The search for a chlorine-resistant reverse osmosis membrane

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SUMMARY

Reverse osmosis membranes processing natural and waste waters are
often exposed to low concentrations of chlorine in feed water. This biocide
is chemically aggressive toward most commercial high performance
membrane polymers. Chemical attack by chlorine ultimately results in
membrane failure as measured by enhanced passage of both salt and water.
Membrane failure is due to certain structural changes within the polymer
in response to chlorine exposure. These changes in polyamide type mem-
branes result from chlorine attack on amide nitrogen and aromatic rings.
The resulting substitution products may cause deformation in the polymer
chain or cleavage at amide linkages. The exact chemical mechanism of
chlorine-polymer interaction and subsequent membrane failure is not, as
yet, clearly understood. A review of published work on membrane-chlorine
interaction will be presented here. Experimental evidence supporting
various models for membrane failure will also be documented. In addition,
certain common structural features known to enhance chlorine resistance of
polymeric membranes are identified. It is anticipated that this paper will
stimulate research efforts toward development of polymeric reverse osmosis
membranes with high levels of chlorine resistance.
INTRODUCTION

Reverse osmosis (RO) technology has come a long way since its humble beginnings in the early 1960's [1]. Despite impressive membrane inventories [2,3] and sophisticated hardware [4], stability and life expectancy of membranes continue to plague this rapidly growing industry [5,6]. A principal cause of membrane failure involves membrane-chemical interaction with disinfectants used for biofouling control [7,8].

Feed water disinfection is an integral part of all RO installations processing natural or waste waters [7-9]. The disinfectant of choice is chlorine, although other biocides have been considered for membrane processes [9-11]. Chlorination is especially important for systems involving wastewater reclamation [12]. A variety of reducing agents is used in dechlorination systems, but partial failure of such systems may result in RO membrane exposure to low concentrations of residual chlorine [13,14].

Chlorine sensitivity of RO membranes varies with polymer type and feed water pH [15-18]. Cellulose acetate blended membranes, for example, are generally quite chlorine resistant, but their application is limited to waters of relatively low salinity. Processing of higher salinity waters, however, demands considerably better levels of membrane performance.

The requirement of high flux and salt rejection has been accomplished by two state-of-the-art membrane configurations [1]. In the first, flux enhancement occurs by providing a large increase in membrane surface area. DuPont B-9 and B-10 hollow fine fiber modules are leaders in this technology [19]. These asymmetric membranes are cast from various modifications of aromatic polyamides. In the second class of membranes, resistance to water flow is minimized with ultra-thin cross-linked polymer layers [20]. These thin films are formed by interfacial polymerization and deposited on a microporous support, usually consisting of polysulfone. Most current high performance composite membranes involve aliphatic or aromatic amines condensed with acyl chlorides, isocyanates, or other reactive groups [3]. The resulting membranes usually contain amide or urea linkages in various states of substitution. A variety of other nitrogen bases may also be present in the polymer.

Why are these "new generation" membranes chlorine sensitive whereas cellulose acetate polymers can tolerate fairly high levels of feed water chlorine? The answer lies in a comparison of structure and reactive functional groups available in these different membrane categories. Our
objective here is to identify chemical entities contributing to chlorine sensitivity contrasted with structural features necessary for high performance levels.

More than 25 years have passed since the first reports on membrane-chlorine sensitivity appeared in the literature [15]. Numerous papers in this area have subsequently been published. Various models for chlorine attack on membranes and mechanisms of membrane failure have been proposed. Most published data are based on polyamide type membranes. In this paper, however, we plan to expand our discussion so as to include other polymeric systems with proven or potential RO application.

At this writing, the literature appears to be in a state of confusion regarding polymer properties necessary for chlorine resistance while maintaining high levels of performance. Motivation for the present paper arose from the need to review existing literature and sort out supporting evidence for the various models describing membrane failure. We believe that the ensuing discussion will help to clarify the mechanism of chlorine attack on aromatic polyamides. In addition, certain chlorine resistant structures will be identified. Our intent is to provide new insights which may be useful in development of high performance chlorine resistant membranes.

CHEMICAL MODELS FOR MEMBRANE-CHLORINE INTERACTION

Since DuPont introduced the first B-9 permasep permeator, polyamides and certain other nitrogen-containing polymers have been adopted as basic chemical structures for a variety of noncellulosic high-performance RO membranes [19]. As a result, published studies on membrane failure resulting from chlorine exposure have focused on this group of polymers. Commercial polyamide type membranes are roughly classified into two categories based on chemical structure of the salt rejecting layer [2,3]. These are fully aromatic and aromatic-(cyclo)aliphatic types. Membranes may be further classified as homogeneous, asymmetric, or composite based on physical structure and method of fabrication [3]. General structures of cellulose acetate and aromatic polyamide membranes are illustrated in Fig. 1.

A major disadvantage of polyamide type membranes is their sensitivity to chemical disinfectants such as chlorine and ozone [18]. Since chlorine is
a most cost-effective disinfectant, there exists a great demand for chlorine-resistant membranes. Reduction in chlorine sensitivity may be achieved through modification of polyamide structure or consideration of alternate polymeric systems. The first part of our discussion will focus on proposed mechanistic models for polyamide-chlorine interaction. Chlorination has been shown to initiate conformational changes or cleavage of the membrane polymer. Either event ultimately leads to permanent membrane failure. Information gained from mechanistic studies helps to identify chlorine sensitive sites and should prove useful in design of membranes with greater chlorine tolerance.

Chlorination of aromatic polyamides

Amide nitrogen is vulnerable to chlorine attack because of electron withdrawing effects of the carbonyl group [21-23]. Aqueous chlorine species react readily with amide nitrogen, resulting in formation of N-chloro derivatives [24]. For example, N-chloro-N-methyl-benzamide is produced from the reaction of hypochlorite ion with N-methyl benzamide [24]. This reaction involves initial chlorination of amide oxygen followed by rapid rearrangement to the N-chloro product. Avlonitis et al. [25]
Fig. 2. Proposed Orton Rearrangement in chlorination of benzanilide (N-phenyl benzamide).
Step 1: N-chlorination through chlorine attack on amidic nitrogen. Step 2: ring chlorination through intermolecular rearrangement.

suggested this mechanism as a pathway for N-chlorination of polyamides in alkaline solution.

Aromatic rings are also susceptible to electrophilic substitution by chlorine [22,23]. Ring chlorination is considered to take place by two possible reaction pathways. In the first, direct electrophilic aromatic substitution is suggested [26]. Aromatic rings bonded to the N-H group of amide linkages are most vulnerable to chlorine attack [22,23]. A second mechanism, known as the Orton Rearrangement, involves initial chlorination of amide nitrogen [27,28]. The resulting N-chloro amide then undergoes intermolecular rearrangement forming various aromatic substitution products. An explanation for this rearrangement suggests elimination of the N-bonded chlorine atom yielding molecular chlorine which then rapidly attacks aromatic rings via electrophilic substitution. The reaction mechanism is illustrated in Fig. 2.

Ring chlorination via the Orton Rearrangement has been verified by Kawaguchi and Tamura [29] who performed chlorine-resistance tests on three model compounds: N-methyl benzanilide, N-phenyl benzanilide, and benzanilide. No evidence of chlorine uptake by the first two tertiary amides was observed. However, the secondary amide, benzanilide, sustained extensive aromatic ring chlorination. These reactions, summarized in Fig. 3, strongly support Orton’s theory involving N-chlorination followed
(a) Tertiary Amides (N-methyl benzanilide, N-phenyl benzanilide)

\[
\begin{align*}
\text{CH}_3 & \quad \text{HOCl} & \quad \text{No Reaction} \\
\text{CH}_3 & \quad \text{HOCl} & \quad \text{No Reaction}
\end{align*}
\]

(b) Secondary Amide (Benzanilide)

\[
\begin{align*}
\text{HOCl} & \quad \text{No Reaction} \\
\text{HOCl} & \quad \text{No Reaction}
\end{align*}
\]

Fig. 3. Chlorination of selected model compounds as reported by Kawaguchi and Tamura [29].

by intermolecular rearrangement. It should also be noted that ring chlorination observed with benzanilide did not occur on chlorination of N-methyl benzamide. Explanation lies in structural differences between these compounds. Benzanilide contains two aromatic rings whereas the single ring present in N-methyl benzamide is deactivated by an adjacent carbonyl group. A discussion of ring substitution patterns will be presented in the following section of this paper.

Kawaguchi and Tamura [29] also studied a variety of other model polyamides representing different alkyl and aryl groups as well as levels of substitution at amide nitrogen. Interaction with HOCl was divided into three general categories: (1) no reaction, (2) reversible amidic nitrogen chlorination, and (3) irreversible aromatic ring chlorination. From their experimental results, it was shown that tertiary amides were unreactive toward chlorine. Secondary amides containing aliphatic nitrogen substituents formed N-chloro derivatives which were easily dechlorinated. Irreversible chlorination occurred only with secondary amides containing aromatic nitrogen substituents. In the reactive polyamides, chlorine in the final product was always associated with aromatic ring substitution. It thus appears that N-chloro amides have limited stability. Spontaneous loss of chlorine or molecular rearrangement most likely takes place.
A more extensive study of model-compound chlorine sensitivity was reported by Lowell et al. [30]. In this work a variety of aromatic model compounds containing amide, urea, and ester linkages were exposed to sodium hypochlorite solutions at pH 4.5 and 10. Following are significant conclusions generated from their results:

- Chlorine sensitivity is pH dependent. Most model compounds in this study were more reactive at pH 4.5.
- Chlorine sensitivity is greatly enhanced when the aromatic group is linked to nitrogen in amides or ureas.
- Ureas were shown to be more chlorine sensitive than amides.
- Ester linkages were generally chlorine resistant.
- Model compounds containing tertiary substituted nitrogen showed the highest levels of chlorine resistance.

The work of Lowell et al. has indeed provided useful guidelines for the design of chlorine resistant polymers.

The chemical literature regarding chlorine substitution mechanisms favors Orton’s Rearrangement, but the possibility of direct aromatic ring chlorination cannot be ruled out completely. Orton et al. [27,28,31] showed that the ratio of N- to C-chlorinated products from the reaction between acetanilide and chlorine was time-independent, implying that N-chlorination and direct ring chlorination were simultaneous and independent of each other. Glater and Zachariah [32] also favored direct chlorination of aromatic rings based on IR and NMR spectral analysis of bromine-substituted benzanilide. Their data indicated only shifting but not weakening of N-H stretch frequencies. No evidence of amide nitrogen bromination was revealed from their studies.

**Aromatic ring substitution patterns**

The mechanism of chlorine attack on polyamide membranes is involved not only with chlorination pathways but also with sites of aromatic ring substitution. In electrophilic aromatic substitution, both reactivity and orientation are influenced by substituents already present on the benzene ring [22,23]. If the ring contains electron-releasing groups, electrophilic aromatic substitution takes place rapidly. On the other hand, aromatic substitution occurs slowly if electron-withdrawing groups are present. Substitution sites are also determined by the directive influence of these groups.
(a) Benzanilide (N-phenyl benzamide)

(b) N-p-bromophenyl benzamide

(c) N-2,4-dibromophenyl benzamide

Fig. 4. Final reaction products from aqueous bromination of benzanilide (N-phenyl benzamide) as reported by Gienger [33].

Bromination studies of the model compound benzanilide by Glater and Zachariah [32] showed that reaction took place first at the para-position of rings linked to the N-H substituent. Upon further exposure, a second bromine was substituted in the ortho position. Rings linked to the carbonyl group could be brominated at the meta position but at a much slower rate. This was anticipated since the N-H portion of an amide linkage is known to be a ring-activating, ortho-para director, while the C=O portion is a deactivating meta director [22,23]. Selection of the benzanilide model in this study was based on its structural similarity to units of DuPont B-9 membrane. Bromine was used as a halogenating agent in this work since steady solution concentration levels could be maintained more readily than with chlorine. Following selected exposure periods, reaction products were examined by IR and NMR spectroscopy. Experiments on halogen interaction with actual B-9 membrane samples were also performed in their work. IR spectra of chlorine or bromine-exposed membrane showed substitution patterns similar to model compound studies.

The above benzanilide substitution pattern was also verified by Gienger [33] who succeeded in isolating and identifying products of this reaction by HPLC-UV. Compounds derived from this reaction (Fig. 4) consisted of
unreacted benzanilide, N-p-bromophenyl benzamide, and N-2,4-dibromophenyl benzamide. Bromine substitution occurred only on the N-H activated ring and was not found on carbonyl deactivated rings. No evidence of amide bond cleavage was observed by Gienger since molecular fragments could not be identified by HPLC.

$^1$H NMR studies reported by Kawaguchi and Tamura [29] are also in good agreement with results observed by Gienger. Experiments performed with poly-m-phenyleneisophthalamide showed initial chlorination at the para-position on the activated ring. A second chlorine atom then adds to the mutual ortho position of this ring. The chlorination pattern of this model aromatic polyamide is shown in Fig. 5. This could be expected since each para position is doubly activated by two N-H groups. The mutual ortho position is also doubly activated but may be less vulnerable to chlorine attack because of steric hindrance. Chlorination of the deactivated ring was not observed from their experimental data.

Membrane failure mechanisms

Several models for polyamide chlorination and aromatic ring substitution patterns have been reviewed in the preceding subsections. A remaining
question involves the impact of these events on ultimate membrane failure. Two general mechanisms are suggested for this process. The first involves membrane polymer deformation with resultant weakening of the salt rejection barrier. In the second concept, complete or partial depolymerization results from amide bond cleavage.

Polymer deformation was proposed by Glater and Zachariah [32] in an attempt to explain the chlorine sensitivity of the DuPont B-9 membrane. Spectral analysis of chlorine exposed membrane samples revealed a marked shift in wave frequency from 3280 to 3420 cm⁻¹. This spectral region is sensitive to hydrogen bonding modes and was interpreted as a transition from intermolecular hydrogen-carbonyl oxygen bonding to intramolecular hydrogen-chlorine bonding. The overall effect caused weakening of the partially cross-linked polymer with resulting polymer chain deformation. Three concerted steps are involved in the overall proposed mechanism: (1) aromatic ring chlorination, (2) disruption of intermolecular cross linkages and conversion to intramolecular hydrogen bonding, and (3) subsequent chain structure deformation. It should be noted, however, that this hypothesis applies only to membranes weakly cross-linked by hydrogen bonds. Chlorine damage to highly cross-linked membranes such as FilmTec FT-30 probably occurs by a different mechanism, possibly partial or complete depolymerization [34].

According to Avlonitis et al. [35], changes in physical properties of DuPont B-10 polyamide membrane were related to length of chlorine exposure at pH 4 and 9. As in other studies, chlorine degradation occurred much more rapidly at pH 4. Extent of chlorination was correlated with changes in melting point, tensile strength, and intrinsic viscosity. All of these properties were found to decrease with increased chlorine exposure. The authors explained these changes on the basis of a structural transition from crystalline to amorphous states. This change is believed to result from a reduction of intermolecular forces (i.e., hydrogen bonding) in response to continued chlorine exposure. Ultimately the amorphous region becomes more susceptible to chlorine, finally causing chain cleavage and complete membrane failure.

Evidence for amide bond cleavage has been suggested by other investigators but the chemical nature of this process remains speculative. Three chemical routes supported by some experimental evidence have been proposed [21,25,34,35]. These are hydrolysis, oxidation, and Hoffman Degradation. The possibility of hydrolysis is questionable since amide
bonds are quite stable at usual feed water pH levels [21-24]. In addition, evidence that N-chloro amides are more vulnerable to hydrolysis could not be found in the literature. Oxidation is also a possibility since HOCl is a fairly strong oxidant, but according to Lee et al. [35], the amide bond is resistant to oxidation in acid solution at low chlorine concentrations. Amine groups, however, are much more sensitive to oxidation which may explain the high chlorine sensitivity of polyethylenimine (PEI) based membranes [35]. In this case, oxidation causes rupture of secondary and tertiary amine linkages but not amide bonds.

Oxidative amide bond cleavage has been proposed by Koo et al. [34]. Electron spectroscopy chemical analysis (ESCA) studies of chlorine damaged FT-30 membrane revealed an increase in membrane carbonyl content. A mechanism proposed by these investigators involves amide N-chlorination followed by bond cleavage and subsequent benzene ring oxidation to substituted quinone derivatives. No effort was made to identify other oxidation products of this reaction.

Hoffman Degradation has also been suggested as a route for amide bond cleavage through chlorination [25,35]. In this process, secondary N-chloro amides are decomposed at high pH in a series of steps yielding primary amines. This is accompanied by loss of the carbonyl group which is converted to carbon dioxide. Bond cleavage by this mechanism appears unlikely at usual feed water pH since Hoffman Degradation occurs only in alkaline solution.

Amide bond cleavage should be reflected in a significant change in membrane physical properties. Among these properties are changes in intrinsic viscosity. Viscosity measurements by Glater et al. [18] and Avlonitis et al. [25] were conducted with chlorine-exposed polymer samples dissolved in dimethylsulfoxide (DMSO). Resulting data revealed an initial viscosity increase followed by a sharp decline in response to continued chlorine exposure. Viscosity data are usually related to polymer molecular weight. An explanation for the first event is chlorine addition accompanied by a corresponding molecular weight increase. Continued chlorination may then be followed by chain cleavage with a resulting decrease in molecular weight.

There may be another interpretation for observed viscosity changes. The first event is indeed related to chlorine addition. Subsequent viscosity decline, however, may be explained by a different mechanism. According to Glater and Zachariah [32], performance decline of Du Pont B-9 mem-
brane resulted from a reduction in cross-linked hydrogen bonding. This structural change could account for the measured viscosity decrease. Experimental verification of this hypothesis, however, has not as yet been accomplished and a detailed mechanism for B-9 membrane failure remains to be established.

CHEMICAL MODELS FOR MEMBRANE-CHLORINE RESISTANCE

The first successful RO membranes were based on cellulose, a naturally occurring polymer. Since the early work of Loeb and Sourirajan [1], efforts have focused on synthetic polymers with the intent of creating higher performance membranes. This objective has been achieved, but at the expense of enhanced chlorine sensitivity.

Despite its salt rejection limitations, cellulose acetate has proved to be highly tolerant of feed water chlorination. How do we account for the well established chlorine resistance of cellulose acetate type membranes contrasted with chlorine sensitivity of most synthetic membranes? The answer lies in a comparison of structural elements present in these two membrane categories.

The cellulose diacetate polymer "backbone," for example, consists of gluco-pyranose rings connected by β-glycoside (ether) linkages [22]. Two of the three ring hydroxyl groups are acetylated. Essential features of this polymer are cyclo-aliphatic rings and oxygen containing functional groups. It appears from the literature that oxygen functionalities are unreactive toward aqueous chlorination. In addition, chlorination of aliphatic or cycloaliphatic structures is not likely under conditions required for feed water disinfection. It is evident that cellulose acetate meets these chemical and structural requirements.

By contrast, most "new generation" membranes include aromatic polyamides or polyureas. In the preceding section of this paper, we have shown that chlorine sensitivity is enhanced by nitrogen functional groups such as amines, ureas, and secondary amide linkages. Tertiary amides appear to be chlorine resistant. It was also shown that aromatic rings bonded to amide nitrogen are vulnerable to chlorine attack, while rings bonded to the carbonyl group appear to be chlorine tolerant. Polyamides containing alkyl groups bonded to amide nitrogen are also less chlorine sensitive.
Based on these findings, the following structural features should be considered in future development of polymeric membranes with enhanced chlorine resistance:

- Functionalities containing oxygen or sulfur only
- Tertiary amide linkages
- Aromatic rings bonded to carbonyl group of amide linkage
- Alkyl groups bonded to amide nitrogen
- Protective groups on active sites of aromatic rings

Incorporation of these features without loss of performance and structural integrity presents a real challenge for membrane manufacturers. Continued research and development efforts involving these constraints should improve the overall quality of future RO membranes. In recent years, several novel chlorine tolerant membranes have been developed and some are commercialized. Polyamide membranes have also been modified in an effort to improve chlorine resistance. Various aspects of successful polymer modification are presented in the following section. Note that this discussion is not intended as a comprehensive literature survey. It will, instead, be limited to a few illustrations from the vast and rapidly growing body of knowledge on membrane-chemical interaction.

**Elimination of chlorine sensitive sites**

RO membranes generally contain oxygen or nitrogen functional groups to enhance hydrophilicity. Since nitrogen functions are chlorine sensitive, chemical resistance will probably improve if such groups are excluded from the polymer. Several membranes containing oxygen and sulfur functionalities have met with varying degrees of success. Leading polymers in this field are poly(ether)sulfones [36–40]. Chlorine resistance and hydrolytic stability of these polymers are outstanding, but water flux and salt rejection are severely limited [36]. Improvement in water flux has been accomplished by sulfonating aromatic rings in these polymers [37–39]. The resulting negatively charged membrane shows ion exchange capability toward divalent cations and is thus unsatisfactory for natural water desalination [39–41]. Hydrophilicity and performance deteriorate rapidly as sodium ions are exchanged for calcium and magnesium in feed water.

Attempts to develop composite membranes by combining polyamide with polysulfone have been reported in recent publications [42,43]. The resulting improved chlorine resistance of these “polysulfonamide” films was ex-
plained by deactivation of the secondary amide linkage through enhanced resonance stabilization [43]. Only limited performance data were reported in these studies.

Polyvinyl alcohol has also been considered as a candidate for RO membrane development [44–48]. The absence of nitrogen functionalities and aromatic rings are essential features for increased chlorine tolerance. The hydrophilic nature of this polymer provides excellent water flux, but poor salt rejection which has been a major problem [45,46]. Recently developed composite membranes contain a thin polyvinyl alcohol skin deposited on a polysulfone ultrafiltration support [47,48]. These low pressure membranes evidently display excellent chlorine resistance coupled with high levels of salt rejection [48]. The manufacturer has even claimed a chlorine-resistance capability superior to cellulose acetate. This is not surprising, if one considers chemical features of the two polymeric components of this membrane. Continued research and development efforts with these polymers may lead to high quality RO membranes in the future.

Furfuryl alcohol, another monomer containing oxygen functional groups, has met with limited success in membrane development [20]. In early stages of development, sulfuric acid catalyzed condensation polymerization produced a high salt-rejecting but chemically unstable membrane [49]. In addition, chlorine tolerance of these membranes was relatively poor. Further developments included co-polymerization of furfuryl alcohol with an isocyanurate derivative [50]. This polyfuran membrane demonstrated good performance but high chlorine sensitivity. Vulnerability to chlorine attack may be shared by unsaturated furfuryl alcohol and nitrogen functionalities present in the skin layer of this membrane.

**Modifications of polymer structure**

Tertiary amides are expected to enhance chlorine tolerance due to the absence of amidic hydrogen. Membranes containing these linkages were first reported by Credali et al. [51] using piperazine monomers. Continued efforts in this area at North Star Research [20] gave rise to a variety of composite membranes involving piperazine and aromatic acid chloride monomers. Resulting membranes showed some chlorine tolerance but were never commercialized because of wide variations in water flux and salt rejection capability. A recent publication [52] describes preparation of a variety of tertiary amide polymers generally classified as polypiperazine-
amides. These polymers display high levels of chlorine resistance evidently resulting from the absence of N-H linkages. Some of these polymers are, in fact, commercially available as spiral wound membrane modules [53].

In addition to polypiperazineamide, several other polyimide derivatives have been considered for RO membrane development. For example, polyimides received a great deal of attention because of excellent thermal and oxidative stability [54]. It was initially believed that the absence of N-H groups would enable these membranes to resist chlorine attack. Chlorine resistance of these membranes, however, turned out to be inadequate. This is probably due to incomplete conversion of the polyamic acid to polyimide or to direct aromatic ring chlorination [54]. As a result, polyimides are not considered commercially attractive at this time.

Benzimidazole and benzimidazolone polymers have also been used in potential RO membrane development [54,55]. The resulting membranes exhibited good pH and thermal resistance but failed on long-term exposure to mildly chlorinated feed water. Chlorine sensitivity probably results from amidic hydrogen and aromatic rings presented in both polymers.

Various aromatic-cycloaliphatic polyamide membranes have recently been described by Sundet et al. [56] and Arthur [57]. Introduction of aliphatic monomers was motivated by the possibility of improved membrane performance due to structural flexibility of these compounds [57]. No significant change in chlorine resistance resulted, however, from these polyamide variants. This could be anticipated since aromatic rings and secondary amide linkages were not eliminated. Improved chlorine resistance might result from polyamides containing cyclo-aliphatic monomers only. RO applications of such monomers, however, have not appeared in the literature.

It appears that high levels of cross-linking improves resistance to chlorine attack. An example is the commercial FilmTec membrane FT-30 [58]. This highly cross-linked polyamide membrane is relatively tolerant of chlorine at low concentrations and pH levels less than 7. Another highly cross-linked commercial membrane, Fluid Systems TFCL, also shows good chlorine resistance under mildly acidic conditions [13,14]. Both membranes are severely damaged at pH levels greater than 8.

**Protection of chlorine-sensitive sites**

At this time, most of the successful high performance commercial RO
membranes are variants of aromatic polyamides. Aromatic substitution by chlorine is known as an important step in the overall mechanism of membrane failure. Protection of active sites on aromatic rings has been suggested as a method for improving chlorine resistance [25]. Deactivating functional groups such as $\text{-NO}_2$ or $\text{-SO}_3\text{H}$ substituted at appropriate ring positions can block attack by aqueous chlorine. Such altered ring structures would then inhibit subsequent steps in the overall membrane failure mechanism. Aromatic monomers containing blocking groups may be suggested as candidates for future polymerization studies.

CHEMICAL REQUIREMENTS FOR THE "IDEAL" RO MEMBRANE

An "ideal" membrane would be one demonstrating high levels of performance (i.e., high water flux and low salt passage) coupled with chemical stability and good chlorine resistance. Requirements for performance enhancement are largely speculative, but relationships between polymer structure and membrane function should be given careful consideration. A variety of models and explanations for solute and water transport through RO membranes have been proposed in the literature [59,60; and references therein]. Some provide good agreement with membrane performance data, but none are concerned with relationships to chemical structure.

The reader should carefully note that the province of this paper is not to discuss the many existing models for membrane transport. Instead, we are attempting to emphasize the importance of chemical and structural features in designing stable membranes with high performance levels.

Most publications in this area do not specify chemical features necessary for rejection of ionic species while providing for adequate water flux. Such requirements are generally overlooked not only by theoreticians but also by polymer chemists. Membrane fabrication at this time is still largely an empirical "art." Polymer chemists are well versed in poly-condensation reactions and are also familiar with long lists of monomers capable of providing films with good structural integrity. The ability of certain of these films to reject salts and pass water has been established, however, primarily on a trial-and-error basis. Development of a molecular-level understanding of the relationship between chemical structure and membrane performance and stability is a major challenge for membrane scientists.
What then are the chemical features necessary for optimum desalination capability coupled with high resistance to chlorine attack? Requirements for the first category should be considered in greater detail by groups engaged in membrane development. It appears to the authors that the most successful desalination membranes contain two distinguishing chemical features. These are (1) ring structures, usually containing five or six carbon atoms; and (2) functional groups associated with unshared electron pairs.

Rings may provide optimum structural features necessary for formation of molecular-size hydrophilic voids. Indirect evidence for such voids in cellulose acetate and polyimide membranes has been reported in the literature [61–65]. Electron pairs must be involved in hydrogen bonding with water molecules. The latter requirement is necessary for hydrophilicity and facilitated water transport. Electron pair participation and water transport via hydrogen bonding has been suggested by several investigators [54,60–65].

Scherer and coworkers [64] emphasized the importance of polymer-polymer, polymer-water, and water-water interactions within the membrane active layer. Such interactions are involved in controlling the transport of water and solutes through RO membranes. It has been suggested that cellulose acetate membranes contain a random array of interconnected hydrophilic voids. These voids are separated by hydrocarbon-like areas associated with gluco-pyranose rings. The periphery of each void is lined with acetyl and hydroxyl groups. Both functional groups, containing unshared electron pairs, form a variety of hydrogen bonded structures which facilitate water transport through the membrane.

The second category, chlorine resistance, is better understood as a result of a growing body of experimental evidence. Existing chemical models for membrane-chlorine interaction and chlorine resistance have been reviewed in preceding sections of this paper. Alteration in polymer structure and functionalities will undoubtedly result in diminished chlorine sensitivity. However, polymer manipulation to enhance chlorine resistance must be concerned with those features necessary for adequate levels of performance. Consideration of both phenomena is essential to membrane optimization. We may still be a long way from producing “tailor-made” membranes, but some of the information discussed here should provide a stimulus to research groups engaged in membrane development.
CONCLUDING REMARKS

The literature on membrane-chlorine interaction has expanded rapidly during the past decade. In this paper we have attempted to characterize those features of RO membranes which enhance chlorine sensitivity and others which tend to resist chlorine damage. A review of published mechanisms for polyamide membrane-chlorine interaction has been presented.

Chlorine sensitive features of membranes consist of nitrogen functional groups and aromatic rings. Secondary amide and urea linkages are most vulnerable to chlorine attack. Chlorine addition is followed by subsequent membrane failure. The nature of this process is not, as yet, clearly understood but is considered to involve polymer chain deformation or amide bond cleavage. Future efforts must be directed toward clarification of the overall mechanism of membrane failure.

Progress in development of chlorine tolerant membranes is reviewed in this paper. Membranes involving oxygen or sulfur functional groups have met with some success. Attempts to prepare membranes with tertiary amide linkages is also discussed. In addition to chlorine sensitivity, future membrane development should focus on a better understanding of the chemical basis for water transport and salt passage. Consideration of both phenomena must proceed hand in hand since they share equal importance in membrane function and durability. There is indeed much work to be done before a truly "ideal" RO membrane becomes a reality.

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