

128 (2018) 34–38 October

Regeneration and long-term chemical stability of heterogeneous anion exchange membrane in perchloric acid

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Received 22 March 2018; Accepted 8 May 2018

ABSTRACT

Drinking water quality has been a global problem in recent years. With the growing specific industry, groundwater and surface water are contaminated with certain substances, so drinking water concentration limits for these substances must be defined. Fortunately, with the evolving industry, there is a range of methods that can be used to treat water dedicated to potable purposes. Among them, an electromembrane process with anion exchange membranes can be found. These membranes can be used approximately to remove perchlorate ions from purified water. The paper deals with regeneration and long-term stability of anion exchange membranes in 3% perchloric acid solution. For anion exchange membranes, electrochemical properties such as an areal resistance and a permselectivity were observed for 5 months. At the same time, a change in the mechanical and optical properties of the reinforcing fabrics used in the anion exchange membrane was monitored. Long-term exposure did not have a major effect on the anion exchange membrane permselectivity, and the mechanical properties of the reinforcing fabric did not show significant changes. Differences were determined only for the areal resistance, which grew slightly with the increasing exposure time.

Keywords: Anion exchange membrane; Heterogeneous membrane; Perchloric acid; Long-term chemical stability

1. Introduction

Perchlorate contamination of surface water and water dedicated to potable purposes has become a big global problem, especially where perchlorate contamination from military and aerospace industries, agriculture, industry or water disinfection occurs. Perchlorate can interfere with iodine by the thyroid glands and harm the regular growth of new born and young children and thyroid activity in general. Although it is a strong oxidant (the most oxidised form of chlorine), perchlorate is very persistent in the environment [1–3].

Nowadays, controlled restrictions are in Canada and in the United States, while the Czech Republic currently regulates perchlorate level mainly in food and drinking water according to Council Directive 98/83/EC on the quality of water intended for human consumption [4]. The permissible limits are expressed in μ g L⁻¹ (WHO: Guidelines for Drinking Water Quality, Geneva 2011).

Perchlorates can be removed from the water in several ways: pressure-driven processes such as reverse osmosis [5], ultrafiltration [6], electromembrane processes with anion exchange membranes (AEMs) [7], biodegradation [8] or combinations of biodegradation and AEMs – bioreactors [1,9,10], anion exchange in the columns [11,12] or catalytic reactors [13]. Comparison of individual perchlorate removal methods is discussed in detail in Ref. [2].

Since AEMs are used in many perchlorate removal processes, this work focuses on the long-term stability of these AEMs in perchloric acid solution. AEMs are separation membranes capable of separating anions from cations in solution. AEMs transport anions and retain cations [14].

Commercially available AEMs can be classified into two major groups, which are homogeneous and heterogeneous

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Presented at the XII Scientific Conference 'Membranes and Membrane Processes in Environmental Protection' – MEMPEP 2018 13–16 June 2018, Zakopane, Poland.

membranes. A homogeneous AEMs' comprise one polymer, which is used to form a membrane structure and to carry functional sites needed for ions transport. In heterogeneous AEMs, two different polymers are involved. The first polymer acts as a structural former or a matrix polymer. The second polymer, which is usually a finely ground anion exchange resin, is used to carry the functional sites [15].

Both types of AEMs can be reinforced with reinforcing fabrics to achieve the desired mechanical properties. This paper compares the long-term stability of AEMs reinforced with six types of reinforcing fabrics, which differ mainly in material.

2. Experimental

2.1. AEMs preparation

Heterogeneous AEMs were prepared by a hot pressing on a hydraulic press (ZHOT60MT, Presshydraulika, Czech Republic). Nonreinforced heterogeneous AEMs Ralex® (Mega a.s., Czech Republic) were used. Before pressing, 10 min heating of the mixture at 135°C was carried out. Next, AEMs were reinforced at 135°C for 10 min at a pressure of 25 bar. AEMs were subsequently cooled to 60°C under pressure. The pressing was applied to guarantee the homogeneity [14,16]. Subsequently, AEM samples were soaked in 3% $HClO_4$ for 5 months in total (see Section 2.2). The reinforcing fabrics PET (polyethylene terephthalate), PP (polypropylene), PEEK (polyether ether ketone), PVDF (polyvinylidene fluoride) and PAD *p*-aramid (Kevlar, poly-*p*-phenylene terephthalamide) were selected for lamination of AEMs. The names of the individual samples and parameters of the reinforcing fabrics are shown in Table 1.

2.2. Regeneration and chemical stability

Chemical stability tests were focused on the reinforcing fabricitself and heterogeneous AEMs. All samples were soaked in 3% HClO₄ for 5 months in total. Scanning electron microscope (SEM) images of reinforcing fabrics were made already after a month to check whether further testing was needed. After 3 months, tensile tests were performed on the reinforcing fabrics. AEM samples were taken out from the soaking solution once a month to measure electrochemical properties.

After the first week, AEMs areal resistances increased and it was necessary to perform the regeneration using 15% NaCl solution or FeCl_4^- solution [11]. The latter solution was prepared by mixing 1 mol dm⁻³ FeCl₃ and 4 mol dm⁻³ HCl

Table 1

Names and the AEMs composition

(Eq. (1)). The regeneration solutions were changed three times over a regeneration period of 2 d to guarantee a full regeneration. This regeneration step was applied for all samples.

$$\operatorname{FeCl}_{3}(\operatorname{aq}) + \operatorname{Cl}^{-} \longleftrightarrow \operatorname{FeCl}_{4}^{-} \tag{1}$$

2.3. Characterisation of reinforcing fabrics

2.3.1. Mechanical properties

The mechanical properties (ultimate force, N/5 cm and strain, %) of reinforcing fabrics were measured using wet samples of dimensions 50 mm × 200 mm (clamping length) according to the standard EN ISO 13934-1 by means of an H5KT (Tinius Olsen, USA) tensile testing machine with a speed of 100 mm min⁻¹. The direction loading was aligned to the transverse direction due to the small amount of sample, which was chemically treated.

2.3.2. Microscopy

The change in the structure of the reinforcing fabrics was investigated using a FEI Quanta 250 FEG SEM equipped with large field detector for secondary electrons. The conditions for measurement were 5 kV voltage and low vacuum (80 Pa pressure). Samples of reinforcing fabrics were sputtered with a 10 nm layer of chromium before measurement by the Quorum Technologies Q150T S/E/ES.

2.4. AEMs characterisation

2.4.1. Areal resistance

AEMs for measuring areal resistance $(R_{A'} \Omega \text{ cm}^2)$ were neutralised with 0.5 mol dm⁻³ NaCl for 24 h. Electrochemical resistance was measured using a 0.5 mol dm⁻³ NaCl solution at 25°C in a special experimental cell (especially manufactured by MemBrain s.r.o., Czech Republic) using the compensation method [17]. Electrochemical resistance was measured between reference electrodes (calomel electrodes) and followed by the application of constant direct current (I = 10 mA) between platinum electrodes. Electrochemical resistance was determined from two measurements of potential difference, and the first measurement was performed in the solution without an AEM (U_{solution}), while the second was run with a 0.785 cm² (active area, *S*) AEM ($U_{\text{solution + AEM}}$) installed [18,19]. Areal resistance was determined by Eq. (2) as follows:

Name of samples	Reinforcing fabric				
	Name of fabric	Manufacturer	Thickness (µm)	Warp/weft (1 cm ⁻¹)	Threads
AEM PET	Ulester 32S	Silk & Progress	100	32/35	Monofilament
AEM PP	Popsilk 32S	Silk & Progress	140	32/35	Monofilament
AEM PVDF	Fluortex 02-70/22	Sefar	158	63/63	Monofilament
AEM PAD	Style 240	C. Cramer	65	8/8	Multifilament
AEM PEEK 115	Peektex 17-115x145/58	Sefar	50	73/52	Monofilament
AEM PEEK 220	Peektex 17-220/56	Sefar	128	34/34	Monofilament

$$R_{A} = \frac{S(U_{\text{solution}+AEM} - U_{\text{solution}})}{I}$$
(2)

2.4.2. Permselectivity

Permselectivity describes the ability of AEMs to prevent coions pass through [20] and it is often discussed with a transport number [21]. Permselectivity (P, %) of AEMs was determined using Henderson's method in the same measuring cell as the electrochemical resistance, but using a KCl solution of 0.1–0.5 mol dm⁻³ in the separated parts and without direct current applied. Potential (U_{meas}) was measured between reference (silver–silver chloride) electrodes. Permselectivity was determined by Eq. (3). The AEMs were equilibrated with 0.5 mol dm⁻³ KCl for 24 h before the measurement [22,23].

$$P = \frac{U_{\text{meas.}}}{U_{\text{theor.}}} \times 100 \tag{3}$$

where U_{theor} is a theoretical potential from Nernst's law.

3. Results and discussion

The changes in mechanical properties of the reinforcing fabrics were tested after a 3-month exposure to determine the effect of $HClO_4$. After already a month, SEM images of the reinforcing fabrics were taken in order to decide whether to continue the testing. At the same time, the electrochemical properties of heterogeneous AEMs prepared from the available reinforcing fabrics were tested, and AEMs' samples were taken monthly for 5 months.

Fig. 1 shows the tensile curves of unloaded reinforcing fabrics and after 3 months of exposure to 3% HClO₄. The *p*-aramid fabric (Style 240) was not included in the tensile tests due to slippage from the jaws of the tensile testing machine. This PAD reinforcing fabric is made of high-threads multifilament and exhibits high strength. It is the problem to tear the samples by the method based on the ISO standard. Therefore, PAD reinforcing fabric was excluded from testing. In Fig. 1, the average curves are based on five determinations performed for each sample. It is well evident that both PEEK fabrics slightly lost the ductility and strength. The differences



Fig. 1. Comparison of the tensile curves of unloaded reinforcing fabrics and after a 3-month exposure to $HClO_4$.

are well noticeable in Fig. 2. There was practically no change noted for the PP reinforcing fabrics. There was a slight decrease in the PVDF reinforcing fabric, which was in the range of the measurement error. For PEEK and PET fabrics, the deviations were higher, and degradation of reinforcing fabrics was not conclusive, because the changes moved to the limit of the measurement error. So, we assumed that if some degradation occurred, it was relatively low (in confrontation with SEM images). HCIO_4 had no significant effect on the mechanical properties of selected reinforcing fabrics.

The SEM images for individual reinforcing fabrics are shown in Fig. 3. Narrowing of the diameter or another sign of thread's degradation could not be seen for a single, among selected, reinforcing fabrics.

Due to the much different constructional parameters of the individual reinforcing fabrics, the magnification of SEM image is different. If we do not observe or compare the reinforcing fabric samples with each other, then the same magnification is not required.

The PEEK 115 fabric was obviously calendered to reduce the resulting thickness. Calendering was well visible in the warp and weft monofilament cross.

It was also possible to determine the thread density in the multifilament of the PAD fabric. This reinforcing fabric is very different from the other ones. If this material proved successful, it would be necessary to get a supplier of *p*-aramid monofilament reinforcing fabrics or get a monofilament and weave reinforcing fabric according to our requirements.



Fig. 2. Comparison of ultimate force and ultimate strain for pristine reinforcing fabrics and after 3-month exposure to HClO₄.



Fig. 3. SEM images of reinforcing fabrics after 3-months exposure in $HClO_4$. (a) PET, (b) PP, (c) PVDF, (d) PAD, (e) PEEK 220 and (f) PEEK 115.

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The benefits and comparison of reinforcing fabrics made of different types of fabrics were mentioned in detail in the article [24]. *p*-Aramid is conventionally and extensively used in composite materials based on epoxy and other resins as a reinforcing component.

On PP or PVDF monofilament, there were noticeable scratches or small unevenness on the surface. This threads' defect already originated from the production of the monofilament and it was determined by conditions or the setting of the lubrication during the process. These deficiencies resulted in the preferred degradation of monofilaments. However, this was not apparent basing on the obtained results.

In the next phase, the electrochemical properties of heterogeneous AEMs were tested. After the first week, areal resistances of all samples increased sharply, as shown in Figs 4 and 5. However, the permselectivity of the AEM samples remained unchanged. If there was a significant degradation, the permselectivity would decrease, but that did not happen. The reason for the increased values of the areal resistance was the blocking of the functional groups of membranes by ClO_4^- anions. This anion has a high affinity for the quaternary ammonium group over other anions. The selectivity of strong functional groups in AEMs towards different anions can be arranged in a series [25,26]:

OH⁻ (selectivity coefficient = 1 – reference) $< Cl^{-}(22)$ $< NO_{3}^{-}(65) < SO_{4}^{2-}(150) < ClO_{4}^{-}(<500)$

High selectivity of ClO₄⁻ is given by a low hydration energy and a large size. The high affinity of ClO₄ requires the use of large volumes of concentrated salts solutions for regeneration [11]. Before the measurement, AEMs were only equilibrated with 0.5 mol dm⁻³ NaCl. Low Cl⁻ ion concentrations, together with the low affinity of Cl- anions to AEMs functional groups were unable to fully regenerate the membranes. In Ref. [11], the effect of the used regenerative agent is discussed. According to Ref. [11], the 12% NaCl solution can recover only 20% of AEMs functional groups, compared to the solution with tetrachloroferrate FeCl₄ anion (discussed in Section 2.2), which is able to regenerate nearly 100% of functional groups of AEMs. ClO₄⁻ is one of the most strongly extracted anions by HCl solution by either liquid-liquid solvent extraction or anion exchange. By decreasing Cl- concentration (added 0.01 M HCl), the FeCl₄ anion converts to positively charged Fe(III) species (Fe³⁺, FeCl²⁺ and FeCl²), which are desorbed from AEMs by charge repulsion. Thus, AEMs are regenerated to original state with Cl- [11]. In our case, both regeneration solutions were tested. The result and comparison of regeneration is presented in Fig. 4.

The areal resistance decreased in average by 10.9 Ω cm² (range 7.5–16.2 Ω cm²) with NaCl and by 10.2 Ω cm² (range 6.6–13.2 Ω cm²) with FeCl₄⁻ regenerative solution. This means that, with NaCl, areal resistance of AEMs decreased by 48.1% and FeCl₄⁻ by 42.5%. This result does not correlate with the results found in the article [11]. This may be due to the higher NaCl concentration used, batch regeneration instead of continuous one and longer contact time. Conversely, the recovery of FeCl₄⁻ did not reach as high level as it was advised. Due to the easier use of NaCl solution and with the promising first regeneration results, further samples were regenerated with 15% NaCl.



Fig. 4. Increase of areal resistance in AEMs after exposure to HClO, and their regeneration with NaCl and FeCl_i.

Fig. 5 shows the development of areal resistance in regenerated samples of AEMs over time. Areal resistances slightly increased for almost all samples of AEMs. It is questionable whether the areal resistances increased due to the effect of $HClO_4$ solution over time, whether it would be necessary to increase the dose, concentration or frequency of changes of the NaCl recovery solution.

The development of permselectivity is also depicted in Fig. 5. It did not change over the 5 months testing. Its values varied within the definition error, or the change could be due to the heterogeneous AEMs character. For each permselectivity assessment, samples from another location of prepared AEMs were used. This issue is discussed in the article [15]. The polymer matrix used in the heterogeneous AEM is inert, while the functional groups are located only on the resin powder, therefore the groups are nonuniformly distributed. The heterogeneous model [27,28]. Even a homogeneous membrane contains two phases (gel – functional groups on the matrix and intergel phases – gap and gaps filled with



Fig. 5. Development of permselectivity and areal resistance for all samples during exposure to perchloric acid. Areal resistance values are given already after regeneration in NaCl and FeCl_{4}^{-} .

liquid), while in the heterogeneous membrane the gel phase can be divided into a pure gel – ion exchange resin and inert gel – polymer matrix phases. Consequently, heterogeneous AEMs exhibit more inhomogeneity [15].

In AEMs with PAD reinforcing fabric, separation of the reinforcing fabric from the surface of AEM was observed due to poor lamination. Unqualified lamination was caused by high threads density per centimetre in a multifilament of the tested fabric. Due to partial separation, there was a local increased swelling of the sample and thus, a decrease in permselectivity was observed. This phenomenon occurred in AEMs samples after 2 and 4 months exposure to $HClO_4$. For other samples, permselectivity was higher than 90%, and exposure to $HClO_4$ did not affect the parameter values.

4. Conclusions

This article is focused on the long-term stability of AEMs with 6 types of reinforcing fabrics in the perchloric acid. $HClO_4$ had no significant effect on the mechanical properties of the selected reinforcing fabrics. If some degradation occurred, it was relatively low. SEM images also did not show degradation of the reinforcing fabrics.

In the next phase, the electrochemical properties of heterogeneous AEMs were tested. After the first week, the areal resistances of all the samples sharply increased. This was due to the high affinity of ClO_4^- ions to functional groups of AEMs. Two regenerating agent solutions (NaCl, FeCl₄) were tested for regeneration of AEMs. Their utility was similar, and eventually all samples were regenerated with NaCl solution. Even after regeneration, there was a slight increase in the areal resistances during the exposure of AEMs to perchloric acid. Permselectivity, however, was higher than 90%, and exposure to $HClO_4$ did not affect the parameter values.

Acknowledgement

The work was carried out within the framework of the project no. LO1418 'Progressive development of Membrane Innovation Centre' supported by the program NPU I of Ministry of Education Youth and Sports of the Czech Republic, using the infrastructure of the Membrane Innovation Centre.

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