Abstract

JOSHUA POWELL: Degradation by Free Chlorine of Aromatic Polyamide Active Layers of Thin-Film Composite Membranes

(under the direction of Orlando Coronell)

Polyamide-based thin-film composite membranes are the current technology of choice to meet the growing demand for drinking water desalination applications. One significant drawback to the use of this class of membranes is the high sensitivity of their polyamide active layer to oxidation by free chlorine. The current understanding of the mechanisms of chlorine uptake and eventual polymer degradation that lead to membrane failure has been gained mostly through the quantitative study of the effects of chlorination on molecular model polyamide compounds and membrane surfaces (top ~5 nm) with X-ray photoelectron spectroscopy (XPS), as well as through qualitative analyses of chlorinated membrane samples with attenuated total reflectance-Fourier transformed infrared (ATR-FTIR) spectroscopy. The physico-chemical changes induced by chlorination within the bulk of the active layer, however, have not been characterized by means other than ATR-FTIR, and therefore it has not been confirmed in the literature that the physico-chemical changes observed at the membrane surface are representative of the volume-averaged changes in the active layer, and that the mechanisms that have been proposed as leading to membrane failure based on studies with model compounds are consistent with observations for the bulk region of the active layer.

Accordingly, we exposed a polyamide thin-film composite membrane to free chlorine at a range of concentrations, exposure times and pH values and quantified *in situ* the

volume-averaged kinetics of chlorine uptake and resulting de-polymerization of the polyamide active layer. We performed volume-averaged measurements for the membrane active layer using Rutherford Backscattering Spectrometry (RBS) as an analytical technique. Our results indicate that the trends observed for the kinetics of chlorine uptake into the *bulk* region of the active layer are mostly consistent with the corresponding trends reported in the literature for chlorine uptake into the active layer *surface*. Our results also show that consistent with mechanisms proposed in the literature based on studies with model compounds, chlorine uptake into the bulk region of the active layer can be explained by chlorination of the amidic nitrogen by hypochlorous acid at all pH conditions and ring chlorination. Analysis of chlorine uptake results at acidic conditions indicates that ring chlorination occurs by Orton rearrangement, not direct ring chlorination. We also provide the first measurements of the kinetics of chain scissioning in the active layer as a result of exposure to free chlorine. Our results indicate that de-polymerization of the active layer occurs when the membrane is exposed to alkaline conditions following or during chlorination of the amidic nitrogen. Chain scission of the amide linkage also occurs via a hydrolysis mechanism as is dependent on both exposure to hypochlorous acid and hydroxyl ion. By contrast, ring chlorination does not result in polyamide de-polymerization.

Key Words: reverse osmosis, nanofiltration, polyamide, free chlorine, chain scissioning, ion probing, RBS, charge density, amide N-Cl, ring chlorination

Table of Contents

List of Abbreviations and Symbols vii

List of Figures viii

1. Introduction 1

1.1. Importance of Polyamide-Based Membranes in the Water Treatment Industry 1

1.2. Biofouling and Susceptibility of Polyamide Thin-Film Composite (PA-TFC) Membranes to Free Chlorine 1

1.3 Structure of Polyamide Reverse Osmosis and Nanofiltration Membranes 3

1.4 Changes in Membrane Performance upon Exposure to Free Chlorine and Associated Changes in the Physical and Chemical Properties of Polyamide Active Layers 6

1.5 Mechanisms of Chlorine Uptake by Crosslinked Aromatic Polyamide Active Layers 7

1.6 Mechanisms of Chain Scission in Crosslinked Aromatic Polyamide Active Layers 13

1.7 Mechanisms of Membrane Performance Degradation as a Result of Chlorine Uptake and Chain Scission in the Active Layer 18

1.8 Review of *in Situ* Measurements of the Interaction between Free Chlorine and Polyamide Active Layers 19

1.9 Experimental Motivation 24

2. Materials and Methods 25

2.1 Membranes 25

2.2 Reagents, Chemicals and Solutions 25

2.3 Measuring the Concentration of Free Chlorine 26

2.4 Chlorination Tests 28

2.5 Rinsing Procedure 29

2.6 Quantification of the Concentration of Carboxylic Groups in Active Layers 30

2.7 Rutherford Backscattering Spectrometry (RBS) Analyses 31

3. Results and Discussion 32

3.1 Measuring Chlorine Uptake and Chain Scission in the Polyamide Active Layer 32

3.2 Evaluation of Chlorine Uptake Reversibility upon Alkaline Rinsing 35

3.3 Effect of Total Free Chlorine Concentration on the Uptake of Chlorine into the Bulk Region of Polyamide Active Layers 42

3.4 Effect of pH on the Uptake of Chlorine into the Bulk Region of Polyamide Active Layers 45

3.5 Heterogeneity of Chlorine Uptake into the Active Layer 50

3.6 Chain Scission Dependence on the Hydrolysis Mechanism 53

3.7 The Effect of Total Free Chlorine Concentration on the Chain Scission Potential in the Bulk Region of the Polyamide Active Layer 57

3.8 Effect of pH during Chlorination on Chain Scission Potential in the Bulk Region of the Polyamide Active Layers 60

3.9 Discussion on the Practical Recommendations of Chlorine Damaged Membranes 62

4. Conclusion 64

References 67

Appendix A. 71

List of Abbreviations and Symbols

ATR-FTIR - Attenuated total reflectance Fourier transform infrared spectroscopy

CA - Cellulose acetate

$C_{T,Cl}$ - Total concentration of chlorine species (i.e., HOCl, OCl^- and Cl_2) in solution

$CT_{T,Cl}$ - Total membrane exposure to chlorine calculated as the integral of $C_{T,Cl}$ as a function of time during the time of membrane exposure to the chlorine solution

C_{HOCl} - Concentration of hypochlorous acid (HOCl) in solution

CT_{HOCl} - Total membrane exposure to HOCl calculated as the integral of C_{HOCl} as a function of time during the time of membrane exposure to the chlorine solution

MPD - m-phenylenediamine

NF - Nanofiltration

PA - Polyamide

PSf - Polysulfone

RBS - Rutherford backscattering spectrometry

RO - Reverse osmosis

SBM - Sodium bisulfite

SMBM - Sodium metabisulfite

TFC - Thin-film composite

TMC - Trimesoyl chloride

XPS - X-ray photoelectron spectroscopy

List of Figures

Figure 1. Macroscopic structure of polyamide thin-film composite membrane

Figure 2. Chemical structure of polyamide active layers

Figure 3 (a). Mechanism of amide N-Cl by OCl^-

Figure 3 (b). Mechanism of ring chlorination by the Orton rearrangement

Figure 4 (a). Oxidative chain scission of amide linkages by hypochlorous acid

Figure 4 (b). Hoffman degradation mechanism of chain scission

Figure 4 (c). Hydrolysis mechanism of chain scission

Figure 5 (a). Calibration curve for spectrophotometric measurement of total free chlorine at pH=4

Figure 5 (b). Calibration curve for spectrophotometric measurement of total free chlorine at pH=10

Figure 6. Confirmation of chlorine uptake and chain scission in the AL of SWC4+

Figure 7. The binding nature of chlorine in the AL of SWC4+

Figure 8. Assessing the concentration of reversibly bound chlorine in samples chlorinated at pH = 4 and 10

Figure 9. Quantification of precipitated AgCl in the PSf support resulting from membrane rinsing at pH = 4 and 10

Figure 10. The effect of chlorine concentration on the uptake of free chlorine into the active layer for hypochlorous dominated systems and hypochlorite ion dominated systems

Figure 11. The effect of pH during chlorine exposure on the uptake of chlorine into the active layer as a function of $CT_{T,\,Cl}$ and CT_{HOCl}

Figure 12. The depth heterogeneity of chlorine uptake into the active layer

Figure 13. The dependence of chain scission induction by hydroxyl ion

Figure 14. The effect of chlorine concentration on the chain scission potential of amide linkages in the active layer for hypochlorous acid and hypochorite ion dominated systems

Figure 15. The effect of chlorine pH on the chain scission potential of amide linkages in the active layer

Figure A.1. The effect of chlorine exposure on chlorine uptake and chain scission in PSf support layers

1. Introduction

1.1. Importance of Polyamide-Based Membranes in the Water Treatment Industry

The increasing world population and associated water demand, the increasing scarcity of high-quality fresh water resources, and the increasingly strict water treatment regulations, have made lower-quality water resources (e.g., seawater and effluent wastewater) economically feasible options as drinking water sources[1–3]. Reverse osmosis (RO) and nanofiltration (NF) membranes are arguably the best suited technologies to treat these lower-quality waters as they are able to remove a broad range of contaminants in one treatment step, including salts and small organic molecules[3].

Over the past few decades, the use of RO and NF membranes has increased largely for the desalination of seawater and brackish groundwater. Within this niche, polyamide (PA) thin-film composite (TFC) membranes have gained a majority market share due to their overall more efficient performance in terms of water permeation and salt rejection compared to other options such as cellulose acetate (CA) membranes[4].

1.2. Biofouling and Susceptibility of Polyamide Thin-Film Composite (PA-TFC) Membranes to Free Chlorine

In a membrane water treatment system, it is essential that disinfection occurs before feed water reaches the membrane stages. Without disinfection pretreatment before the membrane stages, viable microorganisms can deposit on the membrane and form biofilms on the membrane surface[5]. The presence of extensive biofilm fouling (i.e., biofouling) can quickly deteriorate membrane performance (i.e., decreased water flux and corresponding higher

operating pressure, as well as need for cleaning), resulting in costly operation and maintenance costs and premature membrane failure[6].

Chlorine is the disinfectant most widely used in water treatment plants, and the most typical form of chlorine is free chlorine (Cl_2/HOCl/OCl^-). Unfortunately, one major weakness of polyamide thin-film composite (PA-TFC) membranes is their sensitivity to oxidative degradation by free chlorine which has received much attention by numerous investigators since the early 1980s[7–9].

In RO/NF membrane treatment facilities where chlorine is used, two approaches are currently employed to minimize membrane degradation by chlorine. The first approach is removing the free chlorine before the water reaches the membrane stages. Removal of free chlorine before the membrane stages is achieved through the application of sodium metabisulfite (SMBS) or sodium bisulfite (SBS)[10,11].

The second approach employed to minimize membrane degradation by chlorine is utilizing chloramines, instead of free chlorine, as the active chlorine species for disinfection[10]. Chloramines have been shown to be much less aggressive on degrading membrane performance[12,13]. However, when chloramines are at chemical equilibrium, there is still some minute concentration of chlorine present as free chlorine. In systems where the presence of free chlorine is significant enough, SMBS or SBS may be added to control free chlorine exposure to the membrane[10,11]. Membrane manufacturers list in corresponding product data sheets a maximum chlorine feed concentration (i.e., reported as chlorine and not free chlorine) to limit rate of degradation of the membrane. For example, the manufacturer of the membrane used in this study recommend a maximum chlorine feed concentration of

<0.1 ppm[14]. Accordingly, understanding the mechanisms by which free chlorine interacts with polyamide thin-film composite membranes and how this interaction leads to membrane failure is essential to the development of more chlorine-tolerant membranes.

1.3 Structure of Polyamide Reverse Osmosis and Nanofiltration Membranes

To understand the causes of performance degradation of polyamide membranes by free chlorine, we start by giving a brief overview of the membrane structure. Thin-film composite polyamide membranes are composed of three distinct layers: a top ultra-thin (~20-200 nm) polyamide active layer supported by a polysulfone porous support (~20-50 μm) which is backed by a polyester fabric (~300 μm) (see Figure 1)[15]. The polyamide active layer is the layer that provides salt rejection properties to the membrane and also the layer that represents the main barrier to water permeation.

Figure 1. Schematic of the structure of polyamide (PA) thin-film composite (TFC) reverse osmosis (RO) membranes.

The polyamide material most commonly used in RO and NF membranes is crosslinked aromatic polyamide produced by interfacial polymerization between *m*-phenylenediamine

(MPD) in aqueous solution and trimesoyl chloride (TMC) in an organic solvent (e.g., hexane)[15]. The membrane is prepared by first soaking the polysulfone support in the aqueous MPD solution whose wetted surface is then interfacially contacted with the TMC organic solution[15]. The reaction between TMC and MPD results in the formation of an ultra-thin cross-linked aromatic polyamide active layer (AL) atop the polysulfone support. The corresponding reaction scheme is presented in Figure 2a.

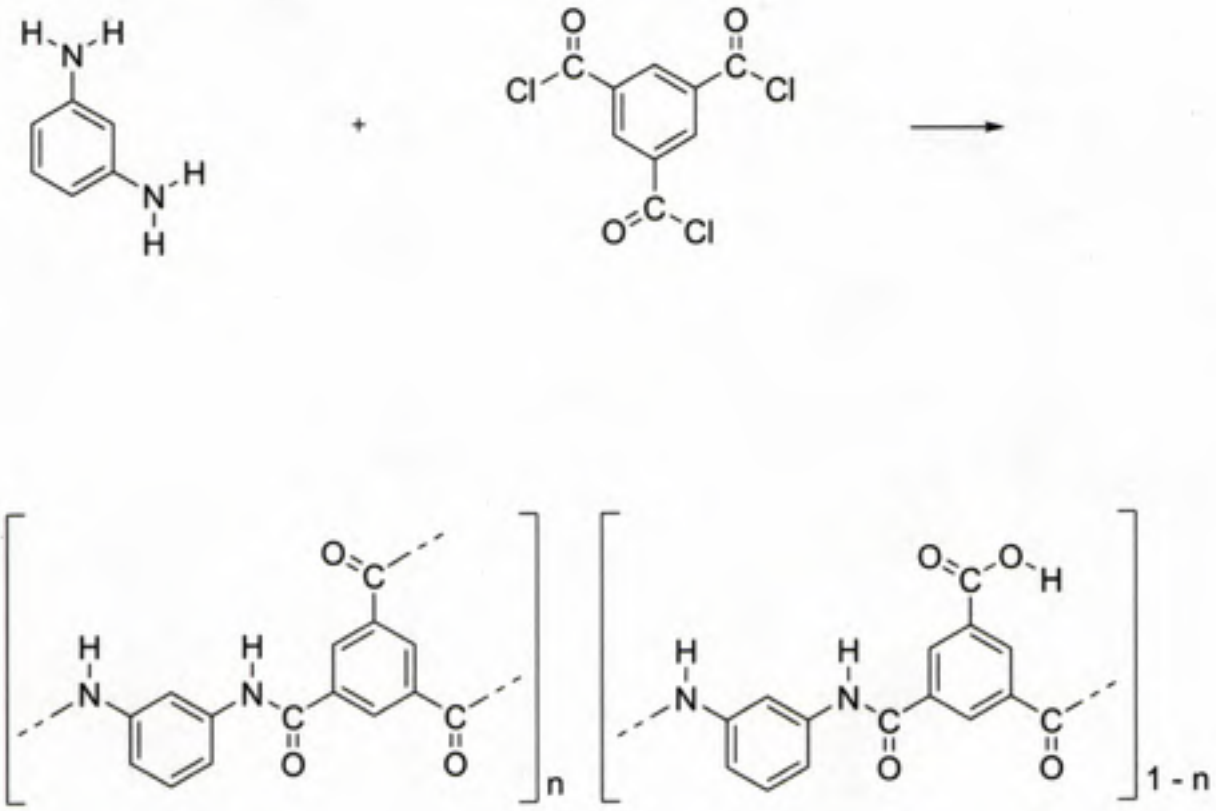


Figure 2 (a). Schematic of the reaction between m-phenylenediamine (MPD) in aqueous solution and trimesoyl chloride (TMC) in organic solvent that results in the formation of cross-linked aromatic polyamide.

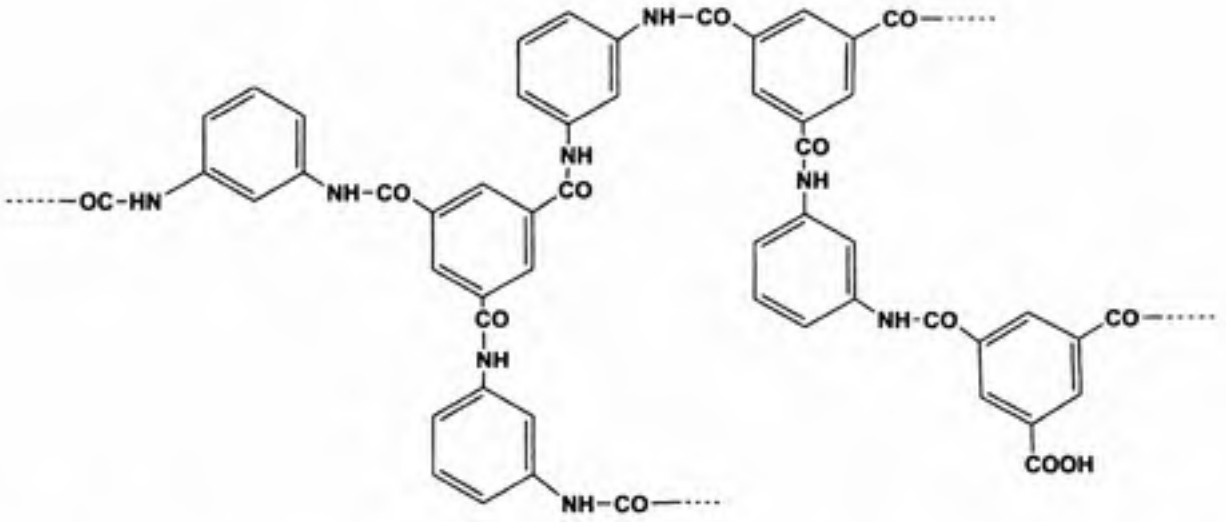


Figure 2 (b). Schematic representation of the molecular structure of crosslinked aromatic polyamide active layers which are characterized by large concentrations of amide linkages and benzene rings with minor amounts for free carboxylate and amine groups.

The general structure of crosslinked aromatic polyamide is presented in Figures 2a and 2b. The figures show that the polyamide layer is composed primarily of benzene rings and amide linkages, where the latter are the result of the reaction between the acyl chloride and amine moieties from the TMC and MPD, respectively. Unreacted acyl chloride moieties hydrolyze and become carboxylic groups in the final polymer structure. Unreacted amine moieties remain as pendant amine groups in the final polymer structure. Given the weak acid-base properties of carboxylic and amine groups, these pendant groups in the polyamide structure provide charge to the membrane, an important property in the exclusion of ionic solutes. More relevant to the present study, given that these pendant carboxylic and amine groups are amide links that did not form during the polymerization reaction, they represent broken links in the polymer structure. A recent study by Coronell *et al.*[16] showed that the concentration of

carboxylic groups in crosslinked aromatic polyamide active layers is about an order of magnitude higher than the corresponding concentration of amine groups.

1.4 Changes in Membrane Performance upon Exposure to Free Chlorine and Associated Changes in the Physical and Chemical Properties of Polyamide Active Layers

Numerous studies have been conducted to characterize changes in the performance (i.e., water flux and salt rejection) of polyamide membranes caused by exposure to free chlorine[9,17–20]. In general, it has been found that upon prolonged chlorine exposure, membranes will eventually have a significant level of increased water flux and decreased salt rejection[13,17,21,22]; however, there have also been studies reporting decreases in membrane water flux and decreased salt rejection after prolonged chlorine exposure[9,17,18,23,24]. Results from studies in which changes in performance are measured are sometimes contradictory, and the degree of change in water flux and salt rejection for a given level of chlorine exposure is not consistent between different studies[20,23].

There are numerous studies that have investigated experimentally the physical and chemical changes that occur in the polyamide active layer as a result of exposure to free chlorine, and that accompany membrane performance deterioration. The experimental approaches used in these studies could be grouped in: (i) semi-quantitative studies of the membrane surface (~5 nm) mostly by X-ray photoelectron spectroscopy (XPS), (ii) qualitative studies of changes in the bond signature of the membrane by Fourier transform infrared spectroscopy (FTIR), and (iii) studies using model compounds, instead of the membranes themselves, to gain insight into the mechanisms by which polyamide and chlorine react. The combined body of literature has revealed that changes in membrane performance are correlated to chlorine

uptake by the polyamide active layer and scission of amide links in the polyamide active layer. We present in Sections 1.5 and 1.6 details about the mechanisms proposed in the literature that lead to said chlorine uptake and chain scission, respectively. We then discuss in Section 1.7 the mechanisms by which chlorine uptake and chain scission result in changes of membrane performance. Finally in Section 1.8 we specify what type of studies of chlorine uptake and chain scission have been performed *in situ* on polyamide membranes as opposed to on model compounds.

1.5 Mechanisms of Chlorine Uptake by Crosslinked Aromatic Polyamide Active Layers

1.5.1 Overview of chlorine uptake mechanisms. The uptake of chlorine (Cl) into the polyamide active layer structure has been studied through experiments using model compounds[8,18,25,26]. It has been found that Cl can be uptaken by the polyamide structure at three locations: (i) at the nitrogen in the amide linkages (i.e., amidic nitrogen)[7,8,18,23,25], (ii) at the benzene rings attached to the amidic nitrogen[8,20,25–28], and (iii) at the free amine groups[26]. In the remainder of Section 1.5.1 we present the most important aspects of these three mechanisms, and in Sections 1.5.2-1.5.4 we present further details about each of them.

Chlorine uptake by polyamide active layers partly occurs via chlorination of the amidic nitrogen forming a N-Cl functionality[7,8,18,25]. In acidic conditions, the amide N-Cl functionality can evolve into the chlorination of the benzene rings attached to amidic nitrogen via the Orton rearrangement mechanism[8,25–27]; ring chlorination occurs at the *para* and *ortho* positions. Ring chlorination is also speculated to occur directly (i.e., without the need for previous existence of a chlorinated amidic nitrogen) by reaction of the polyamide structure with aqueous Cl_2 gas[13,20]. Research performed using model compounds, however, has shown that direct ring chlorination is likely negligible under operating conditions used in

water treatment plants, and thus that Orton rearrangement is the ring chlorination mechanism that is relevant for the study of degradation of polyamide membranes by free chlorine[8,26].

Soice *et al.*[26] also showed that amine compounds are much more reactive to chlorine than amide compounds, and therefore that the free amine groups in the polyamide structure also react with free chlorine[26]. Soice *et al.*[26] hypothesized that chlorination of free amine groups may play a role in initial membrane performance loss upon membrane exposure to chlorine, caused by amines reacting to completion before amides do. Given that the concentration of amine groups in polyamide active layers is orders of magnitude lower than the corresponding concentration of amide links or benzene rings[29], chlorination of amine groups is not expected to play a major role in chlorine uptake of membrane performance degradation at extended chlorine exposures.

1.5.2 Chlorination of the amidic nitrogen. This mechanism for chlorination of amidic nitrogen was presented by Hardy and Robson in 1967[30]. The mechanism described by Hardy and Robson was presented in a review paper shown by Barassi *et al.*[25] to help explain the observed amidic N-Cl in polyamide membranes. As depicted in Figure 3a, in this mechanism OCl^- interacts with the O and H atoms of the amide link opening up to nucleophilic attack the OH^- from the coupling of the OCl^- and N-H functionality. The weakly bonded OH^- can be released into the system. The resulting unstable O-chloroimidate will rapidly rearrange to form a bond between the lone pair of electrons on the amidic nitrogen and the Cl atom.

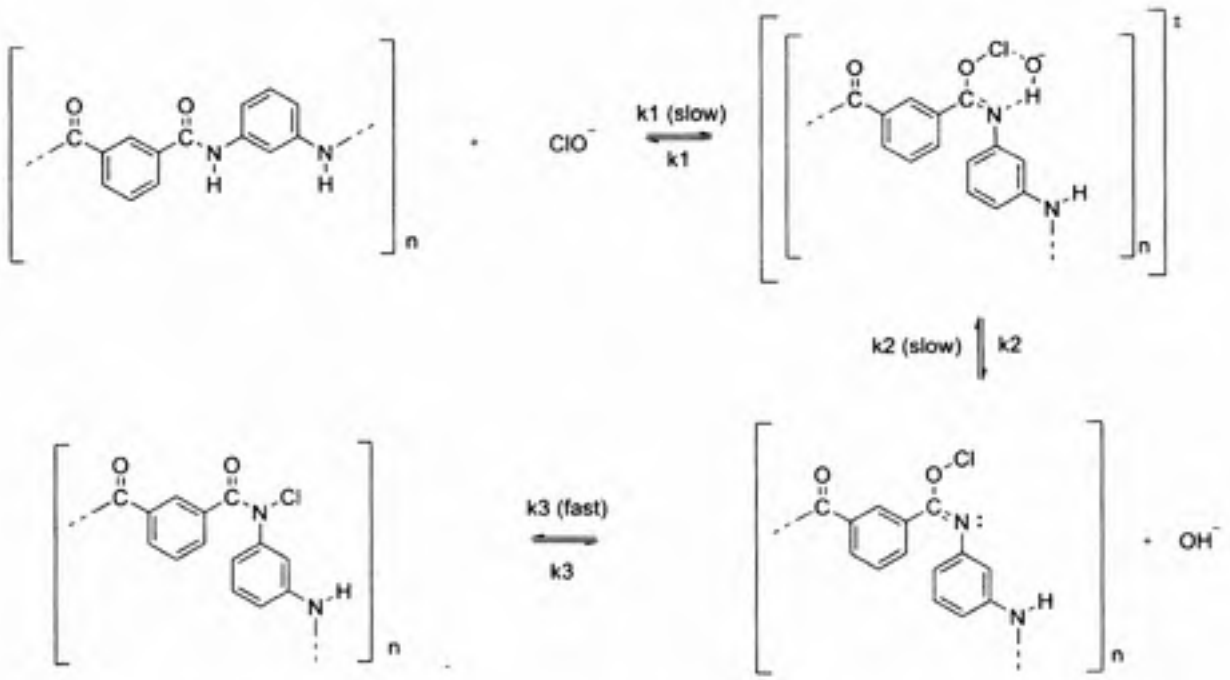


Figure 3 (a). Mechanism of the chlorination of amidic nitrogen in polyamide as presented by Barassi *et al.*[25].

The kinetics proposed by Hardy and Robson in the mechanism described above implies that the amide N-Cl can be reversed back to the N-H utilizing an alkaline rinse[25]. Hardy and Robson[30] observed that amide N-Cl functionalities slowly reacted in alkaline media to generate N-H functionalities. Consistent with this observation, a study by Kang *et al.*[9] showed that upon alkaline rinsing of a chlorinated membrane, the FTIR spectrum of the chlorinated membrane reverted back to a spectrum more similar to that of a virgin membrane. Additionally, after the alkaline rinsing the membrane performance also improved compared to the performance of the chlorinated membrane before the alkaline rinsing. Besides these indirect demonstrations of the reversibility of the chlorination of polyamide active layers, and a study by Kawaguchi and Tamura[8] that showed that N-Cl molecular

compounds could be completely dechlorinated when exposed to a reducing agent, we could not find in the peer-reviewed literature studies that directly quantified chlorination reversibility.

It is important to note that the mechanism described in Figure 3a for chlorine uptake at the amidic nitrogen involves OCl^- as the reactive free chlorine species; however, it has been shown experimentally that the amount of Cl incorporated into the polyamide structure is much higher at acidic conditions where HOCl is the predominant free chlorine species[8,20,26,31,32]. We could not find in the literature a mechanism directly involving HOCl.

1.5.3 Chlorination of the benzene rings bound to amidic nitrogen. The second location at which the polyamide active layers are believed to uptake chlorine are the benzene rings attached to the amidic nitrogen[8,20,21,26]. This type of chlorination is believed to be irreversible. Two mechanisms by which ring chlorination may occur have been proposed. The most widely accepted mechanism in the literature is the Orton rearrangement[21,25–27,33] which was also reviewed by Barassi *et al.*[25] to explain the observed ring chlorination in polyamide membranes (see Figure 3b).

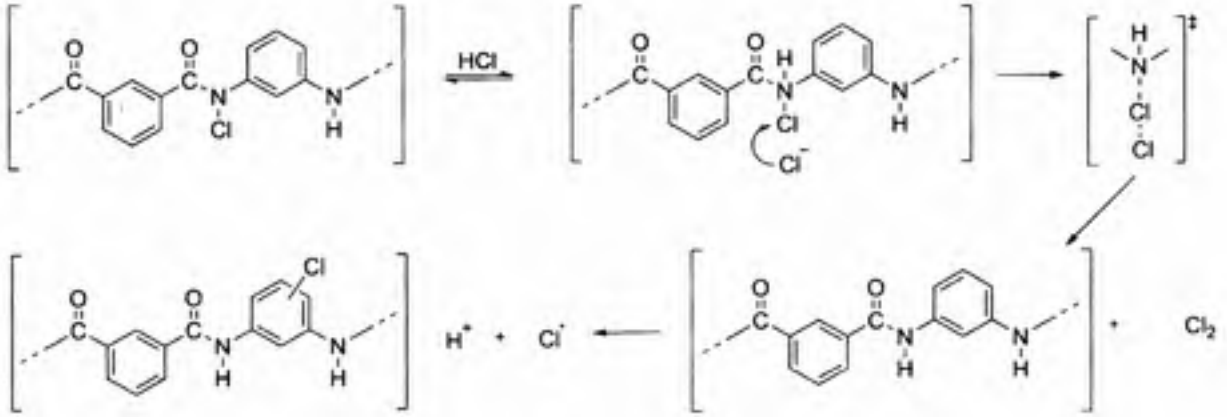


Figure 3 (b). Mechanism of ring chlorination by the Orton Rearrangement mechanism as presented by Barassi *et al.*[25].

The Orton rearrangement requires the initial chlorination of the amidic nitrogen and consists of the intermolecular rearrangement of the N-Cl product in the amide linkage in acidic conditions resulting in the chlorination of the benzene ring attached to the amidic nitrogen. The reaction is initiated by a protonation of the amide N-Cl functionality in acidic conditions. The presence of the additional H on the N-Cl functionality causes an electron withdrawing effect on the N-Cl bond, weakening it. The Cl in the bond becomes positively charged and the bond is opened up to further attack, which occurs from an interaction between the bonded Cl and free Cl^- in solution. The attack results in the formation of Cl_2 gas which can directly rearrange in the membrane and chlorinate the aromatic ring attached to the amidic nitrogen[25]. Glater and Zachariah[28] showed that ring chlorination occurs first at the para position and then, upon further chlorination, at the ortho position.

The other less widely presented mechanism proposed for ring chlorination consists of direct ring chlorination due to exposure to aqueous Cl_2[20,26,28]. It has been speculated that the low

concentrations of Cl_2 in free chlorine solutions at acidic conditions (i.e., pKa = 2.56[34] for the Cl_2/HOCl pair) can directly chlorinate the aromatic rings bound to amidic nitrogen. Direct ring chlorination is thus not dependent on existing chlorinated amidic nitrogen. Kawaguchi and Tamura[8] and Soice *et al.*[26] showed using model compounds that direct ring chlorination is likely less prevalent in polyamide active layers than ring chlorination by Orton rearrangement. The studies showed that ring chlorination is dependent on the presence of a N-H functionality attached to the aromatic ring. When the hydrogen on the N-H functionality was substituted by various other functionalities, little to negligible amounts of N-Cl functionality and ring chlorination were detected upon chlorination. Soice[26] did observe minor amounts of ring chlorination in compounds lacking the N-H functionality; however, the levels of chlorine exposure required to observe ring chlorination in model compounds lacking a N-H functionality in the amide groups were significantly higher than the exposures necessary to cause membrane failure. Since ring chlorination was significant at conditions that cause membrane failure only for compounds with N-H functionalities attached to the aromatic ring, then the results showed that membrane failure caused by ring chlorination on polyamide membranes must be governed by the kinetics of the Orton Rearrangement mechanism[26].

1.5.4 Chlorination of the free amine groups. Soice *et al.*[26] hypothesized that free chlorine can also interact with the free amine groups in the polyamide active layer and even cause the formation of azo compounds that will further increase membrane cross linking. Soice *et al.* explored this mechanism utilizing amine model compounds and found that the amine compounds were much more reactive to free chlorine than amide compounds and yielded the production of various chloramine and azo products. The concentration of free amine groups

in polyamide active layers, however, is about two orders of magnitude or more lower than the concentration of amide links or benzene rings[29]. As a result, compared to chlorination of the amidic nitrogen or ring chlorination, the chlorination of free amine groups likely plays a minor role in total chlorine uptake by the polyamide layer and in changes of membrane performance upon prolonged chlorine exposures.

1.6 Mechanisms of Chain Scission in Crosslinked Aromatic Polyamide Active Layers

1.6.1 Overview of chain scission mechanisms. Polyamide chain scission as a result of membrane chlorination was first proposed by Koo *et al.* in 1985[7]. In this study Koo *et al.* observed by XPS analyses an increase of carbon associated to carboxylic groups in chlorinated membrane samples compared to their non-chlorinated counterparts. While Koo *et al.* did not propose any specific chain scission mechanism other than by oxidative degradation of the polyamide structure by free chlorine, resulting in the formation of additional carboxylic groups in the polymer structure (see Figure 4a), two more detailed mechanisms for chain scission were proposed later on by other researchers: (i) Hoffman degradation[23], and (ii) hydrolysis mechanism[20]. In the remainder of Section 1.6.1 we present the most important aspects of these two mechanisms, and in Sections 1.6.2-1.6.3 we present further details about each of them.

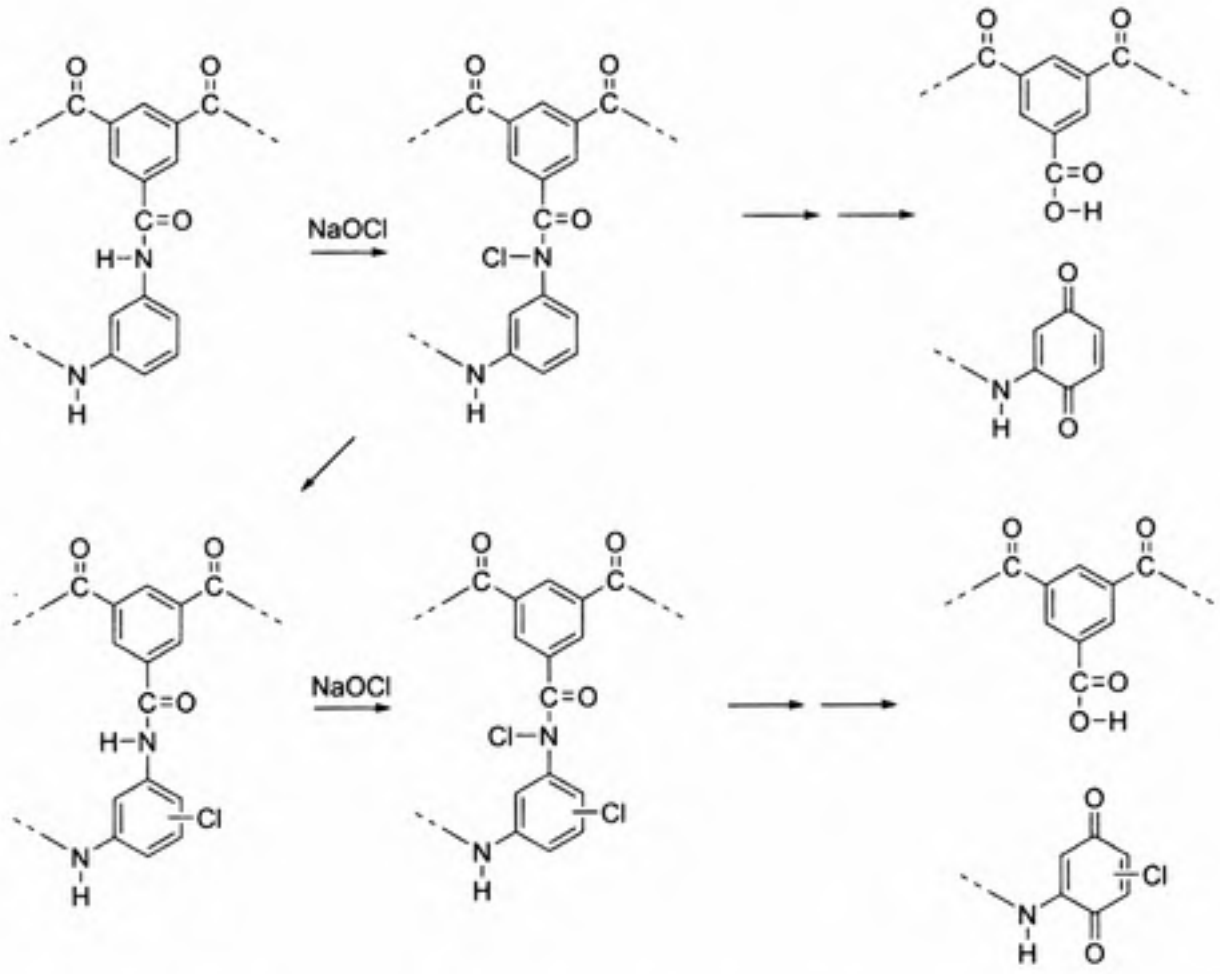


Figure 4 (a). Mechanism of polyamide chain scission by oxidative degradation as presented by Koo *et al.*[7].

Both Hoffman degradation and hydrolysis mechanisms require as a first step the chlorination of amidic nitrogen (see Section 1.5.2) and the presence of hydroxyl ions for subsequent steps in the reactions[20,23]. This is consistent with the observation by Soice *et al.*[26] that chain scission in polyamide model compounds was produced much more readily when they were first exposed to acidic conditions (at which chlorination of the amidic nitrogen is favored, see Section 1.5) and then to alkaline conditions, than in the opposite case. Soice *et al.* proposed

that as a result, membrane performance degradation may occur more readily in systems where chlorination is performed at acidic conditions but cleaned at alkaline conditions; however, membrane performance degradation occurs even under neutral conditions, thus chain scission is probably not the central mechanism of membrane failure.

The Hoffman degradation mechanism predicts the production of additional free amine groups in the polymer structure[23], while the hydrolysis mechanism predicts the production of additional free carboxylic groups[19] in agreement with what was previously proposed by Koo *et al.*[7]. While there is no study available in the literature quantifying the increase of amine or carboxylic groups in polyamide membranes as a result of chlorination, there exist various XPS and FTIR studies which have qualitatively shown that carboxylic groups do increase upon membrane chlorination.

1.6.2 Chain scission by the Hoffman degradation mechanism. The schematic of the Hoffman degradation mechanism for polyamide chain scission is depicted in Figure 4b. The reaction is initiated by the chlorination of the amidic nitrogen (see Section 1.5.2). It is believed that the chlorinated amide link can hydrolyze slowly in alkaline conditions releasing $CO_{2\,(g)}$ and leaving behind an amide N-Cl anion. The N-Cl anion quickly dechlorinates to form nitrene, which undergoes a Hoffman rearrangement to produce isocyanate and eventually a primary amine.

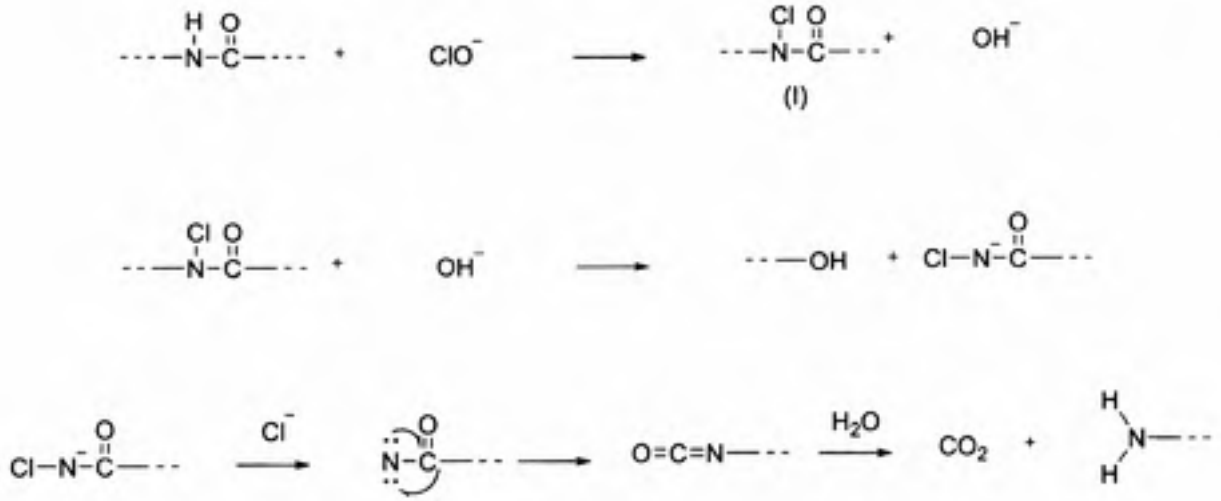


Figure 4 (b). Mechanism of polyamide chain scission by the Hoffman degradation mechanism as presented by Lee *et al.*[23].

Bond scission by this mechanism appears unlikely at usual feed water pH conditions since Hoffman Degradation is favored by alkaline conditions. The validity of the Hoffman Degradation as the primary source of chain scission is also unlikely as the literature has reported an increase in the presence of carboxylic groups in polyamide active layers after exposure to free chlorine in alkaline conditions[7,20], and the Hoffman mechanism does not predict the creation of carboxylic groups but rather of amine groups.

1.6.3 Chain scission by the hydrolysis mechanism. The possible chain scission by hydrolysis of the amide linkage in the active layer structure has come into question because of the stability of amide compounds against hydrolysis at neutral pH conditions[33]. A mechanism to explain the possibility of chain scission by hydrolysis was presented by Do *et al.*[20] and is depicted in Figure 4c.

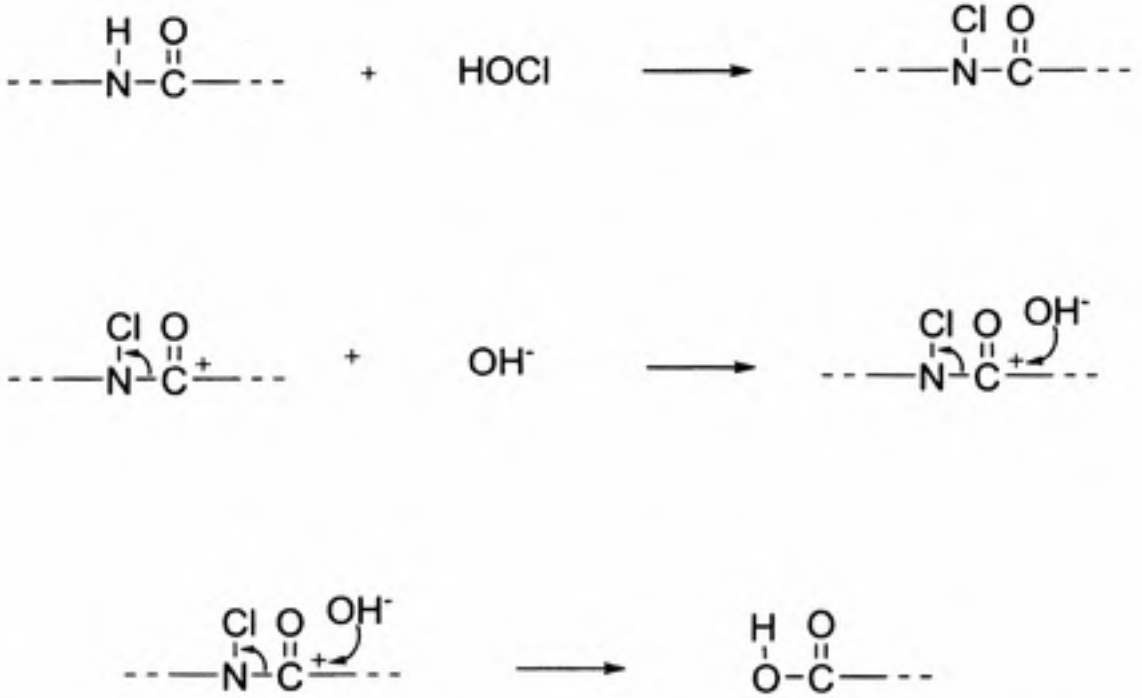


Figure 4 (c). Mechanism of polyamide chain scission by the hydrolysis mechanism as presented by Do *et al.*[20].

The mechanism requires exposure to OH^- after amidic N chlorination has occurred to cause chain scission. HOCl attacks the lone pair of electrons of the amidic nitrogen resulting in amidic nitrogen chlorination (see Section 1.5.2), which weakens the C-N bond in the amide linkage as the shared pair of electrons are drawn to the N atom by the pulling of electrons towards the electronegative Cl now bound to the amidic nitrogen. The withdrawing of electrons from the N-C bond, results in a net positive charge of the C atom which opens the C atom to neuclophilic attack by OH^- to stabilize the positive charge on the carbon. This charge neutralization of the carbon results in further weakening and chain scission of the

amide linkage at the C-N bond, forming a free carboxylate group. However, it has not been explained what happens to the amidic N in the final product of the mechanism.

1.7 Mechanisms of Membrane Performance Degradation as a Result of Chlorine Uptake and Chain Scission in the Active Layer

There are three commonly presented major mechanisms of membrane performance degradation as a result of chlorine uptake and chain scission in the active layer[33]: (i) polymer deformation[17,28], (ii) increased hydrophobicity[20,26,35] and (iii) scission of the amide linkages in the polymer chain[7,18,20]. The polymer deformation mechanism was proposed by Glater and Zacharia[28] based on studies with aramide membranes for which chlorination resulted in ring chlorination but not in chlorination of the amidic nitrogen. The authors hypothesized that upon ring chlorination, the hydrogen bonding structure shifted in the membrane from intermolecular hydrogen-carbonyl oxygen bonding to intramolecular hydrogen chlorine bonding. This change in hydrogen bonding causes an increase of void spaces within the polymer structure which allows for a higher passage of water and solutes through the membrane. The polymer deformation mechanism, however, is only valid for membranes that are weakly cross-linked with hydrogen bonding and not strongly cross-linked with amide linkages[33]. It is believed that the lack of flexibility of the polymer chains of a highly cross-linked polyamide (e.g., the crosslinked aromatic polyamide shown in Figure 2) would most likely not have the rotational freedom to form H-Cl intramolecular bonds.

The mechanism of increased hydrophobicity of the membrane active layer[20,26,35] occurs as Cl is incorporated into the polyamide structure in place of hydrogen. The substitution of Cl in place of H affects the ability of polyamide to hydrogen bond with water. Given that the hydrogen bonding capacity of polyamide is strongly dependent on the N-H functionality of

amide links[26], chlorination of the amidic nitrogen increases the hydrophobicity of the active layer. Soice *et al.*[26] proposed that this increased hydrophobicity leads to extrusion of water from the active layer, irreversible compression of the active layer, and decreased membrane water flux. The mechanism of increased hydrophobicity of polyamide upon chlorination has been proposed to explain the observed lower water flux of polyamide membranes after exposures to free chlorine[20,26,35].

The final mechanism proposed to cause membrane performance degradation is chain scission[33]. The cleavage of amide linkages results in increased water flux and decreased solute rejection due to decreased cross-linking of the polymer structure, and corresponding increased polymer flexibility and opening up of void spaces[7,18,20,23].

1.8 Review of *in Situ* Measurements of the Interaction between Free Chlorine and Polyamide Active Layers

1.8.1 Overview. We present in this section a brief review on what has been reported in the literature for *in situ* measurements (not measurements on model compounds) of various aspects of the interaction between free chlorine and polyamide active layers. We discuss measurements of chlorine uptake (Section 1.8.2) and chain scission (Section 1.8.3), as well as and mechanistic studies of chlorine uptake and chain scission (Section 1.8.4). The majority of the data reported in the literature have been gathered through surface characterization techniques, i.e., XPS, and qualitative FTIR analyses. Verification of the membrane chlorination aspects reviewed in this section, and of the mechanisms discussed in Sections 1.5-1.7, is largely lacking in the literature for the bulk region of the active layer.

1.8.2 In situ measurements of chlorine uptake by polyamide active layers

Chlorine uptake by polyamide active layers has been measured *in situ* in the literature only at the membrane surface (top ~5 nm) using XPS[19,24,31]. We discuss below the two main practical aspects of chlorine uptake by the membranes: chlorine concentration effect, and pH effect.

Effect of chlorine concentration on chlorine uptake by polyamide active layers. Chlorine exposure ($CT_{T,Cl}$) is typically reported as the integral of chlorine concentration and exposure time, usually simplified as the product of total free chlorine concentration ($C_{T,Cl}$) and exposure time (t). This method of quantifying chlorine exposure implies that it is $CT_{T,Cl}$ and not chlorine concentration, $C_{T,Cl}$, or exposure time, t, alone that determines the level of chlorine incorporation into the active layer. Do *et al.*[20] attempted to validate the use of $CT_{T,Cl}$ as a metric of chlorine exposure by chlorinating a polyamide NF membrane at pH = 5 using free chlorine concentrations in the 1-1,000 ppm range and measuring chlorine uptake into the membrane surface using XPS. Total chlorine exposures were in the 1-100,000 ppm·hr range. Do *et al.* concluded that the concentration of chlorine did make a difference in the amount of chlorine incorporated into the active layer surface with higher free chlorine concentrations resulting in higher levels of chlorine incorporation.

Effect of pH on chlorine uptake by polyamide active layers. The relationship between pH and chlorine uptake into the surface of polyamide active layers has been studied using XPS in a number of studies[20,31]. There is agreement in the literature that lower pH values lead to higher levels of chlorine incorporation into the active layer surface[19] and that HOCl is the dominant chlorine species reacting with the membrane[18,24,26]. Kwon and Leckie[31] used XPS

to measure the change in chlorine content in the surface of the active layer at constant levels of total free chlorine exposure and eight different pH values in the 3-10 range. The data showed that as pH decreased, the amount of chlorine incorporated into the surface of the active layer increased. Kwon and Leckie proposed that because at higher pH values there is an increase in both the negative charge of polyamide active layers and the OCl^-:HOCl ratio in solution, then the increased electrostatic repulsion of OCl^- by the membrane leads to a lower level of interaction between the membrane and chlorine. In addition, Ettori *et al.*[24] found, also using XPS, a strong correlation between membrane exposure to HOCl and chlorine uptake into the surface of the active layer which indicated that HOCl (not OCl^-) was the dominant free chlorine species reacting with the membrane.

1.8.3 In situ measurements of chain scission in polyamide active layers. The extent of occurrence of chain scission in polyamide active layers has been studied in a limited manner using XPS and FTIR[7,13,20,24,35]. Typically, researchers look at the changes that occur as a result of chlorination in the signal of the carboxylic carbon in XPS spectra[7] and the peaks corresponding to carboxylic and amide groups in FTIR spectra[13,24,35]. These two approaches are largely qualitative. Do *et al.*[20] tried to be more quantitative by using the ion probing+XPS method reported by Coronell *et al.*[36] for measurement of carboxylic groups in RO/NF membrane active layers. After membrane chlorination, Do *et al.* probed carboxylic groups at pH = 7 using Ca^{2+} as ion probe and evaluated the concentration of Ca^{2+} at the active layer surface using XPS to quantify chain scission as a result of membrane chlorination. Do *et al.* indicated that the Ca^{2+} probing+XPS method at a probing pH of 7 was not sensitive enough to quantify accurately the low levels of Ca^{2+} bound to the active layer. The results obtained for six chlorinated membrane samples, however, seemed to support that

higher chlorine exposure and higher pH values resulted in a larger concentration of calcium bound to the active layer. Do *et al.* recommended careful interpretation of the results and need for more detailed studies both because the calcium content measured in the chlorinated samples (0.1%, 0.3% and 0.8%) was similar to the detection limit of the method (~0.1% [19]) and because of the possibility of nonspecific binding of Ca^{2+} to moieties other than carboxylate groups. No accurate, direct results to measure chain scission in the active layer have been shown. A few studies, however, have shown that upon extensive chlorine exposure signals corresponding to PA active layers completely disappear, implying a complete de-polymerization of the active layer explained by the occurrence of chain scission[20,35].

1.8.4 In situ studies of the mechanisms of chlorine uptake and chain scission in polyamide active layers. Most mechanisms proposed in the literature for chlorine uptake and chain scission in polyamide active layers have been based on studies with model compounds, not on *in situ* measurements in polyamide active layers. The limited attempts to correlate *in situ* results to the mechanisms proposed based on model compounds have been performed based on surface characterization studies with XPS and qualitative studies with FTIR. A review of the literature indicates that there has been little work done to verify that chlorine uptake by the bulk of polyamide active layers is consistent with the mechanisms proposed in the literature based on studies with model compounds, or with chlorine uptake measurements taken for membrane surfaces. The same is true regarding the mechanisms of chain scission. We discuss below some *in situ* measurements in active layers that have been reported in the literature to study the mechanisms of chlorine uptake. The only *in situ* measurements that we

found in the literature studying the mechanisms of chain scission were those discussed in Section 1.8.3.

Chlorine uptake reversibility. One aspect of chlorine uptake by polyamide active layers that has not been thoroughly studied is the possibility of its reversibility. As discussed in Section 1.5, polyamide chlorination at the amidic nitrogen should be at least partially reversible at alkaline conditions[25]according to studies performed with model compounds[30]. While Kang *et al.*[9] showed that upon alkaline exposure of a chlorinated membrane, membrane performance improved and the FTIR spectrum of the chlorinated membrane reverted back to a spectrum similar to that of a virgin membrane, there are no *in situ* studies directly measuring chlorination reversibility in polyamide active layers.

Location (in the polyamide structure) of chlorine uptake. As discussed in Section 1.5, studies with model compounds have shown that chlorine uptake occurs at the amidic nitrogen and at the benzene rings[8]. Some insight into the reactive sites for chorine in the PA network has been *qualitatively* shown with FTIR[37]. Changes in peaks associated with inter-chain hydrogen bonding have been observed and speculated to occur because of chlorination of the amidic N followed by subsequent breaking of inter-chain hydrogen bonding that was formed via interactions of the neighboring amide link N-H- - - O=C bonds within the polymer network[37]. It has also been proposed that ring chlorination may occur by two different mechanisms: direct ring chlorination[20,28] and Orton rearrangement[8,26]. However, there are no *in situ* studies evaluating these different mechanisms for the bulk of the active layer. The closest related *in situ* study is that by Do *et al.*,[20] who measured chlorine uptake as a function of HOCl exposure as CT_{HOCl} and noticed a larger chlorine uptake on the active layer surface for samples chlorinated in acidic conditions. Do *et al.* proposed that, consistent with studies

with model compounds[26], at acidic conditions ring chlorination occurred in addition to chlorination of the amidic nitrogen. Do *et al.* speculated that ring chlorination might have occurred as a result of direct ring chlorination via interactions with minute amounts of Cl_2 in solution; however, this was not proven experimentally.

1.9 Experimental Motivation

From the critical review above of the existing body of literature on the chlorination of polyamide membranes, it is clear that most information about chlorine uptake, chain scission and related mechanisms has been gathered through studies using model compounds or studies of the surface (top ~5 nm) of the polyamide active layer. As a result, very little quantitative data have been reported about the interactions between free chlorine and the bulk of the polyamide active layer. In particular, there is no quantitative information available in the literature on chlorine uptake and chain scission in the bulk of the polyamide active layer. Given the lack of these data, there is also no confirmation of whether chlorine uptake and chain scission in the bulk of the active layer are consistent with the relevant mechanisms proposed in the literature. Accordingly, in this study we present for the polyamide active layer of a seawater reverse osmosis membrane: (i) quantitative data on the volume-averaged uptake of chlorine at a wide range of chlorine exposure and pH conditions, (ii) volume-average chain scission results at these conditions, (iii) discussion of whether these results support or not polyamide chlorination and chain scission mechanisms proposed in the literature, (iv) quantification of the level of reversibility of chlorine uptake by polyamide active layers, and (v) additional insights into the mechanisms of membrane failure. This study is the first to provide quantitative results on the interaction between free chlorine and the bulk of polyamide active layers.

2. Materials and Methods

2.1 Membranes

Experiments were performed with samples of the thin-film composite SWC4+ RO membrane (Hydranautics/Nitto Denko Corporation, Oceanside, CA) which has a polyamide active layer. Membrane samples were obtained by cutting 2.5 x 5.0 cm^2 coupons from a spiral-wound element obtained from the manufacturer. Coupons were thoroughly rinsed with ultrapure water and then soaked also in ultrapure water overnight at least three times before storing in ultrapure water until use.

2.2 Reagents, Chemicals and Solutions

Reagent grade ~5% w/w sodium hypochlorite (NaOCl, Fisher Scientific USA, Pittsburg, PA), 12.1 N hydrochloric acid (HCl, Fisher Scientific USA, Pittsburg, PA), ACS grade granular sodium hydroxide (NaOH, Mallinckrodt Baker, Inc, Paris, Ky), 15.8 N nitric acid (HNO_3, Fisher Scientific USA, Pittsburg, PA) and granular silver nitrate ($AgNO_3$, Fisher Scientific USA, Pittsburg, PA) were purchased from Fisher Scientific (Hampton, NH). All solutions were prepared using ultrapure water (18 MΩ·cm) produced using a Dracor Water System (Durham, NC) water purification system. All procedures were performed at room temperature (20±1°C).

The NaOCl stock was diluted with ultrapure water to produce the NaOCl solutions used in membrane chlorination procedures. Chlorine solutions were prepared with concentrations of ≈75 $mg \cdot L^{-1}$, ≈750 $mg \cdot L^{-1}$ and ≈7,500 $mg \cdot L^{-1}$ as Cl_2 and their pH was adjusted to values of 4, 5, 7.5 and 10 using HCl and NaOH. All chlorine solutions were contained in glassware covered in aluminum foil to minimize the photo-degradation of free chlorine.

2.3 Measuring the Concentration of Free Chlorine

The concentration of total free chlorine ($HOCl/OCl^-/Cl_2$) in solution was measured by spectrophotometric analyses at a wavelength of 292 nm using calibration curves prepared as described below[38]. The concentration of total free chlorine in the stock solution (~51,400 mg/L as Cl_2) was measured using a standard iodometric method[39]. Standard solutions with concentrations in the 20-1,000 ppm range were prepared by dilution of the stock solution to generate the calibration curves for spectrophotometric analyses. A calibration curve for free chlorine concentration at pH = 4 was generated by adjusting the pH of the standard solutions to pH = 4, measuring their absorbance at 292 nm, and plotting the absorbance values as a function of concentration (see Figure 5a). This curve had a linear range for measuring total free chlorine at pH 4 for concentrations between 0 - 1,000 ppm. A similar method was used to produce a calibration curve for free chlorine at pH=10 by adjusting the pH of the standard solutions to pH = 10 (see Figure 5b). This calibration curve had a linear range of about 0 - 100 ppm. The pH of samples whose pH was different from pH = 4 or 10 was adjusted to pH = 4 or 10 for determination of their chlorine concentration.

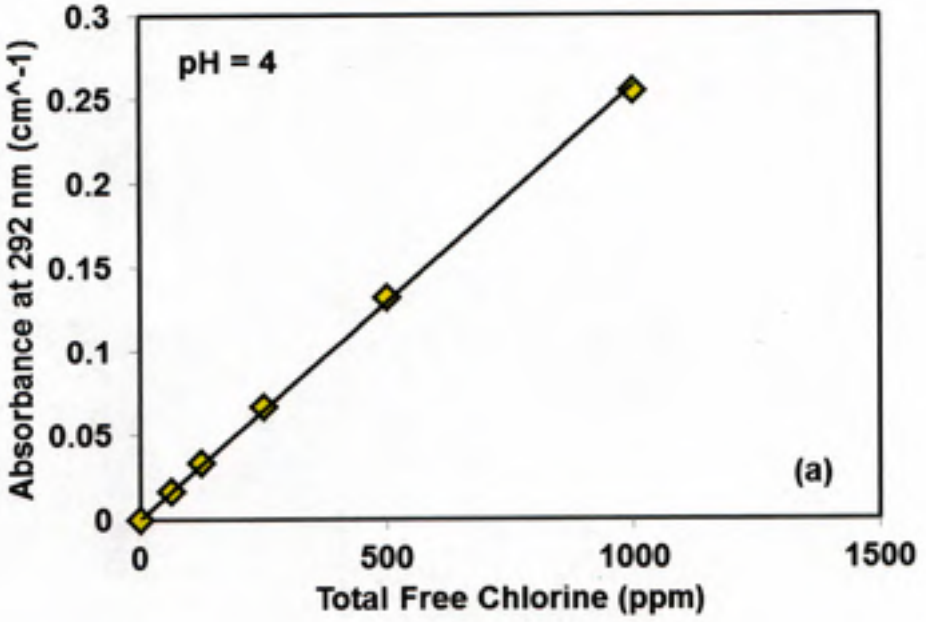


Figure 5 (a). Calibration curve for determining the concentration of total free chlorine at pH = 4 in NaOCl solutions. The slope is equal to 2.63×10^{-4} $ppm^{-1} \cdot cm^{-1}$.

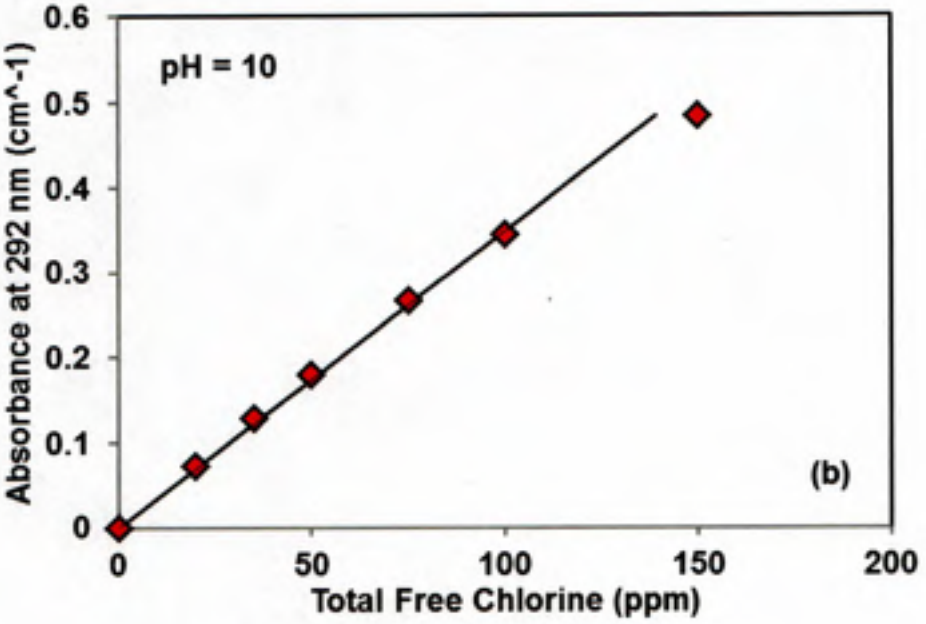


Figure 5 (b). Calibration curve for determining the concentration of total free chlorine at pH = 10 in NaOCl solutions. The slope of the linear segment is equal to 3.48×10^{-3} $ppm^{-1} \cdot cm^{-1}$.

It was assumed that the concentration of HOCl and OCl^- measured at pH = 4 and 10, respectively, were equal to the total concentration of free chlorine, $C_{T,Cl}$, as the pK_a of the HOCl/OCl^- system is pK_a = 7.50 at 20°C[40].

The free chlorine concentration in test solutions was measured spectrophotometrically by adjusting the pH to 4 or 10 and using the appropriate calibration curve. In cases where the total free chlorine concentration in a sample was determined to fall outside of the linear range of the calibration curves, the sample was diluted with ultrapure water at the same pH as the solution to a concentration within the linear range of the calibration curves. The total free chlorine in the diluted samples were then determined spectrophotometrically as described above and corrected by the dilution factor.

2.4 Chlorination Tests

It is important to note that the chlorine concentrations used in this study are much higher than those that would be observed in membrane water treatment plants. Concentrations of free chlorine in the feed to the membrane during desalination would be expected to be below the limit specified by the manufacturer (0.1 ppm) over the lifetime of the membrane, which could be up to 10 years[14]. However, to study the effects of free chlorine on the membrane, rapid aging tests are typically used where free chlorine concentrations can be orders of magnitude higher to allow for shorter exposure times and reasonably feasible laboratory protocols.

Membrane coupons were exposed to chlorine solutions in amber bottles kept at static, non-mixing conditions. The following combinations of pH and total chlorine concentration in solution were used: (i) pH 4 and 75 mg·L^{-1}, 750 mg·L^{-1} and 7,500 mg·L^{-1} as Cl_2; (ii) pH 5

and 750 mg·L^{-1} as Cl_2; (iii) pH 7.5 and 750 mg·L^{-1} as Cl_2; and (i) pH 10 and 75 mg·L^{-1}, 750 mg·L^{-1} and 7,500 mg·L^{-1} as Cl_2. Membrane exposure to chlorine ($CT_{T,Cl}$ (mg·L^{-1}·hr)) was calculated as the integral under the curve of total chlorine concentration ($C_{T,Cl}$) versus contact time (t) (i.e., $CT_{T,Cl} = \int C_{T,Cl}\, dt$). Chlorine exposures in the 0-75,000 mg·L^{-1}·hr range were used. Membrane exposure to chlorine was also calculated in terms of exposure to only hypochlorous acid (CT_{HOCl} (mg·L^{-1}·hr)) as the integral under the curve of HOCl concentration (C_{HOCl}) versus contact time (t) (i.e., $CT_{HOCl} = \int C_{HOCl}\, dt$). To calculate $CT_{T,Cl}$ and CT_{HOCl}, the total chlorine concentration and pH of the solutions were monitored as a function of time, and the $pK_a = 7.50$[40] of hypochlorous acid was used.

2.5 Rinsing Procedure

In general, once membrane coupons were taken out of the chlorine solution at the corresponding target exposure time, the coupons were thoroughly rinsed using ultrapure water (~25 minutes) followed by 0.1 M $NaNO_3$ at pH = 10 (~10 minutes), rinsed again thoroughly with ultrapure water (~10 minutes), and rinsed with and stored in 0.1 M $NaNO_3$ at pH = 10 for ~10 hours. Finally, the samples were thoroughly rinsed again with ultrapure water (~25 min) before further use. The 0.1 M $NaNO_3$ at pH =10 rinsing/soaking solution was used to rid the membrane of any remaining ionically bound chloride or reversibly bound Cl that could result in silver precipitation during the silver probing procedure described below. The silver probing procedure was used to quantify the total concentration of carboxylic groups in the polyamide structure and to gain insight into the kinetics of chain scission and its dependence on exposure to hydroxyl ion. In addition to using 0.1 M $NaNO_3$ at pH = 10 as a rinsing/soaking solution, additional rinsing/soaking solutions were used for various purposes as follows: (i) ultrapure water at pH ≈ 5.5 rinsing only to provide a baseline

for comparing other rinsing procedures; (ii) 0.1 M $NaNO_3$ at pH = 4 to determine total amount of chlorine present in the membrane prior to release of reversibly bound chlorine; and (iii) 0.1 M $NaNO_3$ at pH = 5.5 to confirm that reversibly bound chlorine was in fact covalently bonded and not ionically bonded chloride and also to determine the effects of pH induced chain scission.

2.6 Quantification of the Concentration of Carboxylic Groups in Active Layers

The concentration of carboxylic groups in active layers of membrane samples was measured to evaluate the extent of chain scission by comparing the concentration of carboxylic groups in chlorinated and non-chlorinated samples. The concentration of carboxylic groups was measured using the methods reported previously by Coronell *et al.*[16,29] with some modifications. In brief, the method consists on probing carboxylic groups with silver ions (Ag^+) and quantifying the silver content in the active layer using Rutherford backscattering spectrometry (RBS) analysis (see Section 2.7). Since there is a 1:1 correspondence between Ag^+ and ionized carboxylic groups (R–COO–), then the concentration of silver in the active layer is equal to the concentration of carboxylic groups when samples are prepared at pH conditions (pH≈10.5) at which carboxylic groups are fully ionized.

Silver nitrate ($AgNO_3$) solutions at concentrations in the 2×10^{-6}-10^{-3} M range were used during ion probing procedures. All solutions were prepared in 1L batches in glassware covered with aluminum foil and using ultrapure water. The pH of $AgNO_3$ solutions was adjusted using 0.1 M NaOH and 0.1 M HNO_3. To probe carboxylic groups with Ag^+, membrane samples were immersed in $AgNO_3$ as follows: once for > 10 minutes in 10^{-3} M $AgNO_3$, twice in 10^{-5} M $AgNO_3$ at pH ≈ 9.85 (+/- 0.10), and three times in 2×10^{-6} M $AgNO_3$

at pH ≈ 10.50. The silver concentration was always kept well below the solubility limit to avoid silver precipitation[41]. Probed samples were dried between two Whatman Qualitative Grade filter papers by applying fingertip pressure. Samples were stored in petri dishes open to the atmosphere overnight to allow for air drying before RBS analyses. All procedures involving silver were performed in a dark room under dim red light to prevent photo-induced silver precipitation.

2.7 Rutherford Backscattering Spectrometry (RBS) Analyses

Membrane samples were analyzed with RBS to determine the chlorine and silver content in membrane active layers. The RBS analyses were performed at the Triangle Universities Nuclear Laboratory (TUNL, Durham, NC). RBS analyses were performed at room temperature with a 2-MeV He^+ beam generated with a tandem Van de Graaff accelerator (High Voltage Engineering Corporation, Burlington, MA). A dedicated target system for analyses of polymeric membrane samples was used for semi-automatic rastering of the membrane sample surface with the He^+ beam. Further details about the target system can be found elsewhere[42]. The incident angle (i.e., angle between the incident beam and the normal to the sample surface), exit angle (i.e., angle between backscattered beam and the normal to the sample surface), and scattering angle (i.e., the angle between incident and backscattered beam) were set at 22.5°, 42.5°, and 160°, respectively. To avoid membrane damage caused by beam irradiation, the He fluence over any spot of the membrane sample was kept below 1×10^{14} He/cm^2, which is lower than the damage threshold of 3×10^{14} He/cm^2 reported by Mi *et al.*[43] for the polysulfone support. The total area scanned over any given sample was about 400 mm^2 and an average beam current in the 50-75 nA range was used for analyses. Samples were analyzed until a minimum of 100 particle counts were collected for energy channels

corresponding to the sulfur plateau of the polysulfone support. The commercial computer simulation software SIMNRA v 6.06[44] was used to analyze RBS spectra. More extensive details about RBS analysis and analysis of RBS spectra can be found elsewhere[16,45].

3. Results and Discussion

3.1 Measuring Chlorine Uptake and Chain Scission in the Polyamide Active Layer

Figure 6 compares the RBS spectra of SWC4+ membrane samples before and after chlorination. The chlorinated sample had been subjected to a total chlorine exposure of $CT_{T,Cl}$ = 7,500 ppm-hr using a solution at a pH = 4 with a total chlorine concentration of $C_{T,Cl}$ = 750 mg/L as Cl_2. The main elements composing the polyamide active layer (C, O, N) and polysulfone support layers (C, O, S), except hydrogen, can be clearly identified in the spectra. The isolated peaks at the far right of the spectra correspond to the silver used to probe the carboxylic groups of the membrane samples. Figure 6 shows that the chlorine content (6.90% atom/atom) and silver content (0.50% atom/atom) in the spectrum from the sample exposed to free chlorine are much larger than the corresponding chlorine content (0.05% atom/atom) and silver content (0.073% atom/atom) in the spectrum from the sample that was not exposed to chlorine.

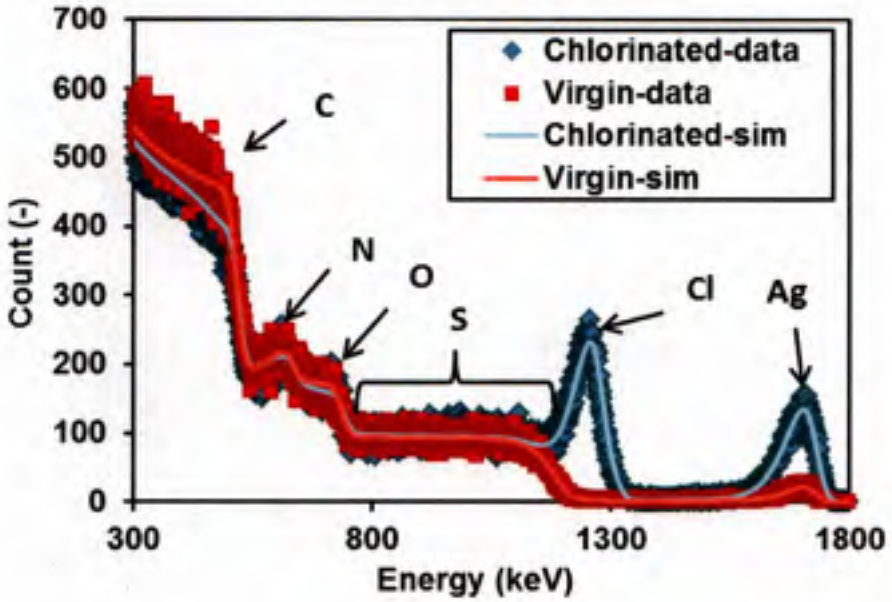


Figure 6. Representative RBS spectra showing peaks for chlorine (Cl) and silver (Ag) within the active layer of virgin and chlorinated SWC4+ membrane samples. The chlorinated sample was chlorinated to a total chlorine exposure of 7,500 ppm*hr with 750 ppm of chlorine at pH=4. After chlorination, the sample was rinsed with ultrapure water followed by 0.1 M $NaNO_3$ at pH = 10. Experimental data are shown as symbols and SIMNRA simulations of the RBS spectra are shown as continuous lines. The chlorine content and silver content for the virgin membrane are 0.05% atom/atom and 0.073% atom/atom, respectively. The chlorine content and silver content for the sample exposed to free chlorine are 6.9% atom/atom and 0.50% atom/atom, respectively.

The increases in chlorine content and silver probe content in the active layer of the membrane after chlorination is consistent with chlorine uptake and chain scission resulting in an increase in carboxylic groups in the polyamide active layer. Samples of the polysulfone

support were also chlorinated, rinsed and probed in the same manner as the polyamide membranes, and no evidence of chlorine uptake or silver binding during the silver probing procedure was observed (see Figure A.1 in Appendix A). This is in agreement with the previously reported chemical stability of polysulfone-based membranes against attack by free-chlorine[20,46]. The results in Figure 6 (and Figure A.1 in Appendix A) indicate that chlorine uptake and chain scission resulting in formation of carboxylic groups in polyamide active layers can be monitored using RBS and the silver probing+RBS procedure as analytical techniques.

Figure 7 presents the chlorine content measured in membrane samples chlorinated to a total chlorine exposure of up to $CT_{T,Cl} \approx 75{,}000$ ppm·hr at pH = 4. The figure compares the chlorine content measured in samples rinsed with ultrapure water only and in samples rinsed with 0.1 M $NaNO_3$ at pH = 4. Rinsing with $NaNO_3$ at pH = 4 allowed for the evaluation of whether some of the chlorine detected in the samples rinsed with ultrapure water corresponded to ionically bound chloride (Cl^-). If there were a significant amount of Cl^- in the membrane, the NO_3^- from the rinsing solution would replace it by ion exchange and thus result in a chlorine content lower than that measured in samples rinsed with ultrapure water only. Figure 7 clearly shows that the chlorine content measured in samples rinsed with ultrapure water and samples rinsed with $NaNO_3$ was approximately the same, and thus that any ionically bound Cl^- remaining in the membrane samples after any of the rinsing procedures is negligible compared to the extent of chlorine uptake. Furthermore, the results in Figure 7 indicate that the chlorine content measured during RBS analyses corresponds to chlorine covalently bound to the polyamide structure as a result of the reaction with free chlorine in solution.

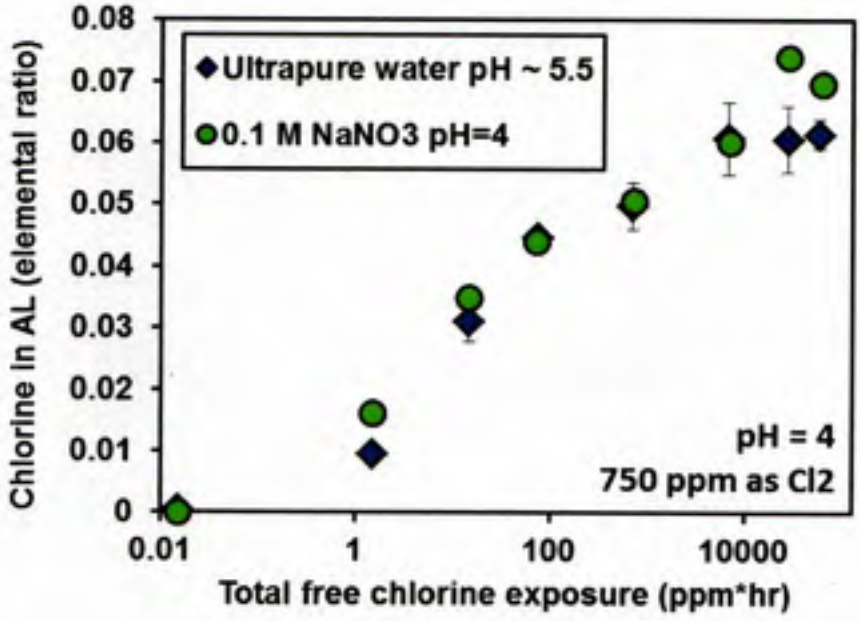


Figure 7. Chlorine uptake into the polyamide active layer (AL) of SWC4+ RO membrane samples as a function of total chlorine exposure. All samples were chlorinated at pH = 4 with $C_{T,Cl}$ = 750 ppm for $CT_{T,Cl}$ = 0-75,000 ppm·hr. Samples were rinsed with (i) ultrapure water at pH ≈ 5.5, and (ii) ultrapure water followed by 0.1 M $NaNO_3$ at pH = 4.

3.2 Evaluation of Chlorine Uptake Reversibility upon Alkaline Rinsing

As described in Sections 1.5.2 and 1.8.4, based on studies with model compounds, it has been suggested[25,30] that chlorination of the amidic nitrogen is reversible by alkaline rinsing. Thus, we evaluated whether the chlorine content presented in Figure 7 for the samples chlorinated at pH = 4 and rinsed with ultrapure water only (pH ≈ 5.5) and with 0.1 M $NaNO_3$ at pH = 4 could be released from the membrane by alkaline rinsing. The data presented in Figure 7 as a function of $CT_{T,Cl}$ was re-plotted in Figure 8a as a function of CT_{HOCl} consistent

with our findings presented in Section 3.3 below that chlorine uptake is a function of exposure to HOCl, not to exposure to total free chlorine.

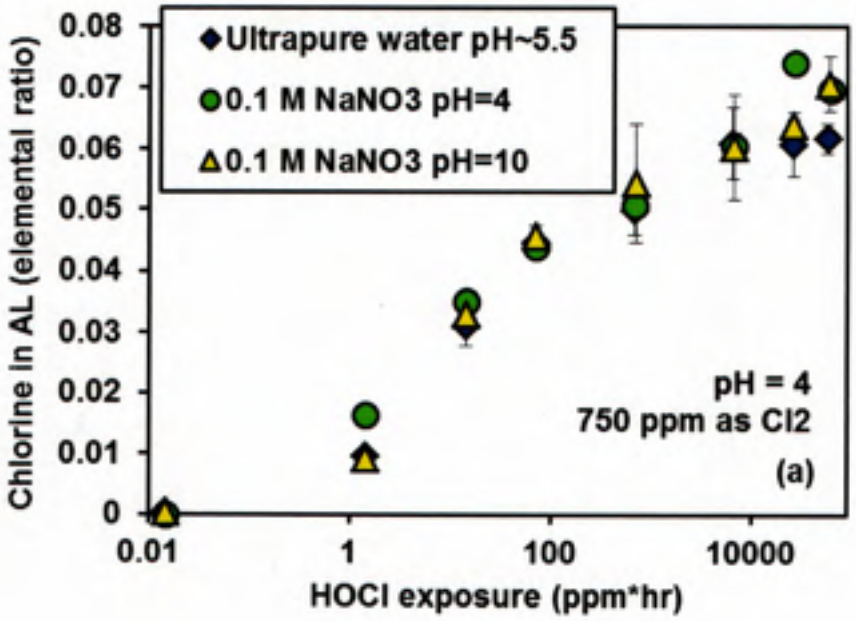


Figure 8a. SWC4+ samples chlorinated at pH = 4 with a $C_{T,\,Cl}$ = 750 ppm for exposures of $CT_{T,\,Cl}$ = 0-75,000 ppm·hr. Samples were rinsed with (i) ultrapure water at pH ≈ 5.5, (ii) 0.1 M $NaNO_3$ at pH = 4 and (iii) 0.1 M $NaNO_3$ at pH = 10. The elemental ratio of chlorine in the active layer was measured with RBS and plotted against CT_{HOCl}.

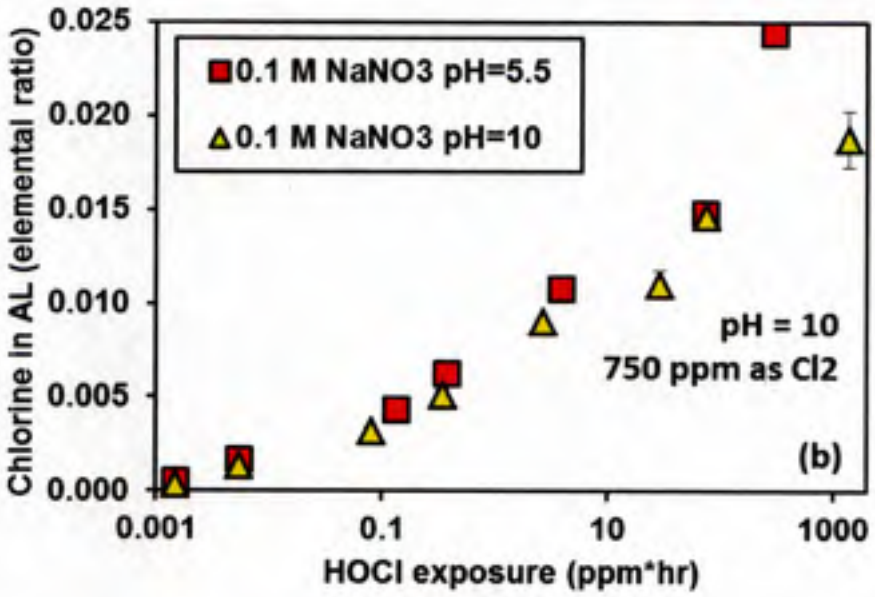


Figure 8b. SWC4+ samples were chlorinated at pH = 10 with a $C_{T,\,Cl}$ = 750 ppm for exposures of $CT_{T,\,Cl}$ = 0-75,000 ppm·hr. Samples were rinsed with 0.1 M $NaNO_3$ at pH ≈ 5.5 and 0.1 M $NaNO_3$ at pH = 10. The elemental ratio of chlorine in the active layer was measured with RBS and plotted against CT_{HOCl}.

The test consisted of rinsing samples chlorinated at pH = 4 with 0.1 M $NaNO_3$ at pH = 10. Figure 8a clearly shows that the chlorine content measured for membrane samples subjected to the same chlorine exposure was approximately the same for samples rinsed at acidic and alkaline conditions. Thus, the results in Figure 8a demonstrate that if chlorine uptake is reversible by alkaline rinsing, the extent of reversibility is negligible compared to the extent of chlorine uptake.

Figure 8b shows that the same trend of similar chlorine content measured for samples rinsed with acidic (0.1 M $NaNO_3$ at pH = 5.5) and alkaline (0.1 M $NaNO_3$ at pH = 10) solutions was

obtained for membrane samples chlorinated at pH = 10. In this case, however, given that chlorination itself was performed at alkaline conditions, no chlorine uptake reversibility was expected. The results in Figures 8a and 8b therefore indicate that the rinsing procedure and pH history of membrane samples after chlorination do not appreciably affect the chlorine content in the polyamide active layer.

While Figure 8 demonstrates that chlorine uptake reversibility upon alkaline rinsing was negligible compared to chlorine uptake, we also demonstrated that some chlorine is indeed released by the membrane when exposed to alkaline conditions after chlorination. Figure 9a presents representative RBS spectra for membrane samples chlorinated at pH = 4 using a $CT_{T,Cl}$ of 7,500 ppm·hr. One of the data sets corresponds to a sample that was rinsed after chlorination with ultrapure water followed by 0.1 M $NaNO_3$ at pH≈5.5 (blue diamonds), and the other data set corresponds to a sample that was rinsed with ultrapure water followed by 0.1 M $NaNO_3$ at pH=10 (yellow triangles). After the rinsing, both samples were subjected to the ion probing procedure described in Section 2.6. For the purpose of this discussion, we focus on the fact that during the ion probing procedure, the membrane samples were immersed in $AgNO_3$ alkaline (pH=10.5) solutions.

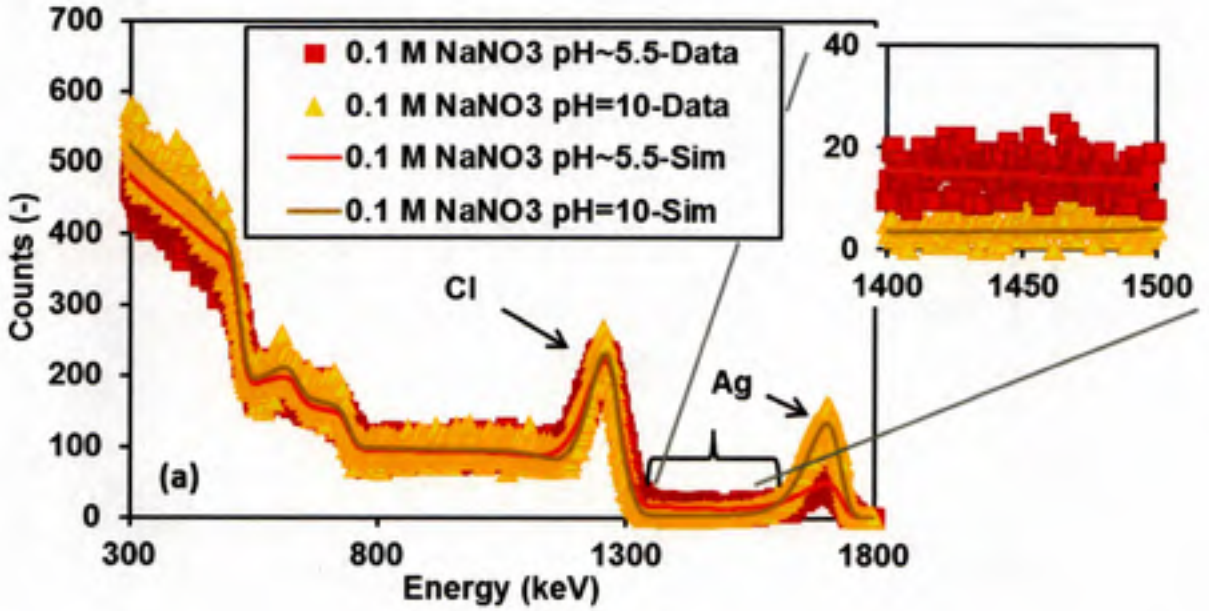


Figure 9 (a). Shown are RBS data collected for samples exposed to $CT_{T,\,Cl}$ = 7,500 ppm·hr with $C_{T,\,Cl}$ = 750 ppm. Data for the Sample rinsed with 0.1 M $NaNO_3$ at pH ≈ 5.5 can be seen as the red square data points and the corresponding fitted SIMNRA simulation is the pink fitted line. Data for the sample rinsed with 0.1 M $NaNO_3$ at pH = 10 can be seen as the yellow triangles and the corresponding fitted SIMNRA simulation is the brown line.

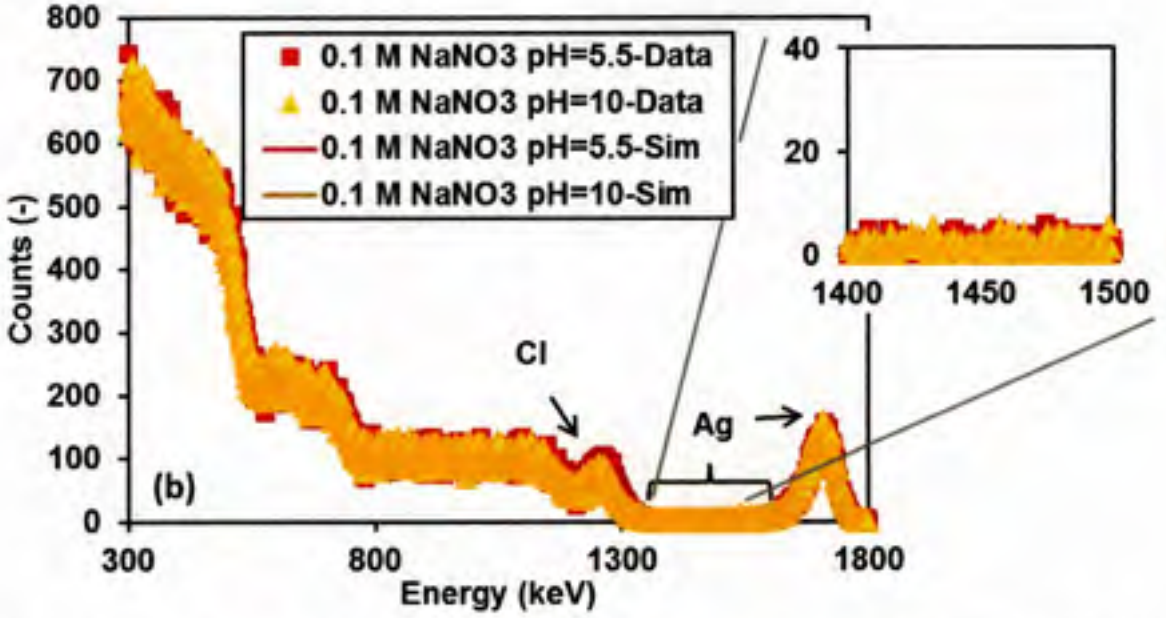


Figure 9 (b). Shown are RBS data collected for samples exposed to $CT_{T,Cl}$ = 75,000 ppm·hr with $C_{T,Cl}$ = 750 ppm. Data for the sample rinsed with 0.1 M $NaNO_3$ at pH ≈ 5.5 can be seen as the red square data points and the corresponding fitted SIMNRA simulation is the red line. Data for the sample rinsed with 0.1 M $NaNO_3$ at pH = 10 can be seen as the yellow triangle data points and the corresponding fitted SIMNRA simulation is the brown line.

Figure 9a shows that the RBS spectrum of the membrane sample that was rinsed with ultrapure water and 0.1 M $NaNO_3$ at pH ≈ 5.5 before the silver probing procedure has a silver content in the polysulfone support much larger than the corresponding silver content in the sample that was rinsed in alkaline solution before the silver probing procedure. This is explained by the insolubility of silver chloride (AgCl) in water as follows. For the sample rinsed with ultrapure water and 0.1 M $NaNO_3$ at pH ≈ 5.5, chlorine is released back into solution while the membrane is immersed in the alkaline $AgNO_3$ solution. As a result, AgCl precipitates inside the membrane and is detected by RBS analysis as silver content within the

polysulfone support. By contrast, for the sample rinsed in alkaline conditions before the silver probing procedure, there is no chlorine released by the membrane while immersed in the alkaline $AgNO_3$ solution. As a result, there is no AgCl precipitation and the silver content measured within the polysulfone support is negligible (≈0.00008 atom/atom). As mentioned in Section 3.1, the RBS spectrum of a polysulfone support sample chlorinated at pH = 4 and subjected to silver probing at pH = 10.5 showed negligible silver content (see Figure A.1 in Appendix A). This indicates that the silver content in the polysulfone support of the samples whose RBS spectra is presented in Figure 9a is not the result of the interaction between chlorine and polysulfone, but rather between chlorine and polyamide.

The peak at the far right of the spectrum of the sample rinsed at alkaline conditions in Figure 9a corresponds to the silver content that neutralizes the carboxylate groups in the polyamide active layer. Further discussion on the total concentration of carboxylic groups measured in chlorinated samples is presented in Sections 3.6-3.8.

Figure 9b shows that for samples chlorinated at alkaline conditions (pH = 10), there was no silver precipitation during the silver probing procedures regardless of whether the samples were rinsed with acidic (0.1 M $NaNO_3$ at pH = 5.5) or alkaline (0.1 M $NaNO_3$ at pH = 10) solutions. Given that for the samples represented in Figure 9b chlorination itself was performed at alkaline conditions, no chlorine release during immersion in the alkaline $AgNO_3$ solution was expected; this is consistent with the absence of detectable silver precipitation in the spectra in Figure 9b.

The results in Figure 9 therefore indicate that while chlorine uptake reversibility is negligible compared to chlorine uptake, there is indeed a minute level of reversibly bound chlorine

when samples are chlorinated at acidic conditions. We estimate that the level of reversibly bound chlorine for samples chlorinated at acidic conditions is ≤6% of the level of chlorine uptake. This estimate is based on the observation that the level of chlorine reversibility is within the experimental error of chlorine measurements (see Figure 8a), and the analysis of the extent of silver precipitation in the polysulfone support for samples rinsed only at acidic conditions before the silver probing procedure.

3.3 Effect of Total Free Chlorine Concentration on the Uptake of Chlorine into the Bulk Region of Polyamide Active Layers

We studied the effect that the concentration of total free chlorine in solution had on the chlorine uptake into the bulk of the active layer. For this purpose, we chlorinated SWC4+ membrane samples to total free chlorine exposures in the $CT_{T,Cl}$ = 0-75,000 ppm·hr range using total free chlorine concentrations of $C_{T,Cl}$ = 75, 750 and 7,500 ppm. Membrane chlorination tests were performed at pH values of 4 and 10 and the corresponding results are presented in Figure 10a and Figure 10b, respectively. The figures show the chlorine elemental ratio observed in the active layer as a function of $CT_{T,Cl}$.

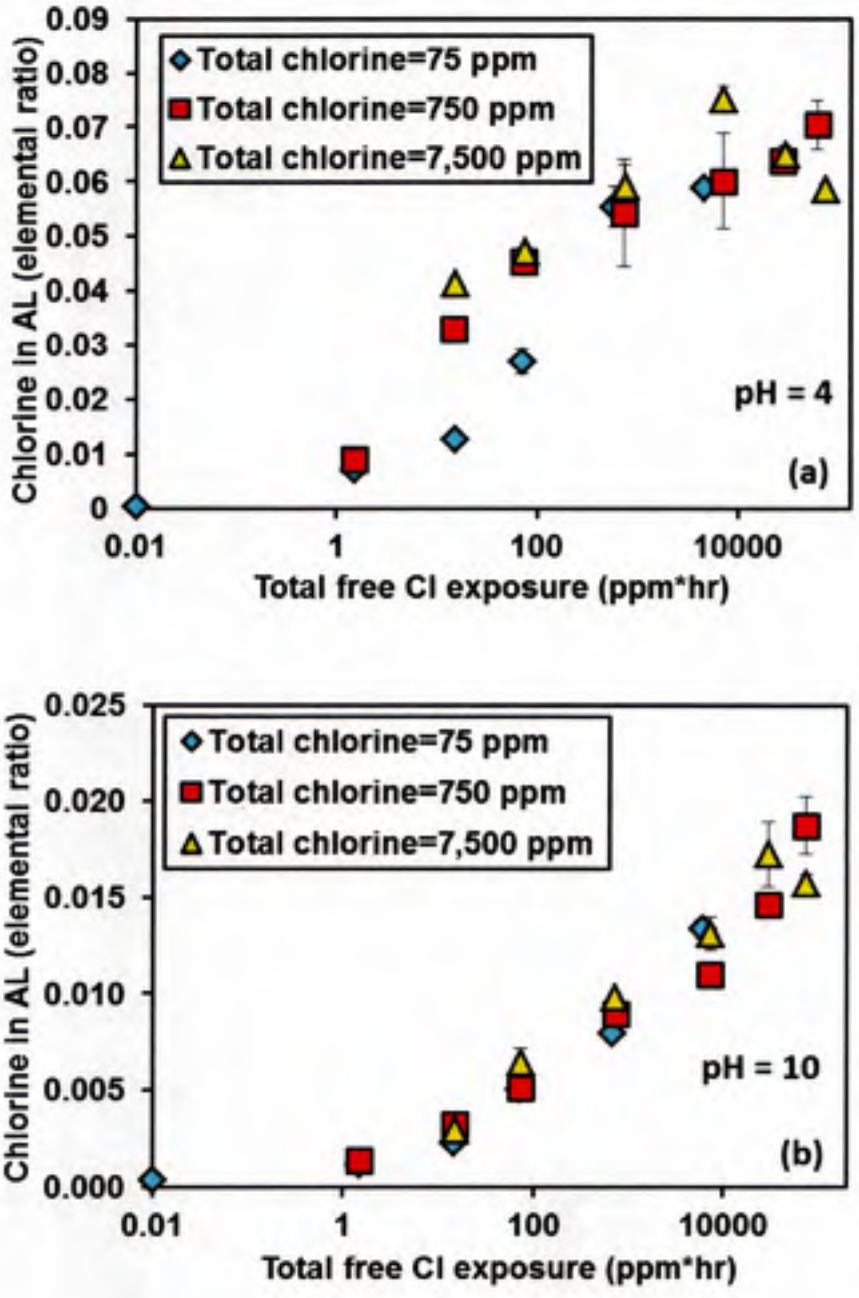


Figure 10. Elemental ratio of chlorine in the active layer of SWC4+ RO membrane corrected for hydrogen concentrations gathered from RBS experiments as a function of $CT_{T,\,Cl}$ (total concentration of free chlorine species * time of exposure). All samples were rinsed with 0.1 M $NaNO_3$ at pH = 10. (a) Samples chlorinated at pH=4 with $C_{T,\,Cl}$ = 75, 750 and 7,500 ppm; (b) Samples chlorinated at pH=10 with $C_{T,\,Cl}$ = 75, 750 and 7,500 ppm

Figure 10 shows that when membrane samples were chlorinated at either of the two pH conditions studied (pH = 4 and 10), the amount of chlorine uptaken into the bulk of the polyamide active layer was approximately constant for any given level of chlorine exposure regardless of the concentration of free chlorine or contact time used during chlorination. This indicates that free chlorine concentration alone or exposure time to chlorine alone are not appropriate metrics of chlorine exposure. Instead, both free chlorine concentration and exposure time must be known to calculate the appropriate metric of chlorine exposure, i.e., $CT_{T,Cl}$.

As part of a chlorination study where the chlorine uptake into the *surface* of a polyamide active layer was measured using XPS, Do *et al.*[20] reported data for chlorination tests at pH = 5 indicating that the uptake of chlorine as a function of $CT_{T,Cl}$ was independent of chlorine concentration in the 100-1,000 ppm range; however, lower concentrations of 1-10 ppm resulted in ~10-50% lower levels of chlorine uptake into the polyamide active layer surface. Do *et al* concluded that, in general, higher chlorine concentrations seem to result in higher chlorine uptake into the *surface* of the active layer. Our results for chlorine uptake into the *bulk* of the active layer do not appear to be in agreement with the conclusion by Do *et al.*, since in Figure 10 only two chlorination conditions (i.e., pH = 4, 75 ppm of chlorine, $CT_{T,Cl}$ ≈15 and ≈75 ppm·h) resulted in chlorine uptake levels statistically different (i.e., lower) from those measured for samples exposed to the same $CT_{T,Cl}$ but different chlorine concentrations. As stated above, from the results in Figure 10 we conclude that chlorine uptake into the *bulk* region of the polyamide active layer can be described as a function of $CT_{T,Cl}$.

Figure 10 also shows that for a given $CT_{T,Cl}$ the extent of chlorine uptake was higher at pH = 4 than at pH = 10. As a result, Figure 10 indicates that chlorine uptake is a unique function of $CT_{T,Cl}$ only when chlorination occurs at a constant pH condition. We therefore proceeded to study the effect of pH on the level of chlorine uptake into the bulk of polyamide active layers.

3.4 Effect of pH on the Uptake of Chlorine into the Bulk Region of Polyamide Active Layers

We chlorinated SWC4+ membranes samples to total free chlorine exposures in the $CT_{T,Cl}$ = 0-75,000 ppm·hr range at pH values of 5, 7.5 and 10. Membrane chlorination tests were performed at a total free chlorine concentration of $C_{T,Cl}$ = 750 ppm and the corresponding results for volume-averaged chlorine uptake by the polyamide active layer are presented in Figure 11a as a function of $CT_{T,Cl}$. The results indicate that the kinetics of chlorine uptake increased with decreasing pH, which is in agreement with previously reported results for the *surface* of polyamide active layers showing that chlorine uptake was larger at acidic conditions[20,31].

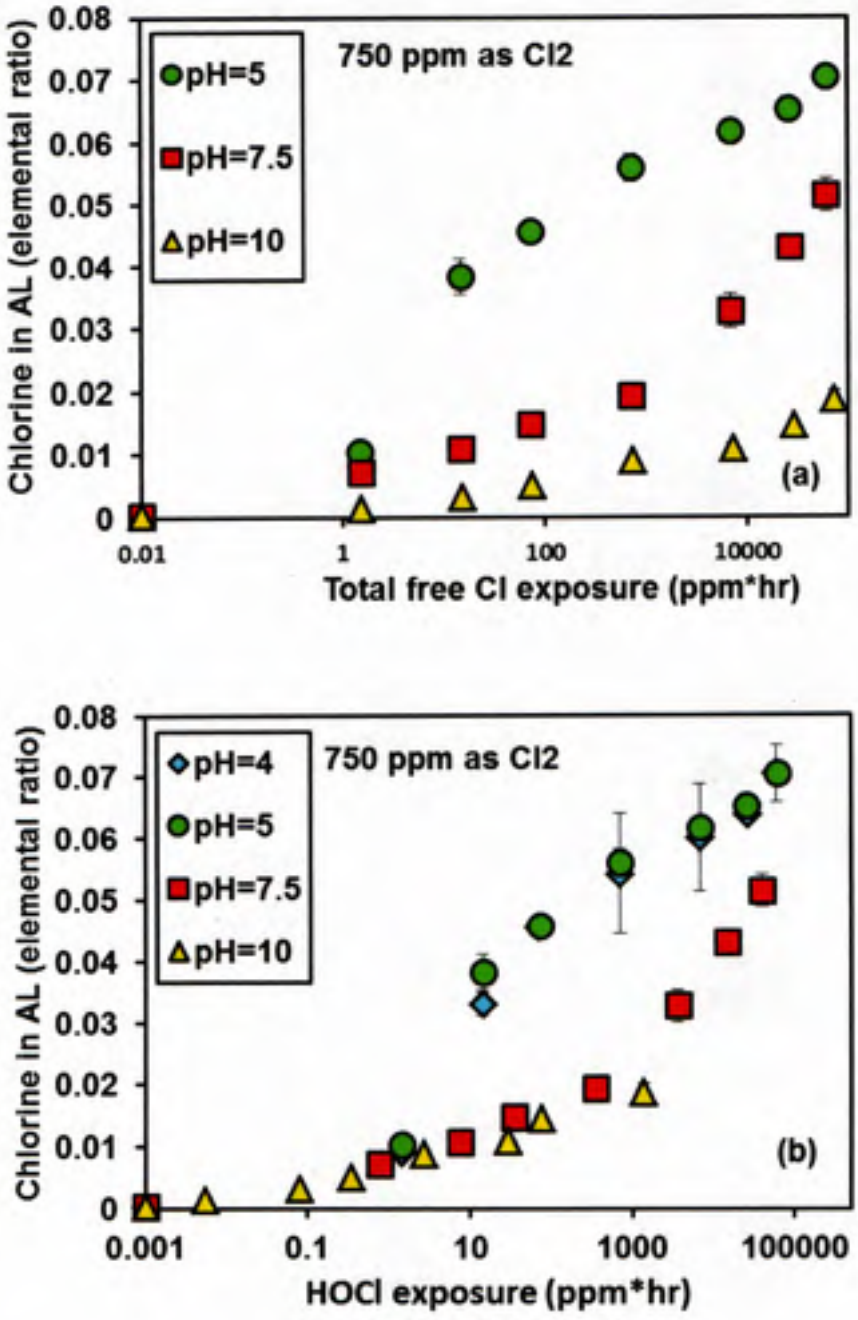


Figure 11. Effects of pH on the chlorine uptake (elemental ratio) into the membrane active layer (AL). Samples were chlorinated with pH = 4, 5, 7.5 and 10 and exposed to $C_{T,\,Cl}$ = 750 ppm. Panel (a) shows data plotted as a function of $CT_{T,\,Cl}$. Panel (b) shows data plotted as a function of CT_{HOCl}, neglecting all other free chlorine species.

Given that $pK_a = 7.50$ for free chlorine, then at acidic conditions hypochlorous acid (HOCl) is the dominant free chlorine species over hypochlorite ion (OCl^-). As a result, it has been hypothesized in the literature that the higher chlorine uptake by the surface of polyamide active layers at acidic conditions indicates that HOCl is the main reactive free chlorine species driving chlorine uptake into polyamide [18,20,21,26,31]. To test this hypothesis, Ettori *et al.*[24] plotted chlorine uptake at the *surface* of the membrane as a function of HOCl exposure for pH conditions of 5, 6.9, 8 and 12. Ettori *et al.* observed a constant trend for chlorine uptake based on HOCl exposure. Do *et al.*[20] also observed a dependence of chlorine uptake on HOCl exposure. Do *et al.* also noted a higher level of chlorine uptake in acidic conditions which they speculated might be due to direct ring chlorination.

We thus evaluated whether chlorine uptake into the *bulk* region of the active layer followed the same trend reported by Ettori *et al.*[24] and Do *et al.*[20] for the *surface* of the active layer. We plotted in Figure 11b as a function of exposure to HOCl (CT_{HOCl}) the same chlorine uptake data presented in Figure 11a as a function of exposure to total chlorine ($CT_{T,Cl}$). Figure 11b shows that samples chlorinated at pH = 7.5 and 10 followed the same chlorine uptake kinetics as a function of HOCl exposure, and that samples chlorinated at the more acidic condition of pH = 5 had faster chlorine uptake kinetics. Thus, our results for the *bulk* region of the active layer are in agreement with those of Ettori *et al.*[24] and Do *et al.*[20] for the *surface* of the active layer with chlorine uptake dependent on HOCl exposure and additional chlorine uptake at lower pH.

The percentages of free chlorine in solution in the form of HOCl at pH = 7-10 are in the ≈0.3-76% range, and that the chlorine uptake kinetics as a function of HOCl exposure in the pH range of 7-10 were the same in both this and Ettori *et al.*'s[24] study. Thus our

measurements strongly support the conclusion that chlorine uptake in which HOCl is the main reactive free chlorine species which dominates chlorine uptake kinetics at pH>7. The higher chlorine uptake kinetics at pH = 5 at which >99% of free chlorine is in HOCl form can be understood based on the mechanisms of chlorine uptake proposed in the literature from studies with model compounds[8,26]. It has been reported that chlorination of the amidic nitrogen (see Section 1.5.2) occurs at all pH conditions, but that ring chlorination (see Section 1.5.3) only occurs at acidic conditions. As a result, chlorination of the amidic nitrogen occurred at all pH conditions studied here and by Ettori *et al*; however, the additional mechanism of ring chlorination observed by Do *et al.* only occurred at pH = 5. Thus, net faster kinetics of chlorine uptake were observed at pH = 5 compared to at pH = 7-10. This rationalization of the results of the effect of pH on chlorine uptake as a function of exposure of HOCl was presented by Do *et al.*[20] for their results of chlorine uptake by the surface of the active layer and can be applied to our results for chlorine uptake by the bulk region of the active layer.

Based on studies with model compounds, two mechanisms have been proposed in the literature[8,26,33] to explain how ring chlorination occurs (see Section 1.5.3): (i) direct ring chlorination, and (ii) Orton rearrangement. No studies have been reported evaluating which of the two mechanisms is the dominant ring chlorination mechanism in membrane active layers; however, Do *et al.*[20] speculated that the larger chlorine uptake at the surface of the active layer that they observed at acidic conditions might be the result of direct ring chlorination. Accordingly, we performed tests to evaluate whether direct ring chlorination or Orton rearrangement was responsible for the additional chlorine uptake observed in Figure 11 at pH = 5 compared to pH = 7.5 and 10.

We performed additional chlorination tests at pH = 4 at total free chlorine exposures in the $CT_{T,Cl}$ = 0-75,000 ppm·hr range and at a total free chlorine concentration of $C_{T,Cl}$ = 750 ppm. The corresponding results for the volume-averaged chlorine uptake by the polyamide active layer as a function of exposure to HOCl are presented in Figure 11b. Given that direct ring chlorination is believed to be dependent on membrane exposure to Cl_2[20] and that the pK_a between Cl_2 and HOCl is $pK_a = 2.56$[34], then if direct ring chlorination were taking place at pH = 5, there would be a larger chlorine uptake at pH = 4 compared to at pH = 5 because there is ≈10 times more Cl_2 at pH = 4 than at pH = 5. Figure 11b shows that there was no additional chlorine uptake at pH = 4 compared to at pH = 5, and thus does not support direct ring chlorination as a significant chlorination mechanism at pH > 4.

Regarding Orton rearrangement, this mechanism is a second step to the chlorination of amidic nitrogen[25–27]. Since the chlorination of amidic nitrogen is a function of exposure to HOCl, as supported above by the matching chlorine uptake kinetics at pH = 7.5 and 10 in Figure 11b, chlorine uptake by the Orton Rearrangement should also be a function of HOCl exposure. Given that the percentage of free chlorine in solution in the form of HOCl at pH = 4 and 5 is almost the same (i.e., ≈99.9% and ≈99.7% for pH = 4 and 5, respectively), then if the Orton rearrangement mechanism were taking place at pH = 5, there would *not* be a larger chlorine uptake at pH = 4 compared to at pH = 5 because the Orton rearrangement depends on the concentration of HOCl, and this concentration is the same at pH 4 and 5. Accordingly, the matching kinetics of chlorine uptake as a function of HOCl exposure at pH = 4 and 5 in Figure 11b support the Orton rearrangement mechanism as the mechanism responsible of the faster kinetics for chlorine uptake at pH = 4-5 compared to at pH = 7.5-10.

3.5 Heterogeneity of Chlorine Uptake into the Active Layer

What has been presented in the literature for quantification of chlorine uptake into the active layer has been performed solely at the surface using X-ray photoelectron spectroscopy (XPS). To determine the heterogeneity of chlorine uptake into the bulk of the active layer, we decided to compare data on chlorine uptake into the surface of the membrane using XPS to the data on chlorine uptake into the bulk of the active layer using RBS. To do this, we exposed membrane samples to free chlorine with a $C_{T,Cl}$ = 750 ppm at pH = 4 and 10. Chlorinated samples were rinsed with 0.1 M $NaNO_3$ at pH = 10 prior to ion probing. Samples were ion probed at pH = 10.5 and analyzed with both XPS and RBS. The results can be seen in Figure 12.

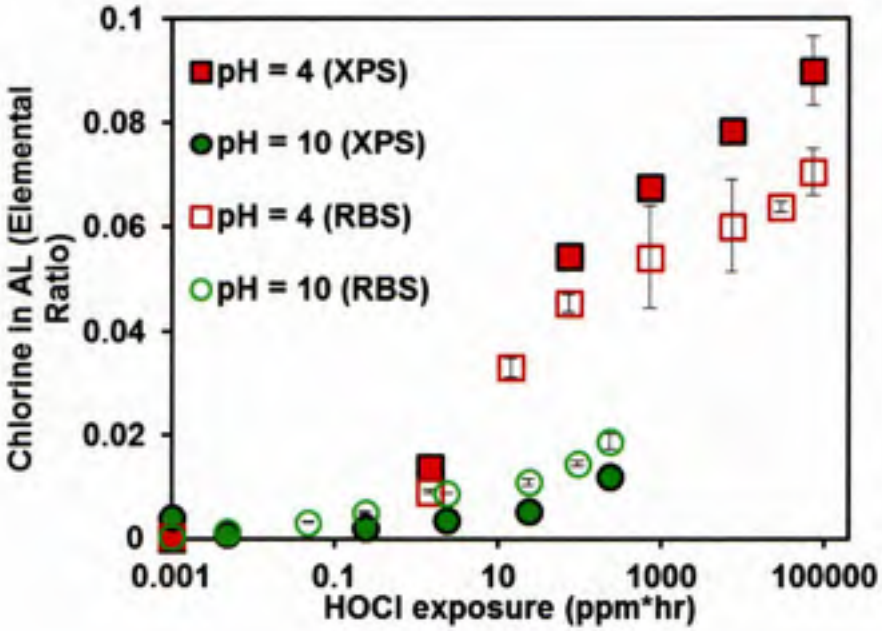


Figure 12. Comparison of chlorine uptake into the *surface* of the active layer (XPS) and into the *bulk* of the active layer (RBS) for samples exposed to free chlorine at pH = 4 and 10.

From the data we can see that there is not a significant difference in the amount of chlorine detected at the surface of the active layer compared to the chlorine uptake into the bulk of the active layer. This observation allows us to see that diffusion of free chlorine into the membrane is not a limiting process affecting the kinetics of chlorine interactions with the membrane (i.e., there is not more chlorine bound to the surface of the membrane).

Kwon and Leckie[31] observed chlorine uptake into the active layer of a PA-TFC membrane using XPS. Samples exposed to chlorine up to $CT_{T,Cl}$ = 2,000 ppm·hr at pH 4 and 9 saw surface concentrations of chlorine at ~0.014 and 0.0073 atoms/atom (corrected for H concentration), respectively. Our samples exposed to similar chlorine exposure conditions at pH = 4 contained much higher levels of chlorine (~0.073 atoms/atom) at the active layer surface. While our samples exposed to chlorine at alkaline conditions showed similar chlorine uptake.

Kwon and Leckie chlorinated LFC1 membrane at pH = 4 with $CT_{T,Cl}$ = 2,000 ppm*hr and $C_{T,Cl}$ = 2,000 ppm and saw a chlorine uptake of ~0.017 atoms/atom. We did not have a sample exposed to the same level, but we did expose samples of SWC4+ to $CT_{T,Cl}$ = 750 and 7,500 ppm·hr at pH = 4. We observed levels of chlorine at the surface of these samples of 0.068 and 0.078 atoms/atom, respectively. This is much higher (~4 times higher) than the results observed by Kwon and Leckie.

Samples chlorinated to the same CT_{HOCl} for alkaline conditions between the samples in this study and the study by Kwon and Leckie saw similar amounts of chlorine at the surface of samples. Kwon and Leckie chlorinated LFC1 membrane to $CT_{T,Cl}$ = 2,000 ppm·hr with $C_{T,Cl}$

= 2,000 ppm. They observed a chlorine uptake of ~0.0072 atoms/atom. As we did not expose membrane samples to this particular exposure and pH we compared results based on CT_{HOCl} where there would be ~10 times as much HOCl at their test conditions of pH = 9 compared to our test conditions at pH = 10. For comparison, we equated chlorine uptake in our samples at pH = 10 with a $CT_{T,\,Cl} \approx 20{,}000$ ppm·hr to their chlorine uptake at pH = 9 with a $CT_{T,\,Cl} = 2{,}000$ ppm·hr where the CT_{HOCl} between the two samples is approximately the same. They observed a chlorine uptake of ~0.0072 atoms/atom compared to our observation of between 0.011 - 0.012 atoms/atom. Our chlorine uptake results in alkaline conditions are in similar agreement (~1.6 times higher) with Kwon and Leckie[31].

Do *et al.*[20] also measured chlorine uptake at the surface of NF90 membrane using XPS for various pH conditions. For samples chlorinated at low pH, Do *et al.* observed an elemental ratio of ~0.069 atoms/atom (corrected for hydrogen) for a chlorine exposure at pH = 5 and $CT_{HOCl} = 100{,}000$ ppm·hr. Our SWC4+ samples chlorinated in acidic conditions agreed fairly consistently with the surface chlorine content measured by Do *et al.* For samples exposed to free chlorine at acidic conditions, we observed an elemental ratio of 0.090 atoms/atom for a sample exposed to free chlorine at pH = 4 and a $CT_{HOCl} = 75{,}000$ ppm·hr.

Do *et al.* observed the effect of alkaline chlorination on chlorine uptake at the surface of the NF 90 membrane by exposing samples at pH = 9 up to about $CT_{HOCl} \approx 40$ ppm·hr. They observed a chlorine uptake for this condition of ~0.036 atoms/atom. We did not have samples at this particular exposure to compare directly, but did expose samples to free chlorine at pH = 10 up to $CT_{HOCl} \approx 240$ ppm·hr. For a sample of SWC4+ exposed to free chlorine at pH = 10 for a $CT_{HOCl} \approx 25$ ppm·hr, we observed a chlorine uptake at the surface of

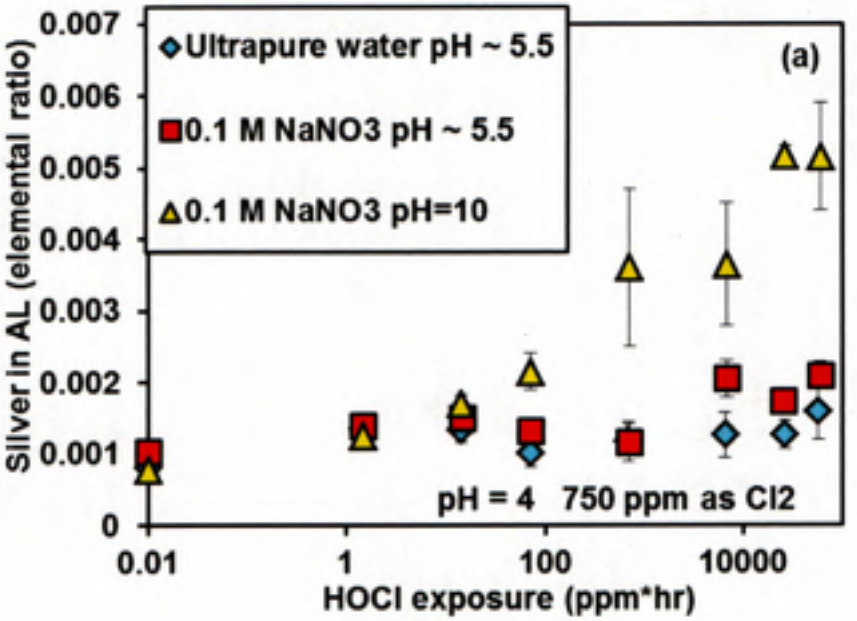
the membrane of about 0.0054 atoms/atom. The observations by Do et al are ~6.67 times higher than our results.

From this, we can see that there is a wide amount of variation for chlorine uptake at the surface of different membranes based on XPS measurements. Due to the proprietary nature of membrane manufacturing, differences in membrane production processes yield variations on membrane chemical structure which can affect the uptake kinetics of chlorine into the polyamide active layer. This is consistent with the range of values reported by manufacturers for membrane chlorine sensitivity.

3.6 Chain Scission Dependence on the Hydrolysis Mechanism

The hydrolysis mechanism presented by Do *et al.*[20] is speculated to be dependent on the presence of significant amounts of hydroxyl ions to induce chain scission. During this study all ion probed samples were rinsed with 0.1 M $NaNO_3$ at pH = 10 prior to ion probing with Ag^+ at pH = 10.5. Based on the mechanics of the hydrolysis mechanism, it is speculated that rinsing samples at high pH can induce chain scission of chlorinated amide linkages. The dependence of environmental pH to induce chain scissioning of the active layer after chlorination was investigated. For this, we chlorinated SWC4+ membrane samples to total free chlorine exposures in the $CT_{T,Cl}$ = 0-75,000 ppm·hr range using total free chlorine concentrations of $C_{T,Cl}$ = 750 ppm. Membrane chlorination tests were performed at pH values of 4 and 10. Rinsing was performed using three different conditions to determine the ability for pH induced chain scission to occur. Rinsing conditions were: (i) rinsing only with ultrapure water at pH ≈ 5.5; (ii) rinsing with ultrapure water at pH ≈ 5.5 followed by 0.1 M $NaNO_3$ at pH ≈ 5.5 and ultrapure water again; (iii) rinsing with ultrapure water at pH ≈ 5.5 followed by 0.1 M $NaNO_3$ at pH = 10 and ultrapure water again. Results can be seen for

samples chlorinated at pH = 4 and 10 in Figure 13 a and Figure 13 b respectively. The figures show the silver elemental ratio observed in the active layer as a function of CT_{HOCl}.



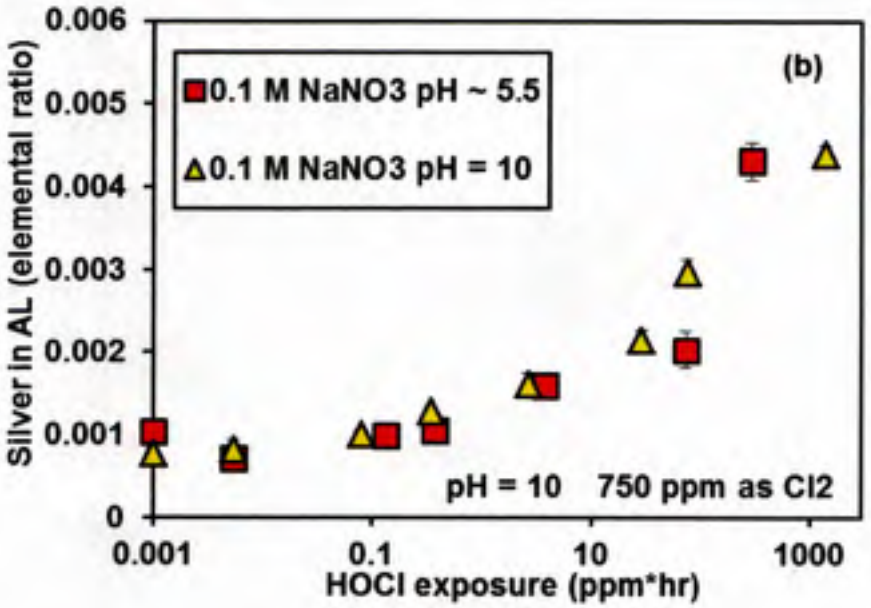


Figure 13. Elemental ratio of Ag in the active layer of SWC4+ RO membrane chlorinated with $C_{T,\,Cl}$ = 750 ppm gathered from RBS plotted as a function of CT_{HOCl}. (a) samples chlorinated at pH = 4 and rinsed prior to ion probing at pH = 10.5 with (i) ultrapure water at pH ≈ 5.5, (ii) 0.1 M $NaNO_3$ at pH ≈ 5.5 and (iii) 0.1 M $NaNO_3$ at pH = 10; (b) samples chlorinated at pH = 10 and rinsed prior to ion probing at pH = 10.5 with (i) 0.1 M $NaNO_3$ ≈ 5.5 and (ii) 0.1 M $NaNO_3$ = 10.

Figure 13 a shows results for samples chlorinated at pH = 4 with $C_{T,\,Cl}$ = 750 ppm. Samples rinsed in acidic conditions (pH ≈ 5.5) experienced very little to only minor amounts of chain scission after exposure to free chlorine up to levels much higher than was necessary to induce membrane failure at constant pH. However, when samples chlorinated in acidic conditions were exposed to alkaline rinsing conditions (pH = 10) prior to ion probing, extensive levels of chain scission in the active layer of the membrane was observed. This implies that chain

scission of the amide linkage does not occur spontaneously after incorporation of chlorine into the active layer chemical structure when chlorine exposure occurs in acidic conditions. It would imply that the presence of hydroxyl ions is necessary to induce chain scission as described by the hydrolysis mechanism (Section 1.6.3).

The effect of rinsing pH on chain scission in samples chlorinated in alkaline conditions was also investigated by rinsing samples that were chlorinated at pH = 10 with $C_{T,Cl}$ = 750 ppm in acidic (pH ≈ 5.5) and alkaline (pH=10) conditions. The measured chain scission in the active layer for these samples can be seen in Figure 13 b. There was no detectable difference in the kinetics of chain scission between samples rinsed in acidic or alkaline conditions. This seems to imply that chain scission of the amide linkage will occur spontaneously in alkaline environments.

These observations made from Figure 13 give insight into the kinetics by which chain scission occurs. These conclusions are in agreement with the hydrolysis mechanism described by Do *et al.*[20] and the observation by Soice *et al.*[26] that extensive chain scission can be produced by chlorinating samples in acidic conditions where extensive amide N-Cl (Section 1.5.2) can occur, followed by exposure to alkaline conditions to induce chain scission by the hydrolysis mechanism (Section 1.6.3). Samples that were chlorinated in acidic conditions and rinsed in acidic conditions did not show evidence of chain scission after rinsing in acidic conditions for the duration in this experiment (~10 hrs). The hydrolysis mechanism requires free hydroxyl ions to cause scission of the chlorinated amide linkage. Chain scission is not predicted to occur readily in acidic conditions because of a lack of hydroxyl ions to induce chain scission during chlorine exposure. However, once samples chlorinated in acid conditions with high levels of amide N-Cl were exposed to alkaline

conditions, extensive chain scission was observed resulting from the interaction of the chlorinated amide linkage with free hydroxyl ion. Samples chlorinated in alkaline conditions showed extensive chain scission in the active layer regardless of rinsing conditions. The kinetics involved in inducing chain scission in alkaline chlorinating environments is not limited by a lack of hydroxyl ions, but instead the lack of HOCl to induce chlorination of the amide linkage.

3.7 The Effect of Total Free Chlorine Concentration on the Chain Scission Potential in the Bulk Region of the Polyamide Active Layer

As we showed in the previous section (Section 3.6), chain scission of the amide linkages occurs by the hydrolysis mechanism (Section 1.6.3). As the methods used in this study required alkaline pH to ionize all carboxylic groups for ion probing, chain scission was induced in all samples by exposing to alkaline pH rinsing condition with 0.1 M $NaNO_3$ at pH = 10 after chlorine exposure was performed. This allowed for chlorinated samples to hydrolyze and induce the maximum possible amount of chain scission for the corresponding chlorine exposure. Based on this, we can now study the effect that the concentration of total free chlorine in solution had on chain scission potential in the bulk region of the polyamide active layer. For this purpose, we chlorinated SWC4+ membrane samples to total free chlorine exposures in the $CT_{T,Cl}$ = 0-75,000 ppm·hr range using total free chlorine concentrations of $C_{T,Cl}$ = 75, 750 and 7,500 ppm. Membrane chlorination tests were performed at pH values of 4 and 10. Chlorinated samples were rinsed with ultrapure water followed by 0.1 M $NaNO_3$ at pH = 10 prior to ion probing at pH = 10.5. The corresponding results for samples chlorinated at pH values of 4 and 10 are presented in Figure 14a and

Figure 14b, respectively. The figures show the silver elemental ratio (i.e., proportional to the concentration of free carboxylic groups) observed in the active layer as a function of CT_{HOCl}.

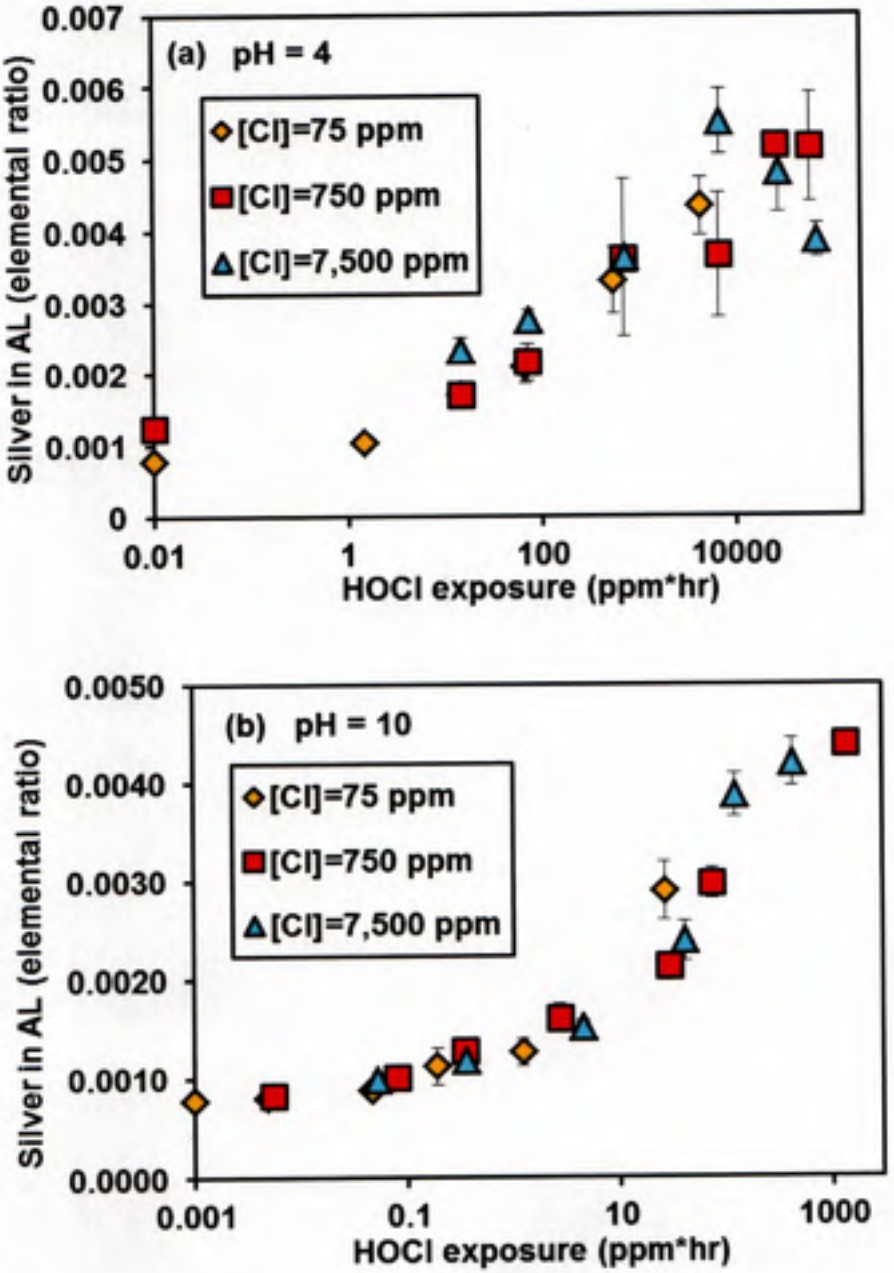


Figure 14. Concentration of Ag in active layer of SWC4+ as detected by RBS and plotted as a function of CT_{HOCl} for $C_{T,\,Cl}$ = 75, 750 and 7,500 ppm: (a) Shows data for chlorinating at a pH of 4; (b) Shows data for chlorinating at a pH of 10.

Figure 14 shows that when membrane samples were chlorinated at either of the two pH conditions studied (pH= 4 and 10), maximum chain scission was induced and chain scission was then quantified, the amount of chain scission in the active layer was approximately constant for any given level of chlorine exposure regardless of the concentration of free chlorine or contact time used during chlorination. This indicates that free chlorine concentration alone or exposure time alone are not appropriate metrics of predicting chain scission. Instead, both free chlorine concentration and exposure time must be known to calculate the appropriate metric of chain scission, i.e., $CT_{T,Cl}$.

This appears to be in agreement with the hydrolysis mechanism (Section 1.6.3) as a result of the dependence of chain scission to occur after chlorination of the amide linkage. It was already shown above (Section 3.3) that chlorine uptake in the amide linkage was dependent on the CT_{HOCl}.

3.8 Effect of pH during Chlorination on Chain Scission Potential in the Bulk Region of the Polyamide Active Layers

We studied the effect that pH of chlorine solution had on the eventual chain scission potential of the amide linkages in the bulk of the active layer. To accomplish this, we chlorinated SWC4+ membrane samples to total free chlorine exposures in the $CT_{T,Cl}$ = 0-75,000 ppm·hr range using total free chlorine concentration of $C_{T,Cl}$ = 750 ppm. Membrane chlorination tests were performed at pH values of 4, 5, 7.5 and 10. Samples were rinsed with 0.1 M $NaNO_3$ at pH = 10 prior to ion probing at pH = 10.5. The corresponding results are presented in Figure 15. The figures show the silver elemental ratio (i.e., proportional to the concentration of free carboxylic groups) observed in the active layer as a function of CT_{HOCl}.

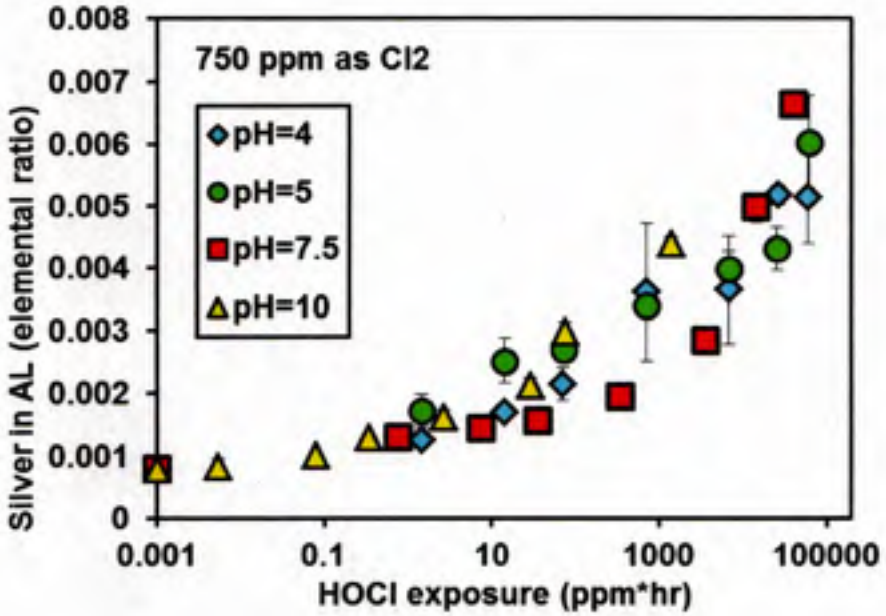


Figure 15. Concentration of Ag in the active layer of SWC4+ RO membrane gathered from RBS experiments plotted as a function of CT_{HOCl} = 0 - 75,000 ppm·hr for samples chlorinated at pH = 4, 5, 7.5 and 10 with $C_{T,\,Cl}$ = 750 ppm. All samples were rinsed with 0.1 M $NaNO_3$ at pH = 10 prior to ion probing at pH = 10.5.

Figure 15 shows that chain scission potential of the amide linkage is predicted well by CT_{HOCl}, and therefore must be a byproduct of a chlorination mechanism that is predicted as a function of CT_{HOCl} over a wide range of pH values. In Section 3.4 it was shown that amide N chlorination occurs at all pH conditions. However, ring chlorination only occurs via the Orton rearrangement (Section 1.5.3) at sufficiently acidic conditions. Because no additional Ag was observed in the active layer of the membrane for samples in Figure 15, corresponding to the additional Cl observed in the active layer of the membranes in Figure

11b as a function of CT_{HOCl}, it is clear that chlorination of the benzene ring via the Orton rearrangement did not induce any additional chain scission. Therefore, the data in Figure 15 show that chlorination of the N-H functionality of the amide linkage precedes chain scission.

3.9 Discussion on the Practical Recommendations of Chlorine Damaged Membranes

From the results of this study, some insight into membrane failure due to chlorine exposure can be gained. As shown in the literature, membrane failure is a complex system of competing mechanisms. Membrane failure is speculated to occur through three primary pathways as shown in Section 1.7. From this study a clear insight has been given on the mechanisms of chain scission and how they can affect the performance of the membrane. Based on these results, the maximum amount of chain scission will occur when conditions are right to achieve the maximum amount of chlorine uptake into the amidic N. This occurs at acidic conditions where HOCl is most dominant. However, the hydrolysis mechanism also needs hydroxyl ion to induce chain scission. This is characteristic of many cleaning solutions used in membrane treatment operations where pH can be as high as 11. Therefore, membrane plants operating with chlorine exposure occurring at low pH followed by cleaning at high pH will induce extensive amounts of chain scission in the active layer and accelerate membrane de-polymerization and failure. It has also been shown that alkaline conditions will only cause a minor amount of chlorine to come off of the amide linkage as speculated in the kinetics by the mechanism presented by Hardy and Robson[30]. However, based on the results in this study, this amount of reversibly bound Cl is minor in comparison to the total amount of chlorine bound to the membrane affecting membrane performance. Consequently, it would also not be recommended to use an alkaline post treatment in attempts to improve membrane performance after chlorine exposure as has been previously speculated[9,25]. The

kinetics in this study imply that membrane failure caused by chlorine-uptake-induced chain scission will not often occur without sufficient hydroxyl ions to induce chain scission through the hydrolysis mechanism. It seems that membrane failure following chlorine exposure in systems operating at constant acidic or neutral pH is most likely caused by another mechanism other than hydrolysis-induced chain scission. For membranes constantly operating in acidic conditions, the failure mechanism by chlorine uptake is probably not related to scission of the amide linkage.

It would be recommended that conditions where chlorine exposure occurs should be operated at an intermediate pH where HOCl and OH^- concentrations are both relatively low to minimize chlorine uptake and chain scission. However, there is probably not a pH condition to significantly satisfy these conditions due to the overlying pKa values of free chlorine (pKa=7.50) and water (pka~7).. Therefore, the best recommendation would be to monitor chlorine exposure and try to keep it as low as possible and to avoid using cleaning protocols where pH is excessively high to accelerate chain scission.

As was observed from review of the literature, there are conflicting results of chlorine exposure leading us to believe that membrane failure is not just a function of chlorine uptake. From the results of this study, we will further investigate the effects of operating conditions on chlorine uptake and chain scission leading to membrane failure. The ability shown in this study to accurately monitor both chlorine uptake and chain scission of a membrane sample will allow us to relate performance change as a function dependent on both chlorine uptake and chain scission in the membrane. The results of this future study will allow us to determine if membrane failure is dependent on only chlorine uptake and chain scission and what affect ring chlorination has on membrane failure.

4. Conclusion

This is the first study that quantifies chlorine uptake and chain scission in the *bulk* region of polyamide active layers of RO/NF membranes. We used Rutherford backscattering spectrometry (RBS) as an analytical technique to quantify the chlorine content and silver probe concentration (a surrogate for chain scission) in the bulk region of the active layer. Our results showed that when membrane chlorination occurs at acidic conditions, a minor fraction (<6%) of the chlorine uptaken is released upon alkaline rinsing. Our results also showed that for a given pH condition, chlorine uptake into the bulk region of the active layer was not dependent on the chlorine concentration or exposure time, but rather on the chlorine exposure defined as the integral of chlorine concentration versus exposure time. This result was mostly consistent with results reported in the literature for chlorine uptake into the surface of the active layer, though it has also been reported in the literature that lower chlorine concentrations at the same chlorine exposure may lead to lower chlorine uptake. We also observed that lower pH conditions lead to faster kinetics of chlorine uptake into the bulk of the active layer, which is consistent with reports in the literature for the uptake of chlorine by the active layer surface. Our results are consistent with chlorine uptake taking place through chlorination of the amidic nitrogen at all pH conditions, and through Orton rearrangement at acidic conditions. For both mechanisms, chlorine uptake is a function of exposure to HOCl, not of exposure to total free chlorine in solution. We also demonstrated that direct ring chlorination does not take place at pH > 4. It was also shown that chain scission of the amide linkage occurs through the hydrolysis mechanism after chlorination of the amidic nitrogen. The occurrence of chain scission of the amide linkage was shown to be dependent on both total exposure to HOCl and OH^-. Chain scission did not occur spontaneously in acidic

conditions, but exposure of membranes chlorinated at acidic conditions to an alkaline environment induced chain scission. The potential for chain scission to occur was shown to be directly proportional to the amount of chlorination of the amidic nitrogen. Ring chlorination was also shown not to lead to chain scission.

We present a brief summary of the results obtained in this study based on the literature review and comprehensive experimental evaluation of chlorine uptake and chain scission potential in the bulk of the active layer:

- The primary free chlorine species causing chlorine uptake into the membrane is HOCl
- Chlorine uptake is not dependent on concentration of free chlorine during exposure, but is instead predicted well based on the CT_{HOCl}
- Chlorine uptake occurs by two separate mechanisms: chlorination of the amidic N in the amide linkage, and chlorination of the benzene ring bound to the amidic N
- Chlorination of the amidic N in the amide linkage occurs at all pH conditions
- Chlorination of the benzene rings bound to the amidic N occurs only in acidic conditions
- Ring chlorination appears to occur as a result of Orton rearrangement, not direct ring chlorination
- A relatively small fraction (<6%) of the chlorine bound to the active layer as a result of chlorination of the amidic N is reversible
- Chain scission potential is directly proportional to chlorination of the amidic N of the amide linkage

- Chain scission potential can be predicted based solely on CT_{HOCl} regardless of the pH of chlorine solutions
- Chain scission occurs via the hydrolysis mechanism (i.e., chain scission is dependent on both CT_{HOCl} to cause amidic N-Cl and OH^- to induce chain scission)
- Exposing chlorine damaged membrane samples to alkaline conditions has the potential to induce additional chain scission

References

(1) Jacangelo, J. G.; Rhodes Trussell, R.; Watson, M. Role of Membrane Technology in Drinking Water Treatment in the United States. *Desalination* **1997**, *113*, 119–127.

(2) Burbano, B. Y. A. A.; Adham, S. S.; Pearce, W. R. The State of Full-Scale RO / NF Desalination — Results from a Worldwide Survey. *Journal AWWA* **2007**, 116–127.

(3) MWH *Water Treatment Principles and Design*; Second edition.; John Wiley & Sons, Inc.: Hoboken, 2005.

(4) Hanra, A. M.; Ramachandhran, V. RO Performance Analysis of Cellulose Acetate and TFC Polyamide Membrane Systems for Separation of Trace Contaminants. *Desalination* **1996**, *104*, 175–183.

(5) Ridgway, H.; Justice, C.; Whittaker, C. Biofilm Fouling of RO Membranes—Its Nature and Effect on Treatment of Water for Reuse. *Journal AWWA* **1984**, 94–102.

(6) Baker, J. S.; Dudley, L. Y. Biofouling in Membrane Systems — A Review. *Desalination* **1998**, *118*, 81–89.

(7) Koo, J.; Petersen, R.; Cadotte, J. ESCA Characterization of Chlorine-Damaged Polyamide Reverse Osmosis Membrane. *Polym. Prepr* **1986**, *27*, 391–392.

(8) Kawaguchi, T.; Tamura, H. Chlorine-Resistant Membrane for Reverse Osmosis. I. Correlation between Chemical Structures and Chlorine Resistance of Polyamides. *Journal of Applied Polymer Science* **1984**, *29*, 3359–3367.

(9) Kang, G.-D.; Gao, C.-J.; Chen, W.-D.; Jie, X.-M.; Cao, Y.-M.; Yuan, Q. Study on Hypochlorite Degradation of Aromatic Polyamide Reverse Osmosis Membrane. *Journal of Membrane Science* **2007**, *300*, 165–171.

(10) Kinslow, J. K.; Hudkins, J. M. The Evolution of Pretreatment Chemicals in Membrane Processes An Analysis of Innovations in Chemical Pretreatment Practices. *Florida Water Resources Journal* **2004**, 21–28.

(11) Kim, D.; Jung, S.; Sohn, J.; Kim, H.; Lee, S. Biocide Application for Controlling Biofouling of SWRO Membranes — an Overview. *Desalination* **2009**, *238*, 43–52.

(12) Dasilva, M.; Tessaro, I.; Wada, K. Investigation of Oxidative Degradation of Polyamide Reverse Osmosis Membranes by Monochloramine Solutions. *Journal of Membrane Science* **2006**, *282*, 375–382.

(13) Koo, J.; Lee, J.; Jung, Y. Chlorine Resistant Membrane and the Mechanism of Membrane Degradation by Chlorine. *Proceedings of the Water Environment Federation 2008* **2008**, 2958–2969.

(14) Hydranautics SWC4+Data Sheet.

(15) Petersen, R. J. Composite Reverse Osmosis and Nanofiltration Membranes. *Journal of Membrane Science* **1993**, *83*, 81–150.

(16) Coronell, O.; Mariñas, B. J.; Zhang, X.; Cahill, D. G. Quantification of Functional Groups and Modeling of Their Ionization Behavior in the Active Layer of FT30 Reverse Osmosis Membrane. *Environmental Science & Technology* **2008**, *42*, 5260–5266.

(17) Kwon, Y.-N.; Tang, C. Y.; Leckie, J. O. Change of Membrane Performance due to Chlorination of Crosslinked Polyamide Membranes. *Journal of Applied Polymer Science* **2006**, *102*, 5895–5902.

(18) Avlonitis, S.; Hanbury, W. T.; Hodgkiess, T. Chlorine Degradation of Aromatic Polyamides. *Desalination* **1992**, *85*, 321–334.

(19) Do, V. T.; Tang, C. Y.; Reinhard, M.; Leckie, J. O. Degradation of Polyamide Nanofiltration and Reverse Osmosis Membranes by Hypochlorite. *Environmental Science & Technology* **2012**, *46*, 852–859.

(20) Do, V. T.; Tang, C. Y.; Reinhard, M.; Leckie, J. O. Effects of Chlorine Exposure Conditions on Physiochemical Properties and Performance of a Polyamide Membrane-Mechanisms and Implications. *Environmental Science & Technology* **2012**, *46*, 13184–13192.

(21) Antony, A.; Fudianto, R.; Cox, S.; Leslie, G. Assessing the Oxidative Degradation of Polyamide Reverse Osmosis Membrane—Accelerated Ageing with Hypochlorite Exposure. *Journal of Membrane Science* **2010**, *347*, 159–164.

(22) Tessaro, I. C.; Da Silva, J. B. a.; Wada, K. Investigation of Some Aspects Related to the Degradation of Polyamide Membranes: Aqueous Chlorine Oxidation Catalyzed by Aluminum and Sodium Laurel Sulfate Oxidation During Cleaning. *Desalination* **2005**, *181*, 275–282.

(23) Lee, E.; Lonsdale, H.; Babcock, W. Novel Composite Membranes. **1983**.

(24) Ettori, A.; Gaudichet-Maurin, E. Permeability and Chemical Analysis of Aromatic Polyamide Based Membranes Exposed to Sodium Hypochlorite. *Journal of Membrane Science* **2011**, *375*, 220–230.

(25) Barassi, G.; Borrmann, T. N-chlorination and Orton Rearrangement of Aromatic Polyamides, Revisited. *Journal of Membrane Science & Technology* **2012**, *2*, 1–3.

(26) Soice, N.; Maladono, A.; Takigawa, D. Y.; Norman, A. D.; Krantz, W. B.; Greenberg, A. R. Oxidative Degradation of Polyamide Reverse Osmosis Membranes: Studies of Molecular Model Compounds and Selected Membranes. *Journal of Applied Polymer Science* **2003**, *90*, 1173–1184.

(27) Orton, K.; Bradfield, A. CXXXVIII.—The Chlorination of Anilides. The Directing Influence of the Acylamido-Group. *Journal of the Chemical Society (Resumed)* **1927**, 986–997.

(28) Glater, J.; Zachariah, M. A Mechanistic Study of Halogen Interaction with Polyamide Reverse-Osmosis Membranes. *ACS Symp. Ser* **1985**, *281*, 345–358.

(29) Coronell, O.; González, M. I.; Mariñas, B. J.; Cahill, D. G. Ionization Behavior, Stoichiometry of Association, and Accessibility of Functional Groups in the Active Layers of Reverse Osmosis and Nanofiltration Membranes. *Environmental Science & Technology* **2010**, *44*, 6808–6814.

(30) Hardy, F.; Robson, P. The Formation and Hydrolysis of Substituted N-chloro-N-methylbenzamides in Aqueous Alkali. *J. Chem. Soc. B* **1967**, 1151–1154.

(31) Kwon, Y.-N.; Leckie, J. O. Hypochlorite Degradation of Crosslinked Polyamide Membranes I. Changes in Chemical/Morphological Properties. *Journal of Membrane Science* **2006**, *283*, 21–26.

(32) Dam, N.; Ogilby, P. R. On the Mechanism of Polyamide Degradation in Chlorinated Water. *Helvetica Chimica Acta* **2001**, *84*, 2540–2549.

(33) Glater, J.; Hong, S.; Elimelech, M. The Search for a Chlorine-Resistant Reverse Osmosis Membrane. *Desalination* **1994**, *95*, 325–345.

(34) Cherney, D. P.; Duirk, S. E.; Tarr, J. C.; Collette, T. W. Monitoring the Speciation of Aqueous Free Chlorine from pH 1 to 12 with Raman Spectroscopy to Determine the Identity of the Potent Low-pH Oxidant. *Applied spectroscopy* **2006**, *60*, 764–772.

(35) Soice, N. P.; Greenberg, A. R.; Krantz, W. B.; Norman, A. D. Studies of Oxidative Degradation in Polyamide RO Membrane Barrier Layers Using Pendant Drop Mechanical Analysis. *Journal of Membrane Science* **2004**, *243*, 345–355.

(36) Coronell, O.; Mariñas, B. J.; Cahill, D. G. Depth Heterogeneity of Fully Aromatic Polyamide Active Layers in Reverse Osmosis and Nanofiltration Membranes. *Environmental Science & Technology* **2011**, *45*, 4513–4520.

(37) Kwon, Y.; Tang, C.; Leckie, J. Change of Chemical Composition and Hydrogen Bonding Behavior Due to Chlorination of Crosslinked Polyamide Membranes. *Journal of Applied Polymer Science* **2008**, *108*, 2061–2066.

(38) Lei, H.; Mariñas, B. J.; Minear, R. Bromamine Decomposition Kinetics in Aqueous Solutions. *Environmental Science & Technology* **2004**, *38*, 2111–2119.

(39) *Standard Methods for the Examination of Water & Wastewater*; Franson, M. A. H.; Clesceri, L. S.; Greenber, A. E.; Eaton, A. D., Eds.; 20th ed.; APHA, AWWA and WEF: Washington, DC, 1999.

(40) Brezonik, P.; Arnold, W. *Water Chemistry: an Introduction to the Chemistry of Natural and Engineered Aquatic Systems*; Oxford University Press, 2011.

(41) Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; 1st English Edition.; Pergamon Press: Great Britian, 1966.

(42) Attayek, P. J.; Meyer, E. S.; Lin, L.; Rich, G. C.; Clegg, T. B.; Coronell, O. A Remotely Controlled, Semi-Automatic Target System for Rutherford Backscattering Spectrometry and Elastic Recoil Detection Analyses of Polymeric Membrane Samples. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* **2012**, *676*, 21–25.

(43) Mi, B.; Cahill, D. G.; Mariñas, B. J. Physico-Chemical Integrity of Nanofiltration/Reverse Osmosis Membranes During Characterization by Rutherford Backscattering Spectrometry. *Journal of Membrane Science* **2007**, *291*, 77–85.

(44) Mayer, M. SIMNRA, a Simulation Program for the Analysis of NRA, RBS and ERDA. *AIP Conference Proceedings* **1999**.

(45) Mi, B.; Coronell, O.; Marinas, B.; Watanabe, F.; Cahill, D.; Petrov, I. Physico-Chemical Characterization of NF/RO Membrane Active Layers by Rutherford Backscattering Spectrometry. *Journal of Membrane Science* **2006**, *282*, 71–81.

(46) Park, H. B.; Freeman, B. D.; Zhang, Z.-B.; Sankir, M.; McGrath, J. E. Highly Chlorine-Tolerant Polymers for Desalination. *Angewandte Chemie* **2008**, *120*, 6108–6113.

Appendix A.

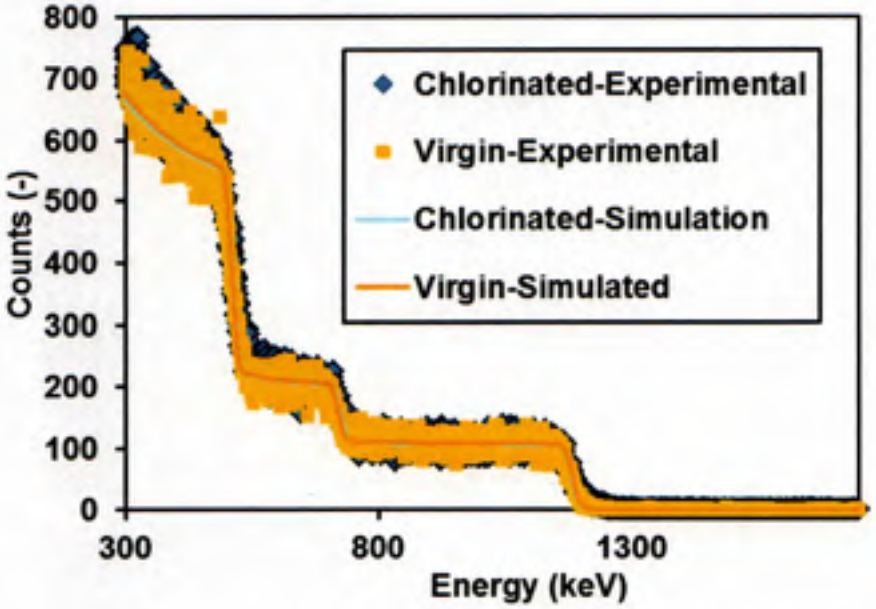


Figure A.1. Polysulfone virgin support and polysulfone support exposed to $CT_{T,Cl}$ =30,000 ppm·hr with $C_{T,Cl}$ = 750 ppm at pH=4. Both samples were rinsed with ultrapure water at pH ≈ 5.5 prior to ion probing at pH 10.5. Experimental data taken with RBS for the virgin support is shown as yellow square data points and the chlorinated support as dark blue diamond data points. The simulation RBS experiment performed using SIMNRA can be seen for the virgin support as the yellow fitted line while the Simnra simulation for the chlorinated support can be seen as the light blue fitted line.