JACEK A. WIŚNIEWSKI[1], MAŁGORZATA KABSCH-KORBUTOWICZ[1]

ELIMINATION OF SELECTED ANIONS AND CATIONS FROM WATER BY MEANS OF THE DONNAN DIALYSIS

The usefulness of the Donnan dialysis has been assessed for the elimination of harmful (bromide, bromate and nitrate) or troublesome (calcium and magnesium) ions from water. The rate and efficiency of ion exchange were examined. For anion removal Selemion AMV or Neosepta ACS membranes were used while for cation removal – Neosepta CMX or Selemion CMV ones. The influence of membrane properties and salt concentration in the receiver was investigated.

1. INTRODUCTION

The use of water for industrial or municipal purposes often requires removal of certain ions that can be harmful to health (in drinking water) or hinder subsequent processes of water purification (e.g., desalination of brackish water in the electrodialysis). Nitrates, bromates as well as bromides (indirectly), among others, belong to ions which are harmful for health. In turn ions which greatly hinder desalination by electrodialysis are calcium and magnesium ions.

Concentration of nitrates in drinking water should not exceed 50 mg NO_3^-/dm^3, and the recommended value is 25 mg NO_3^-/dm^3 [1]. At higher concentrations of nitrates in water, there is a risk of methemoglobinemia, often referred to as blue baby syndrome. Currently in Europe, 87% of agricultural land is characterized by a concentration of nitrates in groundwater above the recommended level of 25 mg NO_3^-/dm^3, and 22% – above 50 mg NO_3^-/dm^3 [2]. The reason for this phenomenon (so called nitrate problem) was an intense use of mineral and organic fertilizers on farmlands, which as a result of infiltration and surface runoff caused contamination of groundwater and surface water. Elevated nitrates concentration in natural waters means a need to remove them from drinking water. In the group of effective

_____

[1]Wrocław University of Science and Technology, Faculty of Environmental Engineering, Department of Water and Wastewater Treatment Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland, corresponding author J. Wiśniewski, e-mail address: jacek.wisniewski@pwr.edu.pl

methods of nitrate removal from water should be mentioned first of all: ion exchange, reverse osmosis, electrodialysis and biological denitrification processes using membrane bioreactor. These methods are effective to remove nitrate ions from water but the use of certain (reverse osmosis (RO) and electrodialysis (ED)) means simultaneous water desalination, which is not desirable for water with a low salt content.

Bromide ions are present in all natural waters and their concentration ranges from a few to ca. 2000 µg/dm^3 (beside the waters of seas and oceans, in which the level of Br$^-$ is ca. 65 mg/dm^3). Natural source of bromides is water contact with a substrate material and intrusion of sea and ocean waters. Bromides may also come from anthropogenic sources: runoffs from salted roads in winter and runoffs from agricultural land on which brominated pesticides are used. Although bromide ions have no detrimental effect on human health, chlorination of water containing bromides and natural organic matter may result in the formation of chlorinated and brominated derivatives of organic compounds, amongst which trihalomethanes (THM) and haloacetic acids (HAA) constitute the biggest group [3]. Due to a carcinogenic nature of these compounds, their concentration in drinking water is limited in the EU (THM) and the USA (THM, HAA) [1, 4]. It should be emphasized that brominated THMs and brominated HAAs are much more mutagenic and carcinogenic, therefore, pose a greater danger to human health than their chlorinated analogues.

Another risk associated with the presence of bromides in water is oxidation of these ions to bromates during water ozonation. Popularity of this method of water disinfection is due to the effective inactivation of microorganisms including those resistant to common disinfectants (e.g., protozoa *Cryptosporidium parvum* which are resistant to chlorine and chlorine dioxide) [5]. It is also important that ozonated water is devoid of used disinfectant flavor, which is particularly important in the production of bottled water [6]. In the ozonation of water containing bromides, bromide ion is oxidized to hypobromous acid (HOBr), which after dissociation to hypobromite ion (OBr$^-$) is further oxidized to bromate ion (BrO$_3^-$) [7]. Concentration of bromates in water after disinfection with ozone increases together with the concentration of bromides, pH of water and ozone dose [7]. Data presented in this work [8] indicate that as a result of ozonation of water with a relatively low concentration of bromides (160 µg/dm^3), the content of bromates in water after ozonation reaches up to 30 µg BrO$_3^-$/dm^3. Bromates have a carcinogenic effect on human health. Research conducted by USEPA have shown that for an adult human drinking daily 2 dm^3 of water containing 5 µg BrO$_3^-$/dm^3, the risk of cancer is 10^{-4}, and in the case of water containing 0.5 µg BrO$_3^-$/dm^3 the risk is 10^{-5} [6]. For this reason, allowable concentration of bromates in drinking water in the US and in the EU currently stands at 10 µg/dm^3 [1, 4]. The same value is recommended by WHO [9].

Among the methods of removing bromide ions from water, there are three noteworthy processes: exchange of anions using a magnetic ion-exchange resin MIEX$^{®}$, coagulation and membrane processes. The efficiency of bromide removal using MIEX$^{®}$ resin

is strongly dependent upon the presence of competing anions, especially bicarbonates and natural organic compounds (NOM) [10]. Under preferred conditions (water of low alkalinity and low NOM content), the efficiency of bromide removal reaches 94%, although with an increased concentration of competing anions efficiency of the process is reduced up to 43% [11]. Effect of accompanying anions and humic acids on the efficiency of Br^- ion removal was also observed in the coagulation with aluminum sulfate: 62–87% removal of ions from natural waters was obtained, in comparison with 83–99% removal from deionized water [12]. In turn, high efficiency of bromide ion removal characterizes membrane processes: in the nanofiltration (NF) it is possible to obtain up to 97% removal, and in the electrodialysis – 80% [10]. It was noticed even close to 100% removal of Br^- ions from water which has a very high concentration of these ions (10.6 mg /dm^3) [13].

Among the methods used for the removal of bromates from drinking water it is necessary to mention primarily adsorption on granular activated carbon. In this process, bromate ions are reduced at the surface of carbon to a bromide ones [14, 15]. However, it was observed that the effectiveness of adsorption over time is significantly reduced as a result of gradual development of biofilm on the surface of activated carbon [14]. The decrease in the efficiency of bromate removal in the process can also be caused by adsorption of organic compounds on the carbon surface [15]. High efficiency of bromate removal was obtained in a hybrid process of coagulation – nanofiltration [16]. Ferrous sulfate, which is used in this process, completely reduces bromates to bromides, while ferric hydroxide formed effectively removes humic acids. It should be noted, however, that bromides remain in water; in the nanofiltration they are only removed up to 17%. High efficiency of bromate removal from water was observed in high pressure membrane processes: reverse osmosis (96%) [17] and nanofiltration (89%) [18]. In contrast, in a reverse electrodialysis (EDR) bromate removal efficiency is significantly lower (64%) [17]. Although the efficiency of nitrate, bromide or bromate removal in RO or NF processes is relatively high, the use of these techniques results in the removal, apart from harmful ions, all other ionic compounds. This effect is undesirable in water for human consumption.

Another technological problem occurring during deep desalination of brackish water with increased content of calcium and magnesium salts by electrodialysis technique is precipitation of troublesome precipitates ($CaCO_3$, $CaSO_4$, $Mg(OH)_2$) at membrane surface in the concentrate cells. This process, known as scaling, deteriorates the membrane properties, increases system resistance and power consumption during electrodialysis. The effect of scaling can be reduced by changing the polarity of electrodes [19] or addition of appropriate chemicals to the concentrate. These actions, however, do not eliminate troublesome ions from water. This implies the use of high doses of reagents to concentrate or suitably frequent changing electrodes polarity (especially at higher initial concentration of calcium and magnesium ions).

The problem of the presence of harmful or troublesome ions in water can be solved by replacing these ions with an neutral ones, which poses no threat to human health and do not create sediment with counter ions. This can be accomplished by ion exchange in the membrane Donnan dialysis (DD). In this process, the ion-exchange membrane separates two solutions: a feed solution (which contains harmful or troublesome ions) and a receiving solution (which contains an electrolyte having relatively high concentration). As a result of high difference of chemical potentials of components on both sides of the membrane, there is a flow of counter ions of ionic groups of the membrane from the receiver to the feed solution. Because the flow of co-ions in the same direction is not possible (they are rejected by the ionic groups of the membrane) so that to keep electroneutrality of the two solutions there is a transfer of equivalent amount of counterions from the feed solution to the receiver [19]. As a result of ion exchange, harmful or troublesome ions which are present in water are replaced by neutral ions (chlorides or sodium ions, depending on the type of ion-exchange membrane). Figure 1 shows the principle of the Donnan dialysis with anion and cation-exchange membrane.
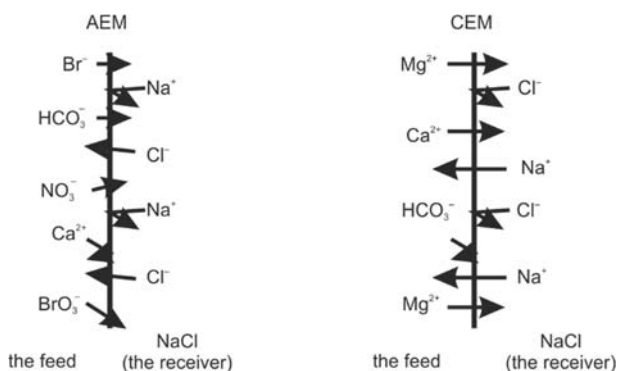

Fig. 1. Scheme of the Donnan dialysis with an anion-exchange membrane (AEM)
and with cation-exchange membrane (CEM)

This paper presents the results of the research on elimination of bromide, bromate and nitrate ions from water in the the Donnan dialysis with anion-exchange membranes and on removal of calcium and magnesium ions with cation-exchange membranes in the investigated process.

2. METHODS

The process was conducted in the laboratory set-up equipped with 20 cell pairs with the proper ion-exchange membranes. In the experiments with anion-exchange membranes, Selemion AMV (Asahi Glass) or Neosepta ACS (ASTOM Corp.) have been used. As a cation-exchange membranes, Selemion CMV (Asahi Glass) or Neosepta

CMX (ASTOM Corp.) were applied. The effective surface area of the membranes was 0.140 m^2. The most important parameters of the examined membranes are given in Table 1.

<div align="right">T a b l e 1</div>

Parameters of anion-exchange and cation-exchange membranes
used in the Donnan dialysis process [20, 21]

Parameter	Membrane			
	AMV	ACS	CMV	CMX
Electric resistance, $\Omega \cdot cm^2$	1.5–3.0	2.0–2.5	2.0–3.5	2.5–3.5
Transport number of ions Cl^- SO_4^{2-} Na^+ Ca^{2+}, Mg^{2+}	>0.94	>0.98 <0.005	>0.92	0.70 0.28
Exchange capacity, mmol/g	1.85	1.4–2.0	4.31	1.5–1.8
Water content, %	19.9	20–30	39.9	25–30
Thickness, mm	0.11–0.15	0.15–0.20	0.13–0.15	0.17-0.19
Membrane type	anion-exchange	monoanion-exchange	cation-exchange	

The process was conducted with the recirculation of feed solution and receiver to achieve a minimum ion concentration in the feed solution. In the Donnan dialysis with anion-exchange membranes, the feed solution contained the following ingredients: NaHCO₃, NaNO₃, NaCl (concentration of each component was 3 mM) and NaBrO₃ (50 µg BrO$_3^-$/dm^3 = 0.391 µM) or NaBr (500 µg Br$^-$/dm^3 = 6.258 µM). In turn, in the Donnan dialysis with the cation-exchange membranes, the solution containing 5 mM CaCl₂ and 5mM MgCl₂ was applied. In all experiments, the volume ratio of the feed solution and the receiver was 10:2.5 (dm^3/dm^3). 100, 200 or 300 mM NaCl solution was used as a receiver.

Anion concentrations in the water being treated were measured in the course of the processes. Concentrations of bicarbonates and chlorides were determined by titration with color indicators [22]. The concentration of sulfate ions was determined using a DREL 2000 spectrophotometer. Bromide ions concentration was measured using a DIONEX ICS 1000 ion-chromatograph equipped with a IONPAC AS9-HC analytical column. Bromate concentration was determined photometrically with 3,3′-dimethyl-naftidin and iodine [23], using a UV mini 1240 spectrophotometer (Shimadzu) and 50 mm glass cuvettes. Sample absorbance was measured at the wavelength of 550 nm. Each anion concentration was measured twice. The mean measurement error did not exceed 10%.

Based on the concentrations of ions in the feed solution, the salt removal efficiency and the salt flux from the feed to the receiver were calculated.

The ion removal efficiency (R) was calculated according to:

$$R = \frac{c_0 - c_t}{c_0} \times 100\%$$

where, c_0 – initial ion concentration, c_t – ion concentration after time t.

The ion flux (J) was determined with the use of the following equation:

$$J = \frac{M_t V_t - M_{t+1} V_{t+1}}{At} \ [\text{mol/(m}^2 \cdot \text{h)}]$$

where: M_t, M_{t+1} – concentrations of ions at time t and $t + 1$ [mol/m^3], V_t, V_{t+1} – volume of the feed solution at time t and $t + 1$ [m^3], A – total membrane surface area [m^2].

3. RESULTS

3.1. REMOVAL OF BROMIDE, BROMATE AND NITRATE IONS IN THE DONNAN DIALYSIS

In the Donnan dialysis with anion-exchange membranes, the gradient of concentration of chloride ions causes their transport from the receiver to the treated water, which in turn causes movement of an equivalent amount of anions in the opposite direction: from the treated water to the receiver. Following the exchange of anions, bromide or bromate ions (and other anions) are replaced by chloride ions.
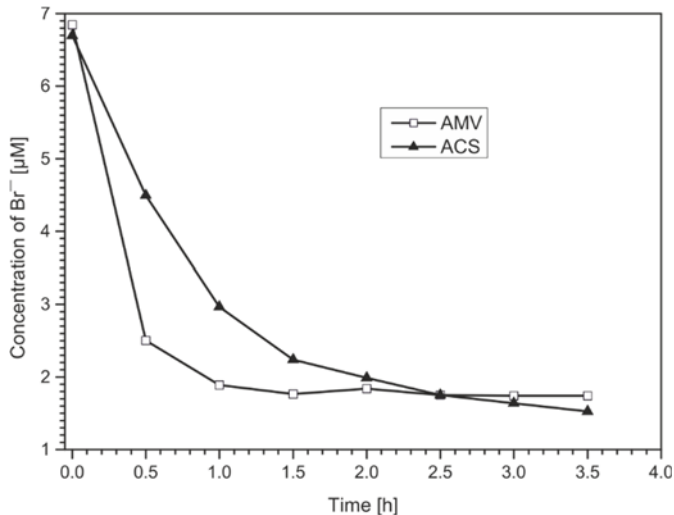

Fig. 2. Removal of bromides in the DD process with Selemion AMV
and Neosepta ACS membranes (salt concentration in the receiver C_{NaCl} = 200 mM)

Figure 2 shows the process of removing bromides from the solution using the studied membranes: Selemion AMV and Neosepta ACS. For both types of the membranes, bromide ion removal was similar (74% and 77%, for AMV and ACS membranes, respectively), but the time required to attain a minimum concentration of bromides in the treated solution was significantly shorter for AMV membranes (1.5 h) than for the ACS membrane (3.5 h). This results from the differences in the construction of the membranes: Neosepta ACS has a thin, highly cross-linked layer on the surface [19], which slows down the flow of anions, thus lengthening the time necessary to achieve a minimum concentration of investigated ions in the treated water.
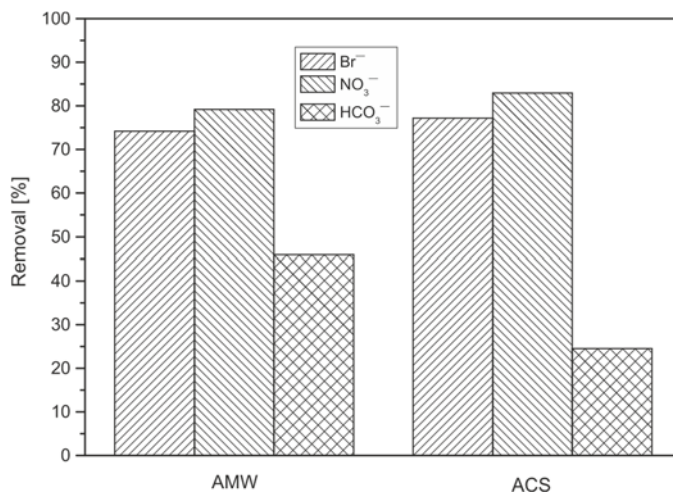

Fig. 3. Comparison of the effectiveness of bromide and accompanying anion removal with the use of Selemion AMV and Neosepta ACS membranes (salt concentration in the receiver C_{NaCl} = 200 mM)

The removing bromides from the solution accompanies the removing the remaining anions: nitrates and bicarbonates. Figure 3 shows the effect of anion exchange using the studied membranes. It can be seen that both membranes allow achieving high efficiency of bromide and nitrate ions exchange on chloride ions. In the process with Selemion AMV membrane, 74% of bromides and 79% of nitrates are removed with significantly reduced bicarbonate removal (46%). This is due to the size of the transported anions: bromide and nitrate anions are relatively small. The radius of a hydrated Br^- ion is equal to 0.330 nm, and NO_3^- ion – 0.335 nm; while HCO_3^- ion is a large one (0.394 nm) [24] which makes it difficult to transport it through an anion-exchange membrane. As a result, there is also a different transfer rate measured by ion flux from the feed solution to the receiver (Table 2). Nitrates are removed the most quickly (average flux of these ions to achieve a minimum concentration of bromides in the feed solution is 0.130 mol/(m^2·h)), while bicarbonates are transported much more slowly (0.070 mol/(m^2·h)). On the other hand, low value of bromide flux (0.247·10^{-3} mol/(m^2·h))

results from a very low concentration of these ions in the solution and the share of bro-
mides in a flux of counter-ions transported from the feed solution to the receiver is cor-
respondingly low.

However, in the Donnan dialysis using Neosepta ACS membrane, a slightly higher
efficiency of small anion removal was achieved (bromides – 77% and nitrates – 83%)
at the reduced effectiveness of large bicarbonates ion removal (24%). This indicates the
suitability of a membrane with a dense surface structure to remove bromides from the
solution in which large anions (HCO_3^-) are present.

Table 2

Effects of removing bromides, and associated anions
using various anion-exchange membranes ($C_{NaCl} = 200$ mM)

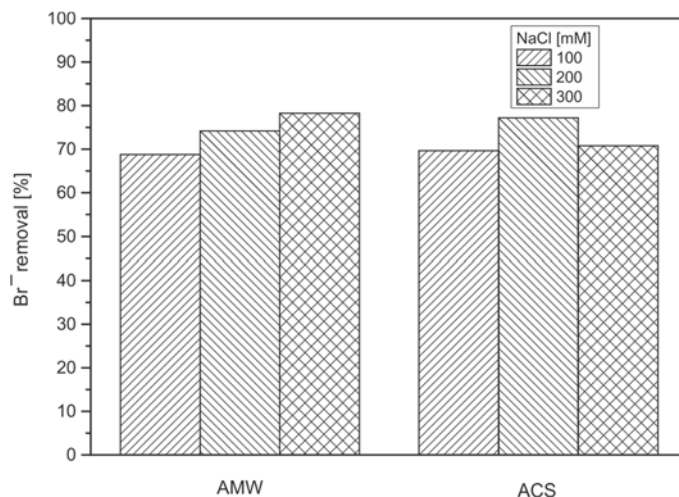| Membrane	Duration [h]	Br$^-$		NO$_3^-$		HCO$_3^-$	
		J_{Br} [mol/(m$^2\cdot$h)]	R_{Br} [%]	J_{NO_3} [mol/(m$^2\cdot$h)]	R_{NO_3} [%]	J_{HCO_3} [mol/(m$^2\cdot$h)]	R_{HCO_3} [%]
Selemion AMV	1.5	0.247×10^{-3}	74.2	0.130	79.2	0.070	45.9
Neosepta ACS	3.5	0.110×10^{-3}	77.2	0.058	83.0	0.021	24.5

Fig. 4. The efficiency of bromide removal from water with Selemion AMV
and Neosepta ACS membranes at various salt concentrations in the receiver

Analyzing the effect of salt concentration in the receiver on the effectiveness of
bromide ion removal from water (Fig. 4), it was observed that only in the process with
Selemion AMV membrane improvement in the efficiency and in the rate of bromide
removal together with the increase in salt concentration occurs. By increasing the NaCl
concentration in the receiver from 100 to 300 mM an increase in the efficiency of Br$^-$

ion exchange into Cl$^-$ ones from 69 to 78% was obtained, with simultaneous increase of bromide ion flow through the membrane from $0.214 \cdot 10^{-3}$ to $0.266 \cdot 10^{-3}$ mol/(m^2·h). This effect is due to an increased concentration gradient of driving ions (i.e., chloride ions), resulting in an increase in flow of these ions from the receiver to the treated water: from 0.111 mol/(m^2·h) at 100 mM NaCl, to 0.249 mol/(m^2·h) at 300 mM NaCl. Increased flow of Cl$^-$ causes increased, oppositely directed transfer of anions (including Br$^-$ ions) from the treated water to the receiver.

However, application of a membrane having a dense surface structure (Neosepta ACS) caused no similar effect – efficiency of bromide removal was practically at a constant level, irrespective of the electrolyte concentration in the receiving solution. This means that a cohesive surface layer of the ACS membrane constitutes a barrier that reduces transport of anions which are removed from water, even with an increased gradient of driving ion concentration.
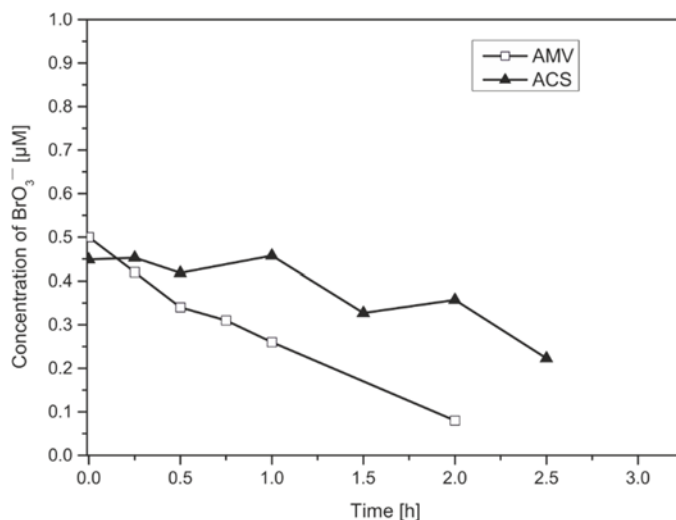

Fig. 5. Removal of bromates in the DD process with Selemion AMV
and Neosepta ACS membranes (salt concentration in the receiver: C_{NaCl} = 200 mM)

In the bromate ion removal from water greater differences in the effectiveness of their removal using the tested membrane were observed (Fig. 5). In the process with Selemion AMV membrane, 83% removal of BrO$_3^-$ ions was achieved, but using a Neosepta ACS membrane gave only 49% efficiency. Significant differences were also observed in the case of other anions. In the process with Selemion AMV membrane, nitrates and bicarbonates were exchanged for chloride ions in 83 and 63%, and with Neosepta ACS membrane, the exchange efficiency of these ions for the chloride ions was 64 and 23%, respectively (Fig. 6).
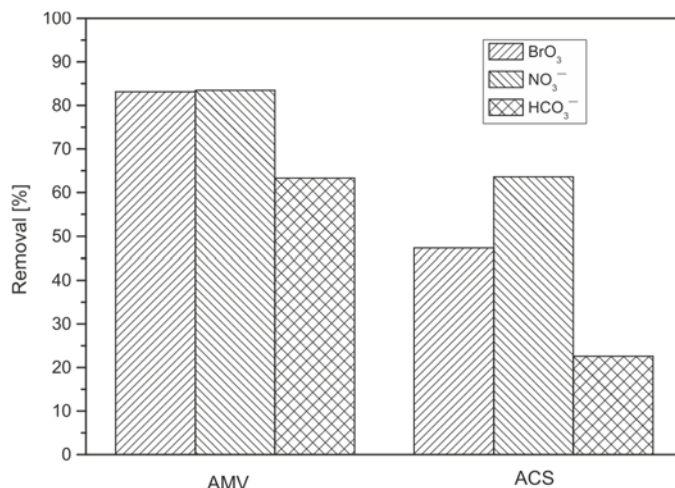
Fig. 6. Effectiveness of removal of bromates and accompanying anions with Selemion AMV
and Neosepta ACS membranes (salt concentration in the receiver: C_{NaCl} = 200 mM)

The bromate ion is bigger than the bromide ion (the radius of the hydrated BrO_3^- ion
is 0.351 nm [24]), thus in the process with a dense surface membrane the efficiency of
ion exchange for chloride ions gave far worse results. These results confirm the earlier
observation that a dense structure of ACS membrane surface makes the flow of anions
more difficult. This is confirmed by data concerning anions flow through the membrane
(Table 3).

Table 3

Effects of removing bromates and associated anions
with the use of different anion-exchange membranes (C_{NaCl} = 200 mM)

Membrane	Duration [h]	BrO_3^-		NO_3^-		HCO_3^-	
		J_{BrO_3} [mol/(m²·h)]	R_{BrO_3} [%]	J_{NO3} [mol/(m²·h)]	R_{NO3} [%]	J_{HCO3} [mol/(m²·h)]	R_{HCO3} [%]
Selemion AMV	2.0	$0.015 \cdot 10^{-3}$	83.1	0.099	83.5	0.071	63.3
Neosepta ACS	2.5	$0.007 \cdot 10^{-3}$	49.3	0.052	63.6	0.027	22.6

The increase of salt concentration in the receiver improves the efficiency of bromate
removal only with Selemion AMV membrane. Upon increasing salt concentrations from
100 to 300 mM NaCl an increased efficiency of bromate ions exchange for chloride
ones from 66 to 85% (Fig. 7) was observed. This results from increased flow of chloride
ions from the receiver to the treated water, resulting in an increase in anion flow (in-
cluding bromates) from treated water to the receiver. On the other hand, the use of Ne-
osepta ACS membrane in the anion exchange did not allow one to obtain a similar

effect: bromate exchange efficiency for chloride ions was almost constant and amounted to 48–49%.
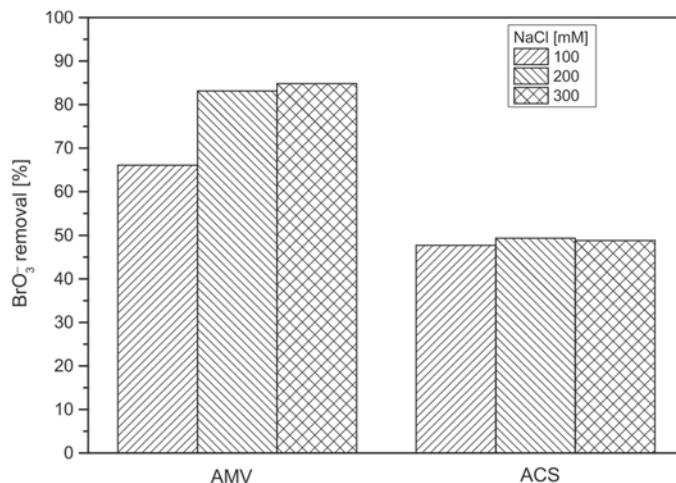

Fig. 7. The efficiency of removal of bromates with Selemion AMV
and Neosepta ACS membranes at various salt concentrations in the receiver

3.2. REMOVAL OF CALCIUM AND MAGNESIUM IONS IN THE DONNAN DIALYSIS

In the cation exchange with a cation-exchange membrane, the concentration gradient of Na^+ ions causes their flow from the receiver to the treated water, leading to removal of an equivalent amount of cations from the treated water. Cations (including calcium and magnesium, responsible for water hardness) are thus replaced with neutral sodium ions. Figure 8 shows the course of removing calcium and magnesium ions using the tested membranes: Selemion CMV and Neosepta CMX.

High efficiency in the exchange of calcium and magnesium into chloride ions was achieved: 87% for CMV membrane and from 80 to 87% for CMX membrane. At the same time, it was observed that the cation exchange with the use of Selemion CMV membrane is faster than the process with Neosepta CMX membrane. This is confirmed by the higher value of Ca^{2+} and Mg^{2+} ion flux through CMV membrane (Table 4). The time required to reach the minimum concentration of the removed cations becomes shorter in the Donnan dialysis using Selemion CMV membrane. It results from a high ion-exchange capacity and increased water content of this membrane (Table 1). These properties facilitate and accelerate the transport of counter-ions (Ca^{2+} and Mg^{2+}) from the feed solution to the receiver.

It was observed that decrease in the concentration of Ca^{2+} in the initial step of cation exchange is faster as compared to Mg^{2+} ions (Fig. 8). Only when calcium ions are in the

majority (over 70%) exchanged for sodium ions, the magnesium ion exchange is intensified. This phenomenon is related to the difference in the size of ions: hydrated ion radius of Ca^{2+} (0.412 nm) is smaller than the radius of Mg^{2+} ion (0.429 nm) [24].
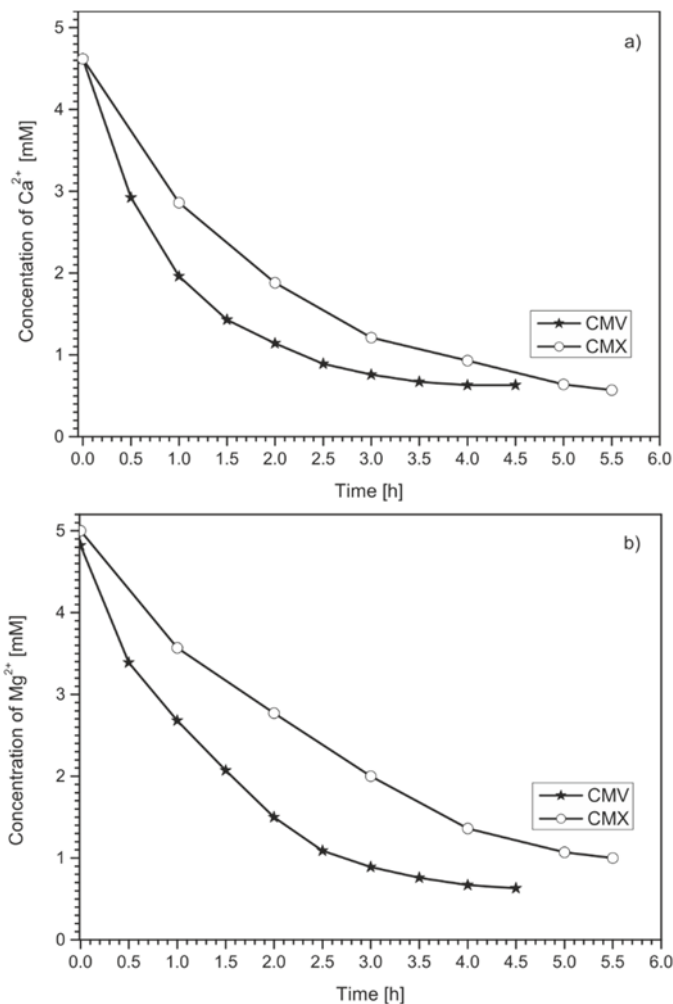

Fig. 8. Removal of calcium (a) and magnesium (b) ions in the DD process with Selemion CMV and Neosepta CMX membranes (salt concentration in the receiver: $C_{NaCl} = 200$ mM)

The concentration of salt in the receiving solution has a significant effect on the efficiency of calcium and magnesium cation removal from water (Fig. 9). Upon increasing NaCl concentration from 100 to 300 mM, an increase of cation exchange efficiency of Ca^{2+} ions for Na^{+} ions from 56 to 95% (CMV) and from 50 to 93% (CMX) was ob-

served. On the other hand, for Mg^{2+} cations there was observed an increase in the process efficiency from 58 to 94% (CMV) and from 58 to 96% (CMX). Despite the beneficial effects of high salt concentration (300 mM) on the efficiency of cation removal, it was found that it is not justified due to the fact that at lower salt concentration (200 mM NaCl), the process efficiency is satisfactory.
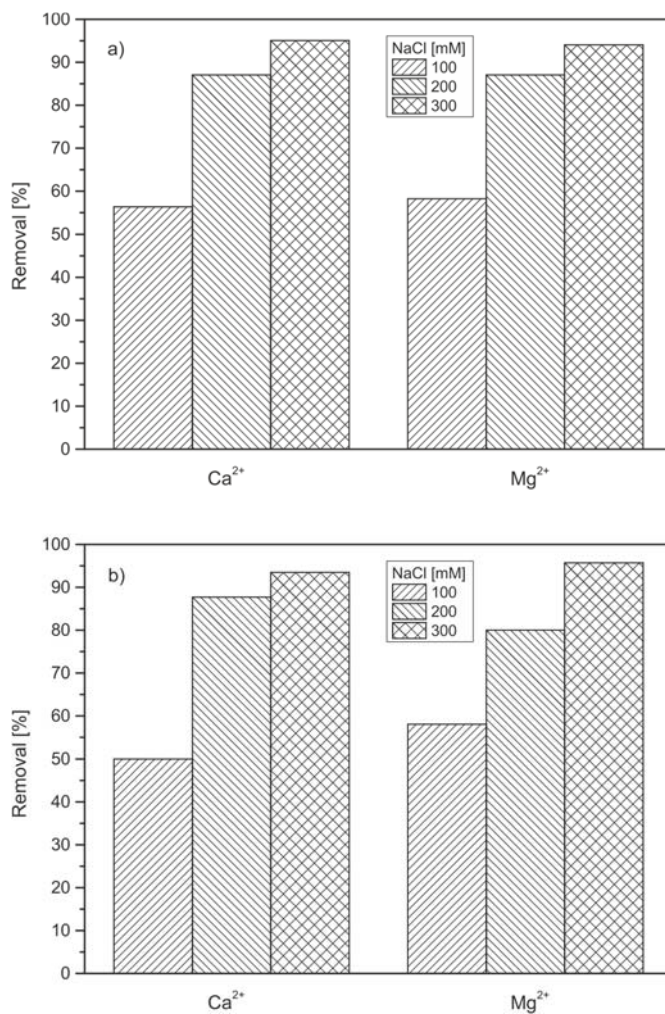

Fig. 9. The efficiency of calcium and magnesium ion removal from water withy Selemion CMV (a) and Neosepta CMX membranes (b) at various salt concentrations in the receiver

After exchange of cations, favorable changes in the ionic composition of the water were obtained (Fig. 10). Molar ratio of Ca^{2+}/Mg^{2+} was reduced from 100% (in raw water) to 5.5% (after the Donnan dialysis with Selemion CMV membrane) and 8.6% (after the dialysis with Neosepta CMX membrane).

Table 4

The effect of removing calcium and magnesium ions using various cation-exchange membranes
(salt concentration in the receiver C_{NaCl} = 200 mM)

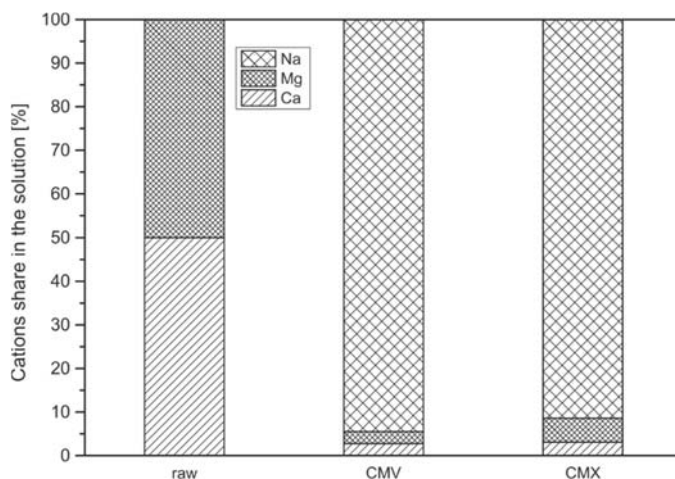| Membrane	Duration [h]	Ca^{2+}		Mg^{2+}	
		J_{Ca} [mol/(m²·h)]	R_{Ca} [%]	J_{Mg} [mol/(m²·h)]	R_{Mg} [%]
Selemion CMV	4.5	0.067	87.0	0.067	87.0
Neosepta CMX	5.5	0.053	87.7	0.052	80.0

Fig. 10. Ion composition of raw water and that after the Donnan dialysis
with Selemion CMV and Neosepta CMX membranes

Changed ionic composition of water has a beneficial effect on its further desalination by electrodialysis. Firstly, limiting current density increases, which allows one to carry out a desalination process at higher current density and thus reduce required membrane surface in the electrodialysis process [25]. This is due to the dominant share of Na^+ cations in water after the Donnan dialysis, so that they become the main cations transferred toward cation-exchange membrane. These ions are of much smaller size in comparison to those of Ca^{2+} and Mg^{2+} ions (radius of the hydrated Na^+ ion is 0.358 nm [24]), which increases their mobility in electric field and causes an increase in the concentration of ions in the boundary layer of a cation-exchange membrane. As a result, limiting current density increases [19]. Changed ionic composition of water after the Donnan

dialysis with cation-exchange membrane also affects the rate of desalination because the flux of sodium salts in the electrodialysis process is higher than the flux of calcium and magnesium salts (Table 5).

<div align="right">T a b l e   5</div>

<div align="center">Mean salt flux in the desalination of raw water
and of the DD product (Selemion CMV membrane) [25]</div>

Current density [A/m^2]	Mean salt flux [eq/(m^2·h)]	
	Raw water	Water after DD
15	0.233	0.279
25	0.433	0.507
30	0.421	0.512

4. CONCLUSIONS

• The Donnan dialysis – a membrane anion exchange process allows effective removal of undesired ions (e.g., bromides or nitrates) from water. The efficiency of the process is dependent on the type of applied membrane. The effectiveness of exchange of Br$^-$ ions for Cl$^-$ ions was from 74% to 77% while in the case of NO$_3^-$ ions from 79% to 83% (concentration NaCl in the receiver of 200 mM) and higher efficienvy of ion removal was reached when anion-exchange membrane with thin, highly cross-linked surface (e.g Neosepta ACS membrane) was applied.

• Only use of the Selemion AMV membrane led to improvement in the efficiency and in the rate of bromide removal from water together with the increase in salt concentration. When membrane with a dense surface structure was applied, the efficiency of bromide removal was practically at a constant level, irrespective of the electrolyte concentration in the receiving solution.

• Bromate ions were effectively removed from water in the anion exchange with Selemion AMV membrane. The effectiveness of BrO$_3^-$ ion exchange for Cl$^-$ ions is 83% (200 mM NaCl in the receiver), which can reduce the concentration of bromates in water to the allowable limit in drinking water (i.e., 10 µg/dm^3).

• The Donnan dialysis with the use of cation-exchange membranes makes it possible to effectively remove calcium and magnesium ions by their exchange for sodium ions. With NaCl concentration in the receiver equal to 200 mM 87% removal of Ca^{2+} ions and 80–87% removal of Mg^{2+} ions was obtained for Neosepta CMX membrane and Selemion CMV membrane, respectively.

• As a result of cation exchange the change of ionic composition of water was obtained: molar ratio of Ca^{2+} to Mg^{2+} was reduced from 100% (in raw water) to 5.5% (Selemion CMV membrane) and to 8.6% (Neosepta CMX membrane).

ACKNOWLEDGEMENTS

REFERENCES

[1] Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Official Journal of the European Communities, 1998, No. L 330/32.

[2] Europe's Environment, *The Dobris assessment, the report on the state of the pan-European environment*. Chapter 5. *Inland waters*, Report EEA for European Environment Agency, 2001.

[3] RICHARDSON S.D., *Disinfection by-products and other emerging contaminants in drinking water*, Trends Anal. Chem., 2003, 22, 666.

[4] United States Environmental Protection Agency, *National Primary Drinking Water Regulations*, 816-F-09-0004, May 2009.

[5] VON GUNTEN U., *Ozonation of drinking water. Part II. Disinfection and by-product formation in presence of bromide iodide or chlorine*, Water Res., 2003, 37, 1469.

[6] DE BORBA B.M., ROHRER J.S., POHL C.A., SAINI C., *Determination of trace concentrations of bromate in municipal and bottled drinking waters using a hydroxide-selective column with ion chromatography*, J. Chromat. A, 2005, 1085, 23.

[7] JOYCE R.J., DHILLON H.S., *Trace level determination of bromate in ozonated drinking water using ion chromatography*, J. Chromat., 1994, 671, 165.

[8] TYROVOLA K., DIAMADOPOULOS E., *Bromate formation during ozonation of groundwater in costal areas in Greece*, Desalination, 2005, 176, 201.

[9] World Health Organization, *Guidelines for drinking-water quality*, 4th Ed., Geneva 2011.

[10] WATSON K., FARRÉ M.J., KNIGHT N., *Strategies for the removal of halides from drinking water sources, and their applicability in disinfection by-product minimisation. A critical review*, J. Environ. Manage., 2012, 110, 276.

[11] SINGER P.C., BILYK K., *Enhanced coagulation using a magnetic ion exchange resin*, Water Res., 2002, 36, 4009.

[12] GE F., ZHU L., *Effects of coexisting anions on removal of bromide in drinking water by coagulation*, J. Hazard. Mater., 2008, 151, 676.

[13] BANASIAK L.J., SCHÄFER A.I., *Removal of inorganic trace contaminants by electrodialysis in a remote Australian community*, Desalination, 2009, 248, 48.

[14] ASAMI M., AIZAWA T., MORIOKA T., NISHIJIMA W., TABATA A., MAGARA Y., *Bromate removal during transition from new granular activated carbon (GAC) to biological activated carbon (BAC)*, Water Res., 1999, 33, 2797.

[15] KIRISTS M.J., SNOEYINK V.L., KRUITHOF J.C., *The reduction of bromate by granular activated carbon*, Water Res., 2000, 34, 4250.

[16] LISTIARINI K., TOR J.T., SUN D.D., LECKIE J.O., *Hybrid coagulation-nanofiltration membrane for removal of bromate and humic acid in water*, J. Membr. Sci., 2010, 365, 154.

[17] VAN DER HOEK J.P., RIJNBENDE D.O., LOKIN C.J.A., BONNE P.A.C., LOONEN M.T., HOFMAN J.A.M.H., *Electrodialysis as an alternative for reverse osmosis in an integrated membrane system*, Desalination, 1998, 117, 159.

[18] MARHABA T. F., BENGRAINE K., *Review of strategies for minimizing bromate formation resulting from drinking water ozonation*, Clean Techn. Environ. Policy, 2003, 5, 101.

[19] STRATHMANN H., *Ion-exchange membrane separation processes*, Elsevier, Amsterdam 2004.

[20] Asahi Glass Company, *Selemion, ion exchange membranes*, 2010.

[21] Tokuyama Corporation, *Neosepta, ion exchange membranes*, 2004.

[22] *Standard Methods for the Examination of Water and Wastewater*, 21th Ed., APHA, AWWA, WEF, Washington 2005.

[23] Merck Applications, Bromate in water and drinking water. Photometric determination with 3,3′- di-methylnaftidin and iodine (private information obtained from Merck's representative).

[24] NIGHITINGALE E.R., *Phenomenological theory of ion solvation. Effective radii of hydrated ions*, J. Phys. Chem., 1959, 63, 1381.

[25] WIŚNIEWSKI J., RÓŻAŃSKA A., *Donnan dialysis for hardness removal from water before electrodialytic desalination*, Desalination, 2007, 212, 251.