Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Marek Gryta[a]
[a] Szczecin University of Technology, Institute of Chemical Technology and Environment Engineering, Szczecin, Poland

To cite this Article Gryta, Marek(2006) 'Water Purification by Membrane Distillation Process', Separation Science and Technology, 41: 9, 1789 — 1798
To link to this Article: DOI: 10.1080/01496390600674950
URL: http://dx.doi.org/10.1080/01496390600674950

Separation Science and Technology, 41: 1789–1798, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600674950

Water Purification by Membrane Distillation Process

Marek Gryta
Szczecin University of Technology, Institute of Chemical Technology
and Environment Engineering, Szczecin, Poland

Abstract: The demineralization of water by membrane distillation (MD) has been investigated. In the first stage of investigations the tap water or boiled tap water was employed as a feed, and the water recovery coefficient exceeding 75% was achieved. The obtained concentrate was supplied to the second stage of MD installation. The quality of distillate was stable and practically independent of the feed concentration. The produced distillate has the electrical conductivity in the range of 1.4–2.5 μS/cm. The precipitation of salt deposit on the membrane surface was observed during the water demineralisation, especially in the first stage of MD. The membrane morphology and the composition of precipitate layer were studied using scanning electron microscopy coupled with energy dispersion spectrometry. The formed deposit caused clogging of the membrane surface (pores), and resulted in a gradual decline of the module efficiency. Moreover, the formation of the deposit on the membrane surface was the major reason of the partial membrane wettability.

Keywords: Membrane distillation, demineralized water, membrane fouling

INTRODUCTION

High purity water is frequently used in various industries. Ion exchange plants are usually applied for the production of large quantities of demineralized water. The major disadvantage of this method is the generation of wastewater during the regeneration of ion exchange resin. Several new membrane

Received 20 October 2005, Accepted 26 February 2006

Address correspondence to Marek Gryta, Szczecin University of Technology, Institute of Chemical Technology and Environment Engineering, ul. Pulaskiego 10, 70-322 Szczecin, Poland. E-mail: marek.gryta@ps.pl

processes have been proposed for water demineralization. One of the most promising processes for this purpose seems to be the process of membrane distillation. The important applications of MD process can be found in the water treatment technology, seawater desalination, and the concentration of aqueous solutions (1–7).

In the direct contact MD variant (DCMD) a hydrophobic membrane separates the hot feed from the cold distillate (1, 5, 7). The volatile components of the feed evaporate through the membrane pores, therefore, the presence of the vapor phase in the pores is a necessary condition for MD. The separation mechanism of the MD process is based on the vapor/liquid equilibrium of a liquid mixture. For solutions with non-volatile solutes (such as tap water), only water vapor is transferred through the membrane, hence, the obtained distillate comprises demineralized water (1, 3, 7).

Natural water contains significant amount of solutes and suspended solids, the presence of which deteriorates the performance of the membrane processes, and therefore water pre-treatment is commonly used (3). Since the costs of water pre-treatment decrease along with the installation capacity, it is advantageous to feed the membrane installation with tap water (from municipal water treatment system). During MD process the tap water is heated and its temperature increases. However, at elevated temperatures a larger amount of CO_2 is required to maintain the bicarbonate ions in water. 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 tap water (1, 3, 8). A part of the membrane surface covered by the deposit undergoes wetting, which implies that the liquid may penetrate the adjacent pores (2, 4). This phenomenon will be accelerated if the formed deposit comprises the salt crystals (scaling), which may grow into the pores (6–9).

The objective of this work was to study the performance of the long term MD process used for demineralisation of tap water.

EXPERIMENTAL

The investigations of the DCMD process used for production of dematerialized water from tap water were performed using the experimental set-up shown in Fig.1. The MD installation was operated in a continuous mode, without the shutdown periods. A membrane module with the diameter of 0.025 m and the effective length of 0.53 m was installed in a vertical position. The module (membrane area 0.0889 m^2) was equipped with 30 hydrophobic capillary polypropylene membranes (Accurel PP S6/2, Membrana GmbH–Germany). The feed flow rate alongside the membrane surface was 1.35 m/s, whereas that of the distillate was 0.25 m/s. The hydraulic pressure of both streams (on the feed and distillate side) at the

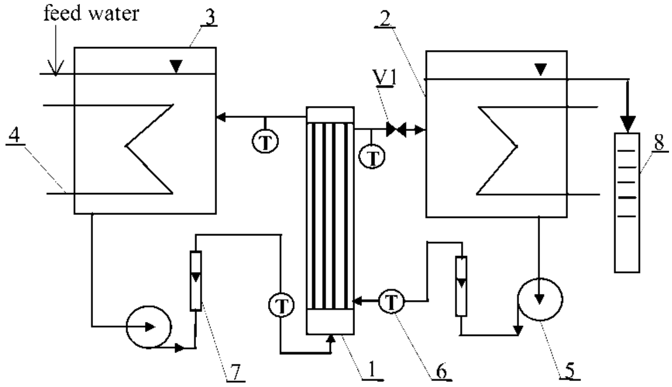

Figure 1. Diagram of the MD experimental set-up. 1—MD capillary module, 2—distillate tank, 3—feed tank, 4—heater, 5—impeller pump, 6—thermometer, 7—flowmeter, 8—measuring cylinder, V1—valve.

module inlet was equal (regulation by throttling valve V1), and amounted to 52 kPa. The inlet temperature of the feed and distillate was 353 and 293 K, respectively, and was maintained constant during the MD process.

The electrical conductivity and the total dissolved solids (TDS) of the used waters were measured with a 6P Ultrameter (Myron L Company). The membrane morphology and the composition of a fouling layer were studied using a Jeol JSM 6100 scanning electron microscopy (SEM) coupled with the energy dispersion spectrometry (SEM-EDS). The accelerating voltage used was 20 kV. The samples were sputter coated with gold (Au) and palladium (Pd). The content of the inorganic carbon (IC) and the total organic carbon (TOC), both in the feed and the permeat, was determined using a TOC-Analyzer multi N/C (Analytic Jena).

RESULTS

The MD installation was supplied with tap water having the electrical conductivity in the range of 605-650 μS cm^{-1}. The corresponding solute content (TDS) was found to be 409–430 mg L^{-1}. The TOC analysis revealed that the tap water contained 29–31 mg L^{-1} of inorganic carbon and 6.8–8.5 mg L^{-1}of the total organic carbon. The average concentrations (in mg L^{-1}) of the major ions were as follows: 29.2 Na, 59.2 Ca, 16.6 Mg, 6.1 K, and 2.8 Si (ICP-AES analysis).

The $CaCO_3$ deposit forming on the membrane surface during the MD process of tap water can be removed by rinsing the module with 2–5 wt.% HCl solutions (1, 3, 8). However, the precipitation of $CaCO_3$ crystals may initiate the membrane wettability. In order to evaluate a scale of this phenomenon in the presented study the MD process with tap water as a feed was carried out in several series. After completing each series, the module was rinsed by a 5% HCl solution. The experimental results are shown in Fig. 2. The presented date confirmed that the direct application of tap water as a feed resulted in a rapid decline of the permeate flux. In the first series the permeate flux decreases from 670 to 430 L $m^{-2}d^{-1}$ during the 100 h of process duration. After rinsing the module its efficiency was increased to 650 L $m^{-2}d^{-1}$, i.e., the permeate flux was closed to the initial value. A similarly large decline of the module efficiency, from 650 to 360 L $m^{-2}d^{-1}$, was observed in the second series (period next 120 h).

The first series of investigation was repeated with a new MD module in order to obtain the samples for membrane autopsy. The SEM examination confirmed that, the major reason of a rapid decline of the permeate flux (shown in Fig. 2) was the formation of a significant amount of the crystalline deposit on the membrane surface (Fig. 3). The composition of this deposit was analysed by the SEM-EDS method (Fig. 4). Beside of the major component (Ca), small amounts of Mg, Na, Fe, Zn, and Si were also determined. The obtained results indicate that $CaCO_3$ comprises the major component of deposit, which was confirmed by previous works (8). The SEM examinations of the membrane after rinsing with a 5 wt. % HCl revealed that all the precipitates from the membrane surface were practically removed (Fig. 5).

In order to limit the magnitude of permeate flux decline, in further studies a module rinsing by HCl solution was applied more frequently (Fig. 2, from 220 h). This allowed to maintain the process efficiency at a level of 500 L $m^{-2}d^{-1}$. Unfortunately, a gradual decline of the maximum permeate flux (distilled water as a feed) was found after a successive rinsing with a HCl solution. The maximum module efficiency was decreased from 670 to 520 L $m^{-2}d^{-1}$ after process duration of 500 h. A reason for the decreasing

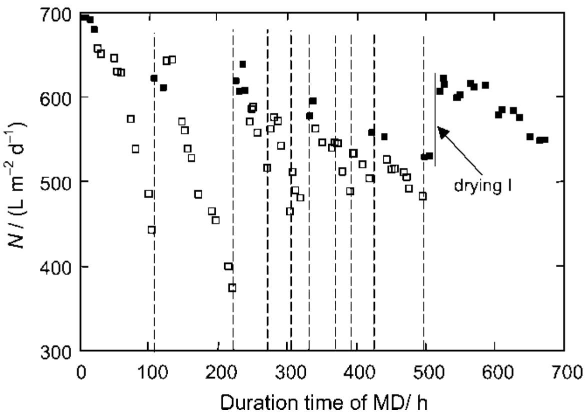

Figure 2. Variation of the permeate flux during the MD process. N—distillate flux for feed: ■—distilled water, □—tap water. Dotted line: module rinsed by HCl solution.

Figure 3. SEM micrograph of $CaCO_3$ deposit on the surface of the Accurel PP S6/2 membrane, feed: tap water.

efficiency was most probably associated with a partial wetting of the membranes. It was confirmed by a fact that the module efficiency increased from 520 to 650 $L\,m^{-2}d^{-1}$ after drying the membranes (Fig. 2, drying I). However, the module efficiency started to decrease again during the consecutive hours of MD process with distilled water.

The SEM investigation of the membrane cross-sections (Fig. 6) allows explaining the mechanisms of the membrane wetting. The $CaCO_3$ deposit covered not only the membrane surfaces but also penetrated into the pores

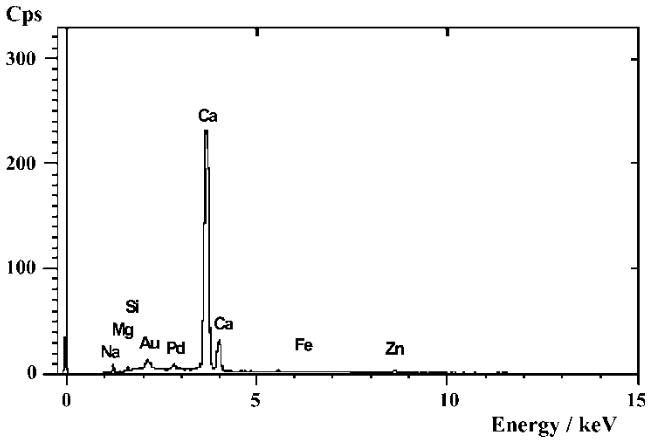

Figure 4. The result of SEM-EDS analysis of deposit formed on the membrane surface (Fig. 3).

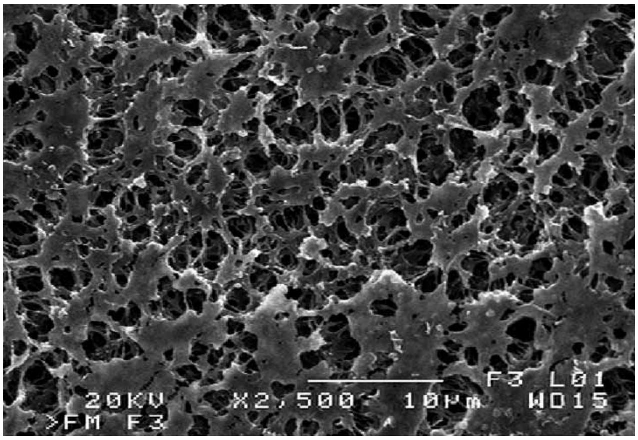

Figure 5. SEM micrograph of the fouled membrane (Fig. 3) after rinsing with HCl solution.

interior. The SEM-EDS line analyses of a change of the Ca content into the membrane wall (Fig. 6–direction A) revealed that the occurrence of calcium up to the depth of almost 40 μm (Fig. 7). This is an average result for the cross-sections of studied membranes. A further dissolution of deposit also proceeded inside the pores during the membrane rinsing with HCl solution, which is synonymous with flooding of these pores by liquid.

In spite of wettability of a fraction of the membrane pores, the quality of obtained distillate was maintained. The electrical conductivity of distillate

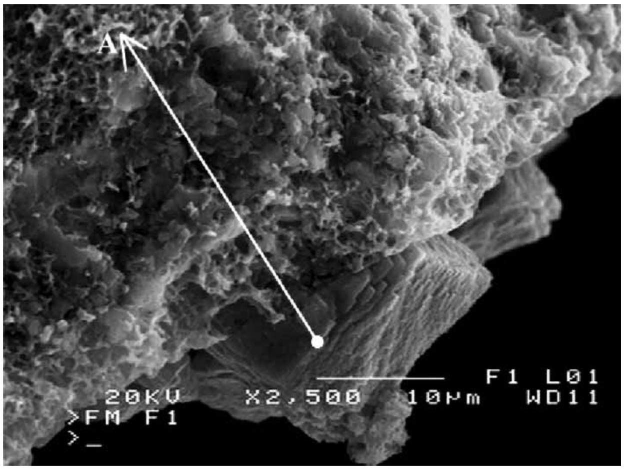

Figure 6. SEM micrograph of the cross-section of the membrane with the $CaCO_3$ deposit (feed side).

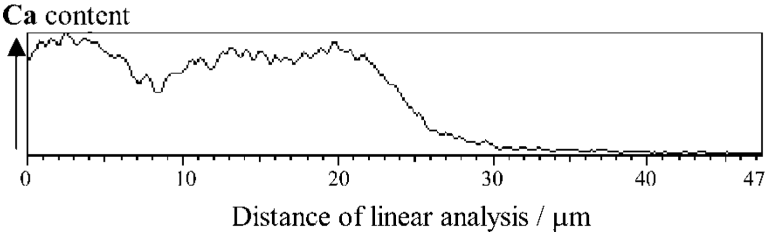

Figure 7. Result of the SEM-EDS line analysis of the calcium concentration in deposit formed inside the membrane wall (Fig. 6, direction A).

varied in the range of 1.4–2.5 μS cm^{-1}. This indicates that the pores were only wetted up to a certain depth of the membrane walls. The wall thickness of used membranes amounted to 400 μm. Therefore, the wettability of the surface pores even on a significant depth, e.g. 100–300 μm, still allows to maintain a gaseous gap between tap water and the obtained distillate. This excludes a leakage of feed and permits to maintain a high purity of distillate. However, a shift of the evaporation surface from the membrane surface deep inside its wall increases the temperature polarization, which causes a decrease of the process efficiency (1, 8, 10).

The degree of recovery of demineralized water from the feed was almost 75% for each series of the experiments. Changes of the feed composition during the process are shown in Fig. 8. Tap water was supplied to the installation in a continuous mode in each series, which caused a gradual increase of

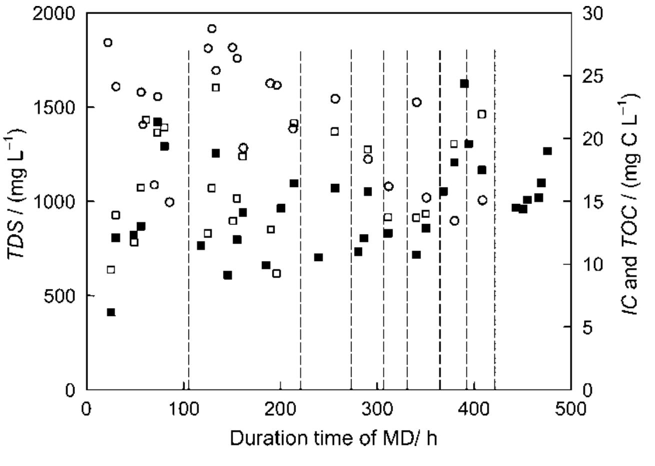

Figure 8. The changes of TDS, TOC, and IC concentration in the feed as a function of the operating time of the MD, feed: tap water; ■—TDS, ○—IC, □—TOC; dotted line: module rinsed by HCl solution.

the feed concentration (TDS). The initial amounts of inorganic carbon in the feed (29–25 mg C L^{-1}) rapidly decreased and the IC content was then stabilized at a level of 14–18 mg C L^{-1}. This confirmed the occurrence of a continuous decomposition of the bicarbonates present in the heated feed. A purity of obtained distillate was independent of the feed concentration, and most frequently the distillate with the electrical conductivity below 2 μS cm^{-1} was achieved. A continuous supply of feed water to the MD installation also caused an increase of organic matter concentration in the feed (Fig. 8, TOC). One should remember that volatile organic components, similarly as water vapor, could be transported through the membrane in the MD process. The presence of a trace amount of organic compounds in distillate (TOC at a level of 1 mg C L^{-1}) was detected.

In the next of the MD investigations the boiled tap water was used as feed water. The boiling of tap water allowed to convert the $HCO_3{}^-$ ions into CO_3^{-2} and CO_2, and as a result the IC concentration in the feed decreases from 30 to 7.5 mg C L^{-1}. The preliminary softening water was continuously added to a feed tank to maintain the constant volume. In this case, a portion of the concentrated water was continuously drained out from the circulating feed, in order to maintain the constant concentration of solutes in the feed (Fig. 9, TDS). However, a decreasing value of IC concentration (Fig. 9, from 700 h) indicates, that the precipitation of deposit still proceeded. This caused a decline of the process efficiency from 550 to 430 L m^{-2}d^{-1} during 175 h of process operation (Fig. 10, period 675–850 h). However, this decline was slower in comparison with a case when tap water was directly used as a feed. It was found that a decline of the permeate flux was associated with the following reasons. The accumulation of deposit at the capillary entrances was observed during the MD process. After its removal, the

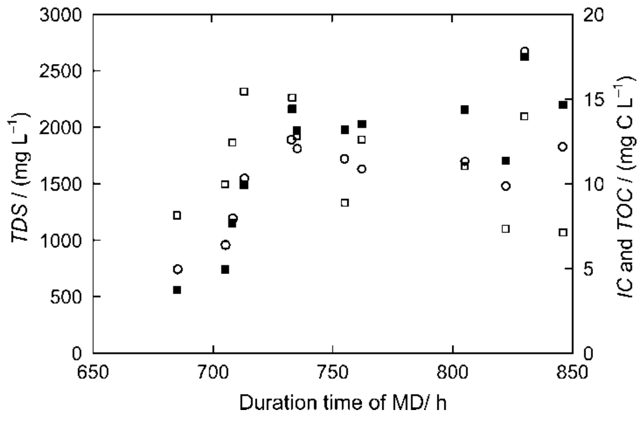

Figure 9. The changes of TDS, TOC, and IC concentration in the feed as a function of the operating time of the MD, feed: boiled tap water, ■—TDS, ○—TOC, □—IC.

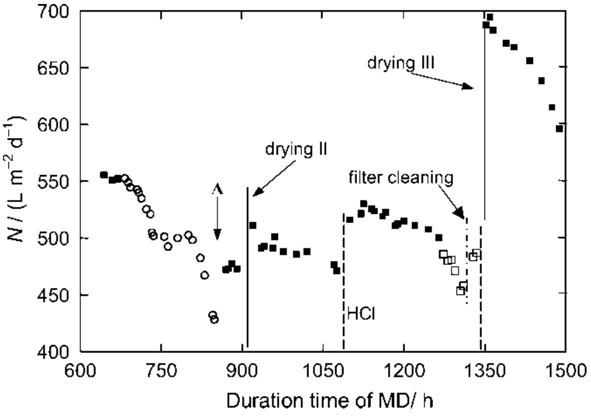

Figure 10. The influence of the operating time of the MD process and the nature of the feed water on the changes of the permeate flux (N), feed: ■—distilled water, ○—boiled tap water, □—MD concentrate; dotted line: module rinsed by HCl solution.

module efficiency was increased from 430 to 475 L m^{-2}d^{-1} (Fig. 10, point A). A further increase of the efficiency, up to 515 L m^{-2}d^{-1}, was achieved after drying the module, which indicates that a decrease of module efficiency was also associated with a progressive wetting of the membranes. Moreover, module efficiency was increased from 470 to 570 L m^{-2}d^{-1} after rinsing with a HCl solution, which indicates that the major reason, which caused a decline of module efficiency, was associated with the formation of deposit on the membrane surface.

In the last stage of the MD investigation the collected concentrates (from the previous series) were used as a feed water (Fig. 10, from 1275 h). The obtained results indicate that a decrease of efficiency was considerably smaller that that in the previous types of feeding water. The efficiency decreased from 475 to 445 L m^{-2}d^{-1} during 70 h. The autopsy of the module revealed, that a decline of efficiency primarily resulted from the accumulation of deposit on a filter net located at the module inlet. Its removal allowed the enhancement of distillate flux to 480 L m^{-2}d^{-1} (Fig. 10, 1340 h).

At the end of the studies the module was rinsed by a HCl solution, then was thoroughly rinsed with distilled water and subsequently subjected to drying over a long period. It was found, that the initial efficiency of a new module, e.g. 700 L m^{-2}d^{-1} was recovered. Unfortunately, similarly as in the previous cases, the module underwent a rapid re-wetting during the consecutive hours of operation. After about 150 h of work with distilled water, its efficiency decreased from 700 to 590 L m^{-2}d^{-1}. Most probably this was caused by the dissolution of salt deposit inside the pores, which were formed in the membrane pores during the membrane drying. A complete removal of solutes from the wetted pores was found to be very difficult.

CONCLUSIONS

The quality of the distillate obtained during MD of tap water was stable and practically independent of the feed concentration. The distillate produced has the electrical conductivity in the range of 1.4–2.5 $\mu S\,cm^{-1}$ with the TOC content below 1 $mg\,C\,L^{-1}$. However, the application of MD for the production of demineralized water from tap water requires the pre-treatment of feed water, in particular, the removal of bicarbonate ions.

The formation of deposit was found to be the major reasons of a decline of the permeate flux during the treatment of tap water in MD process. Rinsing the module with a diluted HCl solution can dissolve the $CaCO_3$ deposit. However, this is associated with the penetration of HCl solution into the pores filled by the deposit, which initiated the process of their wettability. As a consequence, the process efficiency decreases from 700 to 550 $L\,m^{-2}d^{-1}$ during the 500 h of MD process.

The removal of the deposit from the membranes followed by drying facilitates the recovery of the initial efficiency of the membrane module. However, during the consecutive hours of MD process a gradual decline of the permeate flux was again observed. This results mainly from the dissolution of salt deposit, which was formed inside the pores during the membrane drying.

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