branes wetted by NaCl solutions *via* their drying is ineffective.

CONCLUSION

The porous structure of Accurel PP S6/2 membrane did not undergo any significant changes during the MD process carried out for 138 h at 353 K— 358 K. The membranes were partially wetted during the membrane distillation integrated with salt crystallization, which resulted in reduction of the permeate flux by 40 % after elapsed time of 138 h. The salt crystallization on the membrane surfaces accelerates the pores wettability. Low temperatures of the membrane surfaces favour the salt crystallization on the membranes. This phenomenon can be suppressed by the use of a relatively high distillate temperature, *e.g.* 328 K.

The one-stage crystallization system (solution cooled to 303 K, 7 min residence time) did not prevent the salt crystallization in the module. A solution after crystallization, before next feeding into the MD module, was heated to 353 K. However, the heating itself was insufficient to achieve the unsaturated conditions of the salt solution in the layer adjacent to the membrane, thus the salt crystallization occurred in the module.

The concentration of saturated solutions of salt was successfully carried out in the MD installation connected with the three-tank crystallizer. The temperature of both, feed and distillate at the MD module inlet should be relatively high, *e.g.* 358 K and 328 K, respectively. The bulk crystallization process in the first tank was performed by maintaining the temperature of 310 K. This temperature was by 30 K lower than the feed temperature at the outlet of the MD module. In the second tank (without mixing), the crystallization temperature was by 20 K lower than that in the first tank. Moreover, the residence time of the salt solution in each of these tanks was 7 min. The preparation of unsaturated solution in the third tank (heating to 353 K and addition of the feeding solution) allowed to pump the brine to the MD installation without salt crystallization in the module.

It was found that the amount of NaCl separated in the crystallizer was dependent on the quantity of water removed from the concentrated solution (permeate flux) in the MD process. For the case under investigation, the amount of separated salt was about 47 kg m^{-2} d^{-1}—70 kg m^{-2} d^{-1} corresponding to the permeate flux variations from 180 dm^3 m^{-2} d^{-1} to 220 dm^3 m^{-2} d^{-1}.

The regeneration of the membranes wetted by NaCl solution *via* their rinsing with distilled water followed by drying was found to be insufficient method. A rapid partial re-wetting of dried membranes took place probably due to the minor salt deposit remaining in the pores.

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