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REVERSE OSMOSIS MEMBRANE SENSITIVITY TO OZONE AND HALOGEN DISINFECTANTS

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SUMMARY

The sensitivity of commercial reverse osmosis (RO) membranes toward halogen and ozone disinfectants has been measured at carefully controlled concentration and pH levels. Membrane sensitivity varies with polymer type, disinfectant chemical, and solution pH. Aromatic polyamide membranes are damaged by halogen addition to aromatic rings within the polymer. This process follows predictable reaction kinetics. Polymer viscosity changes with increasing membrane damage have also been followed. Results of this study will be useful in planning disinfection strategies for RO units in the field.

INTRODUCTION

Natural water RO systems require feedwater disinfection to prevent slime formation and potential microbiological degradation of membrane polymers. Chlorine, the most common water disinfectant, came under careful scrutiny during the early 1970s because of the appearance of tri-halo methanes in certain municipal drinking water supplies [1]. This discovery motivated the search for alternative disinfection strategies. These included ozone, chlorine dioxide and other halogen agents. This work, sponsored by OWRT, was initiated because of the lack of detailed information on membrane-chemical interactions.

Certain papers on membrane sensitivity to chlorine have been published by Spatz and Friedlander [2], Vos et al. [3] and Fluid Systems Division of UOP [4]. Brief reports on chlorine dioxide and iodine were also presented by Vos et al. [5] and Turby and Watkins [6] respectively. Prior to the onset of our work at UCLA, membrane responses to ozone, bromine, or bromine chloride had not been observed.

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Comprehensive studies of membrane-halogen interactions have recently been published by Glater et al. [7], Glater et al. [8] and McCray et al. [9]. These papers represent a summary of work conducted with five different types of commercial RO membranes. Experiments were carried out with Cl_2, Br_2, I_2, ClO_2, and BrCl under carefully controlled conditions of pH and halogen concentration. Membrane damage was evaluated by performance testing in a two inch flat plate laboratory RO unit. The product flux and percent rejection of a 5,000 ppm sodium chloride solution were compared to baseline performance of unexposed membrane.

In the present study we have continued this series of experiments which include membrane exposure to ozone. We will also report on some additional techniques designed to provide further insights into the nature of membrane-chemical interaction. Additionally these studies include rate studies of membrane deterioration in certain chemical environments.

EXPERIMENTAL

Techniques of soak testing, chemical monitoring, pH regulation, and performance assessment with halogen based disinfectants have been previously presented by Glater et al. [7]. As reported in earlier work, all soak testing was conducted in buffer solutions adjusted to pH levels of 3.0, 5.8, and 8.6. Membrane samples were exposed to ozone by sparging ozone-oxygen gas mixtures into buffered solutions. Ozone was generated by passing pure oxygen gas through an ultraviolet type ozonator. The configuration shown in Fig. 1 was capable of maintaining a maximum concentration of 0.9 ppm O_3 in a 28 liter exposure chamber. Note the elevated position of the gas diffusers. With this arrangement, direct contact between gas bubbles and membrane samples could be avoided.

Because of ozone instability, gas injection must be carried out continuously. A six hour pre-injection period was required to build up steady state levels of dissolved ozone. Ozone levels in the system were periodically monitored by removing bath samples for analysis. These samples were analyzed by iodine release and subsequent titration with sodium thiosulfate according to standard methods.

Certain halogen treated membrane samples were analyzed for halogen uptake following exposure. Membranes were rinsed thoroughly with distilled water, oven dried at 110°C and sent out to Global Geochemical Corp., Los Angeles, CA, a commercial laboratory. The samples were first degraded by sodium fusion, eluted with water, and the resulting solution analyzed by ion chromatography. Halogen incorporated into the membrane was reported as percent by weight of dry sample.

The viscosity of certain membrane samples was measured in an attempt to study possible membrane depolymerization following halogenation. Measure-

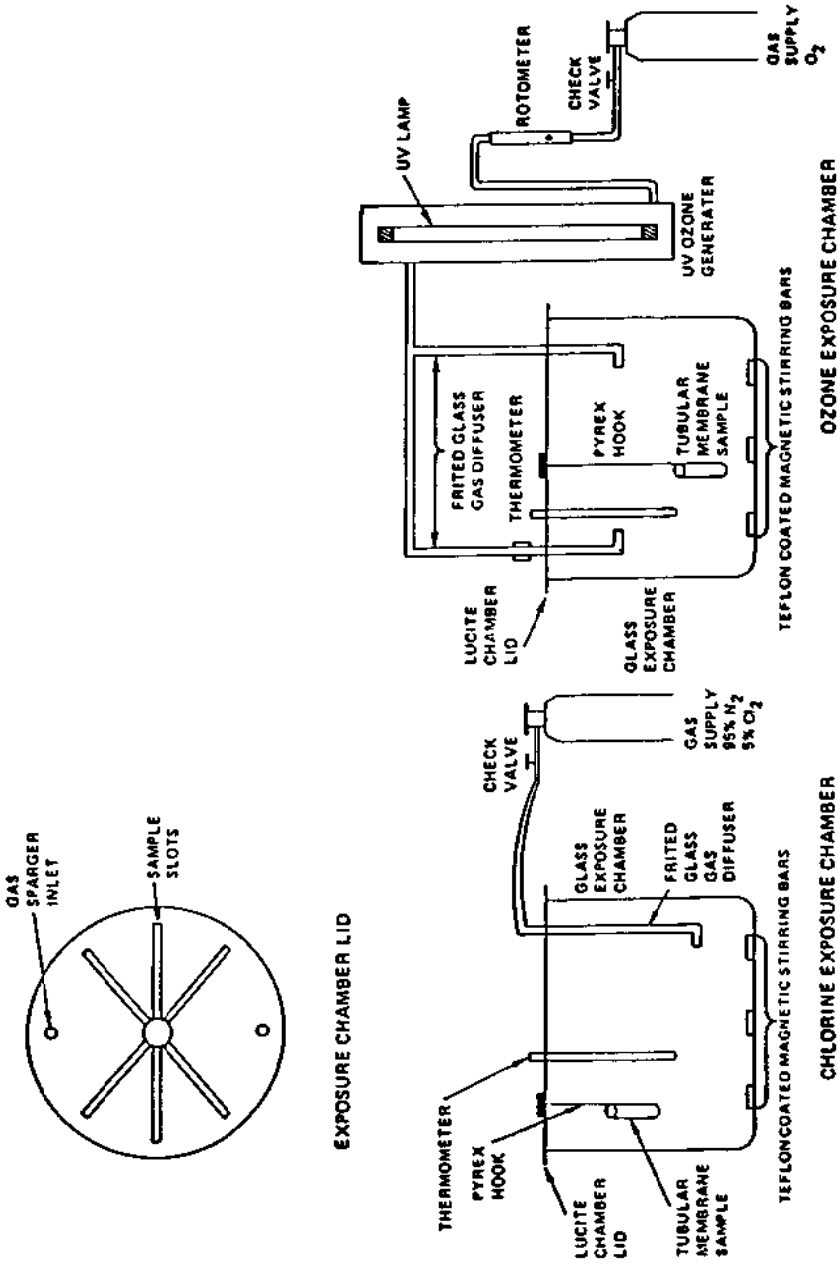


Fig. 1. Experimental apparatus for membrane soak tests with chlorine and ozone.

ments were carried out with a Ubbhelode capillary type viscometer at constant water bath temperature of 25 ± 0.1°C. The experimental procedure, taken from Billingham [10] gives the following equation for solution viscosity.

$$\gamma = A\rho t \tag{1}$$

The viscosity γ is a linear function of solution density ρ and time t in seconds. The constant A is a calibration constant unique to each viscometer.

All viscosity measurements were carried out with B-9 membrane in dimethyl sulfoxide solvent at 1.0% by weight concentration. No accurate assessment of viscosity could be determined since A was not calibrated and values of ρ were not constant because of changes during membrane halogenation. As a result, we simply used time as a rough measure of viscosity changes. It should also be noted that no attempt was made to relate viscosity to molecular weight.

All performance data reported in this paper is compared with baseline data for each membrane. Assessment of membrane damage is based on difference in product flux and percent rejection between exposed and unexposed membranes. A list of commercial membranes used in this work and corresponding baseline data is given in Table I. All performance testing was conducted in a small two inch flat plate laboratory RO unit using 5,000 ppm sodium chloride feed at an operating pressure of 600 psig.

TABLE I

COMMERCIAL MEMBRANE DESIGNATIONS AND BASELINE PERFORMANCE DATA

Manufacturer	Mfg. code	Polymer type	Product flux* (GFD)	Salt rejection (percent)
Fluid Systems	TFC-RC-100	Poly(ether/urea) (thin film composite)	13.8	99.8
Envirogenics	CA blend 72°C cure	CA-CTA blend (homogeneous)	29.5	96.7
Hydranautics	γ	Homogeneous CA (coated with vinyl acetate)	20.2	97.7
DuPont	Aramid B-9	Homogeneous aromatic polyamide	15.7	97.3
FilmTec	FT-30	Composition unknown (thin film composite)	25.8	98.5

*Tested at 600 psig, 5,000 ppm NaCl feedwater at 25 ± 1°C.

MEMBRANE RESPONSE TO HALOGENS

Polyamide type membranes have, in general, been considered sensitive to chlorine as reported in previous work [7, 8, 9]. In light of our recent experimental data, however, this conclusion must be qualified. Considerable work with FT-30 and B-9 have shown these membranes to withstand chlorine attack provided the pH is carefully regulated. Fig. 2 illustrates a prolonged exposure of FT-30 to 30 ppm chlorine. Note the sustained salt rejection capability and reasonably constant product flux at pH 3.0 and 5.8. Note that performance remains fairly constant at pH levels below 5.8. At pH 8.6, however, severe degradation in performance is observed over a 328 hour period.

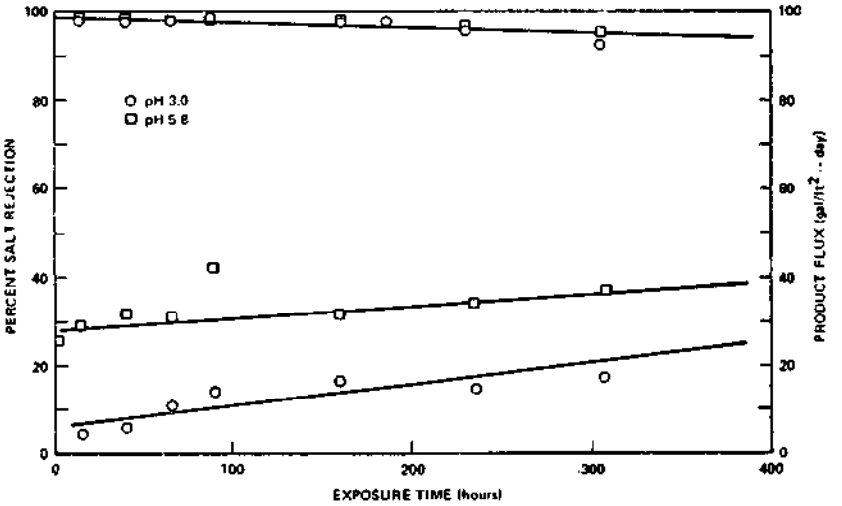


Fig. 2. Change in performance of FT-30 membrane on continuous exposure to 30 ppm chlorine at pH 3.0 and 5.8.

Similar chlorine resistance is demonstrated by B-9 membrane as shown in Fig. 3. Note the similar flat performance profiles at pH levels above 5.8. In this case severe damage occurs at pH 3.0 within 72 hours of exposure. It is interesting to note the opposite pH sensitivity of these polymers. Both membrane types are unresponsive to iodine on prolonged exposure at high concentration but show different performance profiles with bromine. FT-30 displays approximately the same sensitivity to bromine and chlorine. On the other hand, B-9 is severely damaged by bromine over the pH range used in these experiments.

Obviously the chemical structure of FT-30 differs from that of B-9. At this time we are unable to explain the difference in pH response of these

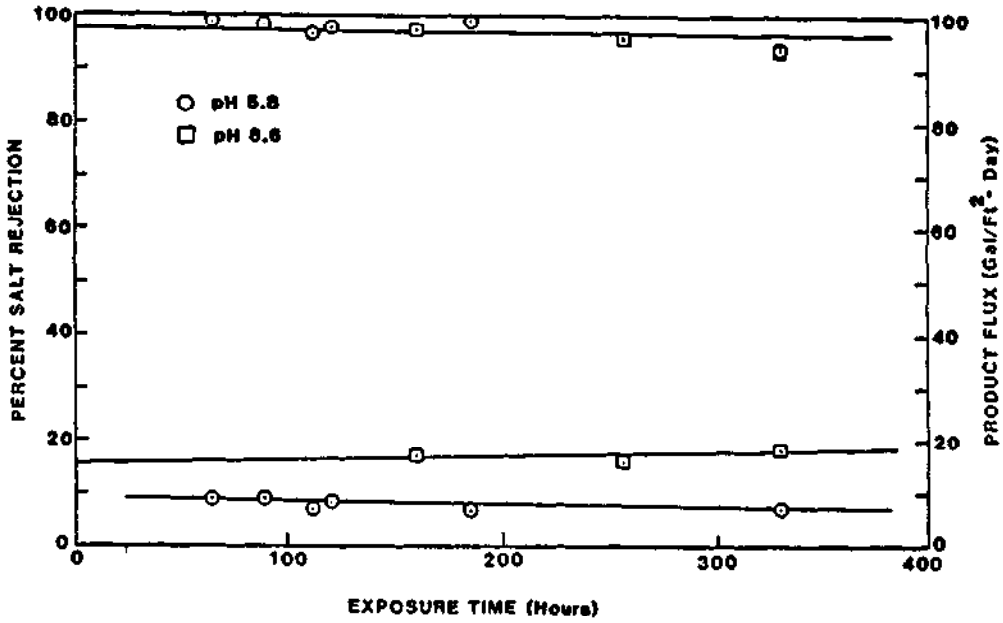


Fig. 3. Change in performance of B-9 membrane on continuous exposure to 30 ppm chlorine at pH 5.8 and 8.6.

membranes to chlorine and the overall difference in sensitivity to bromine. Details on polymer structure may provide further insights into this difference in chemical and pH sensitivity. In order to better understand the nature of halogen-membrane interaction, three different lines of investigation have been followed. The first involves elemental analysis of exposed membrane samples for halogen uptake, the second is a measurement of viscosity of exposed polymer solutions, and the third involves a study of these samples by infrared and NMR techniques. The following discussion will focus on results derived from elemental analysis and viscosity measurements. A report of our instrumental studies will appear in a subsequent paper.

All work on elemental analysis was conducted with DuPont B-9 membrane because of its halogen sensitivity at low pH. Also, this membrane is a homogeneous film of considerable thickness as compared with TFC types. Because of these properties, measurable quantities of halogen could be detected in small membrane samples.

Membranes were exposed at fixed halogen concentration in buffer solutions of constant pH. Following exposure, samples were washed thoroughly in distilled water, oven dried at 110°C, and submitted for halogen analysis. The analytical procedure first involved sodium fusion requried to convert organo-halogen compounds to halide ion. The resulting sample was then eluted with water and halide ion determined by ion chromatography.

Experiments were carried out with chlorine, bromine and chlorine dioxide for varying periods of time at different pH and concentration levels. Experimental data is summarized in Table II. Results are expressed as percent by weight of dry exposed membrane. A blank determination on unexposed membrane showed less than 0.1% halogen and was considered insignificant.

The experimental data in Table II enables us to estimate the level of halogen-polymer addition on a mole-mole basis. As a model for this calculation, we assume that aromatic halogen substitution takes place on one or both rings of the following repeating polymer unit (Fig. 4). This assumption is supported by data from our study of infrared spectra. The proposed unit was

TABLE II

HALOGEN INTAKE OF EXPOSED B-9 MEMBRANE

Disinfectant chemical	Concentration (ppm)	pH	Exposure time (h)	Polymer halogen content (% by wt.)
Cl_2	30	3.0	8	13.4
	30	3.0	24	17.0
	30	3.0	40	17.7
	30	3.0	100	22.1
	30	8.6	112	0.1
Br_2	70	3.0	40	22.2
	70	5.8	40	29.5
	70	8.6	40	19.1
ClO_2	30	3.0	100	0.5
	30	8.6	48	0.3

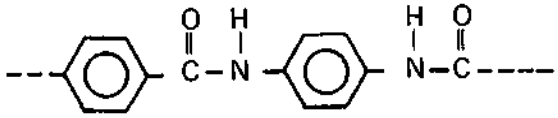
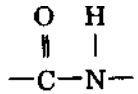
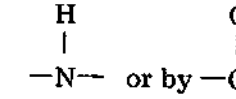


Fig. 4. Repeating polymer unit of B-9 membrane.

suggested by DuPont [11] showing B-9 membrane to consist essentially of a linear aromatic polyamide. The peptide linkages



are arranged so that alternate rings are bonded in the meta position on each side either by



This structure has also been suggested by infrared spectra.

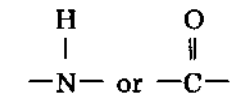
The DuPont patent disclosure for B-9 membrane [12] also shows some of the aromatic rings to contain substituted sulfonic acid groups ($-SO_3H$). This functional group is said to be present on approximately 10% of the aromatic rings. The formula weight of the repeating polymer unit equals 238. If we now consider the addition of one sulfonic acid group to every five repeating units, the formula weight is increased by $-SO_3H/5 = 81/5 \approx 16$ atomic weight units. This gives a corrected formula weight of the repeating unit of approximately 254. By using this figure we can calculate theoretical percentage halogen uptake based on one or two halogen atoms substituted. These calculations are presented in Table III.

TABLE III

THEORETICAL PERCENTAGE HALOGEN IN MONO- AND DI-SUBSTITUTED POLYMER

Substitution pattern	Theoretical % halogen (calculated)
1 Cl per formula unit	12.25
2 Cl per formula unit	21.85
1 Br per formula unit	23.95
2 Br per formula unit	38.64

The chlorine uptake data clearly indicates halogen addition to be initially very rapid. With continued exposure, the rate slows down as shown in Fig. 5. This is easily explained by increased polymer saturation, but, in addition, it is evidently more difficult to substitute a second chlorine atom on mono-substituted aromatic rings. It should be noted that alternate rings are either activated or de-activated by



substituents respectively. Substitution on the de-activated ring would thus

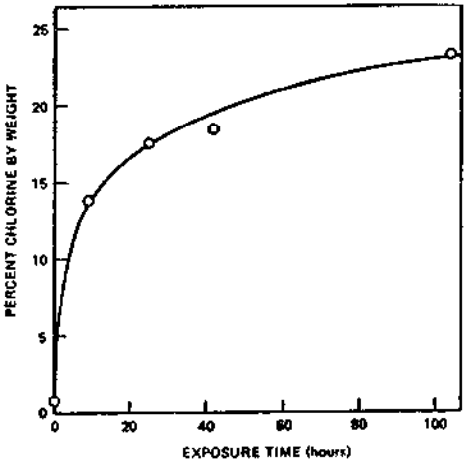


Fig. 5. Chlorine uptake by B-9 membrane on continuous exposure to 30 ppm chlorine at pH 3.0.

proceed at a slower rate. In addition, only one site in the meta position is available.

Note also that mono-substitution is completed in less than eight hours when the chlorine content reaches 13.4%. Two chlorine atoms give a theoretical value of 21.85% chlorine which agrees well with the 22.1% measured after a 100 hour exposure period. We are not certain whether a third chlorine could be substituted on continued exposure.

The effect of pH on chlorine substitution is also clearly illustrated by the data. At pH 8.6 there is no chlorine uptake. Experiments were not conducted at pH 5.8 but we would anticipate results similar to the pH 3.0 data. It is evident that HOCl, which predominates below pH 5.8 is an effective halogenating agent. The species OCl^- which exists in solution at pH 8.6 shows no activity in ring halogenation.

A kinetic analysis of the chlorine data from Table II and Fig. 5 leads to some interesting interpretations. It is assumed that mono-halogenation is a very fast reaction followed by a much slower addition of the second halogen atom. It is also assumed that the di-halogen derivative represents maximum substitution. Thus, the following reaction describes the rate determining step in which MX represents mono-halogenated polymer and K_2 is the rate constant.

$$MX + X \xrightarrow[K_2]{\text{slow}} MX_2 \tag{2}$$

The overall reaction rate may be described by the following equation

assuming that MX is formed instantaneously from M and that both reactions are irreversible.

$$\text{rate} = -\frac{d[M]}{dt} = -\frac{d[MX]}{dt} = K_2\,[MX]\,[X] \tag{3}$$

Since the halogen concentration is kept constant over the duration of the reaction, a pseudo-first order rate constant K_2' may be defined as:

$$K_2' = K_2\,[X]$$

From classical kinetic theory the following integrated form of the rate equation can be derived in which $[MX] = [M]$ and represents the relative concentration of mono-halogenated polymer at time 0 and $[MX_2]$ is the relative concentration of di-halogenated polymer at any time during the reaction. Time in hours is given by t.

$$\ln\ 1 - \frac{[MX_2]}{[MX]_0} = -K_2'\,t \tag{4}$$

The above linear pseudo-first order equation, based on chlorine data from Table II is plotted in Fig. 6. The resulting straight line with a slope of 0.0231 hrs^{-1} is equal to the rate constant K_2'.

This type of analysis may be useful in projecting the life expectancy of RO membranes under field conditions. The methodology is applicable to different membrane types and pretreatment conditions.

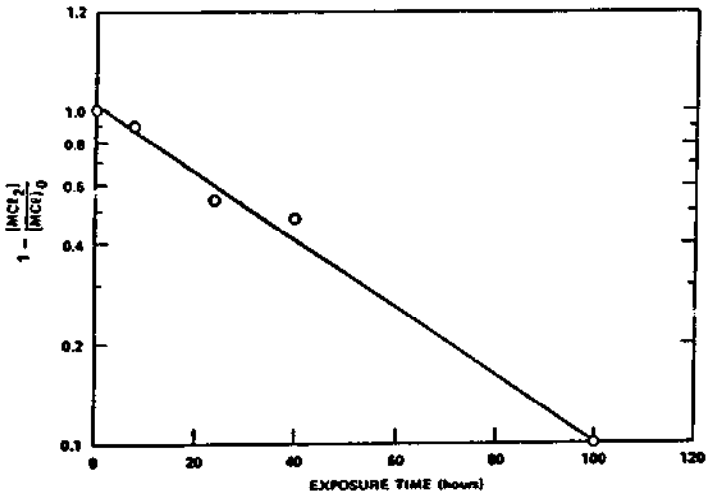


Fig. 6. Rate of chlorine uptake by B-9 membrane showing pseudo first order reaction kinetics.

A series of experiments have also been conducted in an effort to relate performance decline and halogen uptake with membrane degradation. Viscosity measurements of polymer solutions were conducted in an effort to reveal depolymerization or other morphological changes.

Fig. 7 shows changes in viscosity of chlorinated B-9 membrane samples dissolved in dimethyl sulfoxide. Samples were exposed to 30 ppm chlorine at pH 3.0 for time intervals up to 100 hours. All membrane solutions were made up of 1% dry polymer by weight. Superimposed on this figure is the chlorine uptake data also shown in Fig. 5. Note the continually decreasing viscosity as the membrane chlorine content increases. Also note the viscosity increase during the first 10 hours of exposure.

This data suggests a plausible mechanism for membrane deterioration. The initial short rise in the curve is evidently due to chlorine addition accompanied by a corresponding increase in polymer mass and viscosity. Continued exposure possibly results in bond cleavage accompanied by chlorine uptake. The chlorinated polymer fragments are now of significantly lower molecular weight. This sequence of events would appear to follow the initial

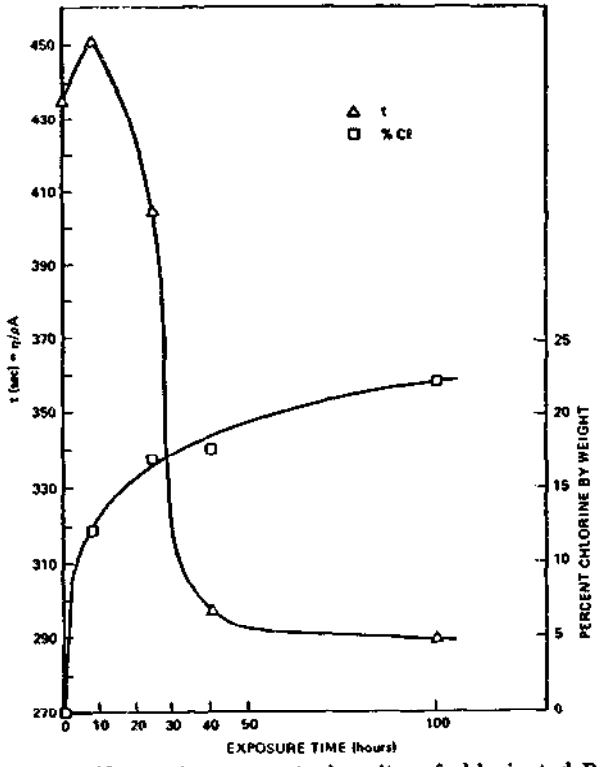


Fig. 7. Change in apparent viscosity of chlorinated B-9 membrane samples dissolved in DMSO plotted with chlorine uptake data.

membrane tightening and subsequent performance decline observed in earlier experiments [8, 9]. At this point we are not sure of the mechanism of viscosity decline which may also result from changes in hydrogen bonding or cross linkage within the halogenated polymer.

The bromine data also indicated pH specificity of polymer halogenation as illustrated in Fig. 8. Bromine is clearly most aggressive at pH 5.8 when the solution is nearly 100% HOBr. At pH 3.0 the approximate species distribution is 11% HOBr and 89% Br_2, and at pH 8.6 it is 56% HOBr and 44% OBr^-. The slightly greater bromine uptake at pH 3.0 compared with pH 8.6 is probably due to concerted attack of HOBr and Br_2. Earlier work has shown OBr^- to be unreactive. From this data we may arrange the overall activity of bromine species in the order $HOBr > Br_2 > OBr^-$.

The extent of bromine substitution is similar to chlorine, showing approximately one bromine atom per polymer unit after a 40 hour exposure. The data also suggests that HOCl at pH 3.0 is somewhat more active than HOBr at pH 5.8.

B-9 membrane exposure to chlorine dioxide (Table II) shows virtually no chlorine uptake. This finding is in agreement with literature reports indi-

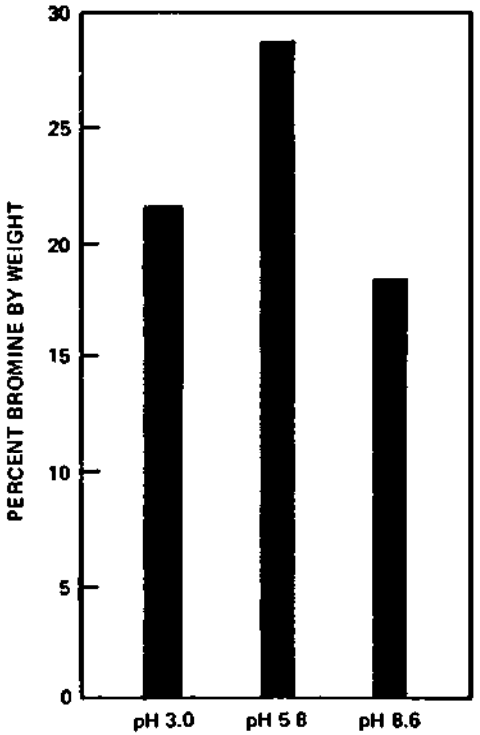


Fig. 8. Bromine uptake of B-9 membrane exposed to 70 ppm bromine for 40 hours at various pH levels.

cating that ClO_2 reacts with organic compounds by oxidation rather than halogenation [13]. The very low measured levels are probably due to traces of chlorine in the ClO_2 solutions.

The response of FT-30 and B-9 membranes to chlorine dioxide has been documented in earlier reports [8, 9]. Both membranes show good resistance at near neutral pH but are severely damaged at pH 8.6. Chemical attack evidently occurs by a mechanism different from chlorination, however, since chlorine is not incorporated into the membrane polymer.

MEMBRANE RESPONSE TO OZONE

Membrane exposure to ozone was carried out by continuous gas injection into the exposure chamber. Steady-state levels of 0.3 ppm were maintained in all experiments. This concentration is approximately six times the average residual used in water treatment applications. As in the case of halogens, experimental conditions represent "accelerated testing".

Ozone was the most aggressive chemical disinfectant tested. All membranes used in this program were damaged during the maximum test period of 90 hours. Even cellulose acetate films which are quite halogen resistant, show a marked sensitivity to ozone within the same exposure period.

All polyamide type membranes tested are very sensitive to ozone. B-9 membrane, for example, shows a marked performance decline within the first few hours of exposure. Complete membrane failure occurs after 15 hours as displayed in Fig. 9. Note that salt rejection drops to less than 10% over the experimental range of pH. Similar results were observed on exposure of RC-100 and FT-30 to ozone.

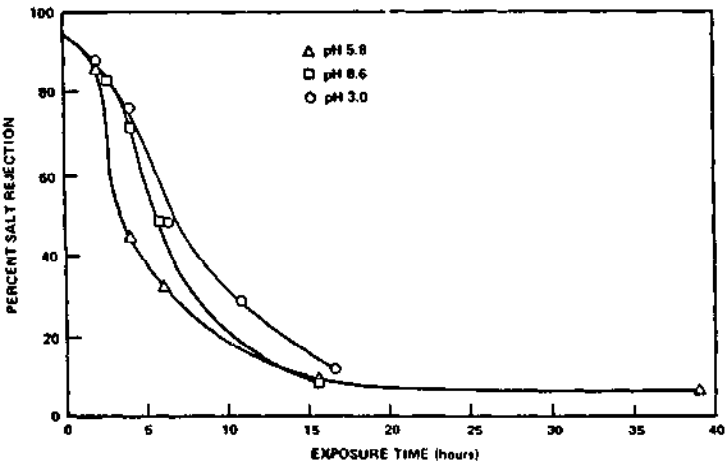


Fig. 9. Change in salt rejection of B-9 membrane on continuous exposure to 0.3 ppm ozone at various pH levels.

The effect of ozone on performance of Envirogenics blended cellulose acetate membrane is displayed in Fig. 10. This membrane is very sensitive at pH 8.6 but sustains only modest performance changes at pH levels below 5.8. It appears that trace ozone concentrations would have minimum effect on membrane life, especially for short exposure periods.

Despite the very aggressive nature of ozone, it seems premature to rule out the use of this disinfectant in RO systems containing cellulose acetate membranes. Following disinfection, deozonation systems based on degasing or chemical treatment could be developed. Even if slight ozone residuals were to remain, it appears that cellulose acetate will resist attack at near-neutral pH. This strategy is not, however, recommended for polyamide containing systems. In this case, the risk of severe membrane damage is too great.

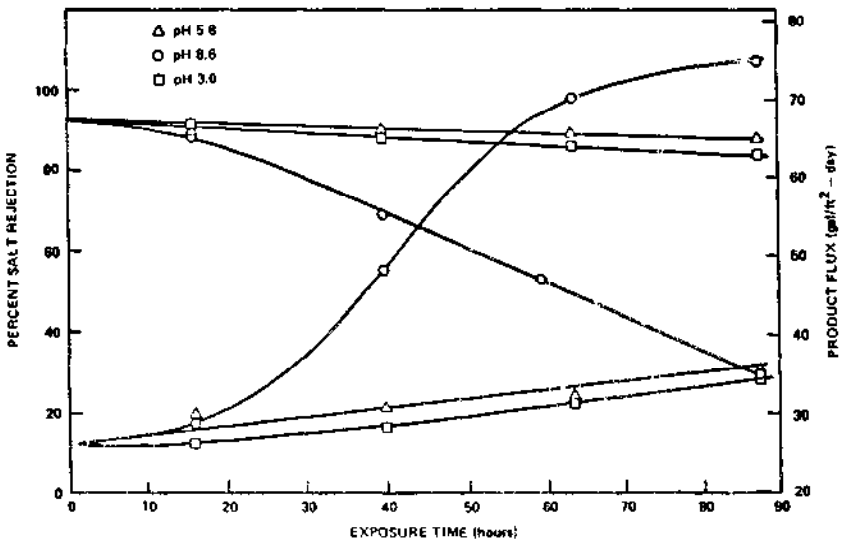


Fig. 10. Change in performance of blended cellulose acetate membrane on continuous exposure to 0.3 ppm ozone at various pH levels.

CONCLUSIONS

Work described in this paper should be useful in planning reasonable disinfection strategies for RO units in the field. Additionally, this research approach may provide techniques for estimation of membrane life expectancy. A better understanding of the nature of membrane-halogen interactions will also aid manufacturers in development of more chemically resistant membranes. Following are the most significant conclusions resulting from this work.

1) Cellulose acetate membranes are generally resistant to halogens and halogen derivatives.

2) Polyamide type membranes are sensitive to chlorine and bromine but show reasonable resistance with appropriate pH control.

3) Ozone will damage any membrane tested, however, cellulose acetate shows some resistance at low pH levels. This type membrane may resist low concentrations in systems designed for ozone disinfection.

4) All membranes are generallly resistant to iodine.

5) Polyamide type membranes are generally resistant to chlorine dioxide at near-neutral pH. This chemical evidently attacks membranes at high pH by oxidation since no halogen uptake is observed.

6) DuPont B-9 membrane chemically combines with chlorine during exposure. This process is accompanied by decreasing viscosity of polymer solutions in dimethyl sulfoxide.

7) Chlorine uptake data follows pseudo-first order reaction kinetics.

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