Relationship between performance deterioration of a polyamide reverse osmosis membrane used in a seawater desalination plant and changes in its physicochemical properties

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Abstract: While it is known that the performance of reverse osmosis membranes is dependent on their physicochemical properties, the existing literature studying membranes used in treatment facilities generally focuses on foulant layers or performance changes due to fouling, not on the performance and physicochemical changes that occur to the membranes themselves. In this study, the performance and physicochemical properties of a polyamide reverse osmosis membrane used for three years in a seawater desalination plant were compared to those of a corresponding unused membrane. The relationship between performance changes during long-term use and changes in physicochemical properties was evaluated. The results showed that membrane performance deterioration (i.e., reduced water flux, reduced contaminant rejection, and increased fouling propensity) occurred as a result of membrane use in the desalination facility, and that the main physicochemical changes responsible for performance deterioration were reduction in PVA coating coverage and bromine uptake by polyamide. The latter was likely promoted by oxidant residual in the membrane feed water. Our findings indicate that the optimization of membrane materials and processes towards maximizing the stability of the PVA coating and ensuring complete removal of oxidants in feed waters would minimize membrane performance deterioration in water purification facilities.

32 **Key Words:** reverse osmosis, membrane, polyamide, desalination, bromination, chlorination

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INTRODUCTION

Thin-film composite reverse osmosis (RO) membranes are the most common membrane type used for seawater desalination (Lee et al., 2011). State-of-the-art RO membranes are typically comprised of a thin polyamide active layer (<200 nm) – which dictates solute and water permeation (Petersen, 1993) – supported by an asymmetric polysulfone support (~20-50 μm) backed by a non-woven polyester mat (~50-150 μm) (Petersen, 1993; Lee et al., 2011). Some polyamide RO membranes also have a coating on top of the polyamide active layer (Hachisuka and Ikeda, 2002; Tang et al., 2009).

The physical and chemical properties of the membrane surface and active layer are known to affect water permeability, contaminant rejection, and fouling propensity, often more than one of these simultaneously. For example, higher membrane surface roughness leads to higher fouling propensity (Bowen and Doneva, 2000; Ramon and Hoek, 2013) and is believed to result in higher water flux (Lee et al, 2011), thinner active layers contribute to higher water and solute permeability (Wijmans and Baker, 1995), more hydrophilic membrane surfaces correlate with higher water permeability and lower fouling (Al-Amoudi, 2010; Kang and Cao 2012), smaller free-volume holes lead to lower water permeability and higher contaminant rejection (Kim et al, 2005), and higher active layer charge increases the rejection of ions (Childress and Elimelech, 2000; Coronell et al., 2013) but exacerbates organic fouling (Xiang et al., 2014). As a result, studies have focused on tailoring the physicochemical properties of membrane surfaces and active layers to optimize performance. For example, membrane surfaces are rendered more neutral and hydrophilic by using a polyvinyl alcohol (PVA) coating atop the polyamide active layer in an effort to minimize membrane fouling (Hachisuka and Ikeda, 2002; Tang et al., 2009),

and approaches have been devised to significantly reduce the thickness of active layers to increase water permeability (Karan et al., 2015).

While great interest has been placed in optimizing membrane physicochemical properties, to the authors' knowledge, no studies exist in the literature that (i) investigate comprehensively the changes that occur to these physicochemical properties as a result of membrane use in full-scale treatment facilities, nor (ii) how these physicochemical changes relate to observed membrane performance deterioration. Existing studies in the literature that use membranes collected from full-scale treatment facilities generally focus on the characterization of their foulant layers and associated performance changes (e.g., Tran et al., 2007; Vrouwenvelder, 2009), not on the physicochemical and performance changes that occur to the membranes themselves. Addressing this gap in the literature would increase the understanding of possible factors that cause membrane physicochemical changes and corresponding performance deterioration in full-scale installations. This understanding can be used to optimize membrane chemistry and/or treatment plant design or operation, so that membrane performance deterioration is minimized during long-term use.

In this study we focus on the physicochemical and performance changes of membranes used in seawater desalination facilities using free chlorine as an upstream disinfectant for membrane biofouling control (Ando and Iwahori, 2001; Sauvet-Goichon, 2007). This water purification scheme was selected because in addition to the common stresses that *may potentially* alter membrane chemistry and structure in any desalination facility (e.g., antiscalants, pH adjusters, cleaning agents), membrane exposure to free chlorine is *known* to cause physicochemical and performance deterioration of polyamide active layers (Kwon and Leckie, 2006; Do et al., 2012; Powell et al., 2015). While upstream disinfection with free chlorine is accompanied by a

dechlorination step ahead of the membranes via the addition of a quencher such as sodium bisulfite (NaHSO_3) (Ando and Iwahori, 2001; Sauvet-Goichon, 2007), the assumption that the dechlorination step removes chlorine continuously may not always be valid. Continuous complete free chlorine removal may be hampered by various practical factors in the operation of a treatment plant such as imperfect mixing of quencher and feed water, dechlorination system upsets, free chlorine concentrations below the detection limit of free chlorine sensors, and the common practice of indirect monitoring of chlorine residuals through oxidation-reduction potential (ORP) sensors (Nitto Denko, 2013; Dow Filmtec, 2015; Masayuki Nakasone, Okinawa seawater desalination plant, personal communication, August 11, 2014). To the authors' knowledge, no studies exist in the literature that investigate whether the dechlorination practice is effective in preventing at full-scale the physicochemical and performance changes reported in laboratory studies for polyamide membranes exposed to free chlorine.

To address the gaps in the literature identified above, we characterized physicochemical and performance properties of a membrane element obtained from a seawater desalination plant using free chlorine as an upstream disinfectant for membrane biofouling control. The membrane obtained from the treatment facility was thoroughly cleaned to enable the evaluation of the physicochemical and performance properties of the membrane itself, instead of its foulant layer. We compared the results for the used membrane to those of a corresponding control virgin membrane provided by the manufacturer in order to: (i) assess membrane performance deterioration as a result of membrane use in the desalination plant; (ii) assess which physicochemical properties changed as a result of membrane use in the desalination plant; (iii) identify which physicochemical changes were the leading factors contributing to membrane performance deterioration; and (iv) assess whether free chlorine quenching ahead of the

membrane feed prevented the well-known detrimental effects of free chlorine on polyamide membranes. The information provided in this study advances the understanding of the fate of polyamide membranes in treatment facilities using free chlorine as an upstream disinfectant, and informs membrane developers and plant operators on specific aspects that should be optimized to minimize membrane performance deterioration at water treatment plants.

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents

Sodium hydroxide (NaOH), citric acid, hydrochloric acid (HCl), sodium chloride (NaCl), sodium nitrate (NaNO₃), boric acid, silver nitrate (AgNO₃), and sodium tungstate (NaWO₄) (Nacalai Tesque, Inc., Kyoto, Japan), and ethylenediaminetetraacetic acid tetrasodium salt (Na₄EDTA) (Dojindo Laboratories, Kumamoto, Japan) were ACS grade or better. Purified Aldrich humic acid (PAHA) was prepared by purifying the Aldrich humic acid (St. Louis, MO, USA) as described elsewhere (Hong and Elimelech, 1997). All solutions were prepared with distilled deionized (DDI) water (>18 Ω.cm). All procedures were performed at room temperature (23±1°C) unless otherwise specified.

2.2. Membranes. Membrane samples were obtained from virgin (unused) and used spiral-wound elements of the seawater desalination SW30HR membrane (Dow Filmtec, Minneapolis, MN, USA). The virgin elements were provided by the manufacturer, and the used element which had been in service for approximately three years was obtained from a seawater desalination plant in Japan (see Section 2.3). At the time of collection, the used element was the lead element in a pressure vessel of the first stage of the desalination plant. SW30HR membranes have a fully aromatic polyamide active layer coated with polyvinyl alcohol (PVA) (Tang et al., 2007). We

confirmed the PVA coating was present in the specific membranes used in this study (data not shown) using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) as reported elsewhere (Tang et al., 2007).

2.3. Seawater Desalination Plant

At the time of this study, the pretreatment for the membrane feed water in the desalination plant from where the used membrane element was obtained consisted of: (i) chlorination (1 mg.L^{-1} as Cl_2 available chlorine using sodium hypochlorite (NaOCl)), (ii) poly aluminium chloride (PAC) coagulation followed by media filtration, (iii) pH adjustment to ≈ 6.5 using sulfuric acid (H_2SO_4), and (iv) dechlorination by NaHSO_3 addition to maintain the ORP of the membrane feed water below 250 mV. The net transmembrane pressure across the RO membranes was in the range of 2.0-3.0 MPa. When the membrane water permeability decreased by 15%, or once every six months, the lead elements in pressure vessels were collected, cleaned off-site with Na_4EDTA (0.1 wt% at pH=11.0 adjusted using NaOH) and citric acid (0.1 wt%), and placed back into the vessels as tail elements. Therefore, while at the time of collection the used membrane element was the lead element in a pressure vessel of the first stage, this element was in various positions (e.g., 5th, 4th, 3rd, 2nd) in the same vessel during the three years of service of the element. Accordingly, our observations on changes in membrane performance and active layer physico-chemical properties are not specific to a given position in the pressure vessel, but rather an average of the changes that occur in the elements of a pressure vessel in a three-year period.

2.4. Membrane Sample Preparation

Samples for permeation and materials characterization tests consisted of $20 \times 25 \text{ cm}^2$ and $2.5 \times 5.0 \text{ cm}^2$ coupons, respectively. The coupons cut from the virgin SW30HR element were thoroughly

rinsed with and stored in DDI water until needed. The coupons cut from the used SW30HR element were first cleaned with the same sequence of chemicals used in the desalination plant, and then rinsed with and stored in DDI water until needed. The cleaning procedure consisted of immersing the coupons for 30 minutes in each 0.1 wt% Na₄EDTA at pH=11.0 and 0.1 wt% citric acid. This procedure was used twice for each coupon, and was followed by thorough rinsing with DDI water. To assess the efficacy of the cleaning protocol, we performed scanning electron microscopy (SEM) and transmission electron microscopy (TEM) cross-sectional imaging, as well as elemental analyses of virgin, uncleaned used, and cleaned used membrane samples (see Supplementary Material) using Rutherford backscattering spectroscopy (RBS), XPS, and energy dispersive X-ray spectroscopy (EDS). The cross-sectional SEM and TEM images show a clear foulant layer in the uncleaned used samples, and absence of a foulant layer in the cleaned used samples. RBS, XPS and EDS elemental analyses did not detect Al, Fe, or Si (the inorganic elements characteristic of the foulant layer) in the cleaned used samples, but did detect these elements in the uncleaned used samples. Therefore, to the best of the capabilities of the thin-film and surface characterization techniques available for membrane studies, the foulant layer was effectively removed by the membrane cleaning procedure. Accordingly, from here on in, we use the term “used membrane samples” to refer to the “cleaned used membrane samples”.

2.5. Performance Evaluation

Permeation experiments were performed with a cross-flow, closed-loop filtration system similar to that described by Urama and Mariñas (1997). The system had two flat-sheet cells in series, each with 140 cm² effective filtration area. Additional details of the filtration system are provided in the Supplementary Material. The system was always operated at constant feed solution temperature of 24±0.3°C and pH=6.5. For performance evaluation, the membrane

samples were initially stabilized for three weeks at 2.5 MPa to allow for membrane compaction, using a feed solution containing 22 mM NaCl, 12 mM NaNO₃, and 1.7 mM boric acid (H₃BO₃). It is important to note that our testing conditions were not exactly the same as those used in the full-scale treatment facility and therefore should not be expected to result in the same membrane performance observed at the treatment plant. However, given that the objective of the performance tests was not to reproduce membrane performance at full scale, but rather to evaluate whether differences in membrane performance existed between virgin and used membranes, the exact testing conditions are not as important as long as they were kept consistent between the tests for virgin and used membranes.

Two types of performance experiments were performed in series for each virgin and used membrane. The first experiment evaluated water flux and solute (Cl⁻, NO₃⁻ and H₃BO₃) rejection in the absence of foulants (0.8-3.5 MPa). The relatively high crossflow velocity of 26 cm.s⁻¹ was used to minimize concentration polarization and estimate more accurately water/solute transport parameters (see Section 2.6). The second experiment investigated fouling behavior using PAHA as a surrogate for hydrophobic foulants under hydraulic pressures that resulted in the same initial water flux (0.3 m.day⁻¹) for virgin (1.7 MPa) and used (2.5 MPa) membranes. A lower crossflow velocity of 19 cm.s⁻¹ was used in the fouling experiments so that membrane fouling could occur more easily in a short-term experiment, thus allowing for the evaluation of differences in fouling propensity. The feed solution for the fouling tests was the same as for stabilization and solute rejection tests but 10 mg-C.L⁻¹ of PAHA and 1 mM of CaCl₂ were added before starting the fouling runs. Water flux was measured every 6 hours for 48 hours. The Cl⁻ and NO₃⁻ concentrations were measured using high-performance liquid chromatography (HPLC) with conductivity detection (Prominence series, Shimadzu Corp., Kyoto, Japan). The H₃BO₃

193 concentration was measured using the azomethine-H colorimetric method (Japanese Standards
194 Association, 2015).

195 **2.6. Water and Solute Transport Model**

196 Experimental results obtained from permeation experiments in the absence of PAHA were
197 analyzed using the solution-diffusion model allowing for the existence of unhindered advection
198 through nano-scale imperfections (Urama and Mariñas, 1997). In brief, the total water flux J_v
199 ($\text{m}\cdot\text{day}^{-1}$) was expressed as

$$200 \quad J_v = A(\Delta p - \Delta \pi) \quad , \quad (1)$$

201 where A ($\text{m}\cdot\text{MPa}^{-1}\cdot\text{day}^{-1}$) is the specific water permeability coefficient, Δp (MPa) is the
202 transmembrane applied pressure, and $\Delta \pi$ (MPa) is the transmembrane osmotic pressure. Solute
203 rejection R (dimensionless), which is operationally defined as $R=1-C_p/C_F$ where C_p and C_F are
204 the solute concentrations in the permeate and feed solutions, respectively, was expressed as

$$205 \quad R = \frac{1}{\left(\frac{\alpha}{1-\alpha} + \frac{B}{1-\alpha} \frac{1}{J_v} \right) \exp\left(\frac{J_v}{k} \right) + 1} \quad , \quad (2)$$

206 where B ($\text{m}\cdot\text{day}^{-1}$) is the solute diffusive permeation coefficient in the active layer, α
207 (dimensionless) is the advective permeation coefficient in the active layer, and k ($\text{m}\cdot\text{day}^{-1}$) is the
208 solute mass transfer coefficient in the concentration polarization layer next to the membrane
209 surface (Matthiasson and Sivik, 1980). In the case of negligible concentration polarization (i.e.,
210 $\exp(J_v/k) \approx 1$), Equation 2 is simplified to

$$R = \frac{1}{\frac{B}{1-\alpha} \frac{1}{J_v} + \frac{1}{1-\alpha}} \quad (3)$$

In all our tests concentration polarization was negligible (see Supplementary Material), and therefore Equation 3 was used to fit solute diffusive (B) and advective (α) transport coefficients from J_v and R experimental data.

2.7. Physicochemical Characterization of Membrane Samples

The following physicochemical properties were characterized in virgin and used membranes: dominant chemical functionalities; membrane surface morphology, roughness, hydrophilicity, charge, and hydroxyl content; and active layer bulk charge, void fraction, free-volume hole abundance, free-volume hole size distribution, halogen content, and water sorption. Dominant chemical functionalities in membrane samples were identified via ATR-FTIR analyses. Membrane surface charge and hydroxyl content, as well as active layer bulk charge and halogen content were quantified via elemental analyses as described in Section 2.8. Membrane surface morphology was evaluated visually from TEM micrographs. Active layer void fraction was calculated via image analysis of TEM micrographs as described by Lin et al. (2016). Membrane surface roughness and hydrophilicity were quantified using atomic force microscopy (AFM) and water contact angle analyses, respectively. Free-volume hole abundance and size distribution in active layers were characterized using positron annihilation lifetime spectroscopy (PALS) analyses as described by Kim et al. (2005). Water sorption by active layers isolated on quartz crystal microbalance (QCM) sensor was measured in humidified nitrogen gas at 96% relative humidity (RH) as described in Lin et al. (2016). Results reported for physicochemical analyses correspond to the average of two (ATR-FTIR, QCM), three (TEM, AFM), or four (contact angle)

replicate samples. For PALS analyses, reported results correspond to the integrated signal generated from 225 mm² of membrane sample. Additional details about physicochemical characterization procedures and equipment are provided in the Supplementary Material.

2.8. Elemental Composition Analyses

For each sample, the membrane surface (top ~10 nm) elemental composition and active layer bulk elemental composition were obtained via XPS and RBS analyses, respectively. Details of the equipment and analyses settings used for XPS and RBS analyses are in the Supplementary Material. In addition to allowing for the comparison of the elemental compositions of virgin and used membranes, elemental composition results were used to evaluate the effect of membrane use at the water desalination facility on the membrane surface hydroxyl content, membrane surface charge, and bulk active layer charge. Results reported for XPS and RBS analyses correspond to the average of four and three replicate samples, respectively.

For comparison of the elemental composition of the membrane samples, membrane coupons were rinsed with HCl solution at pH=3.5 and NaOH solution at pH=10.3 to remove ionically associated ions, thoroughly rinsed with DDI water, blot-dried with filter paper, and finally air dried overnight. For the evaluation of the membrane surface hydroxyl content, hydroxyl groups were chemically derivatized in gas phase with trifluoroacetic anhydride (TFAA) to form trifluoroacetate as described by Pippig and Sarghini (2009). The elemental composition of the membrane surface before and after TFAA treatment was measured by XPS and used to calculate the surface concentration of hydroxyl oxygen (f'_{F} , atom/atom). The reaction scheme of TFAA with hydroxyl groups as well as the rationale behind the calculation of f'_{F} are described in the Supplementary Material.

For the evaluation of membrane surface charge and bulk active layer charge, negatively ionizable sites in the membrane samples were probed at pH=10.5 using silver ion (Ag^+) and positively ionizable sites were probed at pH=3.8 using tungstate ion (WO_4^{2-}). The measured elemental fractions of silver and tungsten were used to calculate the concentrations of negative and positive sites, respectively. The detailed probing and charge calculation procedures are described in Coronell et al. (2008).

3. RESULTS AND DISCUSSION

3.1. Water Permeability and Solute Rejection

Figure 1 presents the water permeation and solute rejection results for Cl^- , NO_3^- , and H_3BO_3 at pH=6.5 for the virgin and used membranes. The corresponding fitted transport parameters A , B and α are presented in Table 1. The water permeation results show that the specific water permeability coefficient, A , was smaller for the used membrane ($0.12 \pm 0.01 \text{ m.MPa}^{-1}.\text{day}^{-1}$) than the virgin membrane ($0.18 \pm 0.02 \text{ m.MPa}^{-1}.\text{day}^{-1}$), indicating that membrane water productivity decreased after three years of use at the treatment plant. The rejection of the three solutes was also shown to be consistently lower for the used membrane than for the virgin membrane. The modeling results show that both B and α values for all solutes were larger for the used membrane, indicating that the lower solute rejection of the used membrane was due to both an increased permeation of solutes through the polyamide layer by the solution-diffusion mechanism (i.e., higher B values) and a larger amount of nano-scale imperfections in the active layer allowing advective transport to occur (i.e., higher α values). Further, the order of solute rejection ($R_{\text{H}_3\text{BO}_3} < R_{\text{NO}_3^-} < R_{\text{Cl}^-}$) and B values ($B_{\text{H}_3\text{BO}_3} > B_{\text{NO}_3^-} > B_{\text{Cl}^-}$) were the same for both virgin

and used membranes (see Figures 1(b)-1(d)), indicating that membrane use at the treatment plant affected the transport of all solutes in relatively the same manner.

3.2. Membrane Fouling

We evaluated the water flux reduction in virgin and used membranes when challenged with waters containing PAHA to compare their organic fouling propensities. Calcium chloride (CaCl_2) was added to the feed solution because calcium ion (Ca^{2+}) is known to exacerbate organic fouling (Hong and Elimelech, 1997). Figure 2 shows that after two days, a 35% decrease in water flux was observed for the used membrane, compared to 10% for the virgin membrane. It should be mentioned that the fouling cake for the used membrane was likely more compact than that for the virgin membrane because of the higher applied pressure, and this partially contributed to the more severe decrease in water flux for used membranes after 48 hours. However, the used membrane showed a significantly greater water flux decline even during the initial stages of the fouling tests (e.g., the first 6 hours) during which a fouling cake does not exist. It is thus reasonable to conclude that the used membrane was more prone to fouling by PAHA than the virgin membrane. Given that higher surface hydrophobicity and roughness are known to be two critical factors leading to higher organic fouling (Kang and Cao, 2012), the results in Figure 2 suggest that the surface of the used membrane was likely more hydrophobic and/or rougher than that of the virgin membrane.

Overall, the permeation and fouling results (Figures 1 and 2) indicate that membrane use in the treatment plant led to membrane performance deterioration. In the following sections, we characterize the physicochemical properties of the membrane surface and polyamide active layer for virgin and used membranes and summarize these results in Table 1. We present in Table 2

the observed qualitative change (i.e., increased, decreased, none) for each property along with the expected effect that the observed change has on the membrane performance metrics tested (i.e., water permeability, solute rejection, and organic fouling) based on known performance-property relationships from the literature (as discussed in Sections 3.3-3.8). In this manner, Table 2 facilitates the analysis of which physicochemical changes account for the observed membrane performance deterioration.

3.3. Membrane Surface Morphology and Roughness

Cross-sectional TEM images (Figure 3) show that the active layers of both the virgin and used membranes had a ridge-and-valley surface structure, as expected for fully-aromatic polyamide membranes (Petersen, 1993). Visual inspection of the TEM images showed no obvious differences in surface morphology between virgin and used membranes. A comparison of the surface roughness (Table 1), a quantitative descriptor of surface morphology, showed no statistically significant difference (Welch's t-test, 95% confidence level) between virgin (106 ± 13 nm) and used (112 ± 4 nm) membranes. Therefore, the results indicate that surface morphology and roughness did not play an important role in membrane performance changes that resulted from membrane use in the seawater desalination plant.

3.4. Membrane Surface Hydrophilicity and Surface Charge

We evaluated surface hydrophilicity through water contact angle measurements (Table 1). In contrast to surface morphology and roughness results showing no difference between virgin and used membranes, the water contact angles for used membranes ($38 \pm 9^\circ$) were statistically significantly larger than those for virgin membranes ($11 \pm 2^\circ$), indicating that the surface hydrophilicity decreased (i.e., surface hydrophobicity increased) significantly during membrane

use in the desalination plant. The decreased surface hydrophilicity in used membranes is consistent with the decreased water permeability, as higher hydrophilicity is known to correlate with higher water flux (Lee et al., 2011). The lower hydrophilicity in used membranes is also consistent with the higher organic fouling tendency of used membranes as more hydrophilic membrane surfaces generally provide better organic fouling resistance because many foulants such as humic acid are hydrophobic in nature (Al-Amoudi, 2010; Kang 2012).

Changes in surface hydrophilicity may be related to changes in membrane surface charge, and therefore, we estimated the total concentration of ionizable sites at the surfaces of virgin and used membranes (Table 1). The concentration of negatively ionizable sites at the surface of the used membrane (0.028 ± 0.008 M) was statistically significantly larger than at the surface of the virgin membrane (0.005 ± 0.005 M), which is contrary to what would be expected from the lower surface hydrophilicity in the used membrane. However, the larger concentration of surface charges in used membranes is consistent with their higher organic fouling tendency in the presence of Ca^{2+} , as organic foulants such as humic acid are known to associate with negatively charged sites at the membrane surface via divalent ion bridges (Xiang et al., 2014).

3.5. Polyvinyl Alcohol Coating

Given that both the surface hydrophilicity and charge of the used membrane were different from those in the virgin membrane, we assessed the change in PVA concentration at the membrane surfaces by comparing their surface concentrations of hydroxyl oxygen (f'_{F}). Table 1 shows that the surface concentration of hydroxyl oxygen for the used membrane (0.068 ± 0.01 atom/atom) was statistically significantly lower than for the virgin membrane (0.22 ± 0.06 atom/atom), indicating that membrane use in the desalination plant resulted in the degradation and/or

detachment of the PVA coating. This is consistent with the lower surface hydrophilicity and higher surface charge in the used membrane. Therefore, PVA degradation and/or detachment as a result of membrane use in the desalination plant is a contributing factor to the reduced water permeability (through hydrophilicity reduction) and increased organic fouling (through hydrophilicity reduction and increased surface charge) in used membranes.

3.6. Active Layer Thickness, Void Fraction, and Water Sorption

Table 1 presents the thicknesses and void fractions obtained for the PVA-coated active layers of virgin and used membranes. The active layer thickness in the used membrane (108 ± 11 nm) was not statistically significantly different from that in the virgin membrane (88 ± 3 nm). Similarly, there was no statistically significant difference between the void fractions obtained for the used ($23.9 \pm 4.6\%$) and virgin ($27.0 \pm 6.4\%$) membranes. The results thus indicate that membrane use in the desalination plant did not have a significant effect on the thickness or void fraction of the membrane active layers. Combined with the finding above (Section 3.3) that there was no statistically significant difference between virgin and used membranes in terms of the surface morphology and roughness, we conclude that membrane use in the desalination plant did not result in appreciable changes in the physical properties of the active layers at the nanometer scale (i.e., thickness, roughness, void fraction). Therefore, changes in physical properties do not account for the performance deterioration observed in used membranes compared to virgin membranes.

Given that (i) the water permeability coefficient A is proportional to the partition and diffusion coefficients of water in the active layer and inversely proportional to active layer thickness (Urama and Mariñas, 1997), (ii) A was found to be statistically significantly lower in used

membranes (Section 3.1), and (iii) the thicknesses of the active layers of used and virgin membranes were statistically the same (this section), the combined results indicate that water partitioning and/or diffusivity in the active layer of the used membrane was lower than in the virgin membrane. Thus, we evaluated the sorption of water by the polyamide active layers of virgin and used membranes under humidified nitrogen gas at 96% RH (Table 1) and found that the water-to-polymer mass ratio in the active layer of the used membrane (6.8 ± 0.04 wt%) was statistically significantly lower than that in the active layer of the virgin membrane (8.6 ± 0.06 wt%). The water sorption results therefore confirmed that water partitioning was lower in the used membrane than in the virgin membrane. No experimental procedure exists to measure water diffusivity in polyamide active layers.

3.7. Free-Volume Holes and Amide Link Integrity in Active Layers

We studied the free-volume holes in the PVA-coated active layers of virgin and used membranes using PALS (Figure 4 and Table 1). Note that the free-volume holes discussed here correspond to sub-nanometer spaces among polymer chains (Kim et al., 2005), which are different from the voids discussed in Section 3.6 corresponding to cavities in the polymer structure with sizes of a few to over a hundred nanometers (Lin et al., 2016) (see example voids in Figure 3). The probability density distribution (Figure 4) and signal intensities (Table 1) of free-volume holes show that their relative abundance was significantly lower in the active layer of used membranes than in virgin membranes. The results also show that the average free-volume hole radius was larger in the used membrane (0.28 nm) than in the virgin membrane (0.23 nm).

We evaluated whether the changes in abundance and size of free-volume holes were the result of amide link scission in the polyamide active layer, where amide link scission would create free-

volume holes larger than those existing in the original fully-crosslinked polyamide, and lead to partial collapse of the polymer structure, thus reducing the number of free-volume holes. We assessed polyamide link integrity by comparing the concentration of ionizable sites in virgin and used membranes, as pendant ionizable groups are believed to be the main potential products of amide link scission (Do et al., 2012; Powell et al., 2015). Figure 5 presents representative RBS spectra of virgin and used membrane samples probed with Ag^+ for detection of negatively ionizable functional groups. The RBS results (Table 1) indicate that there was no statistically significant difference between the concentration of negatively ionizable sites in used membranes (0.58 ± 0.06 M) and virgin membranes (0.57 ± 0.05 M). Similar analyses were performed for positively ionizable functional groups, but in all cases none or a negligible concentration of positively ionizable sites was detected (see Supplementary Material). Therefore, the results indicate that the decrease in abundance and increase in size of free-volume holes were not the result of amide link scission, but other causes discussed in Section 3.10.

The PALS results (Table 1) indicate that the decrease in abundance of free-volume holes in the active layer of the used membrane (i.e., to approximately a quarter of that in the virgin membrane) was more substantial than the observed increase in hole size (22%). Given that (i) lower abundance of free-volume holes indicates lower availability of free space for water to partition into, and (ii) lower free volume is known to be correlated to lower permeability in polymers (Lee, 1980; Rezac and John, 1998), the free volume results are consistent with the lower water partitioning and flux observed in used membranes. Further, larger free-volume hole size has been associated with lower contaminant rejection both experimentally (Lee, 1980; Kim et al., 2005) and by modelling (Bowen and Welfoot, 2002; Szymczyk and Fievet, 2005), and thus

the observation that the used membrane has a larger free-volume hole size than the virgin membrane is consistent with the lower solute rejection observed in used membranes.

3.8. Halogen Content in the Polyamide Active Layer

3.8.1. Chlorine. Studies have shown that upon free chlorine (HOCl/OCl^-) exposure, polyamide active layers take up chlorine (Cl) at the amidic nitrogen (N -chlorination) and benzene ring adjacent to the amidic nitrogen (ring chlorination) (Kwon and Leckie, 2006; Kang et al., 2007; Do et al., 2012; Powell et al., 2014). Cl uptake results in increased hydrophobicity of the active layer (Kwon and Leckie, 2006) and may result in amide link scission (Soice et al., 2003; Powell et al., 2015). These chemical changes in the polyamide structure lead to membrane performance deterioration, including reduced water flux and salt rejection (Kwon and Leckie, 2006; Kang et al., 2007). Given that (i) the treatment plant from which we obtained the used membrane chlorinates and de-chlorinates the feed water upstream of the membranes, (ii) our contact angle results (Table 1) indicate higher surface hydrophobicity, and (iii) our membrane performance results (Figure 1) showed reduced water flux and solute rejection for the used membrane, it is reasonable to hypothesize that complete de-chlorination of the membrane feed water at the treatment plant was not achieved and thus membrane performance deterioration for the used membrane was due, in part, to Cl uptake and/or amide link scission. Since no amide link scission occurred as a result of membrane use in the treatment plant (Section 3.7), we assessed whether Cl was uptaken by the active layer. Elemental composition results (Table 1) showed that no Cl was present in the membrane active layers, and thus that the membrane performance deterioration observed for used membranes was not the result of Cl uptake in the treatment plant.

3.8.2. *Bromine*. While no Cl content was detected in the virgin or used membranes, a relatively high concentration of bromine (Br) was observed in the polyamide active layer of the used membrane (Table 1). From RBS analyses (Figure 5), the bulk bromine-to-nitrogen ratio in the active layer of the used membrane was Br/N=0.45 ($C_{0.48}H_{0.28}O_{0.11}N_{0.084}Br_{0.038}$). Given that no Br was detected in the virgin membrane, the results indicate that Br uptake occurred at the treatment plant. We hypothesize that Br uptake was the result of the reaction between the polyamide active layer and a bromine-containing oxidant, likely hypobromous acid (HOBr) formed from the reaction between HOCl and Br^- in the feed water. This hypothesis is supported by experimental results (see Supplementary Material) showing that Br uptake did not occur in membrane samples exposed to bromide-containing waters lacking HOCl (i.e., artificial seawater and sodium bromide solutions), which indicates that water chlorination at the treatment plant was an important factor leading to Br uptake by the membrane. The mechanism of HOBr formation, as given by

is well-known and occurs relatively fast (rate constant, $k=1.55-6.84 \times 10^3 \text{ L.mol}^{-1}.\text{sec}^{-1}$ (Liu and Margerum, 2001). Although the concentration of Cl^- in seawater is orders of magnitude higher than that of Br^- (19,000 mg.L^{-1} and 65 mg.L^{-1} , respectively (Snoeyink and Jenkins, 1980)), the ratio of $HOBr/(HOCl+HOBr)$ is 0.996 based on the equilibrium constant of 1.54×10^5 (Liu and Margerum, 2001) for reaction 4, indicating that the dominant hypohalous acid involved in the reaction with the polyamide active layer is HOBr, not HOCl. The hypothesis that Br uptake by the polyamide active layer is the result of the reaction between a bromine-containing oxidant and polyamide is consistent with laboratory studies indicating that such reactions occur (Glaser et al., 1983; Kwon et al., 2011; Valentino et al., 2015). Additional bromine-containing oxidant species

that could form in bromide-containing waters treated with HOCl, and could potentially participate in the bromination of polyamide, are molecular bromine, bromochloramine and monobromamine (Heeb et al., 2014).

To further assess whether Br uptake by the active layer was consistent with HOBr as the reacting bromine-containing species, we evaluated whether the used membrane had bromination products consistent with the expected products of the reaction between HOBr and polyamide. Given that the reaction of amino acids, peptides, and proteins with HOBr is analogous to that with HOCl (Davis, 2011; Sharma, 2013), it is reasonable to assume that the mechanism of Br uptake by polyamide active layers upon exposure to HOBr is analogous to that of Cl uptake upon exposure to HOCl (Figure 6). Briefly, analogous to Cl uptake by aromatic polyamide active layers (Kwon and Leckie, 2006; Kang et al., 2007; Do et al., 2012; Powell et al., 2014), Br uptake should occur at (i) the amidic nitrogen to produce N-brominated amide (Product A), or (ii) the ring adjacent to the amidic nitrogen (Product B) via Orton rearrangement of the bromine at the amidic nitrogen (indirect ring bromination) or direct ring bromination.

We confirmed the presence of N-brominated amide links (Product A) in the active layer of the used membrane via ATR-FTIR analyses (Figure 7). For the used membrane, the peak intensities corresponding to the N-H bond ($1,610\text{ cm}^{-1}$ and $1,541\text{ cm}^{-1}$) were significantly smaller than the corresponding intensities for the virgin membrane, which is consistent with Br uptake at the amidic nitrogen replacing N-H bonds for N-Br. Product A formation is further supported by the shift of the amide I bond peak ($1,663\text{ cm}^{-1}$) to higher frequency ($1,669\text{ cm}^{-1}$), indicating that the hydrogen bonds between C=O and N-H were weakened (Kang et al., 2007). ATR-FTIR analysis does not provide information on the presence/absence of the brominated aromatic ring (Product B) nor can it quantify Product A, and therefore it is unclear whether all Br in the active layer is

accounted for by Product A or is a combination of Products A and B. Based on the Cl uptake literature, we would expect that Product B is formed via Orton rearrangement at acidic and neutral conditions (Powell et al., 2014).

The confirmation of Br uptake at the amidic nitrogen strongly indicates that Br uptake is the result of the reaction between the polyamide active layer and HOBr. Also, as mentioned above, halogen uptake by polyamide active layers leads to increased hydrophobicity of the active layer and membrane performance deterioration, including reduced water flux and salt rejection, all of which are consistent with the physicochemical and performance differences observed between the used and virgin membranes. Therefore, our results and analyses indicate that the use of free chlorine as an upstream disinfectant at the treatment plant resulted in Br uptake by the polyamide active layer, and contributed to performance deterioration in the used membranes compared to the virgin membranes.

3.9. Identification of Primary Physicochemical Changes Leading to Membrane Performance Deterioration

As observed in Table 2 and discussed in the previous sections, the observed decrease in water flux as a result of membrane use in the treatment plant was consistent with the observed decrease in surface hydrophilicity, PVA coating coverage, water sorption by the active layer and free-volume hole abundance, as well as with the increase in Br content in the polyamide active layer. Among these physicochemical property changes, the decrease in surface hydrophilicity is likely a direct consequence of the reduction in PVA coating coverage (because PVA is more hydrophilic than polyamide) and Br uptake by the active layer (because N-bromination reduces hydrogen bonding sites). The decrease in water sorption can be attributed to the decrease in free-

volume hole abundance (because there is less free space for water to partition into) and Br uptake (because it reduces the hydrophilicity of the active layer). Finally, the decrease in free-volume hole abundance can be reasonably attributed to Br uptake due to the corresponding polymer change rearrangement caused by the disruption of inter/intra-chain interactions in the polyamide structure caused by N-halogenation (and potential ring bromination) (Kang et al., 2007). Therefore, the reduction in PVA coating coverage and the uptake of Br by polyamide are the primary factors leading to reduced water flux in used membranes compared to virgin membranes.

Similarly, the observed decrease in contaminant rejection as a result of membrane use in the treatment plant was consistent with the observed decrease in free-volume hole size and increased Br content in the polyamide active layer. As discussed above, the changes observed in free-volume holes can be attributed to the disruption of the polyamide structure caused by halogen uptake, and therefore, Br uptake by polyamide is the primary factor leading to reduced contaminant rejection in used membranes compared to virgin membranes.

With respect to organic fouling, the corresponding increase in fouling observed in the used membrane was consistent with the observed decrease in surface hydrophilicity and PVA coating coverage, and increase in surface charge. As discussed above, the decrease in surface hydrophilicity and increase in surface charge are a direct consequence of the reduction in PVA coating coverage. Therefore, the reduction in PVA coating coverage is the primary factor leading to increased organic fouling in used membranes compared to in virgin membranes.

3.10. Potential Debromination of Amide Links through Alkaline Rinse

It has been reported (Kang et al., 2007; Powell et al., 2014) that N-chlorination of fully-aromatic polyamide is partially reversible, where N-chlorinated amide links can undergo dechlorination with alkaline treatment. The reversibility of N-halogenated amide links could be used as a potential strategy to regenerate the polyamide structure and restore membrane performance during membrane cleaning. We evaluated whether N-bromination was reversible by soaking used membrane samples in ultrapure water adjusted to pH=10.3 with NaOH for two months. ATR-FTIR analyses of used membrane samples with and without alkaline treatment showed that the amidic nitrogen was not regenerated by alkaline solution and thus the N-bromination reaction was not reversible (see Supplementary Material). We also note that the rate constants of N-halogenation reactions for HOBr are approximately 1-2 orders of magnitude larger than for HOCl (Deborde and von Gunten, 2008). Therefore, in water purification plants where free chlorine is a dominant oxidant, irreversible polyamide deterioration likely occurs at a significantly faster rate when the feed water is seawater than when it is fresh or brackish water.

4. CONCLUSIONS

We studied the relationship between the performance change observed in polyamide membranes collected from a seawater desalination plant using free chlorine as an upstream disinfectant and the physicochemical changes observed in the membranes. Overall, our results and analyses support the following main conclusions:

- Membrane performance deterioration (i.e., reduced water flux, reduced contaminant rejection, and increased fouling propensity) occurred as a result of membrane use in the desalination facility

- Bromine uptake by the polyamide active layer and the reduction in PVA coating coverage were the two primary factors leading to membrane performance deterioration; both factors led to reduced water flux; bromine uptake was the primary factor leading to reduced contaminant rejection; and reduction in PVA coating coverage was the primary factor leading to increased organic fouling propensity
- Bromination of amide links is not reversible through alkaline rinse

Our findings indicate that the optimization of membrane materials and processes towards maximizing the stability of the PVA coating and ensuring complete removal of oxidants in the membrane feed waters would minimize membrane performance deterioration in water purification facilities. Our results and conclusions are directly applicable to seawater desalination facilities using free chlorine as an upstream disinfectant and are also of interest to facilities using other chlorine-based disinfectants ahead of the membranes.

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SUPPLEMENTARY MATERIAL

Evidence of the removal of foulant layer layers from the surface of used samples. Additional details on materials and methods. Assessment of importance of concentration polarization in permeation tests. Reaction scheme of TFAA with PVA and rationale behind the definition of f_F° . Detailed PALS results. Evaluation of the concentration of positively ionizable groups in active layers. Evaluation of bromine uptake by membranes exposed to artificial seawater and NaBr solutions in the absence of an oxidant. Evaluation of the reversibility of N-bromination in used membrane samples. Supplementary material related to this manuscript is available free of charge via the Internet at <http://www.sciencedirect.com>.

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Graphical abstract