

Water Desalination by Membrane Distillation

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1. Introduction

Water is the most common substance in the world, however, 97% is seawater and only 3% is fresh water. The availability of water for human consumption is decreasing due to increasing the environmental pollution. According to the World Health Organisation (WHO), about 2.4 billion people do not have access to basic sanitation facilities, and more than one billion people do not have access to safe drinking water (Singh, 2006). Moreover, the world's population is expected to rise to nine billion from the current six billion in the next 50 years. Chronic water pollution and growing economies are driving municipalities and companies to consider the desalination as a solution to their water supply problems.

Generally, desalination processes can be categorized into two major types: 1) phase-change/thermal and 2) membrane process separation. Some of the phase-change processes include multi-stage flash, multiple effect boiling, vapour compression, freezing and solar stills. The pressure driven membrane processes, such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF), have found a wide application in water treatment (Charcosset, 2009).

The energy required to run desalination plants remains a drawback. The energy limitations of traditional separation processes provided the impetus for the development and the commercialisation of membrane processes. Membrane technologies (simple, homogenous in their basic concepts, flexible in application), might contribute to the solution of most of the existing separation problems. Nowadays, membranes are used for the desalination of seawater and brackish water, potable water production, and for treating industrial effluents. RO membrane separation has been traditionally used for seawater desalination (Charcosset, 2009; Schäfer et al., 2005; Singh, 2006).

One of the limitations of membrane processes is severe loss of productivity due to concentration polarisation and fouling or scaling (Baker & Dudley, 1998; Schäfer et al., 2005). Membrane pretreatment processes are designed to minimise the potential problems of scaling resulting from the precipitation of the slightly soluble ions. Membrane (MF or UF) pretreatment of RO desalinations plants is now a viable options for removing suspended solids, fine particles, colloids, and organic compounds (Banat & Jwaied, 2008; Singh, 2006). NF pretreatment of seawater is also being used to soften RO feed water instead of traditional softening (Schäfer et al., 2005).

The industrial development of new membrane processes, such as membrane distillation (MD), is now being observed (Banat & Jwaied, 2008; Gryta, 2007). In MD process feed water is heated to increase its vapour pressure, which generates the difference between the partial

pressure at both sides of the membrane (El-Bourawi et al., 2006). Hot water evaporates through non-wetted pores of hydrophobic membranes, which cannot be wetted by liquid water (Gryta & Barancewicz, 2010). The passing vapour is then condensed on a cooler surface to produce fresh water (Alklaibi & Lior, 2005; Charcosset, 2009). In the case of solutions of non-volatile substances only water vapour is transported through the membrane. Thus, MD process has a potential application for the water desalination and the treatment of wastewater (Banat et al., 2007; El-Bourawi et al., 2006; Wang, et al., 2008). The MD has a significantly lower requirements concerning pretreatment of feed water, therefore, it enables the production of pure water from water sources, the quality of which impedes a direct application of the RO for this purpose. However, the feed usually contains various impurities, which in turn lead to the formation of deposit (Gryta, 2008). Deposits both pollute surfaces of membranes and make it easier for water to penetrate membrane pores (Gryta, 2007b; He et al., 2008). Consequently, membranes lose their separation properties and the MD process stops. This is why it is essential to prevent formation of deposits on the membrane surfaces.

2. Principles of membrane distillation

An expanded definition of MD process was created in 1986 at the "Workshop on Membrane Distillation" in Rome (Smolder & Franken, 1989). The term "Membrane Distillation" should be applied for membrane operations having the following characteristics:

- the membrane should be porous and not be wetted by the process liquids;
- no capillary condensation should take place inside the pores of the membrane;
- only vapour should be transported through the pores;
- the membrane must not alter the vapour-liquid equilibrium of the different components in the process liquids;
- at least one side of the membrane should be in direct contact with the process liquid;
- the driving force for each component is a partial pressure gradient in the vapour phase.

In membrane distillation heat is required to evaporate the feed components, therefore, in such context (similarly as in the classical distillation) it can be concluded that MD is a thermal-diffusion driven process. However, it operates at low temperatures (323-363 K), therefore, the feed water can be heated by using renewable energy (Banat & Jwaied, 2008).

The MD is carried out in various modes differing in a way of permeate collection, the mass transfer mechanism through the membrane, and the reason for driving force formation (Gryta, 2005; Smolder & Franken, 1989). These differences were taken into consideration in the nomenclature by the addition to the term "Membrane Distillation" the words, which emphasised a feature of a given variant. Various types of MD are known for several years (Fig.1): direct contact MD (DCMD), air gap MD (AGMD), sweeping gas MD (SGMD) and vacuum MD (VMD). DCMD variant is the most frequently studied and described mode of MD process (Alklaibi & Lior, 2005; El-Bourawi et al., 2006; Gryta, 2010; Wang, et al., 2008).

Several theoretical mass transfer models have been presented to describe membrane distillation. The models of DCMD were based on the assumption that vapour permeates through the porous membrane, as a result of molecular diffusion, Knudsen flow and/or the transition between them (Alklaibi & Lior, 2005; El-Bourawi et al., 2006; Gryta, 2008). Using the Stefan-Maxwell model diffusion of vapour through the air layer, the permeate flux can be described as proportional to the membrane permeability and water partial pressure difference (Alklaibi & Lior, 2007; Gryta et al., 1998):

$$J_v = \frac{\varepsilon D_{WA}}{\chi s_m} \frac{M_w P}{R T_m P_{in}} (p_F - p_D) \quad (1)$$

where p_F and p_D are the partial pressures of the saturated water vapour at interfacial temperatures T_1 and T_2 ; ε , χ , s_m , M_w , R , T_m , P , D_{WA} and p_{in} are membrane porosity, pore tortuosity, membrane thickness, molecular weight, gas constant, membrane temperature, total pressure, vapour diffusion coefficient and air concentration inside the pores, respectively.

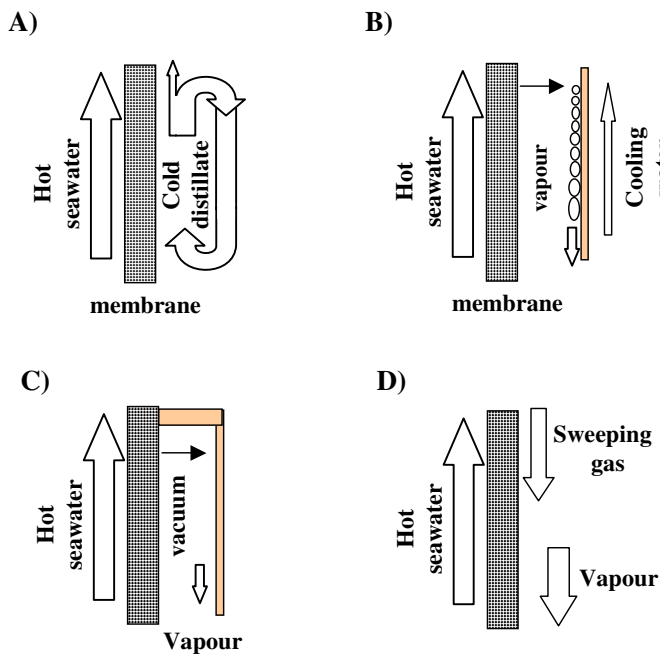


Fig. 1. Types of membrane distillation: A) DCMD, B) AGMD, C) VMD, D) SGMD

In MD process the mass transfer (J_v) occur simultaneously with heat conduction (Q) across the membrane material, and as a results, the temperature of the boundary layer on the feed side is lower, whereas on the distillate side it is higher than that of the bulk (Fig.2). This phenomenon is termed as the temperature polarization (Martínez-Díez & Vázquez-González, 1999). It causes the decrease of vapour pressure difference across the membrane which leads to the reduction of the magnitude of the mass flux (permeate) flowing through the membrane. The interfacial temperatures T_1 and T_2 cannot be measured directly. Several equations used to calculate these temperatures have been presented in the MD literature (Gryta et al., 1998; Khayet et al., 2004; Srisurichan et al., 2006). Their values depend in essential way on the conditions of a heat exchange in the MD module. Thus the correct description of the heat transport across the membrane will determine the accuracy of the mathematical calculation of MD process run (El-Bourawi et al., 2006; Gryta et al., 1998; Gryta, 2008).

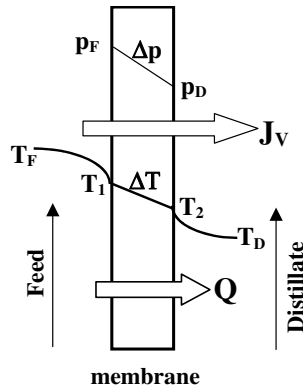


Fig. 2. Principles of DCMD: T_1 , T_2 , T_F , T_D – temperatures at both sides of the membrane, and temperatures of feed and distillate, respectively; p_F , p_D – water vapor partial pressure at the feed and distillate sides, respectively

2.1 Membranes and modules

The porous and hydrophobic MD membranes are not selective and their pores are filled only by the gas phase. This creates a vapour gap between the feed and the produced distillate, what is necessary for MD process operation. However, during the MD a part of the membrane pores may be wetted, that decreases a thickness of vapour gap inside the membrane wall (Gryta & Barancewicz, 2010). Therefore, the properties of membrane material and membrane porous structure are important for MD process performance (Bonyadi & Chung, 2009; Khayet et al., 2006).

Membrane for MD process should be highly porous, hydrophobic, exhibit a desirable thermal stability and chemical resistance to feed solution (El-Bourawi et al., Gryta et al., 2009). These requirements are mostly fulfilled by the membranes prepared from polymers with a low value of the surface energy such as polytetrafluoroethylene (PTFE), polypropylene (PP) or poly(vinylidene fluoride) (PVDF) (El Fray & Gryta, 2008; Gryta, 2008; Li & Sirkar, 2004; Teoh et al., 2008; Tomaszewska, 1996). Apart from the hydrophobic character of the membrane material, also the liquid surface tension, pores diameter and the hydraulic pressure decide about the possibility of the liquid penetration into the pores. This relation is described by the Laplace – Young (Kelvin law) equation (Schneider et al., 1988):

$$\Delta P = P_F - P_D = \frac{-4 B \sigma \cos \Theta}{d_p} \quad (2)$$

where: ΔP is liquid entry pressure (LEP), B is the pore geometry coefficient ($B = 1$ for cylindrical pores), σ is the surface tension of the liquid, Θ is the liquid contact angle, d_p is the diameter of the pores, P_F and P_D are the hydraulic pressure on the feed and distillate side, respectively. Water and the solutions of inorganic compounds have high surface tension ($\sigma > 72 \times 10^{-3} \text{ N/m}$), however, when the organics are present, its value diminishes rapidly. Thus, taking into consideration the possibility of membrane wetting, it is recommended that for MD the maximum diameter of membrane pores does not exceed the $0.5 \mu\text{m}$ (Gryta, 2007b; Gryta & Barancewicz, 2010; Schneider et al., 1988).

Hydrophobic polymers are usually low reactive and stable, but the formation of the hydrophilic groups on their surface is sometimes observed (Gryta et al., 2009). The surface reactions usually create a more hydrophilic polymer matrix, which may facilitate the membrane wettability (El Fray & Gryta, 2008; Khayet & Matsuura, 2003). The amount of hydrophilic groups can be also increased during MD process and their presence leads to an increase the membrane wettability (Gryta et al., 2009; Gryta & Barancewicz, 2010).

The application of membranes with improved hydrophobic properties allows to reduce the rate of membrane wettability. Blending of PTFE particles into a spinning solution modified the PVDF membrane, and enhances the hydrophobicity of prepared membranes (Teoh & Chung, 2009). Moreover, the resistance to wetting can be improved by the preparation of MD membranes with the uniform sponge-like membrane structure (Gryta & Barancewicz, 2010).

Apart from membrane properties, the MD performance also depends on the module design. The capillary modules can offer several significant advantages in comparison with the plate modules (flat sheet membranes), such as a simple construction and suppression of the temperature polarization (El-Bourawi et al., 2006; Gryta, 2007; He et al., 2008; Li & Sirkar, 2004; Teoh et al., 2008). The efficiency of the MD capillary module is significantly affected by the mode of the membranes arrangement within the housing (Fig. 3).

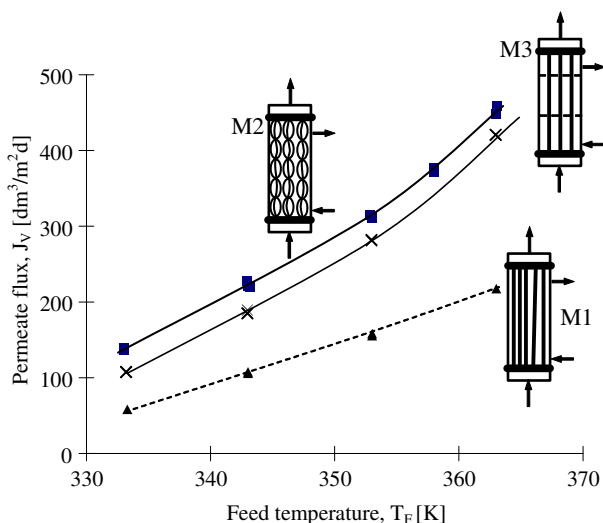


Fig. 3. The influence of feed temperature and the mode of membrane arrangement in a capillary module on the permeate flux. M1 - bundle of parallel membranes; M2 - braided capillaries; and M3 - capillaries mounted inside mesh of sieve baffles

The driving force for the mass transfer increases with increasing the feed temperature, therefore, the permeate flux is also increased at higher feed temperatures. A traditional construction (module M1) based upon the fixation of a bundle of parallel membranes solely at their ends results in that the membranes arrange themselves in a random way. This creates the unfavourable conditions of cooling of the membrane surface by the distillate, which resulted in a decrease of the module efficiency. In module M3 the membranes were

positioned in every second mesh of six sieve baffles, arranged across the housing with in 0.1–0.15 m. The most advantageous operating conditions of MD module were obtained with the membranes arranged in a form of braided capillaries (module M2). This membrane arrangement improves the hydrodynamic conditions (shape of braided membranes acted as a static mixer), and as a consequence, the module yield was enhanced.

2.2 MD process efficiency

Although the potentialities of MD process are well recognised, its application on industrial scale is limited by the energy requirements associated. Therefore, high fluxes must be obtained with moderate energy consumption. DCMD has been widely recognised as cost-efficient for desalination operating at higher temperatures, when waste heat is employed to power the process (Alklaibi & Lior, 2005). The performance of membrane distillation mainly depends on the membrane properties, the module design and its operating conditions (Bui et al., 2010; Li & Sirkar, 2004).

Concerning the operating conditions (Figs. 3 and 4), the feed temperature has the most significant influence on the permeate flux, followed by the feed flow rate and the partial pressure established at the permeate side. This last depending on the distillate temperature for DCMD and on the vacuum applied for VMD (Criscuoli et al., 2008; El-Bourawi et al., 2006).

The results presented in Fig. 4 confirmed that the distillate velocities had a minor role in improving the mass transfer, but a distillate velocity below 0.3 m/s would cause a rapid decrease in mass flux (Bui et al., 2010). Moreover, Bui et al. were indicated, that the distillate temperature has had a significant greater influence on DCMD energy efficiency. It is known that decreasing the water temperature from 283 to 273 K results in a very small increase of mass driving force. Therefore, it is recommended that the DCMD process be operated at a distillate temperature higher than 283 K.

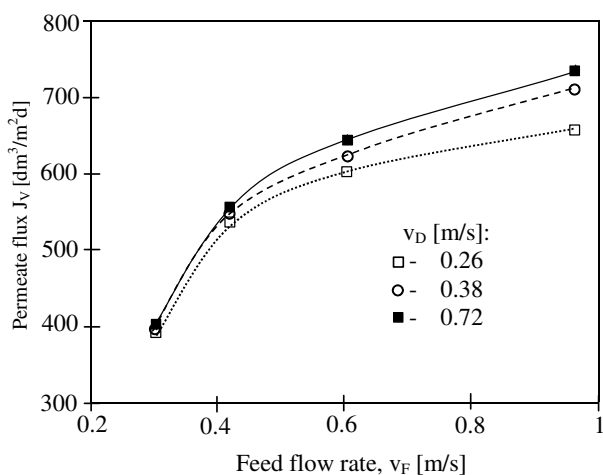


Fig. 4. The effect of the flow rate of streams in a module with braided membranes (module M1) on the permeate flux. $T_F = 353$ K, $T_D = 293$ K

The viability of MD process depends on an efficient use of available energy. The heat transfer inside the membrane (Q - total heat) takes place by two possible mechanisms, as conduction across the membrane material (Q_C) and as latent heat associated with vapour flowing through the membrane (Q_V). The heat efficiency (η_T) in the MD process can be defined by Eq. 3.

$$\eta_T = \frac{Q_V}{Q} = \frac{Q_V}{Q_V + Q_C} \quad (3)$$

The heat transfer which occurs in MD module leads to a cooling of the hot feed and to a heating of the distillate. Therefore, in the DCMD process it is necessary to supply heat to the hot stream and to remove heat from the distillate stream. The heating and the cooling steps represent the energy requirements of the DCMD process.

The amount of heat exchanged in the MD module increases along with an increase of the feed temperature (Fig. 5). However, under these conditions the permeate flux also increases, which causes the limitation of heat losses (heat conducted through the membrane material). As a result, an increase in the module yield influences on the enhancement of heat efficiency of the MD process (Fig. 6). For the highest permeate flux the η_T coefficient equal to 0.75 was obtained. It was concluded that energy efficiency of DCMD process could be maximised if the process were operated at the highest allowable feed temperature and velocity (Bui et al., 2010). A nonuniform arrangement of the capillary membranes in the module housing (module M1) caused a decrease in the energy consumption efficiency.

The unitary energy consumption in the MD process decreases along with temperature of feeding solution. This consumption was reduced from 5000 to 3000 kJ per 1 kg of obtained distillate when the feed temperature increased from 333 to 363 K (Gryta, 2006).

A decrease of the membrane wall thickness significantly increases the obtained permeate flux. However, during the MD process the liquid systematically wetted the consecutive pores, which reduced the thickness of the air-layer inside the membrane wall. In this

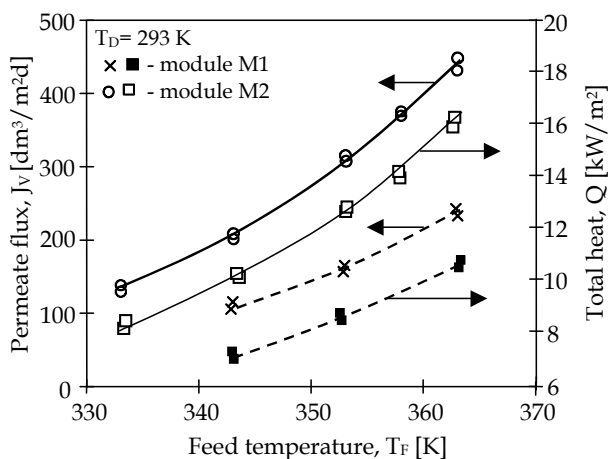


Fig. 5. Effect of feed inlet temperature and mode of membrane arrangement (M1 - parallel, irregular, M2 - braided membranes) on permeate flux and heat transfer in DCMD

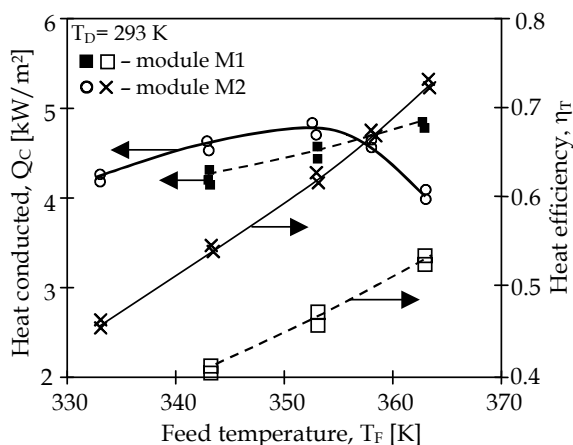


Fig. 6. Effect of feed temperature and mode of membrane arrangement (M1 - parallel, irregular, M2 - braided membranes) on heat conducted and heat efficiency in DCMD

situation, the membranes having a thin wall will be wetted in a relatively short time. Therefore, the hydrophobic membranes with thicker walls are recommended for commercial DCMD applications (Gryta & Barancewicz, 2010).

3. Membranes fouling

Fouling is identified as a decrease of the membrane permeability (permeate flux) due to deposition of suspended or dissolved substances on the membrane surface and/or within its pores (Schäfer et al., 2005). Several types of fouling can occur in the membrane systems, e.g. inorganic fouling or scaling, particulate and colloidal fouling, organic fouling and biological fouling (Baker & Dudley, 1998; Singh, 2006; Srisurichan et al., 2005). Scaling occurs in a membrane process when the ionic product of sparingly soluble salt in the concentrate feed exceeds its equilibrium solubility product. The term scaling is commonly used when the hard scales are formed (e.g. CaCO_3 , CaSO_4) (He et al., 2008; Lee & Lee, 2000). Fouling is also one of the major obstacles in MD process because the deposit layer formed on the membrane surface may cause membrane wetting. This phenomenon will certainly be accelerated if the salt crystals were formed inside the pores (Alklaibi & Lior, 2005; Gryta, 2002; Gryta, 2007; Tun et al., 2005).

The possible origins of fouling in MD process as follows: chemical reaction of solutes at the membrane boundary layer (e.g. formation of ferric hydroxides from soluble forms of iron), precipitation of compounds which solubility product was exceeded (scaling), adsorption of organic compounds by membrane-forming polymer, irreversible gel formation of macromolecular substances and colonization by bacteria and fungi (Gryta, 2002; Gryta, 2005b; Gryta, 2007; Gryta, 2008). The operating conditions of membrane distillation restricted the microbial growth in the MD installation; therefore, one should not expect the problems associated with biofouling in the degree encountered in other membrane processes such as UF, NF or RO (Gryta, 2002b).

A large influence on the fouling intensity has a level of feed temperature. During concentration of bovine serum albumin aqueous solution by DCMD was found that fouling was practically

absent in the process operated at low temperature (i.e. 293–311 K) (Ortiz de Zárate et al., 1998). On the contrary, a severe fouling by proteins was observed at higher feed temperatures (Gryta et al., 2001; Gryta et al., 2006c). The CaCO_3 scaling is also increased with an increase of the feed temperature. As a result of feed heating the HCO_3^- ions, present in the water, undergo the decomposition and a significant amount of CaCO_3 precipitates on the membrane surface (Drioli et al., 2004; Karakulski & Gryta, 2005; Gryta, 2005b; Schneider, et al., 1988). Although the acidification of feed water to pH 4 limited CaCO_3 scaling in the MD process, a slight fouling caused by other compounds (such as silicates), was still observed (Karakulski & Gryta, 2005). The foulants concentration may be reduced in the pretreatment stage, e.g. by using the NF or RO processes (Karakulski et al., 2002; Gryta, 2005b).

The deposit layers can be divided into two basic categories: porous and homogenous (non-porous) - Fig. 7. The deposit covered a part of the membrane surfaces, which reduced the membrane permeability and changed the temperature polarisation (Gryta, 2007). The values of heat transfer coefficients in both liquid phases and the membrane have a dominant influence on the values of T_1 and T_2 temperature of surfaces adjacent to the membrane (Fig. 2). The deposit layer creates an additional thermal resistance, thus decreasing the heat transfer coefficient from the feed bulk to the evaporation and condensation surfaces, and the temperature polarisation increased. As a result, the driving force for mass transfer is reduced and a significant decline of the permeate flux was observed (Gryta, 2008). The formation of non-porous layer causes a significant increase in the mass transfer resistance and the value of the permeate flux approach zero in an exponential way (Gryta, 2008).

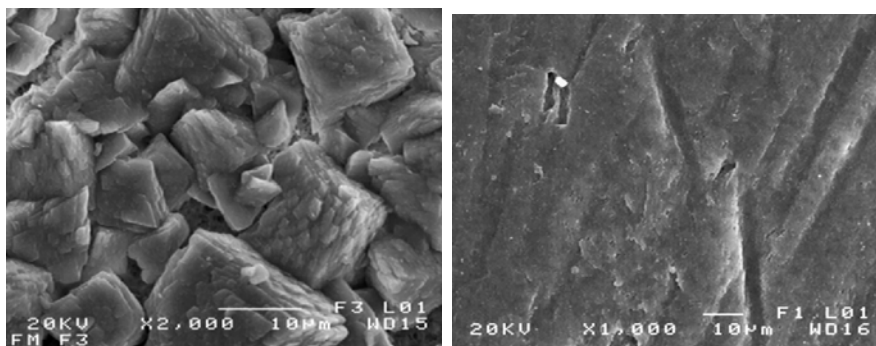


Fig. 7. SEM image of deposit on the MD membranes (Accurel PP S6/2). A) porous (CaCO_3); B) non-porous (proteins)

The supersaturation state enables the nucleation and crystal growth, what in MD is mainly caused by water evaporation and temperature changes (Alklaibi & Lior, 2005; Gryta, 2002; He et al., 2008; Yun et al., 2006). In the case when the solute solubility decreases along with a temperature drop, deposit can be formed as a result of the temperature polarization (He et al., 2008; Gryta, 2002).

The formation of deposit on the MD membrane surface begins in the largest pores (Fig. 8), because they undergo wettability the most rapidly (Alklaibi & Lior, 2005; Schneider et al., 1988). The wetted pores are filled by the feed, what facilitates the oversaturation and formation of deposits. The salt crystallization inside the pores was limited through a reduction of the surface porosity (Gryta, 2007b; He et al., 2008).

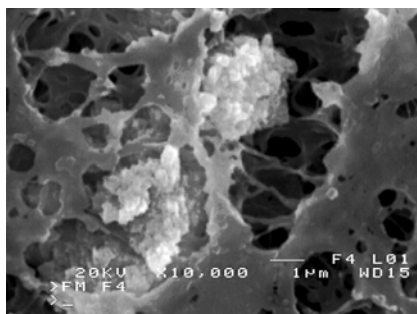


Fig. 8. SEM images of deposits formed inside the large pores (3-5 μm of diameter)

The adherence of the deposit to the membrane surface is a critical factor for MD performance, as well as for other membrane processes (Gryta, 2008; Gryta, 2009). It was found, that the deposit of CaCO_3 on the membrane surface can easily be removed by rinsing the module with a 2-5 wt.% solution of HCl, what allowed to restore the initial permeate flux (Fig. 9). However, the repetitions of module cleaning procedure by this method resulted in a gradual decline of the maximum permeate flux (Gryta, 2008).

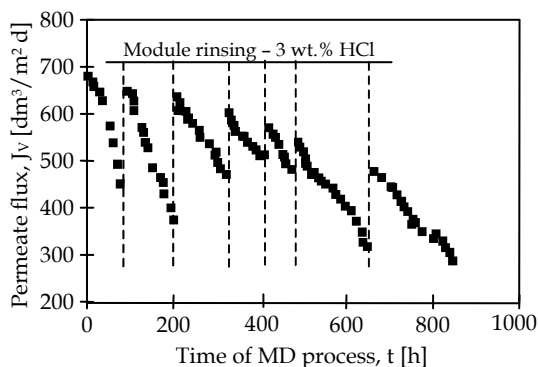


Fig. 9. Changes of the permeate flux during MD process of tap water

The SEM investigation of the membrane cross-sections revealed that the deposit covered not only the membrane surfaces but also penetrated into the pore interior (Fig. 10). The SEM-EDS line analysis of a change of the calcium content located into the membrane wall demonstrated that the deposit occurred up to the depth of 20-30 μm . Although, a rinsing acid solution dissolves the crystals, the wettability of the pores filled by deposit was accompanied to this operation. Therefore, the elimination of the scaling phenomenon is very important for MD process. The application of chemical water softening and the net filters (surface crystallization) allows to limit the amounts of precipitates deposited on the membrane surface during water desalination by MD process (Gryta, 2008c).

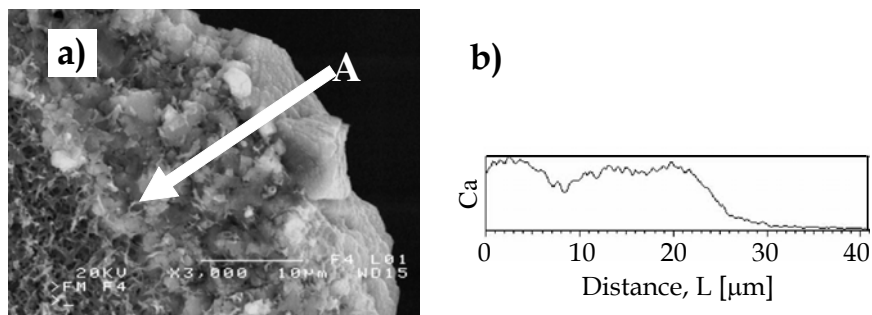


Fig. 10. CaCO_3 deposit on the membrane surface. a) membrane cross section, b) SEM-EDS line analysis (direction A)

4. Water pretreatment and membrane cleaning

The main techniques currently used to control fouling are feed pretreatment and membrane cleaning (Baker & Dudley, 1998; Schäfer et al., 2005, Gryta, 2008). The degree of pretreatment depends on the nature of the feeding water, the kind of membrane, the water recovery level and frequency of membrane cleaning (Karakulski et al., 2006; Schäfer et al., 2005). It was found that a significant amount of foulants from effluents obtained during ion-exchangers regeneration was successfully removed by the addition of the $\text{Ca}(\text{OH})_2$ to treated wastewater (Gryta et al., 2005c). The fouling intensity can be also limited by combining the MD with other membrane processes (Drioli et al., 2004; Jiao, 2004; Karakulski et al., 2006). The UF/MD integrated processes enables the concentration of solutions polluted by significant amounts of petroleum derivatives (Karakulski et al., 2002; Gryta et al., 2001b). On the other hand, an excessively advanced pretreatment system significantly increases the installation costs (Karakulski et al., 2006), which may render the application of MD process as unprofitable. Moreover, an effective water pretreatment by NF and RO processes did not allow to completely eliminate fouling (Karakulski et al., 2002; Karakulski & Gryta, 2005), therefore, its negative consequences should also be limited through the development of appropriate procedure of installation operation.

The majority of problems encountered during the water desalination by MD process are associated with water hardness. As the water is heated, CO_2 content decreases and the precipitation of CaCO_3 takes place due to the decomposition of bicarbonate ions (Figs. 7-11). For this reason, the feed water has to be pretreated before feeding the MD installation (Singh, 2006; Karakulski et al., 2006; Gryta, 2006b). Several operations such as coagulation, softening and filtration are used during the production of technological water. The possibility of such pretreated water utilization as a feed for the MD process is an attractive option (Gryta, 2008b). Contact clarifiers (accelerators) are usually applied to the chemical pretreatment of feed water in power stations (Powell, 1954, Singh, 2006). The chemicals (e.g. lime, aluminum or ferric sulphate) are added directly to the accelerator containing a relatively high concentration of precipitated sludge near the bottom of the tank, and raw water is treated with this mixture. Inside the accelerator, water flowing downward from the mixing and reaction zone passes the outer section of a much larger diameter, which is free of turbulence. Subsequently, the water flows upward, and the removal of flocks by settling takes place. A larger portion of this water passes through the return zone to the primary mixing and to the reaction zone. This recirculation improves the quality of the treated water.

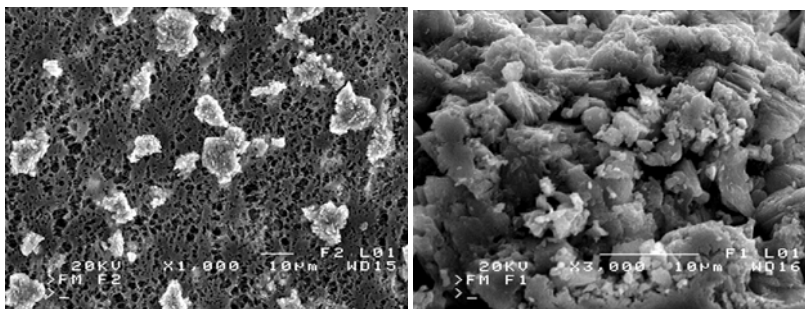


Fig. 11. SEM images of CaCO_3 deposit on membrane surface after: A) 10 h, and B) 50 h desalination of surface water by MD process

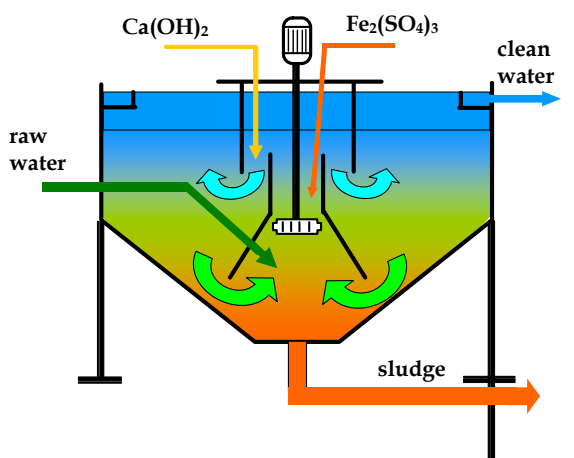


Fig. 12. Water treatment using the contact clarifiers (accelerator)

The chemical pretreatment of ground water caused a significant decrease of the concentration of compounds responsible for the formation of a deposit on the membrane surface during the MD process (Gryta, 2008). However, the treatment of water carried out in an accelerator, employed in the power station for production of demineralized water by the ion exchange process, was found to be insufficient for the MD process (Fig. 13). The formation of crystallites on the membrane surface was confirmed by SEM observations. Thus, a further purification of water produced by accelerator is required in order to use it as a feed for the MD process.

A very efficient method for preventing CaCO_3 precipitation is dosing an acid (Karakulski & Gryta, 2005). In this case HCO_3^- ions are converted into CO_2 according to the following reaction:



A major disadvantage of this method is an increase of concentration of chloride (HCl) or sulphates (H_2SO_4) in the retentate. The later anions (SO_4^{2-}) are particularly hazardous for the membrane (Fig. 14).

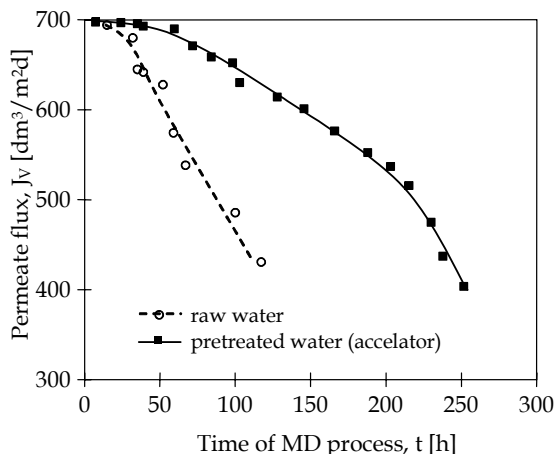


Fig. 13. Effect of the feed pretreatment (accelerator) on the MD permeate flux

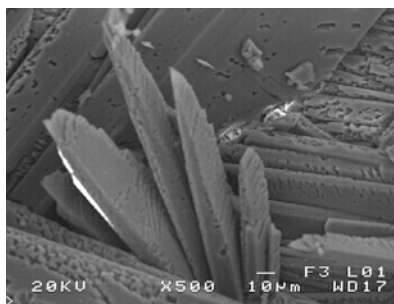


Fig. 14. SEM image of CaSO₄ deposit on the MD membrane surface

Sulphates comprise the second type of fouling components, the scaling of which can be encountered during water desalination by MD. The CaSO₄ solubility often determines the maximum recovery rate of demineralised water from feeding water (Gryta, 2009b).

The feed water before flowing into MD modules is heated in heat exchangers. In this case, a thermal softening of water can also be performed (Gryta, 2006b). As the water is heated, CO₂ content decreases and the precipitation of CaCO₃ takes place due to the decomposition of bicarbonate ions. A precipitated deposit may also cause substantial fouling of membranes; therefore, this deposit should be removed by using an additional filtration (Karakulski & Gryta, 2005). Other option is the application of heat exchanger, the design of which allows to remove the deposit of carbonates formed during water heating (Gryta, 2004).

Thermal pretreatment allows to remove most bicarbonates from water, which in turn reduces the amount of precipitate forming during MD process. However, the degree of water purification sometimes is too low and precipitate is still forming on the membrane surface. The SEM-EDS analysis revealed that apart a large amount of Ca, this deposit also contained Mg, Si, S, Fe, Ni, Al and Na. When the majority of HCO₃⁻ ions was removed from water, the carbonates formed an amorphous deposit with increased content of silicon (Gryta, 2010b). Such a nonporous form of deposit increases the rate of decline of the MD

process efficiency (Fig. 15). For this reason an additional operation of the feed treatment was required to prevent the formation of deposit. The residual of HCO_3^- ions, from the thermally softened water, were removed by acidifying the boiled water down to $\text{pH} = 4$. This operation retained the formation of precipitate and as a result the MD process proceeded without the flux decrease.

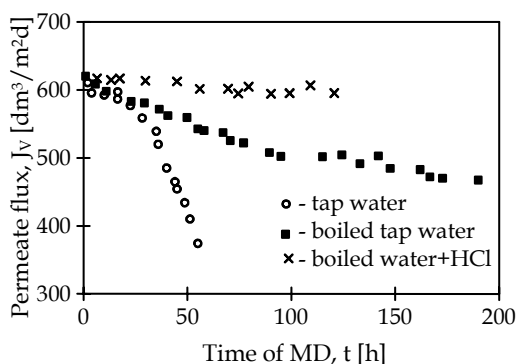


Fig. 15. The dependence of permeate flux as a function of the mode of feed pretreatment

Increasing the speed of the feed flow can reduce the negative influence deposit formation on MD process efficiency. SEM investigations demonstrated that the layer of the deposit was in this case more porous (Gryta, 2008c).

The induction period of CaCO_3 nucleation decreases as the supersaturation increases, but for the low saturation ratios (5-20) the induction period was higher than 30 min. It was reported that the induction time decreased from 12.9 to 1.1 min when the saturation ratio increased from 4 to 16 (Qu et al.; 2009). The elimination of membrane scaling is possible when the induction time will be longer than the residue time of feed inside the MD module. A heterogeneous crystallization performed inside a net filter may decrease the saturation ratio and as a result, the amount of deposit formed on the membrane surface will be reduced (Gryta, 2006b). The application of pre-filter element assembled directly to the MD module inlet allows to significantly limit the amounts of precipitates deposited on the membrane surface during the desalination of natural water by MD process (Gryta, 2009c). The removal of formed deposit from this element (rinsing by HCl solutions) would not result in the membrane wettability. The period between consecutive rinsing operations of the pre-filter is dependent on the several factors, such as a water hardness level, parameters of MD process and the residence time of the feed inside the MD installation. On the basis of the obtained results it can be assumed, that this period would be in the range of 2-5 h. The efficiency of this system was found to decrease along with an increase of distance of pre-filter element from the module inlet.

5. Practical aspects of MD process

The MD separation mechanism is based on vapour/liquid equilibrium of a liquid mixture. For solutions containing non-volatile solutes only water vapour is transferred through the membrane; hence, the obtained distillate comprises demineralized water (Alklaibi & Lior, 2005; Karakulski & Gryta, 2005; Schneider et al., 1988). However, when the feed contains

several volatile components, they are also transferred through the membranes to the distillate (El-Bourawi et al., 2006; Gryta, 2010c). Based on this separation mechanism, the major application areas of membrane distillation include water treatment technology, seawater desalination, production of high purity water and the concentration of aqueous solutions (El-Bourawi et al., 2006; Drioli et al. 2004; Gryta et al., 2005c; He et al., 2008; Karakulski et al., 2006, Li & Sirkar, 2005; Srisurichan et al., 2005; Teoh et al., 2008).

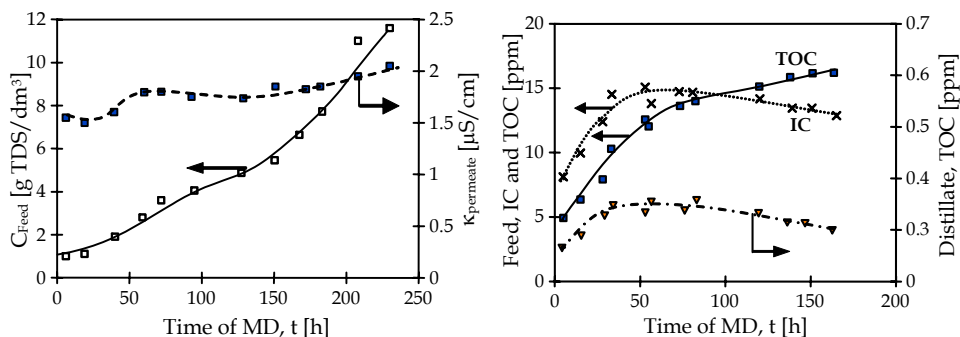


Fig. 16. Desalination of surface water by MD process

The results shown in Fig. 16 indicate that an increase in the feed concentration had a negligible effect on the quality of produced distillate. Despite the increasing value of the feed concentration the content of inorganic carbon (IC) in the distillate was close to the analytic zero. Only a slight amount of total organic carbon (TOC), below 0.5 mg TOC/dm³, was detected in the distillate, which can be associated with the transport of the volatile compounds through the MD membranes. It was found that volatile organic compounds (VOCs) diffuse through the pores of hydrophobic membranes, similarly to water vapour, hence, they are not completely rejected in the MD process (Gryta, 2010c; Karakulski & Gryta, 2005; Lawson & Loyd, 1997).

The produced MD distillate usually has the electrical conductivity in the range 0.5–5 $\mu\text{S}/\text{cm}$ and contained below 0.5 ppm of inorganic carbon. It confirms the fact that regardless of the time of the process duration, the MD membranes demonstrated a high retention of inorganic solutes (Alklaibi et al., 2005; Gryta, 2006b).

The possibility of application of the MD process for the treatment of saline effluents generated during the regeneration of ion exchangers was investigated. The feasibility studies were also performed in the MD pilot plant (Gryta, 2007). A corrosion phenomenon was noticed in this installation during a long-term operation of process. The pilot plant was constructed using a typical heat exchanger made of stainless steel, however, the employed construction material was found to undergo the corrosion in studied solutions. A more appropriate heat exchangers for this process should be made of tantalum, but their price is 2-times higher than the cost of constructed MD installation. Therefore, the treatment of the effluents from ion exchangers regeneration would be unprofitable due to a high investment cost. Moreover, the fouling caused by iron oxides does not always result from the corrosion of installation, but also from the reactions proceeding in the feed. Therefore, the utilization of plastics for the construction of the entire MD installation will not prevent the formation of iron oxides that subsequently will precipitate onto the membrane surface. Such a

phenomenon has been observed in the hybrid MD/absorber system utilised for gas purification by the absorption of SO_2 in a solution of Fe (II) sulphate (VI) proceeding simultaneous with the catalytic oxidation of SO_2 to sulphuric acid (Lewicki & Gryta, 2004). Membrane processes associated with renewable energy for water desalination offer alternative solutions to decrease the dependence on fossil fuels (Charcosset, 2009). The potential use of solar thermal-driven MD process for water desalination has been studied extensively. Although the desalted water was produced using free energy, it was stated that this technology is still expensive compared to other desalination processes (Banat & Jwaied, 2008). However, it was found that increasing the reliability of the MD technology and plant life-time could reduce the cost of the produced water significantly.

6. Conclusion

In comparison with other desalination processes, the main advantages of membrane distillation are: (1) 100% separation (in theory) of ions, macromolecules, colloids, cells etc., (2) lower operating pressures, (3) lower requirements concerning the mechanical properties of the membrane, and (4) less space requirement compared to conventional distillation processes. However, besides these advantages, membrane distillation still faces difficulties for commercialization.

The availability of the industrial MD modules is currently one of the limitations for MD process implementation. Flat-sheet membranes in plate and frame modules or spiral wound modules and capillary membranes in tubular modules have been used in various MD studies. The design of the MD modules should provide not only good flow conditions, but also has to improve the heat transfer and thermal stability. Several advantages offer the capillary MD modules. The efficiency of these modules was significantly improved when the cross flow or a devices with membranes arranged in a twisted or braided form in the housing were used.

The major difficulties are basically associated with a phenomenon of membrane wetting and the formation of the deposit on its surface. The use of an adapted pretreatment minimizes the fouling problems and can provide good protection of the membranes. Moreover, the module scaling may be reduced using the appropriate MD process conditions. The CaCO_3 precipitation was limited by lowering the feed temperature and by increasing the feed flow rate. The HCO_3^- ions concentration may be reduced by chemical water softening or by using pressure driven membrane processes. An effective solution would be the complete removal of the HCO_3^- ions from feed water, which can be achieved by the acidification of water to pH 4. However, the significant amounts of acids are required for feed acidification and as a result, the amount of salt increased in the retentate discharged to the environment.

The fouling and scaling accelerated the membrane wetting; therefore, more work will have to be done for a thorough evaluation of these phenomena.

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The book comprises 14 chapters covering all the issues related to water desalination. These chapters emphasize the relationship between problems encountered with the use of feed water, the processes developed to address them, the operation of the required plants and solutions actually implemented. This compendium will assist designers, engineers and investigators to select the process and plant configuration that are most appropriate for the particular feed water to be used, for the geographic region considered, as well as for the characteristics required of the treated water produced. This survey offers a comprehensive, hierarchical and logical assessment of the entire desalination industry. It starts with the worldwide scarcity of water and energy, continues with the thermal - and membrane-based processes and, finally, presents the design and operation of large and small desalination plants. As such, it covers all the scientific, technological and economical aspects of this critical industry, not disregarding its environmental and social points of view. One of InTech's books has received widespread praise across a number of key publications. Desalination, Trends and Technologies (Ed. Schorr, M. 2011) has been reviewed in Corrosion Engineering, Science & Technology – the official magazine for the Institute of Materials, Minerals & Mining, and Taylor & Francis's Desalination Publications. Praised for its “multi-faceted content [which] contributes to enrich it,” and described as “an essential companion...[that] enables the reader to gain a deeper understanding of the desalination industry,” this book is testament to the quality improvements we have been striving towards over the last twelve months.

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