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# Water desalination using membrane distillation with acidic stabilization of scaling layer thickness

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## HIGHLIGHTS

- Membrane scaling during membrane distillation was studied.
- Acidic stabilization of scaling layer thickness was presented
- Rinsing of MD module with HCl solution maintained the high permeate flux

## ARTICLE INFO

## ABSTRACT

Membrane scaling during water desalination by membrane distillation has been studied. A tap water was applied as a feed and diluted HCl solutions were used for periodical cleaning of module. The membrane morphology and the composition of deposits were determined using scanning electron microscopy coupled with energy dispersion spectrometry. The $CaCO_3$ deposit covered not only the membrane surfaces but was also formed in the pores' interior. During the membrane rinsing an HCl solution dissolved the deposit inside the pores, which is synonymous with flooding of these pores by liquid. Due to the membrane wetting, a significant flux decline was observed. It was confirmed that the rate of membrane wettability might be limited by shorting a period between the cleaning operations. In this work the membranes were cleaned every 1–5 h, and as a result, the penetration of deposit into the pores was restricted up to the depth of 30 μm during 200 h of MD process. A periodical rinsing of membranes by HCl solutions did not have a negative influence on the membrane performance, and the MD module efficiency was stabilized during this period.

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## 1. Introduction

Water evaporation below the boiling point through the pores of non-wetted hydrophobic membranes enables to obtain the fresh water even from the brine water sources. This process was called membrane distillation (MD), and the possibilities of water desalination by MD were presented by several researches [1–7]. A spiral wound MD module for solar desalination applications with 5–14 $m^2$ effective membrane area has been developed by Fraunhofer ISE [8,9]. A number of pilot plants were successfully used for a long-term water desalination based on the spiral and other module configurations, which enhanced the commercial acceptance of MD process [10–13].

The separation mechanism of the MD process is based on the vapor/liquid equilibrium of the liquid mixture; therefore, the presence of the vapor phase in the pores is a necessary condition [3,5–14]. The driving force for the mass transport is a difference in the vapor pressures, resulting from different temperatures and the compositions of the solutions in the layers adjacent to the membrane [5,7–9,14]. In the direct contact MD (DCMD) the membrane separates a hot feed and a cold distillate.

Vapor and non-condensable gases can be only transported through the membrane pores during MD; therefore, the MD membranes must not be wetted by the separated aqueous solutions. The porous hydrophobic membranes, made from polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polypropylene (PP), have been used in MD process. Recently, several new types of membranes designed specifically for MD process were manufactured [14–17]. The modification of PP membranes by the incorporation of functionalized carbon nanotubes significantly enhanced MD flux and the membrane stability [17]. The strong hydrophobic properties of these membranes retarded the pores wetting, but simultaneously increases the fouling intensity when the feed water contains any hydrophobic species. In this case, the hydrophilic surface modification is proposed [18].

A hydrophilization of the membrane surface allows to reduce the adsorption of hydrophobic compounds, and as a result, to limit organic fouling. However, the pores of hydrophilic layer formed will become wetted by the feed (surface wetting — Fig. 1), and the permeate flux

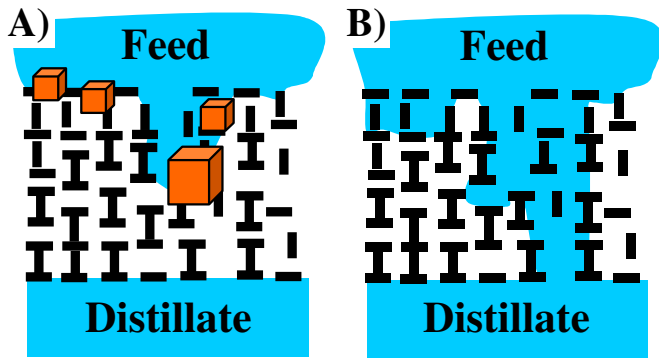*E-mail address:* Marek.Gryta@zut.edu.pl.

**Fig. 1.** Wettability of hydrophobic membrane: A) surface wettability, B) partial wettability. Cubic — salt crystal.

will be decreased. Moreover, the operating conditions of the MD process, such as elevated temperature and the presence of oxygen, facilitate the degradation process of the polymer. The formation of hydrophilic groups (e.g., $C = O$, OH and COOH) on the polypropylene surface was confirmed, and as a result, the surface wetting of hydrophobic polypropylene membranes was observed after 50 h of MD process duration [19]. When the layer of surface pores is wetted, the liquid/vapor interfaces are moved toward the membrane wall (Fig. 1A), which has an adverse effect on the temperature of interfacial surfaces [14]. Consequently, a steady decrease of the permeate flux is observed. After reaching the second stage of wettability (partial wettability — Fig. 1B) some parts of the feed can flow to the distillate, the result of which is an increase of its electrical conductivity [19].

Water evaporation in the MD process caused that the feed is continuously concentrated, and when the feed solution reaches or exceeds the solubility limits of sparingly soluble salts, scaling occurs and it will result in the deteriorations of membrane flux and the separation performance. Different forms of scales were present on the membrane surface, mainly calcium carbonate, barium sulfate and magnesium hydroxide, which are commonly observed in seawater desalination operation applications [12,14]. The surface scaling can be also developed into the internal membrane scaling [1–4,7]. The salt crystals are wetted with the feed solution, and water evaporation from the crystal surface facilitates the secondary nucleation. Due to the crystals growth to all three spatial dimensions scaling was also observed inside the membrane pores [20].

The feed water before entering the MD modules is heated in heat exchangers. The solubility of carbon dioxide in water decreases with increasing temperature. Therefore, the precipitation of $CaCO_3$ takes place due to the decomposition of bicarbonate ions during the MD process. The $CaCO_3$ scaling was indicated as the major problem during MD process of natural water [7,14]. It was found that a deposit of $CaCO_3$ on the membrane surface can be easily removed by rinsing the module with a 2–5 wt.% solution of HCl, which allowed to restore the initial permeate flux. However, the repetitions of module cleaning procedure by this method resulted in a gradual decline of the maximum permeate flux. An acid solution dissolves the salt crystals and the wettability of the pores filled by deposit was accompanied to this operation (Fig. 1B), and as a result, wetting of pores up to the depth of 100 μm of membrane wall was observed [21]. When a shortened period of membrane cleaning was used the deposit penetrated into the pores up to the depth of 30 μm [7]. This indicates that the rate of membrane wettability can be limited by shortening the period of time between cleaning operations. Moreover, the MD modules should be rinsed using HCl solution with concentration below 5 wt.%, which restricted HCl diffusion through the membrane pores [27].

As the surface wetting can affect scaling, the membranes with low surface porosity and a high hydrophobicity are proposed for MD applications [3,14,17,20–22]. Such membranes are resistant for the

surface wetting over a longer period of time, especially when well soluble solutes are solely present in the feed [17]. However, if scaling occurs, the membrane surface is rapidly wetted, and the internal scaling is also observed for membranes with low surface porosity [20,23–26]. Moreover, the application of hydrophilic modifications, which not only reduce the membrane pore size, but also protect the membrane pore mouth from fouling, is proposed [14,18].

The results of MD studies [7,19,21] indicated that the surface wettability, scaling and module rinsing with HCl solutions in a natural way transforms any hydrophobic membrane into two layers hydrophilic/hydrophobic membrane. Therefore, the problem is not in the surface wettability, but how to maintain the pore wetting, internal scaling and other phenomena destructive for MD membrane only inside the thin, e.g., 20–50 μm, external surface layer. In this work an idea of stabilization of scaling layer thickness by applying a frequent short period module rinsing by HCl solutions was examined.

## 2. Experimental

The studies of the direct contact MD process were performed using the experimental set-up shown in Fig. 2. A capillary module (MK1 or MK2) with the diameter of 0.012 m and the effective length of 0.25 m was installed in a vertical position. The modules were equipped with 10 hydrophobic capillary polypropylene membranes (Accurel PP S6/2, Membrana GmbH — Germany) with the outside/inside diameter equal to $d_{out}nd_{in} = 2.6$ mm/1.8 mm, pore sizes with the nominal diameter of 0.22 μm, and the porosity of 73% (the manufacturer's data).

The peristaltic pumps were used, and the volumetric flow rate of distillate and feed streams were equal to $14 \pm 0.2$ ml/s. The feed was introduced inside the membrane capillaries (0.55 m/s), whereas the distillate flowed (0.23 m/s) on the shell-side of MD module. The Reynolds number was 2712 and 790, respectively. The hydraulic pressure on the distillate side was 1.8–2.1 kPa higher than that on the feed side (14 kPa). The inlet temperature of feed and distillate was 353 and 293 K, respectively, and was maintained constant during the MD process.

Tap water produced from the lake water was used as feeding water for the MD experiments. A portion of tap water was stored in a tank with a volume appropriate for all carried out studies. The electrical conductivity of this water was 635 μS/cm, and the average concentrations (in mg/L) of the major ions were as follows: 27.9 $Na^+$, 66.9 $Ca^{2+}$, 16.6 $Mg^{2+}$, 101.3 $SO_4^{2-}$ (IC analysis) and 6.1 $K^+$ and 2.8 Si (ICP-AES
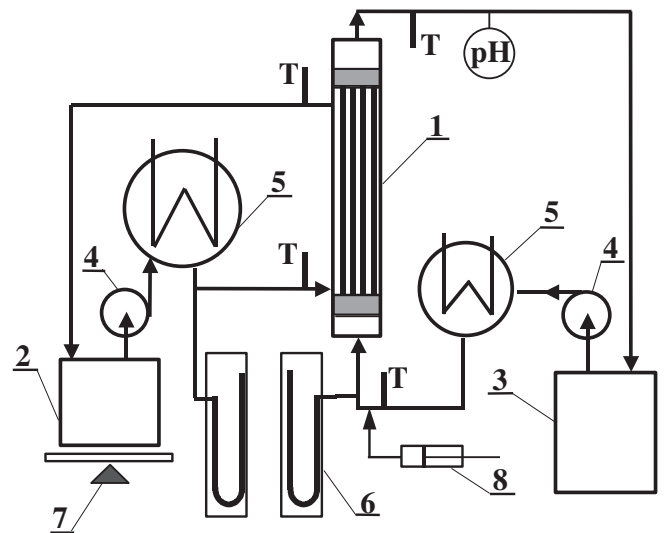


**Fig. 2.** DCMD experimental set-up: 1 — MD module, 2 — distillate tank, 3 — feed tank, 4 — pump, 5 — heat exchanger, 6 — manometer, 7 — balance, 8 — HCl dosing system, T — thermometer, pH — pehameter.