

# Water demineralization by membrane distillation utilizing cooling water from municipal waste incinerator

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The membrane distillation performance was studied for production of demineralized water from surface water (river). Hot water from cooling water system of municipal waste incinerator was considered as an energy source for membrane distillation. The integration of membrane installation with such cooling water system allows to re-use up to 18 kW per 1 m<sup>2</sup> of the membranes. The studies were performed with the application of polypropylene capillary membranes Accurel PP S6/2. The membrane modules were supplied with the feed heated to a temperature of 310 K and 330 K. The permeate flux obtained for these temperatures was 2.8 and 9.7 L/m<sup>2</sup> h, and the distillate conductivity was 6 and 4 μS/cm, respectively. The water demineralisation process was carried out for 1200 h without module cleaning. The behaviour of the permeate flux and distillate conductivity indicate that used membranes maintained their non-wettability over tested period. The performed SEM-EDS examinations confirmed, that the deposits did not fill the pores and were mainly formed on the membrane surface. The scaling intensity was definitely smaller for lower temperature (310 K) of the feed. The amorphous deposits containing beside Ca also substantial amounts of the Si were mainly formed under these conditions, whereas at higher feed temperature dominated CaCO<sub>3</sub> scaling.

**Keywords:** demineralized water, membrane distillation, scaling, waste incinerator.

## INTRODUCTION

The disposal of municipal solid waste is a major challenge especially in a big city. A traditional option for waste treatment is landfilling, recently reduced by recycling and composting. However, only a part of waste volume can be managed by these methods and incineration is a good additional method for the treatment of residual mixed waste. The energy recovery from waste incineration is important and the cogeneration of thermal energy and electricity production is the most effective method of recovering heat from waste incineration<sup>1–3</sup>. In this case the thermal energy is delivered to the district-heating network for supplying urban consumers and the electrical energy is delivered to the public electricity network.

The temperature of combustion process must be maintained to at least 1123 K (850°C), which reduced the synthesis of dioxins and the thermal efficiency close to 90% can be achieved, with typical steam conditions 4 MPa and 673 K<sup>1</sup>. Similarly as in all power stations, the water used in the boiler must be purified using a demineralization process, because besides scaling any ions remaining in the water will corrode the boiler at the high operating temperatures<sup>4</sup>.

The water treatment by ion exchange (IX) process has been used extensively and is a major industrial method for water demineralisations<sup>1, 4</sup>. However, the operation of large-scale industrial IX systems, e.g. in the power stations, is inherently associated with the generation of wastewaters resulting from the regeneration of ion exchange resins. The incorporation of membrane processes, such as ultrafiltration (UF) and reverse osmosis (RO) would result in a substantial saving of costs of the chemicals together with mitigation of waste treatment problems. Moreover, these processes enable the water re-use. The application of UF/RO/IX integrated system allowed the production of demineralised water using the water obtained from municipal wastewater treatment plant<sup>4</sup>.

Demineralised water can be also produced using membrane distillation (MD)<sup>5, 6</sup>. During this process only water evaporates through non-wetted microporous membranes, and as a result the salts present in the feed water are retained and produced distillate is demineralized water<sup>5–7</sup>. A large amount of energy is required for water evaporation, thus a good thermal efficiency is important for industrial implementation of the MD process<sup>8, 9</sup>. The MD process has a low single pass water recovery (below 10%) and usually the feed is re-circulated, which additionally increases the energy consumption<sup>10</sup>. However, the application of MD membrane modules, which enables the heat recovery from distillate, results in a significant reduction of energy consumption<sup>7, 11</sup>. Moreover, as the MD operates with low-grade heat, the coupling of MD with waste energy makes the MD process very attractive<sup>12, 13</sup>. Several sources of waste heat exist in municipal waste incinerator. Most of the energy losses being accounted for the low-pressure steam exiting the turbine and entering the condensers<sup>1, 3</sup>.

A basic problem that hinders a long-term MD module exploitation is a phenomenon of membrane wetting, which is often induced by scaling and membrane fouling<sup>14–16</sup>. The wettability of even a small fragment of the membrane wall causes, that the salts penetrate from the feed resulting in a deterioration of distillate quality and as a result, the possibility of demineralized water production can be eliminated<sup>7, 13–15</sup>. Moreover, crystallization of salts on the membrane surface causes a decrease of process efficiency and the membrane modules are often damaged<sup>17</sup>.

The occurrence of scaling causes, that it is necessary to apply a periodical membrane cleaning and/or to limit a scaling intensity. It was found in several works, that the intensity of scaling could be reduced by lowering of the feed temperature, particularly for the temperatures below 333 K<sup>5, 8, 18–20</sup>. A scaling elimination and stable operation of MD during water desalination was achieved

ved at the feed temperature of 308 K<sup>21</sup>. Although the evaporation efficiency decreased only from 90% to 75% with decreasing feed water temperature from 353 to 313 K; the permeate flux decreased several times what limits such a solution<sup>8, 22, 23</sup>. However, lowering of the feed temperature from 333 to 313 K during water desalination was found to be advantageous in the case of CaSO<sub>4</sub> precipitation, because a decrease of this temperature causes a prolongation of the induction time of CaSO<sub>4</sub> crystallization and delays the development of membrane scaling<sup>18</sup>. Similarly, diminishing of CaCO<sub>3</sub> precipitation was also observed for a low feed temperature<sup>21</sup>. Therefore, the application of post-cooling water, usually having a temperature below 333 K, can be advantageous in the MD process<sup>12, 24, 25</sup>.

In the presented work was studied a possibility of MD application in waste incinerator for boiler water make up system. The actual post-cooling water was applied as a feed. The polypropylene membranes manufactured by Membrana (Germany) were used due to the possibility of application in the industrial modules. These membranes were successfully utilized in a pilot plant tested in the power plant for demineralized water production<sup>26</sup>. The capillary modules having a thermal efficiency close to 80% were assembled in this pilot MD installation.

### MD installation

In the considered waste incinerator the open cooling system was supplied by water extracted from the river. A substantial volume of fresh water (up to 2000 m<sup>3</sup>/h) flowed through the steam condenser and was recycled to the river. The outlet water temperature is at a level of 305 K and this temperature should not exceed 308 K. The smaller heat sources with a higher water temperature are also available, e.g. about 323–333 K for the water used for cooling of the vacuum system of the generator. The effect of water temperature elevation by 10 centigrade causes a loss of 11 MW per each 1000 m<sup>3</sup>/h of cooling water discharged into the river. Although the total energy losses are several times higher, only such amount of energy is equivalent to the production over 8 m<sup>3</sup>/h of distillate in the MD process (assuming 50% thermal efficiency and vapour enthalpy of 2400 kJ/kg).

It is possible to integrate the MD process into the existing water system in several ways; one of the variants is presented in Fig. 1. In this case, the water utilized for cooling the MD installation (distillate side) will be injected into the stream of raw water supplied to the pre-treatment station. Such a solution enables beside

distilled water production also a recovery of heat conducted through the membranes from the feed to the distillate. Moreover, elevation of raw water temperature causes an increase of the efficiency of coagulation and filtration processes used for water pre-treatment<sup>27</sup>. This effect is very important during the winter season, when the water temperature is usually below 278 K. The amount of heat transferred from the feed to distillate can be calculated using equation:

$$Q = m_F c_F (T_{Fin} - T_{Fout}) / A \quad (1)$$

where  $A$  [m<sup>2</sup>] is membrane area,  $m_F$  [kg/s] is feed mass flow,  $c_F$  [kJ/kg K] is specific heat, and  $T_{Fin}$ ,  $T_{Fout}$  are inlet and outlet feed temperature, respectively. Only a fraction of this energy is associated with water evaporation and the thermal efficiency is expressed by equation:

$$E_T = J DH / Q \quad (2)$$

where  $J$  [kg/m<sup>2</sup>s] is the permeate flux and  $DH$  [kJ/kg] is evaporation heat.

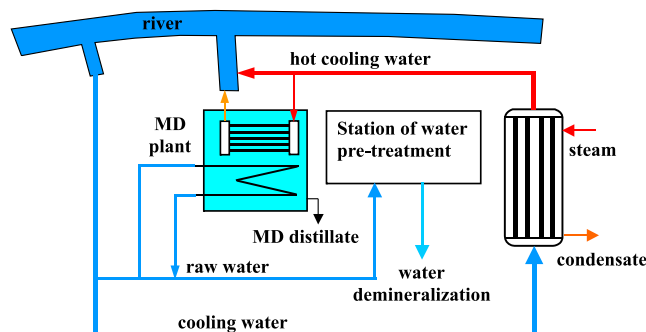
In a case of the considered waste incinerator, an advantage of installation variant presented in Fig. 1 is a beneficial localization enabling a construction of even a large MD installation in the vicinity of building of water pre-treatment station, and the connection of MD installation would require only slight changes in the actual piping system. Although the amount of available waste energy definitely exceeds the demand, a low temperature (305–308 K) of post-cooling water effluent from cooling water system (feed water for MD) necessitates the application of a large membrane area, which can be a financial limitation with regard to the cost of membrane modules. Their number can be reduced three times by using the feed at a temperature close to 333 K<sup>26</sup>. Such a possibility exists, but would require constructing a more complex network of piping. Moreover, a more intensive scaling can expect in this case, which resulting in shorter exploitation time of the MD modules<sup>21</sup>. The resistance of the membranes to wettability is a principal condition permitting to consider the implementation of MD process for the production of demineralized water.

The properties of the membrane surface are changed during exploitation of the modules, thus may influence on the membrane wettability and fouling/scaling intensity. For this reason the water demineralisation was carried out with membrane modules over a period of 1200 h of continuous operation.

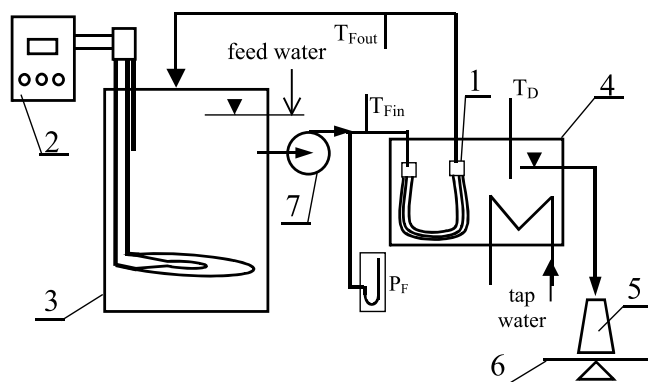
## EXPERIMENTAL

### MD experimental set up

The studies of MD process were performed using an installation based on a variant presented in Fig. 1. The submerged MD modules with single-flow of the feed was planned in this variant. A length of the industrial modules is 1–2 m, which caused a significant concentration of the feed along the module. Therefore, the feed recirculation was applied for shorter laboratory modules in an experimental set-up presented in Fig. 2. Due to the scaling studies, the four similar submerged modules (MK1- MK4) were applied, and each was equipped with 3 hydrophobic capillary membranes made of polypropylene (Accurel PP S6/2, Membrana GmbH – Germany) with



**Figure 1.** The integration of MD installation with water system of waste incinerator



**Figure 2.** DCMD experimental set-up. 1 – MD module, 2 – Nüga temperature regulator, 3 – feed tank, 4 – cooled distillate tank, 5 – distillate collector, 6 – balance, 7 – pump,  $P_F$  – pressure gauge,  $T_{Fin}$ ,  $T_{Fout}$ ,  $T_D$  – thermometer (notation: F – feed, D – distillate, in – input, out – output)

the outside/inside diameter equal to  $d_{out}/d_{in} = 2.6 \text{ mm}/1.8 \text{ mm}$ , pore sizes with the nominal diameter of  $0.22 \mu\text{m}$ , and the porosity of 73% (the manufacturer's data). The working length of capillaries was 30 cm (module area  $50.9 \text{ cm}^2$ ).

A submerged MD module was assembled inside the distillate tank (volume 2 L). The distillate was cooled by tap water and its temperature was maintained at a level of 290–293 K. The temperatures were measured using thermometers with  $\pm 0.2 \text{ K}$  accuracy. At the beginning of each experimental series, the distillate tank was refilled by 2 L of distillate water ( $1\text{--}3 \mu\text{S/cm}$ ). The obtained permeate flux was calculated on the basis of changes in the distillate volume over studied period of time.

The feed tank volume was 4.5 L and the process temperature was fixed at  $310 \pm 2 \text{ K}$  or  $330 \pm 2 \text{ K}$  by Nüga temperature regulator (Germany). The feed flowed inside the capillaries (lumen side) during the MD experiments. A peristaltic pump was used, and the volume flow velocity of feed stream was equal to  $4.5 \pm 0.2 \text{ ml/s}$  ( $0.6 \text{ m/s}$ ). For this flow rate almost  $50 \text{ m}^3$  of cooling water from waste incinerator will be needed for realization of presented studies, if single pass flow through MD installation, as considered in Fig. 1, will be applied. This was the second reason for application of feed recirculation. The constant volume (4 L) of feed was maintained by continuous dosing of the water into the feed tank. A cover of this tank was not airtight; hence, the reduction of water volume inside the feed tank was caused not only by the MD permeate flux but also by the natural evaporation.

### Feed water

Mechanically pre-treated water extracted from the river was used as the cooling water in presented waste incinerator. The actual post-cooling water was used as a feed. The utilization of surface water is associated with mainly alkaline and silicate scaling during demineralisation of this water by MD process<sup>18, 21</sup>. The concentration of Si (ICP-AES analysis) was  $2.6 \pm 0.1 \text{ mg/L}$ . The alkalinity analysis revealed that the  $\text{HCO}_3^-$  concentration was equal to  $2.5 \pm 0.1 \text{ mmol/L}$ . The average concentrations (in  $\text{mg/L}$ ) of the dissolved major ions were as follows:  $27.9 \text{ Na}^+$ ,  $66.9 \text{ Ca}^{2+}$ ,  $16.6 \text{ Mg}^{2+}$ ,  $5.4 \text{ K}^+$ ,  $65 \text{ Cl}^-$ ,  $4.5 \text{ NO}_3^-$  and

$101.3 \text{ SO}_4^{2-}$  (ion chromatography analysis). The electrical conductivity of post-cooling water was  $825 \pm 10 \mu\text{S/cm}$ .

### Analytical methods

Membrane morphology and the compositions of deposit were studied using scanning electron microscopy (SEM) (SU-8000) coupled with the energy dispersion spectrometer (EDS). After accomplishing each MD series the membranes were rinsed using distilled water in order to remove the feed from the membrane surface. The membrane samples were dried at ambient temperature before the SEM examinations. The samples for cross-section observations were prepared by fracturing the capillary membranes in liquid nitrogen. All the samples were sputter coated with chromium.

The electrical conductivity and total dissolved solids (TDS) of solutions were measured with a 6P Ultrameter (Myron L Company, USA). This meter was calibrated for measurements as NaCl mode using TDS/Conductivity standard Solution (Myron L Company).

The anion and cation concentrations were determined using an ion chromatography method with conductivity detector (850 Professional IC, Herisau Metrohm - Switzerland). The separation of anions was performed on  $1.7 \times 3.5 \text{ mm}$  Metrosep RP guard column in series with a  $250 \times 4.0 \text{ mm}$  Metrohm A Supp5-250 analytical column. The eluent was in the form of solution comprising  $3.2 \text{ mM/L Na}_2\text{CO}_3 + 1.0 \text{ mM/L NaHCO}_3$  (flow rate  $0.7 \text{ ml/min}$ ). A C2 Guard column in series with a  $150 \times 4.0 \text{ mm}$  Metrosep C2-150 analytical column was used for the cations separation. In this case, the eluent was a mixture of tartaric acid ( $4 \text{ mM/L}$ ) with  $0.75 \text{ mM/L}$  2-picoline acid.

The concentration of Si was analysed by applying a Yobin Yvon Ultrac 238 JY atomic emission spectrometer with inductively coupled plasma (ICP-AES).

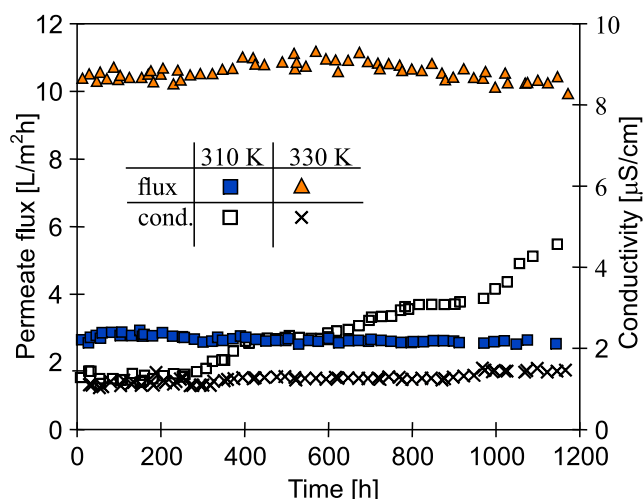
## RESULTS

### NaCl solution as a feed

The resistance for wetting of Accurel PP S6/2 membranes was revealed during over 3 years studies of demineralized water production from RO permeates<sup>28</sup>. However, even the immersion of hydrophobic membrane into distilled water for a longer period may cause the changes of its properties<sup>29</sup>. In this situation it is difficult to evaluate the effect of scaling on wettability without knowledge of membrane wetting only by clean water. For the above reason, a long-term study of the MD process (1200 h) using distilled water with  $1 \text{ g/L NaCl}$  as a feed has been performed. Such a diluted solution does not cause scaling, and the presence of NaCl allows to detect the appearance of possible leakages of the feed through the membrane. The experimental results of MD modules exploitation were presented in Fig. 3.

The initial permeate flux amounted to  $2.9 \text{ L/m}^2 \text{ h}$  (MK1) and  $10.1 \text{ L/m}^2 \text{ h}$  (MK2) at used feed temperature of 310 and 330 K, respectively. The difference in water vapour pressure is a driving force in MD, therefore, as was expected, a significantly larger permeate flux was obtained for higher feed temperature. A stable permeate flux and over 99% degree of salt retention (feed  $1950 \mu\text{S/cm}$ ) was achieved for both feed temperatures used





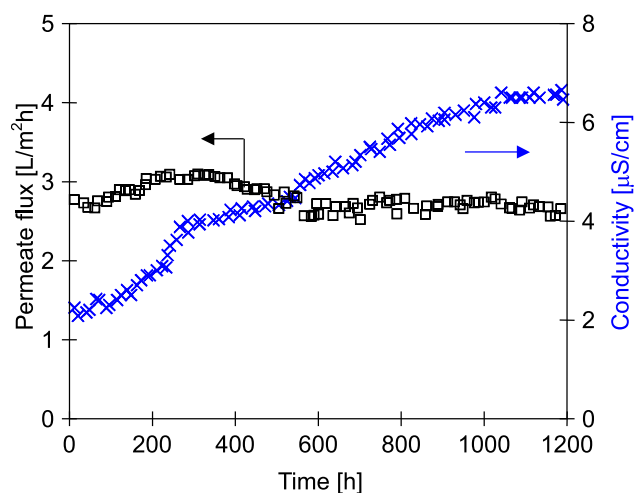
**Figure 3.** Changes of the permeate flux and distillate electrical conductivity as a function of process time. Feed: 1 g NaCl/L. Feed temperature: 310 K (module MK1) and 330 K (module MK2)

during 1200 h of MD process operation. Such results confirm the conclusions from previous works<sup>28–30</sup>, that used Accurel PP S6/2 membranes demonstrate a good resistance for wettability and can be utilized in the MD process.

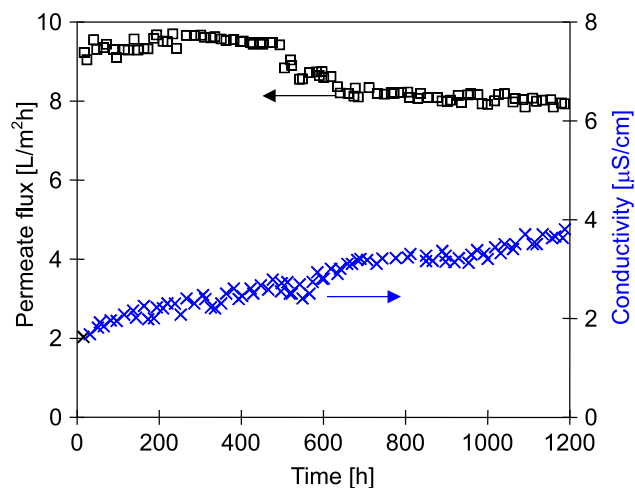
The Accurel PP membranes have the average pores diameters about 0.2  $\mu\text{m}$ , however, a few pores with larger diameters are also existed inside the membrane wall. These pores undergo the wettability during the initial period (50–100 h) of the MD process<sup>31</sup>. Due to a slight local wettability of the wall, a slow increase of the electrical conductivity of distillate to 4.7  $\mu\text{S}/\text{cm}$  (Fig. 3, feed 310 K) was observed during the studies. A slightly smaller increase of the electrical conductivity was noted for the feed at temperature 330 K. Because the permeate flux was 3 times smaller for 310 K, and assuming a similar flux of salt transferred from the feed into the distillate (similar hydraulic pressure on the feed side), a larger increase of the electrical conductivity will be observed for lower feed temperature (smaller permeate flux). If the results will be opposite, this will indicate, that at higher temperature (e.g. due to a more intensive scaling) the membrane underwent the wettability at a larger degree<sup>21, 29</sup>.

### Water demineralisation

In the next stage of studies the demineralisation of water from cooling system by MD with different feed temperatures were carried out. The results obtained for the feed temperature equal to 310 K were presented in Fig. 4, whereas for  $T_F = 330$  K in Fig. 5. In each case the MD installation was operated over a period of 2 months and 1200 h of module exploitation was obtained. After that time, the permeate flux was decreased from 3 to 2.8  $\text{L}/\text{m}^2\text{h}$  for the module MK3 ( $T_F = 310$  K) and the distillate conductivity was stabilized at a value of 6.4  $\mu\text{S}/\text{cm}$ . In the case of the feed temperature of 330 K (module MK4), the permeate flux decreased from 9.8 to 8.2  $\text{L}/\text{m}^2\text{h}$  and the electrical conductivity increased from 2 to 3.8  $\mu\text{S}/\text{cm}$ . The IC analysis indicated that obtained distillate contained 0.7–2.8 mg/L of dissolved salts. The water with such quality cannot be directly supplied to a high-pressure boiler. However, this quali-



**Figure 4.** Changes of the permeate flux and distillate electrical conductivity as a function of process time. Feed temperature 310 K. Module MK3



**Figure 5.** Changes of the permeate flux and distillate electrical conductivity as a function of process time. Feed temperature 330 K. Module MK4

ty is appropriate for treatment by electro-deionisation, which is applied as a last stage in waste incinerator for boiler water preparation.

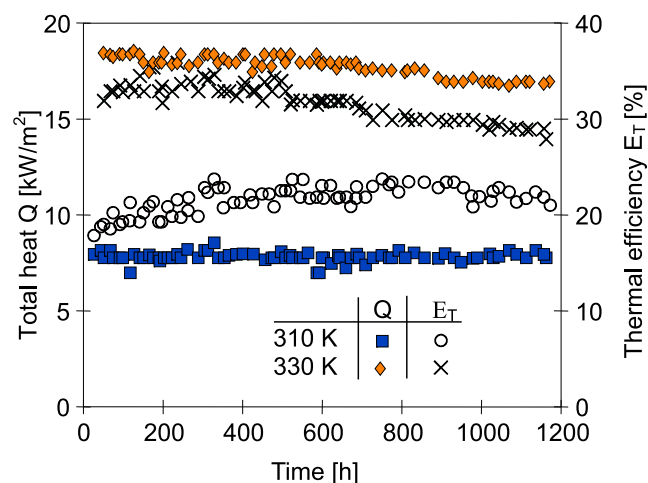
The results of MD process presented in Figs 4 and 5 are slightly worse than those obtained for diluted NaCl solution (Fig. 3). It can be expected that the components present in the treated surface water affect the performance of used membranes. However, a low value of distillate conductivity confirmed a high resistance of Accurel PP S6/2 membranes for wettability. It is worthy to notice, that after the addition of 1 ml of feed into the distillate tank (volume 2000 ml) the electrical conductivity increased from 2 to 4  $\mu\text{S}/\text{cm}$ , thus similarly to the values presented in Figs. 4 and 5. It can be assumed, that only a very small fraction of pores in membrane walls was wetted during 1200 h of MK3 and MK4 modules exploitations.

An analysis of the course of variation of distillate conductivity over time indicated that the highest changes of conductivity occurred in the periods 100–300 h and 600–1000 h in the case of module MK3 (feed 310 K). Moreover, in the former period an increase of the electrical conductivity occurred over 100 h earlier than that observed in the case of NaCl solutions (Fig. 3, MK1),

what suggested the occurrence of scaling, which could accelerate the membrane wettability. This suggestion was supported by the results obtained for module MK4 (feed 330 K), in which the scaling was even larger (data presented in section 3.3), therefore, a higher increase of conductivity was observed in a comparison with the results of studies performed with NaCl solution (Fig. 3, MK2).

In both cases, a larger decline of the permeate flux was observed during the first 400–600 h of MD process operation (Figs 4 and 5). As it has been demonstrated in the previous work<sup>31</sup>, this results from a fact, that Accurel PP S6/2 membranes undergo the surface wettability during the initial period of MD process. Moreover, a slight scaling could also cause the wettability of the surface pores, which will be discussed in the next part of this work. It is interesting, that despite of increasing concentration of solutes (continuous dosing of feed water into feed tank), the module efficiency was almost stabilized after 600–700 h of process operation. This would indicate, that under applied conditions, the deposits were mainly formed on the membrane surface and the salt crystals do not penetrate into the pores interior.

The scaling layer formed on the membrane surfaces decreases the MD thermal efficiency. A low temperature of the feed also decreased its value. In presented studies was obtained the thermal efficiency about 23% and 34% for  $T_F = 310\text{K}$  and  $330\text{K}$ , respectively (Fig. 6). The application of higher feed temperature (330 K) caused that a deposit layer was formed on the membrane surface, mainly as  $\text{CaCO}_3$  (see next section). As a result of scaling the process effectiveness of module MK4 operation started to decrease from 500h and this effectiveness only amounted to 28% after 1200h of process operation. The productivity of module MK3 supplied by the feed at temperature 310 K was only slightly reduced



**Figure 6.** The influence of feed temperature and process time on the value of heat transferred from feed to distillate ( $Q$ ) and thermal efficiency ( $E_T$ ) of MD process

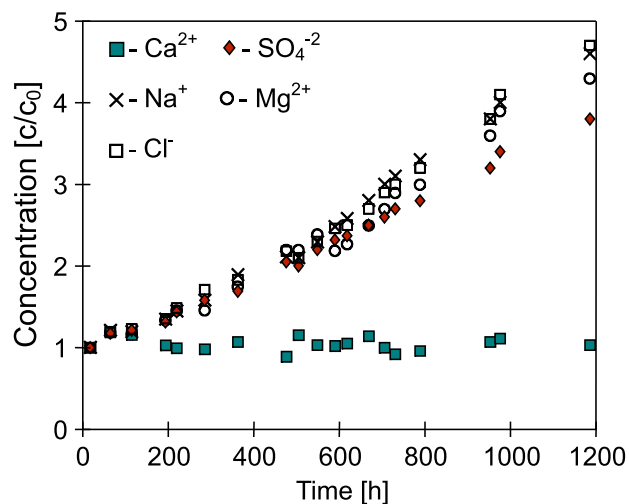
(Fig. 4), hence, the thermal efficiency in this case did not undergo a decrease (Fig. 6).

The heat conducted through the membrane is generally defined as an energy loss in the MD process. However, in the considered waste incinerator, this part of energy can be also re-used. In this case, beside water demineralisation the MD installation performs also other function,

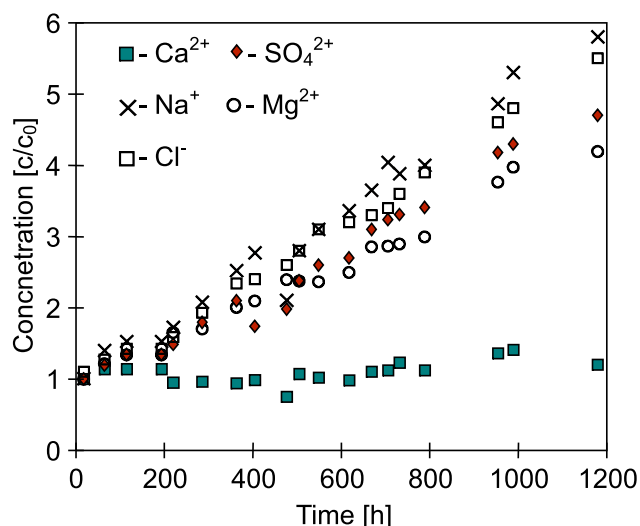
similarly as a traditional heat exchanger, this installation allows pre-heating of raw water (Fig. 1). For the MD installation with e.g.  $100\text{ m}^2$  of assembled membranes the total amount of reused energy will be about 0.8 MW ( $T_F = 310\text{K}$ ) and 1.8 MW (330 K) (Fig. 6).

### Membrane scaling

The intensity of scaling depends not only on the feed composition and temperature, but also on the degree of water recovery. As indicate the changes of salt concentration in the feed (Figs. 7 and 8) the degree of water recovery did not exceed 75–80% in the performed studies (due to  $\text{CaSO}_4$  precipitation). The course of variation of the feed concentration over time was similar in both studied cases, although the solutes concentration in the feed at a temperature 330 K was slightly higher. The obtained results show that the concentration of  $\text{SO}_4^{2-}$  ions was increased in a similar way as that of ions of soluble salts (e.g.  $\text{Na}^+$ ,  $\text{Cl}^-$ ) concentrated over 5 times. However, the  $\text{SO}_4^{2-}$  ions were concentrated only 4-fold, which indicated that a small amount of sulphate deposit was formed, although the obtained final concentration  $400\text{ mg SO}_4^{2-}/\text{L}$  is below the saturation state of calcium sulphate<sup>32</sup>. An opposite course was observed for the  $\text{Ca}^{2+}$  ions, their concentration during the process was



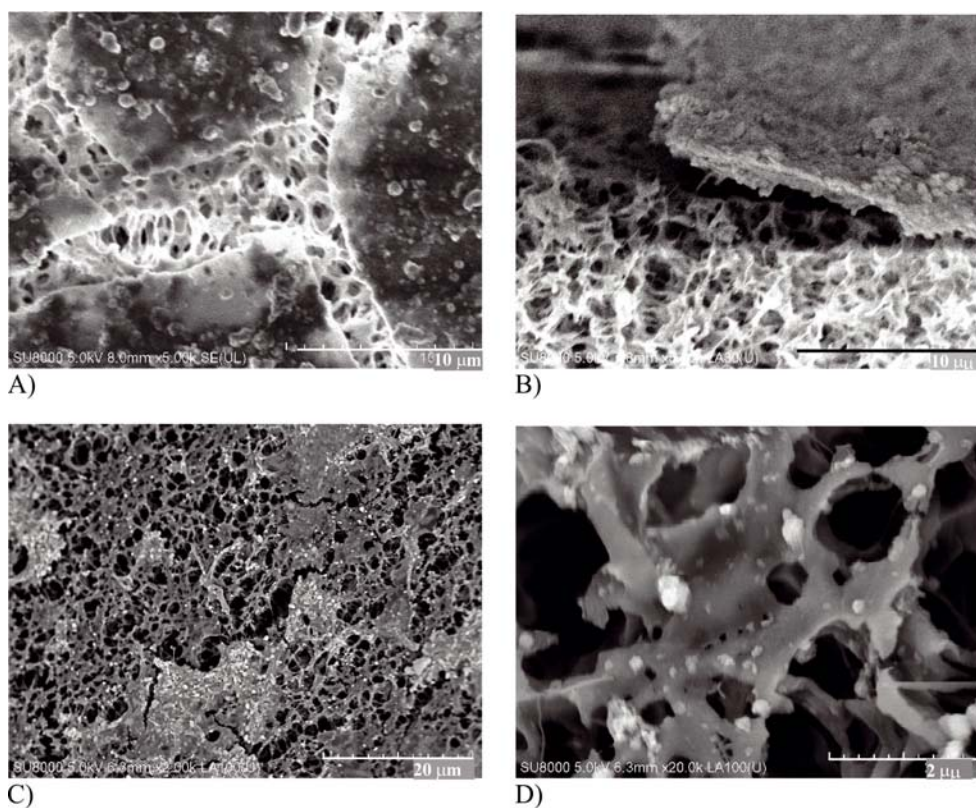
**Figure 7.** Changes of ions concentration in the feed (310 K) during MD process. Module MK3



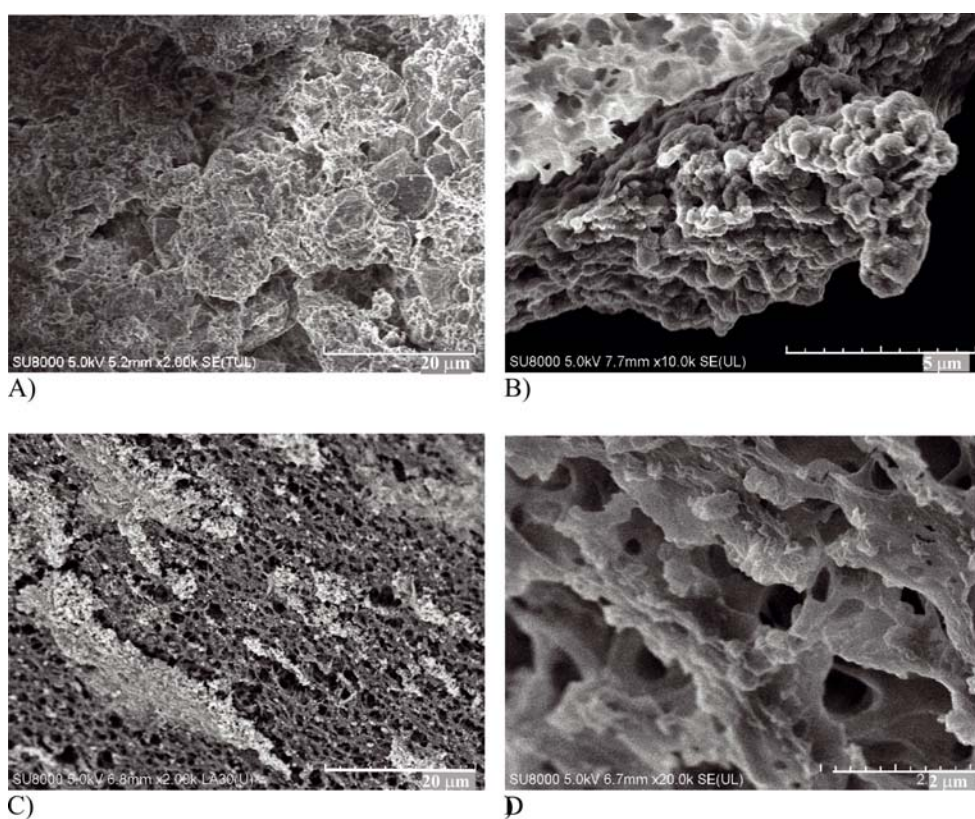
**Figure 8.** Changes of ions concentration in the feed (330 K) during MD process. Module MK4

almost constant despite the continuous concentration of the feed, and can be associated with the formation of  $\text{CaCO}_3$  deposits. However, the  $\text{CaCO}_3$  deposit can be easily removed by module rinsing with HCl solution<sup>30</sup>.

In order to determine the scaling intensity along the module, the samples of capillary membranes were collected at 5 and 15 cm distance from the MK3 and MK4 modules inlet. The SEM examinations confirmed, that definitely larger amounts of deposits were formed in the



**Figure 9.** SEM images of membrane samples collected from MK3 module after 1200 h of MD process (310 K). A) inner surface (lumen side) 5 cm from module inlet, B) membrane cross-section with deposit, C) inner surface (lumen side) 15 cm from module inlet, D) magnified area from image C



**Figure 10.** SEM images of membrane samples from collected MK4 module after 1200 h of MD process (330 K). A) inner surface (lumen side) 5 cm from module inlet, B) membrane cross-section with deposit, C) inner surface (lumen side) 15 cm from module inlet, D) magnified area from image C



vicinity of module inlets (Figs. 9 and 10). This indicated that most of compounds created scaling layer on the membranes have a tendency to precipitate in the bulk solution, most probably as a result of water contact with the heating element (Fig. 2), in the considered waste incinerator inside the steam condenser. Therefore, the connection of MD module with net pre-filter allows to significantly reduce the membrane scaling<sup>30</sup>.

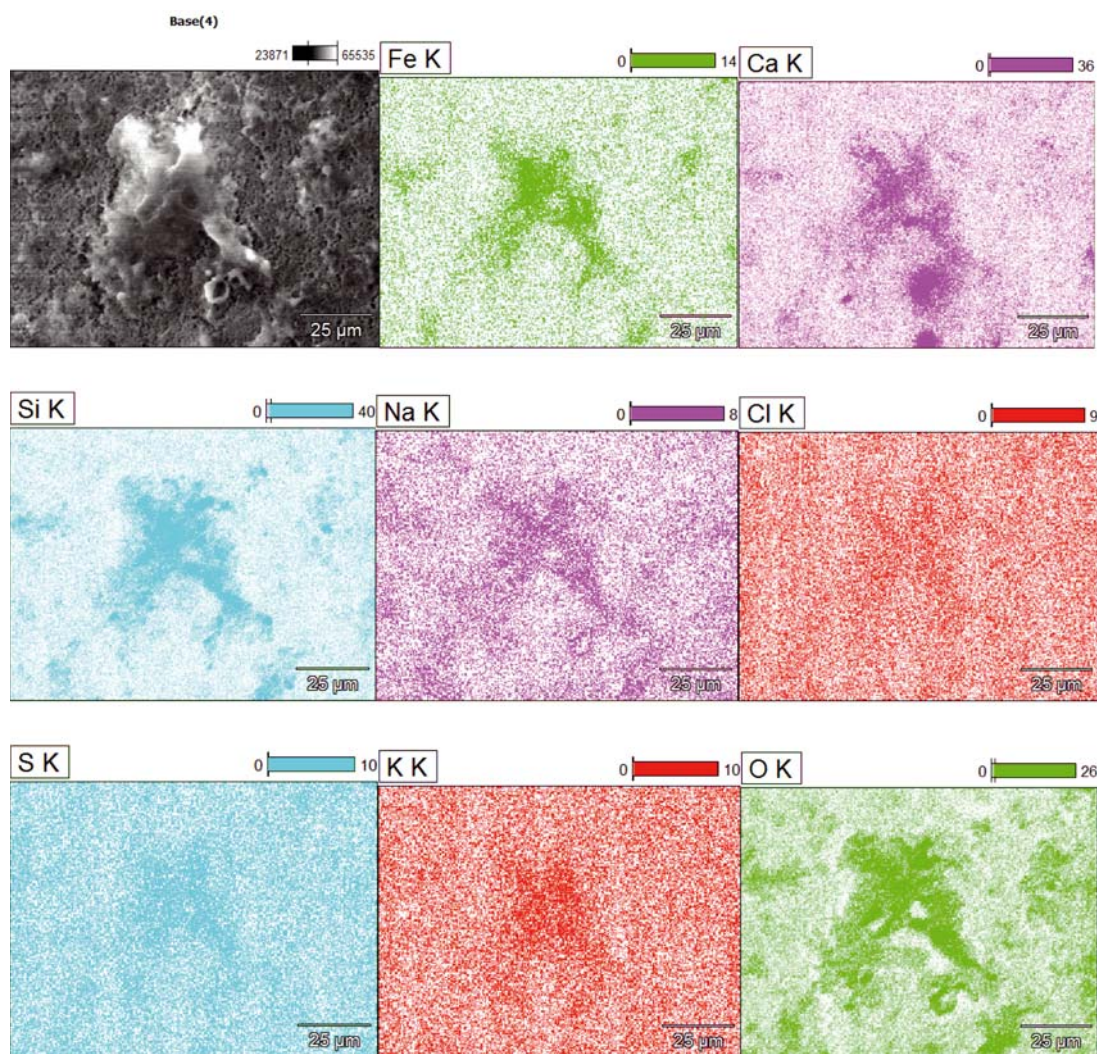
The observations of several membrane samples revealed, that in the majority of cases, the deposit was formed on the membrane surface. As it was expected<sup>21</sup>, compared to  $T_F = 330$  K the scaling intensity was lower at the feed temperature equal to 310 K. A lowering of feed temperature not only decreased the amount of deposits, but also affected their form/shape. At a lower temperature, substantially finer and amorphous deposits were formed. The fine crystallites with the dimensions of 0.5–1  $\mu\text{m}$  were also observed inside these deposits (Fig. 9A). The deposits covered the pores inlets, but these deposits did not exhibit a tendency to penetrate into the pores. This was confirmed by observations of the membrane cross-sections, on which the layers of deposits detached from the membrane surface were visible (Fig. 9B). This may suggest that the deposits were hydrated and they underwent a strong contraction during the preparation of samples for SEM examination (drying). A SEM-EDS analysis revealed that the amorphous

deposits contained small amounts of S, Fe, Zn, Si and substantially larger amounts of Ca and C, characteristic for  $\text{CaCO}_3$  deposits.

A partial composition of deposits can be determined using the SEM-EDS in a variant of the surface analyse. By a comparison the SEM image of deposit with an image obtained for density of elements dispersion, it can be determined which elements contain a deposit. In the case presented in Fig. 11, a substantially larger content of oxygen, silicon and calcium (central part of images) indicates that both carbonates and silicates prevail in these fragments of deposit.

Significantly smaller amounts of amorphous deposits were observed on the surface of membrane samples collected at a distance of 15 cm from the module inlet (Fig. 9C). In this case, only the small groups of deposits were observed. In the remaining places without the deposits, the surface pores were visible (Fig. 9 C, D). The SEM-EDS analysis indicated that the fine crystallites which were formed directly on the membrane surface contained besides C and O also small amounts of Si, which probably was a reason that rhombohedra and cubic crystals characteristic for calcite<sup>33</sup> were not formed (Fig. 9D).

A substantially larger amount of crystalline deposits was observed on the membrane surface in the module MK4 (Fig. 10A). At the module inlet this deposit covered almost the entire surface of the membranes. The

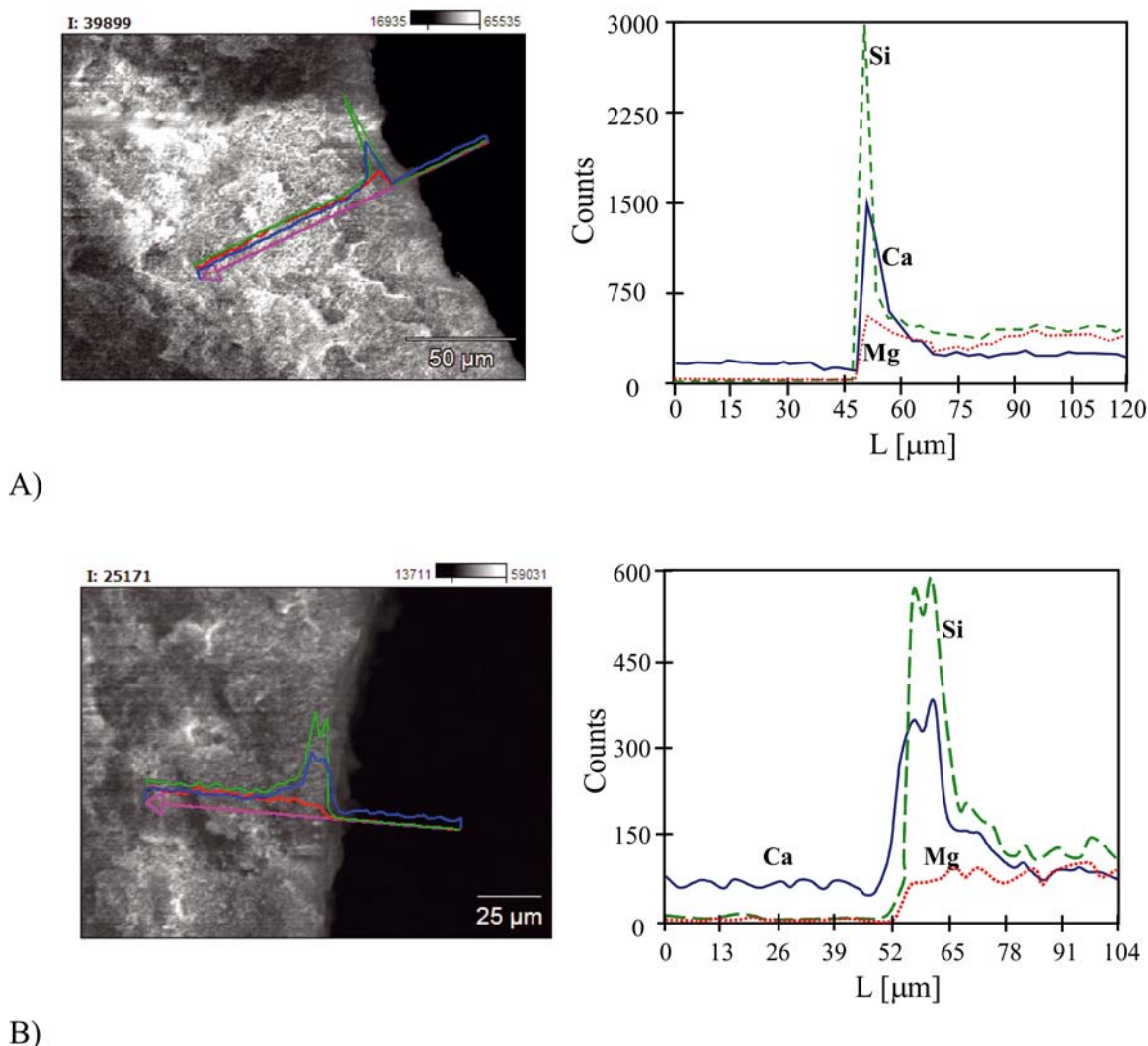


**Figure 11.** The results of SEM-EDS surface analysis presented density of elements dispersion obtained for deposits showed in SEM image. Module MK3

examination of cross-sections confirmed, that a layer of deposits on the membrane surface in the module MK4 was thicker and the deposits were more strongly bonded to the membrane surface (Fig. 10B), in a comparison to that observed in the module MK3. Moreover, these deposits did not exhibit a strong tendency to penetrate into the pore interior (Fig. 15F). The amorphous deposits, similar to those formed in the module MK3 (Fig. 9C) were observed in the sample collected at a distance of 15 cm from the module inlet (Fig. 10C, D). The SEM examinations of the membrane samples revealed, that the scaling layer mainly contained C and O.

In the case of scaling, the observed decline of MD module efficiency results not only from a layer of e.g.  $\text{CaCO}_3$  deposit covering the membrane surface, but also from the fact that the deposit sometimes penetrates into the membrane pores, what accelerates their wettability<sup>28, 30, 31</sup>. The deposit formed inside the membrane pores can be removed e.g. by using a HCl solution, however, this rinsing additionally enhances the degree of wettability and as a result, the advantages resulting from the application of high feed temperature will be rapidly lost<sup>21, 29, 35</sup>. Therefore, the internal scaling is more dangerous for the membrane performance, especially if the production of demineralised water is considered.

A linear SEM-EDS analysis is useful for the evaluation of depth of the membrane wall wettability. The results of linear SEM-EDS analysis performed for the membranes with deposits were presented in Fig. 12. The obtained results allow to determine a depth of layer (deposit+wetted pores) for a given element. The application of software of SEM microscope allow to measure a visible thickness of deposit on the membrane surface (e.g. Fig. 10B) and by subtraction of this value it can be determined how deep the feed penetrated into the wall interior. In the case under study, it was found that the walls were wetted to a depth of 10–15  $\mu\text{m}$  (Fig. 12A, module MK3) and 25–30  $\mu\text{m}$  (Fig. 12B, module MK4). The obtained results indicate that the formation of substantially larger amounts of deposits in the module MK4 in a comparison to the modules MK3 (less deposit) also significantly increased a depth of membrane walls wettability. In the work<sup>35</sup> scaling caused a rapid membrane wetting and the distillate conductivity increased to 250  $\mu\text{S}/\text{cm}$  after 8 h of MD process duration due to a low membrane thickness (36  $\mu\text{m}$  PTFE active layer/53  $\mu\text{m}$  PP support layer). However, the values of wetting depth (10–30  $\mu\text{m}$ ) determined in our studies are small in a comparison with the total thickness of the walls of used membranes (400  $\mu\text{m}$ ). For this reason, the Accurel PP membranes



**Figure 12.** The results of linear SEM-EDS analysis. A) module MK3 (310 K), B) module MK4 (330 K)



maintained their non-wettability in spite of scaling and a long-term period of studies (2–3 months).

## CONCLUSIONS

The performed studies confirmed the possibility of demineralized water production from surface water used in waste incinerator for steam condensation. The integration of MD installation with the cooling water system of incinerator allows to re-use up to 18 kW per 1 m<sup>2</sup> of membranes.

The presented long-term studies of MD process have confirmed, that used polypropylene Accurel PP membranes were resistant to wetting and they can be successfully applied for the production of demineralized water.

It was found, that the operation of MD process at temperature of 310 K is advantageous, because the scaling intensity can be significantly limited, which allows to operate the MD process for several months without necessity to clean the modules.

The SEM examinations revealed, that lowering of the feed temperature from 330 K to 310 K substantially changed the form of deposits and the deposits were mainly formed in the amorphous form. These deposits contained beside calcium also significant amounts of silicon. Moreover, such deposits were weakly bounded with the membrane surface, what indicates that they have small affinity to penetrate into the pores interior. On the other hand, more crystalline deposits, which were strongly bounded with the membrane, were formed in the case of the feed at temperature of 330 K.

The SEM examinations of membrane cross-sections confirmed, that a deposit was mainly formed on the membrane surface. It is advantageous because it allows to avoid the pore wettability taking place during the removal of deposit (e.g. by rinsing of module with HCl solutions).

The experimental results confirmed, that the application of MD process for treatment of surface water (e.g. rivers) using the feed temperature below 333 K allows to achieve the coefficient of water recovery at a level of 75–80%.

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