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Desalination of geothermal water by membrane distillation

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Abstract. Membrane distillation process was used for desalination of hot (333 K) geothermal water, which was applied in the plant producing heating water. The investigated water contained 120 g salts/dm^3, mainly NaCl. The mineral composition was studied using an ion chromatography method. The obtained rejection of solutes was closed to 100%, but the small amounts of NH_3 also diffused through the membrane together with water vapour. However, the composition of obtained distillate allowed to use it as a make-up water in the heating water system. The geothermal water under study was concentrated from 120 to 286 g NaCl/dm^3. This increase in the solution concentration caused the permeate flux decline by a 10-20%. The geothermal water contained sulphates, which was subjected to two–fold concentration to achieve the concentration 2.4-2.6 g SO_4^{2-}/dm^3 and the sulphates then crystallized in the form of calcium sulphate. As a results, an intensive membranes scaling and the permeate flux decline was observed. The XRD analysis indicated that beside the gypsum also the NaCl crystallites were deposited on the membrane surfaces. The fresh geothermal water dissolved the mixed $CaSO_4$ and NaCl deposit from the membrane surface. This property can be utilized for self-cleaning of MD modules. Using a batch feeding of MD installation, the concentration of geothermal water was carried out over 800 h, without significant performance losses.

Keywords: membrane distillation; geothermal water; desalination

1. Introduction

Desalination of seawater and brackish water has been carried out using the standard evaporation methods (multi-stage flash, multi-effect, vapour compression) and reverse osmosis (Singh 2006). These desalination techniques are expensive technologies, particularly when driven by conventional energy sources. For this reason, other forms of alternative energy such as solar and geothermal energy have been attempted for this purpose (Bourouni *et al*. 1999, Gutierrez *et al*. 2009, Mohamed and El-Minshawy 2009).

The application of geothermal water as a feed for membrane distillation was also studied (Bouguecha *et al*. 2002). Membrane distillation (MD) is defined as an evaporation of volatile compounds through the non-wetting, macroporous membrane (El-Bourawi *et al*. 2006, Gryta 2010). For solutions containing non-volatile solutes only water vapour is transferred through the membrane; hence, the obtained distillate comprises demineralized water (Alklaibi and Lior 2004, Karakulski and Gryta 2005). On the basis of this separation mechanism, the MD process can be applied for seawater desalination as well as for the concentration of aqueous solutions (El-Bourawi *et al*. 2006, Drioli *et al*. 2004, Gryta *et al*. 2001, Hsu *et al*. 2002, Martínez-Díez and Florido-Díaz 2001, Wang *et al*. 2008).

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The driving force for the mass transport in MD is a gradient of vapour pressure, which results from the differences in both the temperatures and compositions of solutions in the layers adjacent to the membrane. As evaporation cools the feed solution, heating is required to maintain the vapour flux. In MD the relatively low feed temperatures (below 363 K) are used, therefore, a low enthalpy geothermal energy sources are also appropriate for this process (Bouguecha *et al*. 2002).

In this work were presented the studies on the possibility of utilization of MD process in the plant producing heating water, which was used for residential heating in Pyrzyce town (Poland). The heating power of 48 MW is obtained in 60% from the geothermal water, and the remaining part from the combustion of natural gas. The heating station has access to two wells at a depth of 1620 m, from which water is extracted at depth of 110 m at temperature 335-338 K. The heating water recycled from town is heated to 333 K (hot water) by the geothermal water in the heat exchangers and in the system of heat pump. The geothermal water cooled to 298 K is pumped back under the ground. The energy obtained from the combustion of natural gas is used for reheating of hot water to the temperature 348-363 K.

The losses of heating water due to the leakages were observed in the heating system of town Pyrzyce. The make-up water is produced by the method of reverse osmosis and ion exchange. In the presented work, the distillate obtained in the MD process is proposed to apply as the make-up water.

The ground waters contain several dissolved salts in their composition, in studied case about 120 g NaCl/dm^3. The used geothermal water besides NaCl also contained other salts (bromides, iodides, sulphate, calcium, magnesium, iron, boron and trace elements), which imparts the therapeutic properties (Geotermia Pyrzyce 2010). For this reason, the retentate obtained in the MD process may be applied as the concentrate of therapeutic salts. A high mineralization of water during the MD may result in the formation of deposit on the membrane surface (scaling). This phenomenon is one of the main reasons, which hinder the application of MD process (Gryta 2008). Therefore, the scaling intensity was studied in this work.

2. Experimental

The investigations of water desalination by MD process were performed using an installation presented in Fig. 1. The installation consisted of two thermostatic cycles (feed and distillate) that were connected to a membrane module. The used MD modules had a single capillary membrane (length: 0.7 m – MK1, and 0.01 m – MK2) mounted in the PCV housing with the inner diameter equal to 0.012 m. Hydrophobic capillary polypropylene membranes (Accurel V8/2 HF, Membrana, Germany), with outside/inside diameter equal to d_{out}/d_{in}=8.6 mm/5.5 mm and pore size 0.2 μm, were used for these studies (the manufacturer's data).

The feed and distillate streams flowed co-currently from the bottom to the upper part of MD module. The inlet temperatures of the streams of feed and distillate were kept at a level of 333-353 K and 293 K, respectively. The feed flow rate alongside the membrane surface was 0.34 m/s (inside the capillary bore) or 0.11 m/s (on the shell side), whereas, the distillate flow rate amounted to 0.29 (bore side) or 0.1 m/s (shell side).

The MD process was carried out in two different operating mode. Mode I – desalination of geothermal water at a constant salt concentration. In this case, the feed tank with geothermal water (4 dm^3) was maintained a constant level of liquid by dosing distilled water in the amount equivalent the permeate flux. Mode II – the geothermal water was continuously concentrated. During this

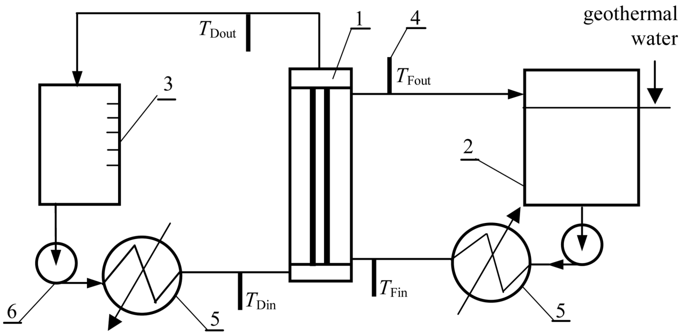


Fig. 1 Schematic diagram of the experimental set-up to study MD of geothermal water. 1 – membrane module, 2 – feed tank with dosing system, 3 – distillate tank, 4 – thermometer, 5 – heat exchanger, 6 – pump, 7 – measurement cylinder

operation the new portions of geothermal water were continuously dosed to the feed tank in order to maintain a constant liquid level (Fig. 1).

The anion and cation concentrations were measured using an ion chromatography method with conductivity detector (850 Professional IC, Herisau Metrohm -Switherland). The separation of anions was achieved on 1.7×3.5 mm Metrosep RP guard column in series with a 250×4.0 mm Metrohm A Supp5-250 analytical column. For cations separation a 150×4.0 mm Metrosep C2-150 analytical column was used.

The morphology and composition of the deposit layer formed on the membrane surface was studied using a scanning electron microscopy (SEM) coupled with energy dispersion spectrometry (EDS). Crystal structure of the precipitates was determined on a Philips X'Pert PRO diffractometer using monochromatized Cu*K*α radiation. The structural models of the precipitated salts were taken from ICPDS database: 74-1905 ($CaSO_4{\cdot}2H_2O$) and 75-0306 (NaCl).

The electrical conductivity and total dissolve solids (TDS) was measured with a 6P Ultrameter (Myron L Company).

3. Results

3.1 Water desalination

The underground water extracted in the geothermal heating station in Pyrzyce is subjected to filtration before flowing into the heat exchangers. The effluent of the filters was used for the MD studies. The analyses carried out with the use of ion chromatography demonstrated that this effluent had the following average ionic composition (ppm): 76100 Cl^-, 29 F^-, 106 Br^-, 196 NO_3^-, 1105 SO_4^{2-}, 46170 Na^+, 113 K^+, 4 NH_4^+, 2200 Ca^{2+} and 631 Mg^{2+}.

A high content of SO_4^{2-} ions (1105 ppm) creates a possibility of the formation of deposit on the membrane surface. The crystals of $CaSO_4{\cdot}2H_2O$ (gypsum) can damage the thin walls of capillary membranes. The precipitation of calcium sulphate was observed during the production of demineralized water from ground water by MD process, when high values of the water recovery coefficient (above 90%) were used (Gryta 2009). After 8 h of MD process duration the crystals were formed also inside the membrane wall, and as a results a feed leakage was observed. The SEM-EDS line analysis of

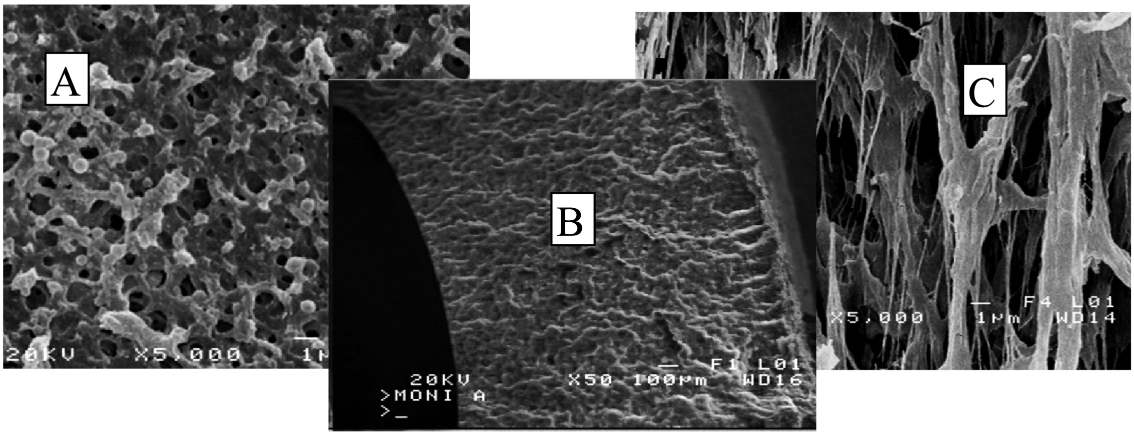


Fig. 2 SEM images of polypropylene capillary Accurel PP V8/2 HF membrane: A – internal surface, B – cross-section, C – external surface

membrane cross-section demonstrated that significant scale amounts were found up to the depth of 50-60 μm inside the membrane wall. Moreover, a small amount of gypsum was detected through the wall of capillary Accurel PP S6/2 membrane (400 μm wall thickness), which explains the reason for the observed feed leakage. It has been demonstrated in the previous works that a cyclic removal of deposits by membrane rinsing one can stabilize the scaling layer inside the membrane wall, e.g. at depth of 50-150 μm (Gryta 2008, Gryta 2009, Gryta *et al.* 2009). However, this method cannot be used in the case of membranes having the thin walls. Therefore, the membranes Accurel PP V8/2 HF, with significantly thicker walls (1550 μm) were used in the presented work.

The utilized Accurel PP V8/2 HF membranes are characterized by a foam structure and they are

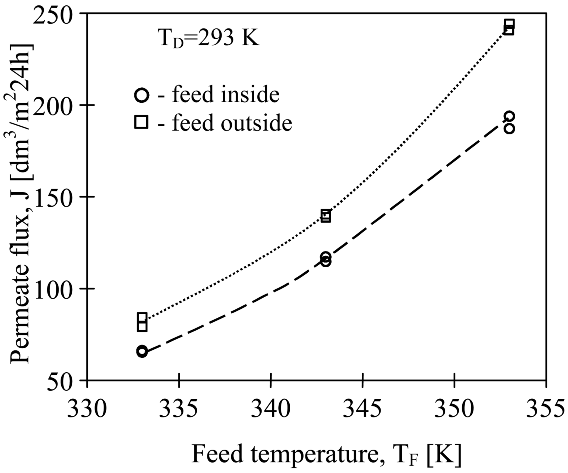


Fig. 3 The influence of feed temperature and flow direction on the permeate flux. Module MK1. Feed – distilled water. Feed inside – feed enters bore of the capillary. Feed outside – feed flowed on the shell side

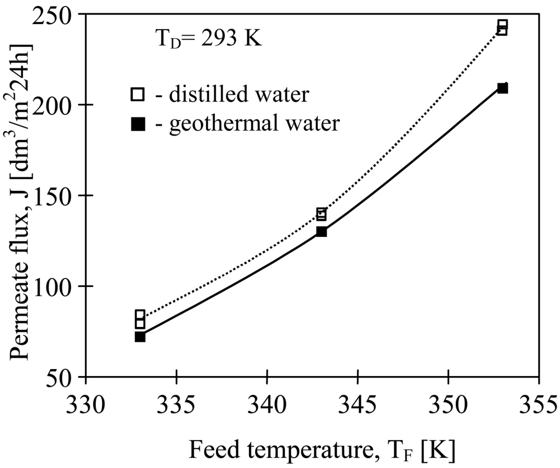


Fig. 4 The influence of feed temperature and salt concentration on the permeate flux. Module MK1. Distilled water (0 g NaCl/dm^3), geothermal water (120 g NaCl/dm^3)

symmetrical. Some differences in the pore size occurred only on the capillary external surfaces (Fig. 2), what was also observed for other capillary membranes (Gryta and Barancewicz 2010). In the studied case, the pores located on the outside surface of Accurel PP membranes are significantly larger than those located on the inside membrane surface (Fig. 2).

The permeate flux in MD process depends on both the condition of module exploitation and the composition of feed introduced into the module. A higher yield of the MD module was achieved for the feed flow on the shell side (Fig. 3). This results from a fact that the evaporation surface defined by the external surface of capillary for Accurel PP V8/2 HF membranes is significantly larger than their internal surface (bore side) due to a large thickness of the membrane wall (1550 μm). When the geothermal water is used as a feed, the permeate flux was lower by 10-15% in comparison with distilled water (Fig. 4). The presence of salts in the feed caused a decrease in the process efficiency, however, the advantageous of MD is a fact that a decline of the permeate flux is not as high as in e.g. reverse osmosis.

The feed temperature has a considerable effect on the magnitude of MD permeate flux. An increase in the feed temperature from 333 to 353 K caused a three-fold increase in the permeate flux (Figs. 3 and 4). The heat transfer inside the MD membrane 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 thermal efficiency (E_T) in the MD process can be defined by Eq. (1)

$$E_T = Q_V/(Q_V + Q_C) \tag{1}$$

Along with the increase in the permeate flux (increase of Q_V) decreases the fraction of heat conducted through the membrane (heat losses), what enhances the thermal efficiency of MD process (Gryta 2006). The permeate flux in MD process decreases along with increase in the thickness of membrane wall. Therefore, it is more advantageous to use the membranes with thinner walls (Fig. 5), providing that the deposits are not formed on the membrane surface. However, if scaling layer is also formed inside the membrane wall, then the thickness of used membrane should be significantly

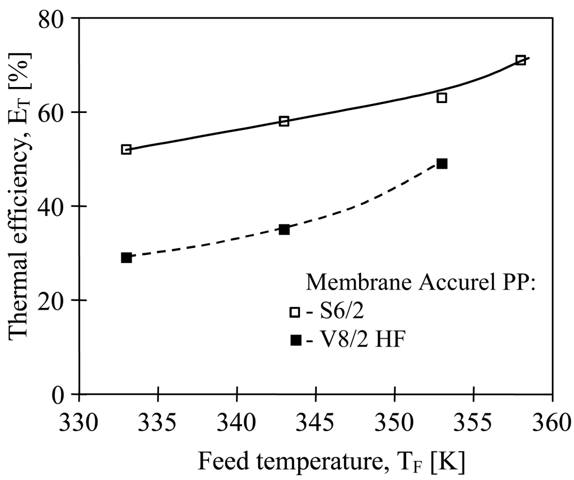


Fig. 5 The influence of feed temperature and membrane wall thickness on the thermal efficiency in MD process. Wall thickness: Accurel PP S6/2 – 400 μm, Accurel PP V8/2 HF – 1550 μm. Data for Accurel PP S6/2 were taken from (Gryta 2006)

larger than the deposit layer, what allows maintain the air gap inside the membrane wall.

The extracted geothermal water has a temperature of 335-338 K for the case considered. The losses of water filling the installation in Pyrzyce heating station are of the level of 1-2 m^3/day. In order to obtain such amount of distillate from geothermal water at temperature of 333 K (Fig. 4 – 70 $dm^3/m^2 24h$) it will be sufficient to use the MD installation containing the membrane modules with the total area of 30 m^2.

The module MK1 was supplied with the feed in the amount of 1.5 m^3/m^2h, hence one should supply 45 m^3/h of geothermal water for feeding of the MD modules having the 30 m^2 membrane area. The heating station in Pyrzyce is supplied by geothermal water stream at a level of 300-400 m^3/h. The feed temperature decreased from 333 to 331 K during the flow through the MK1 module. The same season of changes in temperature of extracted geothermal water has been observed. Thus, a direction of a part of geothermal water stream first to the MD installation, and subsequently to the main stream flowing into the heat exchangers should not cause significant disturbances in the operation of heating station.

The investigations of composition of obtained distillate indicated the presence of (in ppm): 0.02 Ca^{2+}, 0.01 Na^+, 0.29 Cl^-, 0.024 F^-, 0.064 SO_4^{2-} and 0.5-1 NH_4^+. Since ammonia is volatile it can easily diffuses through the membrane pores in the MD process, similarly like water. The heating water flowing back from the town to the geothermal heating station in Pyrzyce contained (in ppm): 8.6 Cl^-, 1.1 SO_4^{2-}, 4.3 Na^+, 1.4 NH_4^+, 2.2 Ca^{2+} and 0.4 Mg^{2+}. As the obtained MD distillate contained significantly smaller amounts of solutes, it can be used directly as make-up water.

The utilization a single flow of the geothermal water through the MD module allows to achieve a low coefficient of water recovery. As a consequence, the salt concentration in the feed would be insignificantly increased, and the possibility of occurrence of scaling can be significantly reduced. However, the determination of resistance of employed membranes for long-term exploitation and the membrane resistance to wettability would be of crucial importance. These parameters were evaluated during investigations with the MK1 module.

The results of MD studies obtained for the module MK1 supplied by the feed with a constant concentration at temperature 333 K over a period of 800 h were presented in Fig. 6. The permeate

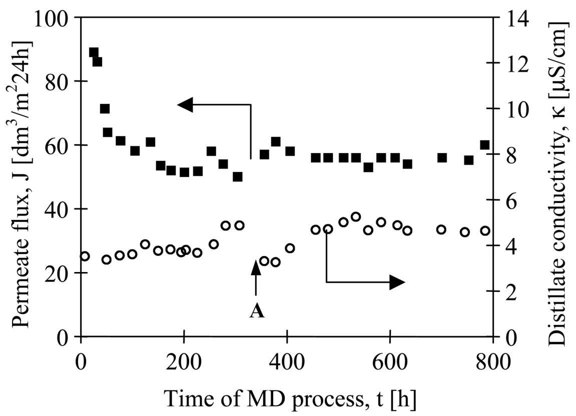


Fig. 6 Changes in the permeate flux and the electrical conductivity of distillate during the long-term geothermal water desalination. Module MK1. Mode: constant feed concentration (120 g NaCl/dm^3). Point A – distillate side refilled with new distilled water (3 μS/cm)

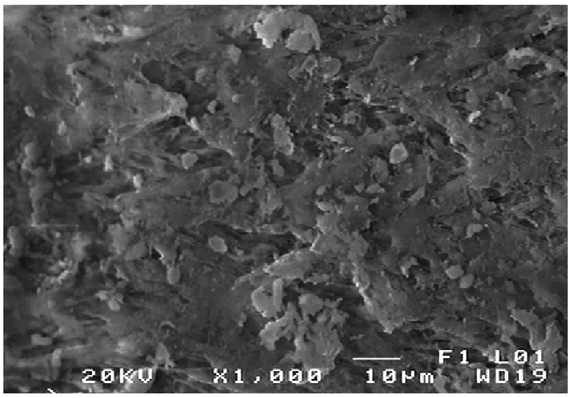


Fig. 7 SEM images of silicate deposit formed on the external surface of Accurel PP V8/2 HF membrane after 800 h of geothermal water desalination

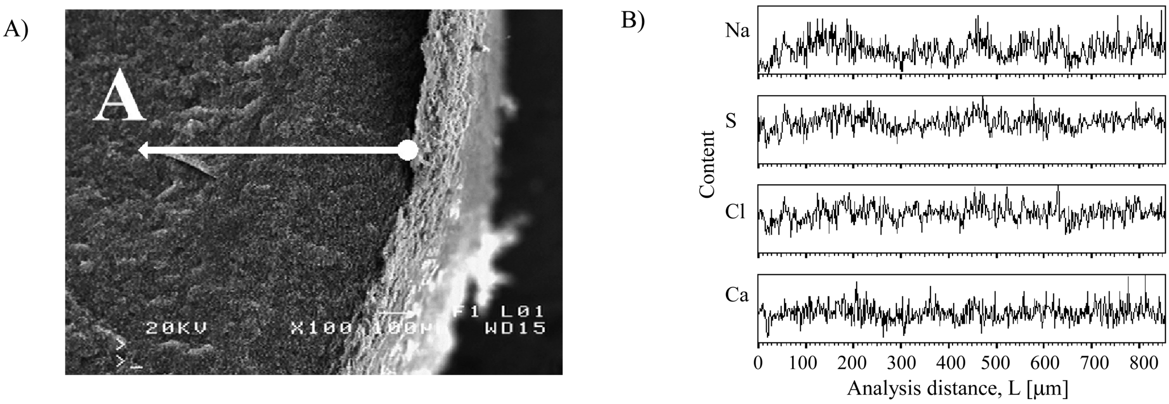


Fig. 8 The results of SEM investigations. A) cross-section of membrane taken from MK1 module after 800 h of geothermal water desalination, B) SEM-EDS line analysis (direction A from Fig. 8A)

flux decreases from 90 to 60 $dm^3/m^2 24$ h, at the initial period of 200 h, and subsequently was stable till the end of the studies. The SEM investigations revealed the presence small amounts of silicate deposit on the external (feed side) membrane surface (Fig. 7). This deposit was located only on the membrane surface. The SEM-EDS line analysis non-indicated the presence the salts deposit inside the membrane wall (Fig. 8). The observed changes of the S, Cl, Na and Ca content are as a consequence of roughness of membrane cross-section (pores). Obtained practically constant value of distillate conductivity (about 3-4 µS/cm) confirmed that the membranes were not wetted. The observed decline of permeate flux resulted most probably from wettability of certain pores located in the layers at the surface of membrane wall, whereas the pores located inside the wall were non-wetted. This result is similar to those observed during other long-term investigations (Gryta 2005, Karakulski and Gryta 2005). The Accurel PP V8/2 HF membranes were also successfully applied for separation saturated NaCl solutions during over one-year MD investigations (Gryta *et al.* 2009). The above results indicated, that the used membranes should not be wetted during long-term geothermal water desalination by MD process.

3.2 Geothermal water concentration

One of the considered new directions of development of the geothermal plant in Pyrzyce is the production of therapeutic brines. In this case the achievement of the highest concentration of salt in the product would be required. During the concentration of geothermal water can occur the precipitation and/or crystallization of sparingly soluble salts on the membrane surfaces what decreases the durability of MD membranes (Drioli *et al.* 2004, Gryta 2008). The possibility of scaling occurrence and its influence on the course of MD process of geothermal water was analysed during continuous long-term studies.

The deposit accumulation proceeds no uniformly on the membrane surface inside the MD module, usually the larger amounts of deposit are observed at the feed inlet (Gryta 2010). In order to limit the influence of differences in the deposit distribution on the module yield, in further studies a shorter MK2 module was used. The results obtained during the concentration of geothermal water were presented in Figs. 9 and 10.

The permeate volume (collected during 24 h) constitutes only 3-4 vol.% of the solution filled the feed tank. In order to achieve a higher degree of salt concentration, the feed was re-heated (333 K) and recycled to the module. A gradual increase in the solute concentration was observed in the recycled feed due to the water vapour permeation through the membranes (Fig. 9, TDS). The electrical conductivity of distilled water, initially filling the distillate tank, was equal to 3-4 μS/cm and was maintained at this level in the recycled distillate over a period of initial 80 h. Subsequently, the electrical conductivity gradually increased and reached a value of 20 μS/cm after about 300 h of MD process duration. The salt concentration in the feed was increased from 120 to 270 g NaCl/dm^3 after this period. The formation of salt crystals in the feed tank was observed; hence, the MD process was interrupted. The XRD analysis confirmed the crystallization of $CaSO_4 \cdot 2H_2O$. The liquid from the feed tank was removed and the feed tank was refilled with a portion of fresh geothermal water. The water was also replaced in the distillate tank by fresh distilled water. This procedure of the

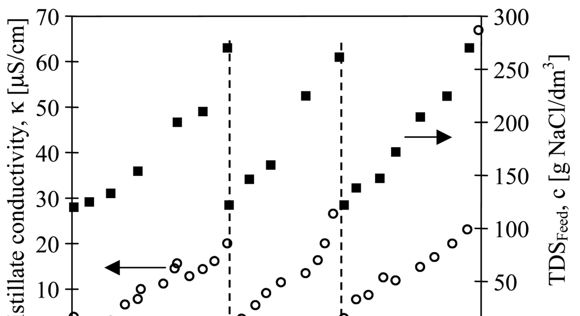


Fig. 9 Changes in the feed concentration (TDS- g NaCl/dm^3) and the electrical conductivity of distillate during the concentration of geothermal water by MD process. Module MK2

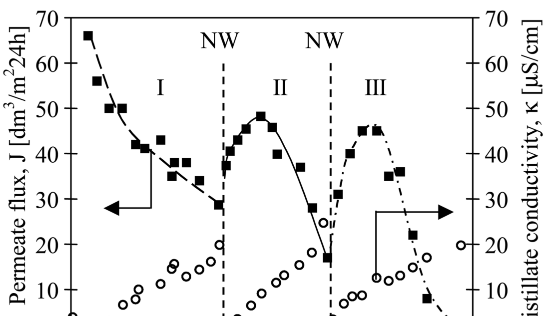


Fig. 10 Changes on the permeate flux and the electrical conductivity of distillate during the concentration of geothermal water by MD process (series I-III). Module MK2. NW – exchange of retentate into a new portion of fresh geothermal water

concentration of geothermal water was repeated twice, and the total operation time of MD installation with MK2 module amounted about 800 h.

An increase in the electrical conductivity of obtained distillate might indicate that some of the pores underwent wetting due to a membrane scaling. However, an analysis of distillate composition by IC method demonstrated that the main reason was associated with an increase in the ammonia concentration (to 4-5 ppm of NH_4^+). It was found that all the volatile compounds diffuse through the pores of hydrophobic membranes, similarly to water vapour (Gryta 2010), therefore, the NH_3 as a volatile compound cannot be totally rejected in the MD process.

The results shown in Figs. 9 and 10 indicated that an increase in the feed concentration caused a flux decline of distillate from 70 do 30 $dm^3/m^2 24h$. A replacement of concentrated retentate by a fresh portion of geothermal water (after 300 h) caused increase in the yield only to a level of 50 $m^3/m^2 24h$. It can be concluded, that the membrane lost a part of their efficiency due to wetting of some pores on the capillary surfaces, similarly as in the case of the module MK1 – Fig. 6.

An increase in the solute concentration of the feed (Fig. 9) caused a reduction of the partial pressure of water vapour. However, taking into consideration also a partial wetting of the membrane, the total decline of yield is larger than that resulting from an increase in the salt concentration from 120 to 270 g $NaCl/dm^3$ (Gryta 2008). Further studies explained, that a reason of this flux decline was the formation of crystallite deposit on the membrane surface. A new portion of geothermal water caused the dissolution of formed deposit; hence the membrane permeability was increased. Therefore, the yield of MD installation was also increased over a period from 300 to 400 h of process operation (Fig. 10). A similar result was obtained in the second series, over a period from 550 to 630 h of MD process.

In the last series, the concentration of geothermal water was prolonged in order to increase the degree of scaling, and the final concentration of 286 g $NaCl/dm^3$ was achieved. The concentration of sulphate ions increased to a value of 2.6 g SO_4^{2-}/dm^3, and subsequently their concentration was reduced to a value of 1.93 g SO_4^{2-}/dm^3. Meanwhile, the module yield decreased to almost zero. An autopsy of module demonstrated that the entire surface of membrane was covered by a thick layer of salt crystals (Fig. 11). SEM images of the scales (Fig. 12) revealed different crystalline shapes formed on the membrane surface. The scale structures were created by numerous plate-like and needle like crystals.

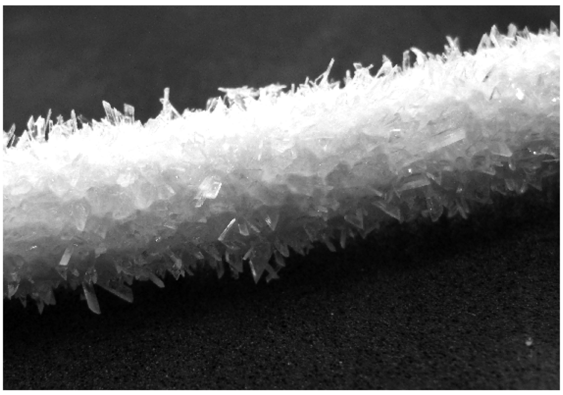


Fig. 11 SEM image of crystallite deposit on the external surface of Accurel PP V8/2 HF membrane

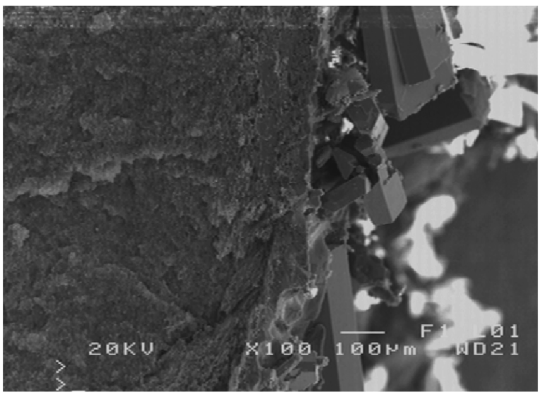


Fig. 12 SEM images of the cross-section of Accurel PP V8/2 HF membrane covered by deposit. Module MK2

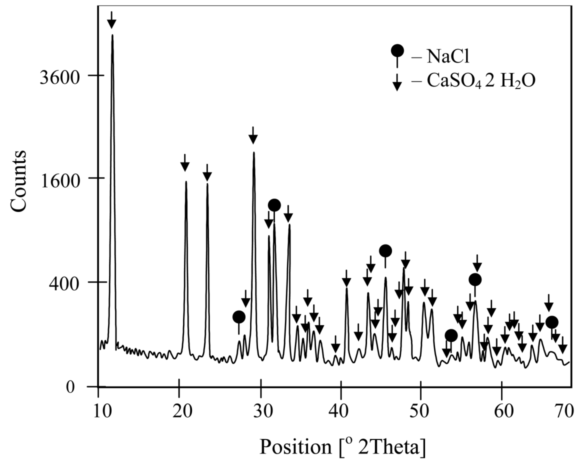
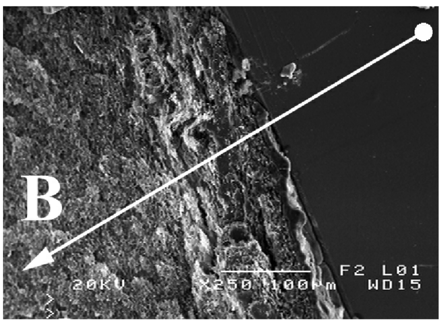


Fig. 13 The results of XRD analysis of deposit taken from the membrane surface (Fig. 11)

A)



B)

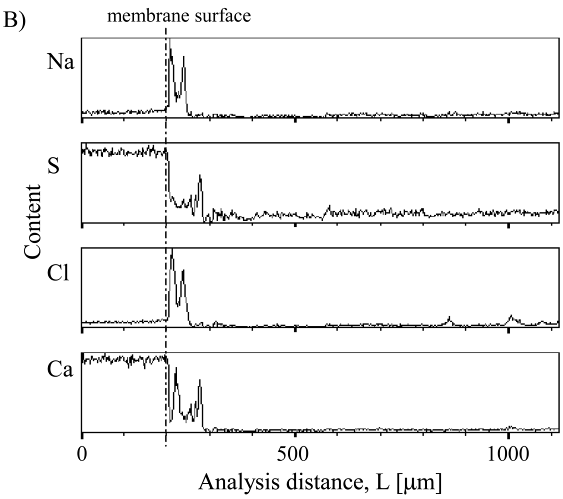


Fig. 14 The results of SEM investigations. A) cross-section of membrane, containing a deposit layer, taken from MK2 module after 800 h of geothermal water concentration. B) SEM-EDS line analysis (direction B from Fig. 14A)

The needles are orthorhombic or hexagonal prismatic, which are the typical forms of gypsum crystals (Gryta 2009).

The XRD analysis indicated that the mixture of $CaSO_4{\cdot}2H_2O$ and NaCl crystallites were deposited on the membrane surfaces (Fig. 13). The presence of NaCl in the deposit probably facilitated its dissolution after the replacement of the retentate for a new portion of geothermal water. In this case can be achieved the effect of self-cleaning of the membrane surface in the MD module when a periodical concentration will be used. The results of SEM-EDS line analysis (Fig. 14) indicated, that despite of the formation of a large amount of deposit, the scaling layer penetrated into the membrane wall interior only at depth of 100 μm during 800 h of the concentration process. Such results allows to assume that by using a periodical removal of deposit it is possible the use of Accurel PP V8/2

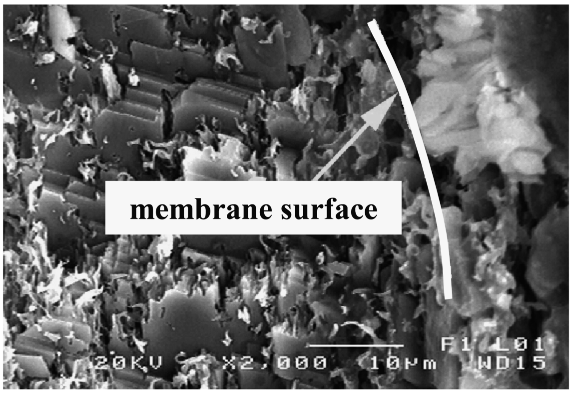


Fig. 15 SEM images of the membrane cross-section with pores destroyed by formed $CaSO_4 \cdot H_2O$ crystallites

HF membranes for the preparation of brines from geothermal water.

The crystallites inside the membrane occupy the space significantly larger than the pore dimensions, what leads to a destruction of the membrane structure (Fig. 15). The application of membranes that are significantly thicker than a layer of crystallizing salt allows to maintain the mechanical strength of the membranes and prevents the membranes from complete wetting.

4. Conclusions

The quality of MD distillate obtained during the desalination of geothermal water was stable and practically independent on the feed concentration. The produced distillate has the electrical conductivity in the range 3.5–20 μS/cm and the content of total dissolved solids was below 6 ppm. The volatile compounds (e.g. NH_3) diffuse from the feed to distillate (similarly to water vapour), therefore, they cannot be completely removed in the MD process. However, the composition of obtained distillate allowed to use it as a make-up water in the heating water system.

During the concentration of geothermal water the severe membrane scaling was observed. A high content of salt in the retentate (270-286 g NaCl/dm^3) increases the solubility of $CaSO_4$, therefore, the feed can be concentrated to the concentration of 2 g SO_4^{2-}/dm^3 without the formation of deposit on the membrane surface. After exceeding this value, the crystallization of $CaSO_4 \cdot 2H_2O$ proceeded and the MD process efficiency was decreased to zero. The formed deposit was dissolved in warm (333 K) geothermal water. The XRD analysis indicated that beside the gypsum also the NaCl crystallites were deposited on the membrane surfaces. The presence the NaCl in the deposit was probably a reason of its fast dissolution, when a new portion of geothermal water replaced the retentate. This property can be utilized for self-cleaning of MD modules by the application of batch feeding of MD installation.

During 800 h of concentration of geothermal water the scaling layer was formed also inside the membrane wall in the depth close to 100 μm. Such amount of deposit should cause the wettability of the membranes with thin wall. One can prevent this phenomenon using the membranes with the thickness definitely larger than the thickness of deposit layer forming inside the membrane pores. For this reason the application of the Accurel PP V8/2 HF, having thick walls (1550 μm), allowed to carry out the desalination and concentration of geothermal water despite of the formation of large amounts of the deposit.

Acknowledgements

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