

Aqueous Chloramine Diffusion into Elastomers

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ABSTRACT: Aqueous chloramine diffusion into styrene butadiene rubber (SBR) and natural rubber was analyzed using approximate analytical and numerical solutions of Fick's second law of diffusion to develop long-term mass intake prediction curves. Diffusion coefficients were calculated for 1 mg/L chloramine concentration at three temperatures (23, 45, and 70°C) and also for 23°C at three chloramine concentrations (1, 30, and 60 mg/L). The reasonableness of using increased temperature and/or chloramine concentration to accelerate the diffusion process to obtain long-term information was discussed. For 1 mg/L chloramine concentration, the activation energy for the diffusion of chloramines into SBR and natural rubber were

computed to be 51.13 and 77.29 kJ/mol, respectively. Also, concentration profiles were developed to understand the extent of penetration through the elastomer thickness over time and temperature. Considering the reports of elastomeric compound failure in chloramine disinfectant water distribution systems because of swelling, this study will be helpful in understanding the performance of the elastomeric compounds in the system. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2597–2611, 2010

Key words: elastomer; diffusion; swelling; aqueous chloramine; drinking water distribution system

INTRODUCTION

Since the early 1900s, chlorine has traditionally been the preferred disinfectant in the drinking water distribution systems. However, because of the increasing health concerns and United States Environmental Protection Agency (USEPA) regulations,¹ chloramines have increasingly been used in the place of chlorine.² The switch to chloramines generally has been beneficial, as the disinfectant has a longer residual life in the distribution system and produces fewer disinfectant by-products than free chlorine. It is notable, however, that after switching to chloramine disinfectant, several utilities have reported substantially higher rates of elastomer failure.^{3,4} The failure mode has been commonly identified as a swelling that grossly distorts shape, thus preventing the product from performing its intended function.⁴ Researchers have postulated failure mechanisms ranging from salt formation to crosslink breakages; however, the fundamental cause of the chloramine-induced elastomer degradation is not clearly understood.^{3,4}

The major challenge in the long-term performance prediction of elastomers is that the degradation is generally a slow process at typical service conditions and would require significant exposure time to provide sufficient data to establish trends. It is a common practice in the elastomer industry to accelerate this degradation by increasing temperature and use the time-temperature superposition (TTS) principle to obtain long-term information by relating temperature with accelerated time.⁵

In previous work,⁶ the research team characterized elastomer chloramine-induced degradation by measuring mass change, volume change, breaking stress, breaking strain, and hardness using accelerated degradation tests. For these tests, elastomers commonly found in the water distribution system were exposed to a combination of temperatures (23, 45, and 70°C) and chloramine concentrations (1, 30, and 60 mg/L) for 30 days. Using the TTS principle, extended-life prediction curves were developed for an equivalent 1 mg/L and 23°C service condition for tensile stress, tensile strain, and hardness.⁶ The mass and volume data associated with swelling behavior, however, could not be extrapolated past the 30-day test windows as the data obtained did not present sufficient information to anchor the TTS curves and enable the data shifts.

The purpose of this research effort was to obtain long-term performance curves for mass intake data, which is an important indicator of elastomeric compound degradation. As TTS principles were

Additional Supporting Information may be found in the online version of this article.

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insufficient to predict long-term swell behavior, aqueous chloramine mass intake into an elastomer was modeled using diffusion theory. The aqueous chloramine mass intake into elastomers can be modeled using Fick's second law of diffusion and can be extrapolated beyond the 30-day test window. With the current literature available, it is not possible to develop single long-term swelling performance curve incorporating accelerated degradation results. However, the diffusion coefficients computed for accelerated conditions would be important indicators of long-term swelling performance. In addition to temperature accelerated swelling, this study would also address chloramines accelerated concentration swelling.

In this study, elastomer degradation has been accelerated by increasing both the temperature and chloramines concentration, because accelerating the degradation by increased chloramine concentration is thought to be a better service condition degradation representative than the increased temperature acceleration. Based on the appropriate solutions of the Fick's second law of diffusion, specific diffusion coefficients were computed for 1 mg/L chloramine concentration at three temperatures (23, 45, and 70°C) and also for 23°C at three chloramine concentrations (1, 30, and 60 mg/L) and used to predict elastomer swell over extended time periods. The diffusion coefficient variation with respect to increasing temperature and chloramine concentration was analyzed. Activation energy for diffusion was computed to assess the accelerated temperature effects on diffusion. Additionally, concentration profiles were also developed to understand the progression of swelling into the elastomer thickness over time. In this manner, long-term swelling behavior was modeled using diffusion theory.

MATERIALS AND EXPERIMENTAL SETUP

Materials

Currently, a wide variety of elastomers are available for use in the water industry. After assessing typical materials and interviewing water utilities and elastomer compounders, six typical backbone polymers were selected for evaluation: natural rubber (NR), styrene butadiene rubber (SBR), nitrile rubber (NBR), neoprene, sulfur-cured ethylene propylene diene monomer [EPDM(S)], and peroxide-cured EPDM [EPDM(P)]. EPDM(P) was added to the test group as it is a relatively new product that is commonly recommended for chloramine environments. For testing, the elastomer compounds were specifically formulated without the proprietary antidegradation additives commonly used in most commercial compounds. A rubber manufacturer (Ashtabula Rub-

ber Co., Ashtabula, OH) compounded and formed the elastomer samples to the required thickness.

Generally, the basic elastomer compounds contain a specific base polymer as the primary ingredient, a filler, a primary vulcanizing agent, a vulcanizing accelerant, and a curing system additive.⁷ The specific composition and molecular structure of the elastomers are presented in Table I and Figure 1. The base polymer compound of NR, standard Malaysia rubber (latex), is *cis*-polyisoprene. SBR is a copolymer of two randomly sequenced monomers, butadiene and styrene. SBR has highest resistance to breaking strain but has poor tensile strength. NBR is also a copolymer of two monomers, butadiene and acrylonitrile. The presence of acrylonitrile makes NBR oil-resistant. Neoprene rubber is essentially polychloroprene. The chloroprene monomer is actually 2-chlorobutadiene, i.e., butadiene with a chlorine atom replacing one of the hydrogens. Ethylene propylene rubbers are also copolymers of ethylene and propylene containing an additional few percent of a diene monomer for unsaturation. Because only one double bond is lost when the diene enters the polymer backbone, the second double bond remains as a pendant group, giving the EPDM elastomers an outstanding resistance to degrading attack by heat, light, oxygen, and ozone.⁷ Peroxide curing [referenced as EPDM(P)] is generally used when additional property enhancements are needed, which cannot be provided by sulfur-curing.⁸

Test procedure

For this study, unless otherwise noted, samples were cut into 2 × 1 × 0.08-inch coupons and were submerged in aqueous chloramine solutions with varying concentrations (1, 30, and 60 mg/L) and temperatures (23, 45, and 70°C) for 30 days.⁹ The elevated temperatures and concentrations were necessary to generate measurable degradation within a reasonable testing period. At 0, 3, 6, 12, 20, and 30 days, the samples were temporarily removed from the bath and subjected to performance tests. Similar experiments were performed for 0.16- and 0.32-inch coupons for NR, SBR, EPDM(P), and EPDM(S), to understand the effect of thickness on diffusion.¹⁰ Because this was meant to provide an additional information, the tests were performed only at the combinations of two chloramine concentrations (1 and 30 mg/L) and two temperatures (23 and 70°C), and the mass change was measured at 10-day intervals for 30 days. Additionally, for 0.32-inch coupons, the 10-day interval mass change was measured for 70 days to obtain saturated mass intake values.

The aqueous chloramine used in this testing was monochloramine (NH₂Cl), which is formed by combining hypochlorous acid (HOCl) with ammonia

TABLE I
Elastomer Composition in Parts-Per Hundred Rubber (PHH) Units

Ingredient	NR (PHR)	SBR (PHR)	NBR (PHR)	Neoprene (PHR)	EPDM(S) (PHR)	EPDM(P) (PHR)	Function
SMR CV 60	100						Base polymer
SBR 1502		100					Base polymer
Paracril BJLT			100				Base polymer
Neoprene W				100			Base polymer
Nordel 1070					100		Base polymer
DSM Keltan 27						100	Base polymer
SRF N762	70		100	60		75	Carbon black
SRF N767		90					Carbon black
FEF N550					100		Carbon black
Sun 4240 (or equiv.)	2	10		10			Extending oil
Sun 2280					110	20	Extending oil
Sulfur	2.5	1	0.3	0.25	2		Primary vulcanizing agent
Zinc oxide	5	5	5	5	5	5	Curing system additive (activator)
Stearic Acid		1	1	0.5	2		Curing system additive
Santocure	0.7	1	1				Accelerant – thiazole based
Dicup 40KE						10	Accelerant
Altax/Butyl Z/M Tuads					4.8		Accelerants
Plasticizer SC			8	9			Harwick plasticizer
M Tuads			1				Accelerant
DOTG/Monex				2.5			Accelerants/processing aid

(NH₃) in a 2 : 1 chlorine-to-ammonia weight ratio.⁶ The solutions were subsequently buffered to a pH of 8.3 ± 0.3 for the preferential formation of monochloramine. The chloramine solutions were replaced every 24 h to maintain its concentration, and thus, the referenced mg/L is the average concentration over the 24-h period.

RESULTS AND ANALYSIS

Elastomer swelling data

During the 30-day testing, measurements were made for the total mass intake of aqueous chloramine diffused into the elastomer as shown in Table II (the data are presented for 1 mg/L chloramine concentration only, while for 30 and 60 mg/L concentration data, please refer Supporting Information). Of the materials evaluated, both the EPDM compounds showed the least amount of mass intake because of heat aging when exposed to the 1 mg/L solutions. Only a small amount of performance degradation was observed in the EPDM(S) material, while very little degradation was observed in the EPDM(P) material. The relatively minimal degradation in the EPDM materials may be due to the lower number of unsaturated bonds and their location as pendent groups.

After the EPDM materials, NBR shows the least amount of mass intake when exposed to the higher temperatures. This is likely due to the presence of nitrile group (C≡N), which makes the elastomer solvent-resistant.⁷ The mass intakes for SBR and NR are about the same at room temperature. However, at

higher temperatures, the NR's mass intake is higher than SBR's mass intake. SBR's better performance at higher temperature is mostly because of the presence of benzene ring as opposed to simple methane groups of NR. The benzene ring provides a more compact molecular network structure. SBR also has more chain links per given area, thereby holding the material intact to resist swelling. Neoprene rubber experienced the highest mass intake as a result of accelerated degradation testing. From the mass intake measurements of three sample thicknesses (0.08, 0.16, and 0.32 inches), it can be concluded that in general the thickness has very little influence on the diffusion rate of aqueous chloramines.¹⁰

Combining this testing data with previous experimental results,⁶ it is evident that breaking strain and breaking stress are highly correlated with mass intake through all temperatures and concentrations. Hardness, however, did not show a correlation through all temperatures. This variation may be due to hardness testing primarily being influenced by surface characteristics, whereas breaking stress and breaking strain are bulk material properties that are dependent on the elastomer crosslink density. Thus, understanding the rate of aqueous chloramine diffusion into an elastomer is necessary to characterize the elastomer degradation in bulk material properties. However, while 30-day data can provide general trends in mass intake behavior, it cannot effectively be used for long-term predictions. As discussed previously, the TTS analysis procedure can be used effectively for some degradation parameters, but cannot adequately model mass intake. Thus, to appropriately assess the

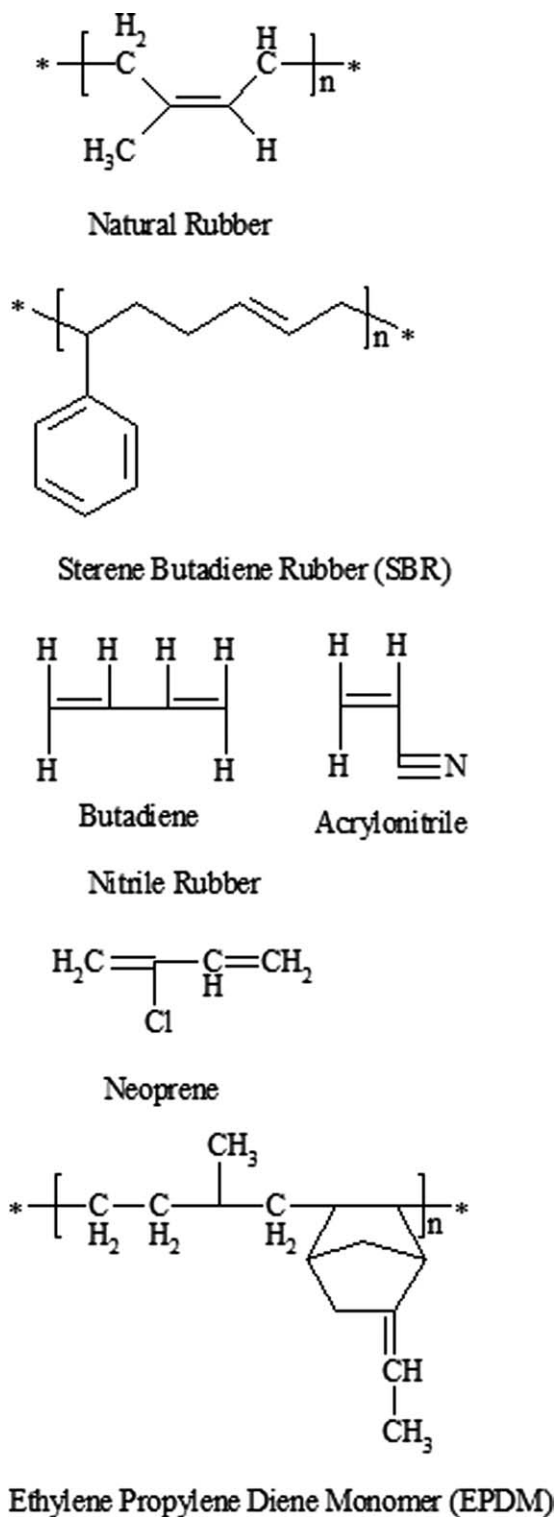


Figure 1 Molecular structure of the elastomers.⁷

long-term performance of mass intake and its subsequent effect on other degradation parameters, it is necessary to fully understand diffusion of chloramines into the elastomer system.

To determine the diffusion coefficient value (D) using an analytical solution of the diffusion equa-

tion, it is necessary to know both the mass intake data over time (M_t) and the saturated mass intake (M_∞) value. However, as evident in Table II, none of the six elastomers reached equilibrium during the 30-day elevated temperature tests. Initially, an attempt was made to calculate both D and M_∞ from the available data, but the solutions were not unique as multiple combinations of D and M_∞ satisfied the criteria.

To obtain the necessary information for diffusion coefficient determination, a subsequent series of tests were performed based on thicker samples (0.32 inches) and longer exposure times (70 days). However, even with the 70-day testing period, EPDM(S), EPDM(P), NBR, and neoprene rubber did not reach equilibrium with respect to mass intake. Only NR and SBR reached equilibrium with a saturated mass intake of 64.57 and 67.12%, respectively. As only NR and SBR provided sufficient information for subsequent diffusion modeling, the scope of the analytical solution investigation was limited to these two materials.

Diffusion coefficients

The diffusion coefficient for the penetration of the aqueous chloramine into the elastomer samples can be characterized by the profile of the sorption M_t/M_∞ versus time using the following equation¹¹:

$$\frac{M_t}{M_\infty} = kt^n \quad (1)$$

where n is the diffusional exponent indicative of the transport mechanism; k is a constant incorporating the characteristics of the macromolecular network and the penetrant.¹² For planar systems, n equal to 0.5 is indicative of pure Fickian diffusion, and n equal to 1 is indicative of Case II diffusion (non-Fickian). In Case II diffusion, diffusion is faster than the material relaxation process.¹³ Case III diffusion is identified by an exponent of n between the values of 0.5 and 1.

The diffusion exponents were computed for 1 mg/L chloramine concentration from the available M_t/M_∞ versus t data using a least square analysis (Table III). Review of the computed n values indicates that the transport mechanism is not pure Fickian diffusion as the calculated n values increase as a function of temperature. Correlating this trend with previous research indicates that the diffusion appears to transit from Fickian to non-Fickian as the swelling progresses over time. This is because as the swelling progresses, the elastomer network opens allowing diffusion to occur unhindered.

The network and penetrant portions of the diffusion equation, k , were also observed to increase

TABLE II
Elastomer Mass Intake Data (1 mg/L Chloramine Concentration)

Elastomer	Temperature	Mass intake (%)				
		3rd Day	6th Day	12th Day	20th Day	30th Day
NR	23°C	0.88	0.66	0.73	0.88	1.21
	45°C	1.33	1.53	2.20	2.74	4.31
	70°C	2.58	3.27	5.42	9.25	17.12
SBR	23°C	0.77	0.69	0.76	0.94	1.16
	45°C	1.23	1.47	2.25	2.71	3.43
	70°C	2.18	3.07	4.00	5.10	6.48
EPDM(S)	23°C	0.47	0.18	0.12	0.12	0.16
	45°C	0.34	0.36	0.36	0.42	0.39
	70°C	0.45	0.48	0.62	0.75	0.76
EPDM(P)	23°C	0.06	-0.18	-0.14	-0.09	-0.10
	45°C	0.13	0.04	0.13	0.17	0.23
	70°C	0.25	0.31	0.63	0.62	0.78
NBR	23°C	0.61	0.60	0.55	0.57	0.80
	45°C	1.17	1.23	1.67	1.75	2.00
	70°C	1.91	2.19	2.70	3.89	4.36
Neoprene rubber	23°C	1.49	1.62	2.15	2.54	3.20
	45°C	3.34	4.46	6.92	9.14	12.68
	70°C	6.10	9.43	17.32	32.05	59.99

systematically with temperature. The value of k for NR is found to be similar to SBR at low temperatures, but slightly higher at elevated temperatures. These increases in k suggest an increase in segmental motion with the rise in temperature.¹⁴

Diffusion coefficients can be determined using sorption experiments, where the mass of solvent per unit area that has entered the elastomer film at time t (M_t) and the limiting mass approached at infinite time (M_∞) are measured. Using the mass balance, one can derive the fundamental one-dimensional diffusion equation, known as Fick's second law of diffusion¹⁵:

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial x^2} \right] \quad (2)$$

where C is the concentration of diffusing substance (aqueous chloramine) in the dimensions of (amount of substance)/(length³); D is diffusion coefficient in the dimensions of (length²/time); t is time; x is space coordinate normal to the section.

TABLE III
Values of n and k for SBR and NR in Aqueous Chloramine Systems (1 mg/L Chloramine Concentration)

Elastomer	Temperature (°C)	n	k
SBR	23	0.703	0.002
	45	0.807	0.004
	70	0.872	0.007
NR	23	0.701	0.002
	45	0.816	0.004
	70	0.931	0.010

Analytical solution of Fick's second law of diffusion

An analytical solution to the Fick's second law [eq. (2)] can be obtained with the boundary conditions shown in Figure 2.

The analytical solution of the Fick's second law when the problem is symmetrical about the central plane of the sheet and with the above boundary conditions is given as follows¹⁵:

$$\frac{C_{x,t}}{C_1} = 1 - \frac{4}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \sin\left(\frac{(2n+1)\pi x}{h}\right) \times \exp\left(\frac{-(2n+1)^2 \pi^2 Dt}{h^2}\right) \quad (3)$$

where $C_{x,t}$ is the aqueous chloramine concentration at any distance x and time t ; h is the elastomer thickness. Integrating the above equation over x and t , $C_{x,t}$ becomes M_t and the following short- and long-term solutions can be obtained.¹⁵

1. Short-term solution ("ierfc" is the complement of the error function):

$$\frac{M_t}{M_\infty} = \frac{4}{h} \left(\frac{Dt}{\pi}\right)^{0.5} + \frac{8}{h} (Dt)^{0.5} \sum_{n=1}^{\infty} (-1)^n \text{ierfc}\left(\frac{nh}{2(Dt)^{0.5}}\right) \quad (4)$$

2. Long-term solution:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-(2n+1)^2 \pi^2 Dt}{h^2}\right) \quad (5)$$

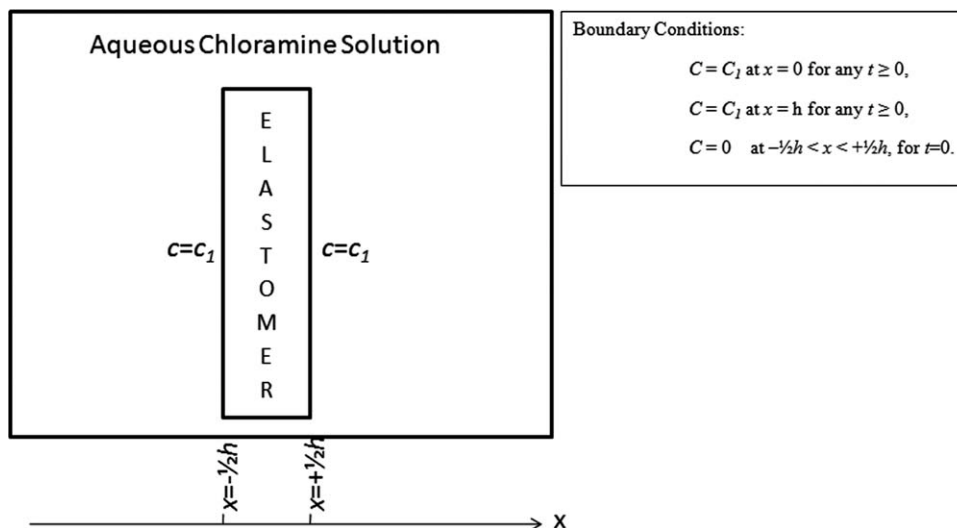


Figure 2 Boundary conditions for analytical solution of Fick's second law.¹⁴

Within the polymer diffusion works, it is a common practice to use the first-term approximation of eq. (4) with the mass intake data up to $(M_t/M_\infty) < 50\%$. Aminabhavi et al.¹⁶ and Geethamma and Sabu¹⁷ used the first-term approximation of Fick's second law of diffusion to predict water diffusivity into elastomers using sorption experiments. Diffusion analysis has expanded these theories to incorporate both the short-term and long-term approximations of Fick's second law into one combined equation such that¹⁸

$$\frac{M_t}{M_\infty} = \phi(x) f(x) + (1 - \phi(x)) g(x) \quad (6)$$

where $f(x)$ and $g(x)$ are the short-term and long-term approximations of Fick's second law; $\Phi(x)$ is the weighting function [$\Phi(x) = 1$, when $x \leq 0.05326$ and $\Phi(x) = 0$, when $x > 0.05326$]; $x = Dt/h^2$, the dimensionless space coordinate.

Numerical solution of Fick's second law of diffusion

Fick's second law of diffusion can also be solved numerically using the following procedure:

- i. Based on the analytical "combine solution" a reasonable range of D values was selected.
- ii. Using finite-difference method, aqueous chloramine concentrations were obtained for discrete finite space-time combinations as explained below: Rewriting the partial derivations in eq. (2) in terms of finite difference derivatives,

$$\frac{c_{i,j+1} - c_{i,j}}{\delta t} = D \frac{(c_{i+1,j} - 2c_{i,j} + c_{i-1,j})}{(\delta h)^2} \quad (7)$$

where i and j are discrete set points of continuous variables h and x , respectively. Rearranging eq. (7) yields¹⁹

$$c_{i,j+1} = c_{i,j} + \frac{D\delta t}{(\delta h)^2} (c_{i-1,j} - 2c_{i,j} + c_{i+1,j}) \quad (8)$$

Equation (8) thus provides a formula for the unknown aqueous chloramine concentration $C_{i,j+1}$ at the $(i,j+1)$ th mesh point in terms of known aqueous chloramine concentration along the j th row. The numerical solution initial and boundary conditions are as follows:

- $C = 0$ at $0 < x < h$, for $t = 0$,
- $C = 1 \text{ gm/cm}^3$ at $x = 0$ for any $t \geq 0$,
- $C = 1 \text{ gm/cm}^3$ at $x = h$ for any $t \geq 0$,
- iii. Solution in (ii) has been integrated to obtain $M_{t(\text{mod})}$ (mass intake at time t calculated using model) for the times 3, 6, 12, 20, and 30 days. Using the simple trapezoidal rule, the concentrations finite space-time grid has been integrated for the "interest" t values. This integration gives us the mass of the amount of aqueous chloramine present along the thickness per unit cross-sectional area. This value multiplied by width and height would provide us the total mass of aqueous chloramine that has been diffused during the time period t .
- iv. Nonlinear regression analysis has been performed using Microsoft Excel Solver tool to minimize the square root of the sum of error between $M_{t(\text{exp})}$ and $M_{t(\text{mod})}$ from Step (ii) and thus optimize the D .

TABLE IV
Diffusion Coefficients for SBR

Temperature (°C)	Diffusion coefficients (cm ² /s)			
	Combined solution	Short-term solution	Long-term solution	Numerical solution
23	1.68 E -12	1.24 E -09	1.72 E -12	1.68 E -12
45	8.68 E -12	1.39 E -08	9.19 E -12	1.71 E -11
70	2.88 E -11	8.06 E -08	2.96 E -11	2.71 E -10

Computed diffusion coefficients

For 1 mg/L chloramine concentration of SBR and NR, the three analytical solutions and numerical solution were calculated in Microsoft Excel using the solver optimization technique²⁰ as presented in Tables IV and V. The combined solution, numerical solution, and the long-term solution values are almost identical and are significantly less than short-term solution. The numerical solution failed to find out the global optimum D value, however, was able to perform D optimization when the minimum and maximum D values were specified as constraints. Numerical solution was reported only wherever the combined solution was available, as the combined solution can reasonably be used to specify the D range for the optimization. Of all the solutions, the combined solution was thought to be more reasonable as it incorporates both short-term and long-term solutions with appropriate weight factors and seems to provide an optimal D value.

The reasonableness of using the combined solution was confirmed by reassessing Schoenbaechler's²¹ analysis of carbon black loss from these rubbers based on atomic force microscopy observations. In his study, he computed the diffusion coefficient for elastomer materials immersed in 30 mg/L aqueous chloramine solution at 45°C for 30 days using the following simplified version of Fick's second law equation:

$$X_{\text{eff}} \approx (Dt)^{0.5} \quad (9)$$

where X_{eff} is the effective penetration distance measured from a clearly discernable zone of expansion at the edges of the sample by digital calipers. As

shown in Table VI, Shoenbaechler's observed diffusion rates were very similar to diffusion rates calculated for his specific data based on the combined solution. Thus, based on these observations, the combined solution has been used in diffusion coefficients for higher chloramine concentrations.

As expected, the diffusion rate is faster into samples studied at higher temperatures for all three diffusion equations. This increase in diffusion rate is due to an increase in kinetic energy of the aqueous chloramine molecules, motion of elastomer molecules, and free volume within the polymer, which are all functions of temperature.

Generally, mass intake should increase as the temperature increases; however, an unexpected trend in the data was observed at 30 and 60 mg/L. The 45°C mass intake curve crossed the 70°C curve at approximately the midpoint of the aging period as shown in Figure 3. Only changes in mass, volume, and to a much lesser extent, hardness displayed this "crossover" behavior. Neither of the EPDM rubbers showed this effect during any of the testing. It was also observed that the tensile properties for all materials did not exhibit this behavior and were not detected at the 1 mg/L concentration condition. A possible explanation for this behavior could be that the elastomer was undergoing degradation that involved loss of base material, while it continued to absorb test solution. Material loss will occur more rapidly at higher temperatures and concentrations. Therefore, although the mass of solution absorbed could have been increasing, the total mass measured could have been "flattening" as shown in Figure 3. It is the conclusion of the research team that this phenomenon is likely the result of testing at conditions too

TABLE V
Diffusion Coefficients for NR

Temperature (°C)	Diffusion coefficients (cm ² /s)			
	Combined solution	Short-term solution	Long-term solution	Numerical solution
23	1.68 E -12	1.24 E -09	1.72 E -12	1.68 E -12
45	1.11 E -11	1.89 E -08	1.14 E -11	1.70 E -11
70	1.24 E -10	4.05 E -07	1.16 E -10	2.60 E -10

TABLE VI
Comparison of Computed Diffusion Coefficients with Schoenbaechler's Study

Material	Diffusion coefficients (cm ² /s) at 30 mg/L, 45°C	
	Schoenbaechler ²¹	Combined solution
SBR	1.26 E -9 ± 0.18 E -9	1.38 E -09
NR	1.42 E -9 ± 0.12 E -9	1.85 E -09

severe for accelerated aging of the elastomer type. Consequently, the diffusion coefficients computed with 30 and 60 mg/L chloramine concentration are not presented here.

Figures 4 and 5 present the variation of diffusion coefficients with respect to temperature and chloramine concentration. Temperature dependence of diffusion coefficients can be fitted with an exponential function as expected. The chloramine concentration dependence of diffusion coefficients can be fitted with an exponential function for NR and a linear function for SBR.

Activation energy

The dependence of the diffusion coefficient on temperature can be further explained with respect to activation energy.⁵ The aqueous chloramine diffusion into an elastomer is the summation of three-component processes, i.e., concentration gradient driven flow, molecular activity driven flow, and chemical reaction driven flow. These processes continue until complete saturation is achieved. As the temperature increases, both molecular activity and

chemical reaction rates increase, thereby increasing the rate of diffusion.

The effects of increasing temperature on elastomer degradation were initially characterized by Arrhenius. He proposed an exponential scale increase of diffusion coefficients as temperature increases by introducing activation energy into the diffusion term [eq. (10)]. This activation energy for diffusion is the energy required for the diffusing atoms to squeeze through the small openings of the host material. However, considering that our diffusion process is the resultant of a reaction rate and a diffusion rate, the activation energy computed includes both the terms. It is thought that at shorter time scales reaction-rate kinetics should be dominant, while at longer time scales diffusion-rate kinetics would be dominant.

$$D = D_0 e^{-E_D/RT} \quad (10)$$

where D_0 is the maximum diffusion coefficient (at infinite temperature); E_D is the activation energy for diffusion; T is the absolute temperature; R is the gas constant [8.314472 J/(K mol) or 1.987 cal/(K mol)].

Taking the natural log of both the sides, eq. (10) can be written as

$$\ln D = \ln D_0 - \frac{E_D}{RT} \quad (11)$$

Using the graphical solution (Fig. 6) of eq. (11), the activation energies of SBR and NR for 1 mg/L

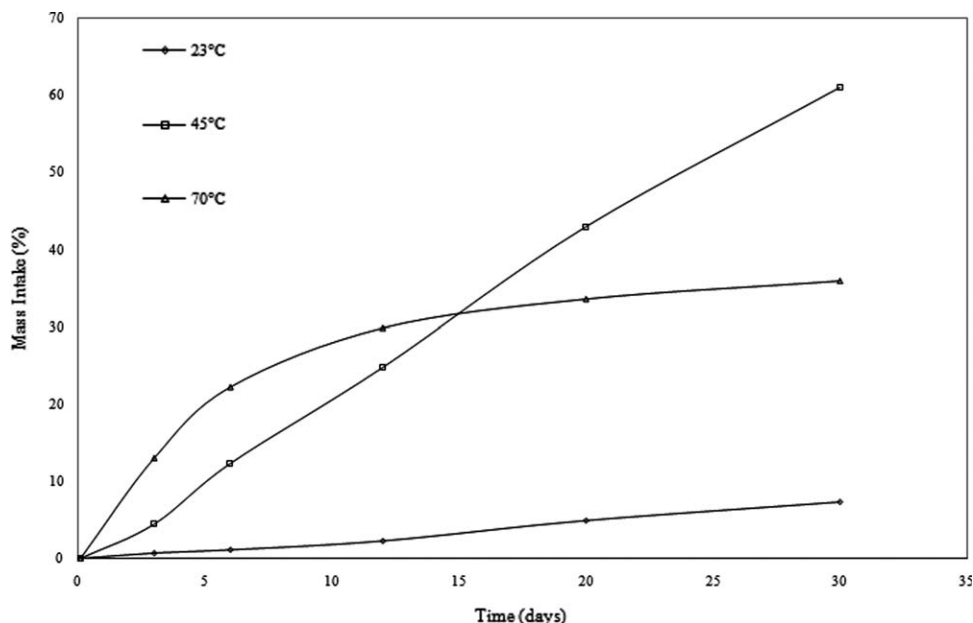


Figure 3 Crossover of 70°C curve over 45°C curve (NR). Source: Awwa Research Foundation. Reprinted with permission.

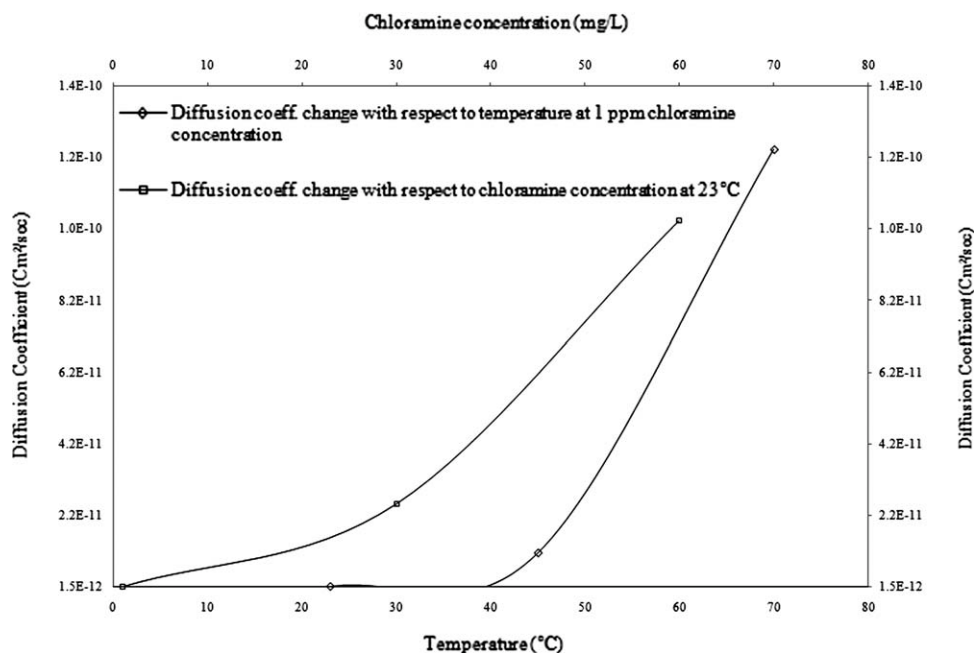


Figure 4 NR diffusion coefficients' dependence on temperature and chloramine concentration.

aqueous chloramine diffusion were calculated to be 51.13 and 77.29 kJ/mol, respectively.

Generally, the increase in the activation energy results in smaller diffusivities and lower probabilities of atomic diffusion.²² NR has higher mass intake than SBR, which means that NR should have lower activation energy. However, the computed NR activation energy for diffusion value is higher than SBR value. This may be due to the inclusion of reaction rate mechanism in activation energy. At 1 mg/L

chloramine concentration, NR performed better than SBR when breaking strain response variable is considered. It may be said that higher reaction rate of SBR rubber may be responsible for its lower activation energy, and another possible reason could be swelling, NR swells more than that of SBR, and thus NR might have higher activation energy as the aqueous chloramine has to pass through that extra swell thickness. To check this possibility, activation energy was also calculated for just 0 and 3rd-day data, as

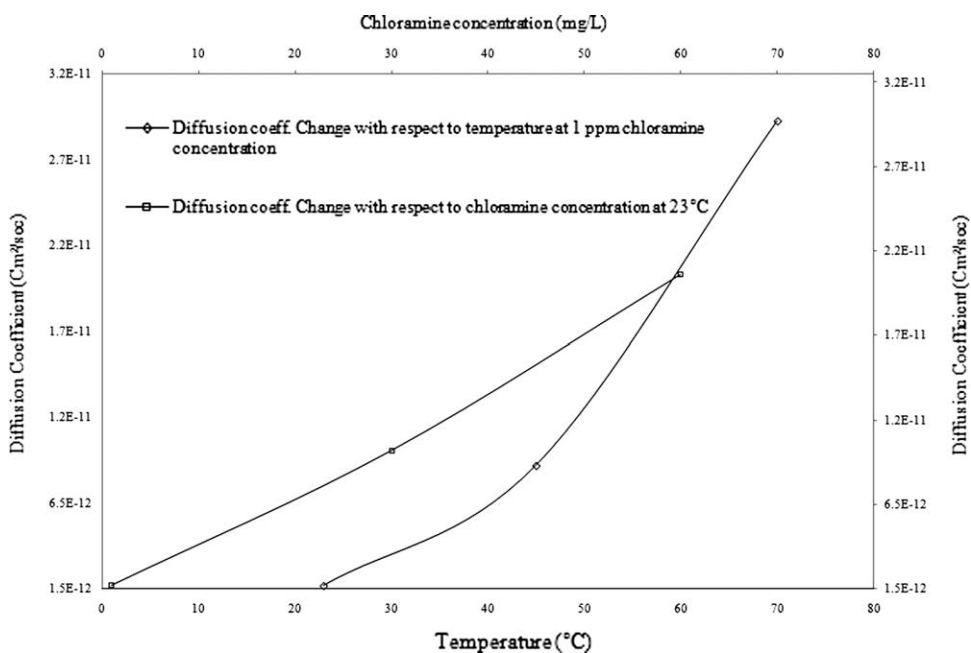


Figure 5 SBR diffusion coefficients' dependence on temperature and chloramine concentration.

these data would not possibly include swelling. For these data, SBR activation energy (39.76 kJ/mol) was computed to be higher than that of NR activation energy (30.49 kJ/mol), suggesting that swelling might be responsible for the higher activation energy of NR.

The literature review of relevant activation energies indicated that the values are available only for reaction rate activation energies computed from breaking strain data. For NR subjected to sea-water aging, an activation energy of 63 ± 3 kJ/mol has been computed using the Arrhenius plot of shift factors.²⁰ For EPDM(S) and EPDM(P) subjected to aqueous chloramine aging, activation energies in the range of 21–28 and 34–48 kJ/mol were computed using the Arrhenius plot of reaction rate.²⁴

Mass intake prediction curve

Once the diffusion coefficients were determined based on laboratory testing, the degree of saturation could be predicted for any exposure time using eq. (6). Long-term performance curves were developed for SBR (Figs. 7 and 9) and NR (Figs. 8 and 10) based on temperature and chloramine concentration accelerated swelling. Interestingly, even during 10,000 days of exposure to 1 mg/L chloramine concentration solution, full saturation was only achieved at 70°C temperature, and the degree of saturation decreased correspondingly with reduced temperatures and chloramine concentrations. It may be noted here that the saturated mass intake used in this study was observed at a combination of higher temperature and chloramine concentration

accelerated degradation test. As expected, the rate of mass intake is similar for SBR and NR at low temperatures and chloramine concentrations; however, NR's mass intake is greater than SBR at higher temperatures and chloramine concentrations. As temperature and chloramine concentration increases, the energy available for diffusion increases, thus increasing the number of molecules with enough energy to overcome activation energy. Hence, the mass intake and degradation would be higher as temperature and chloramine concentrations increase.

As mentioned earlier in the Introduction section, the research team has developed extended-life prediction curves using the TTS principle for an equivalent 1 mg/L and 23°C service conditions for tensile stress, tensile strain, and hardness.⁶ This was achieved by shifting higher temperature and chloramine concentration data to service conditions using William Landel Ferry (WLF) equation. TTS permits the use of short-term accelerated degradation experiments to obtain long-term information by relating the degradation acceleration with accelerated time. From the TTS principle and the long-term performance curves developed in Figures 7–10, theoretically, it can be said that a final composite curve can be developed incorporating all these curves. If 23, 45, and 70°C curves were considered as Type I, Type II, and Type III diffusion curves, theoretically, the final composite curve would initially follow Type I diffusion curve and, at some point of time, switch over to Type II diffusion and finally to Type III diffusion.

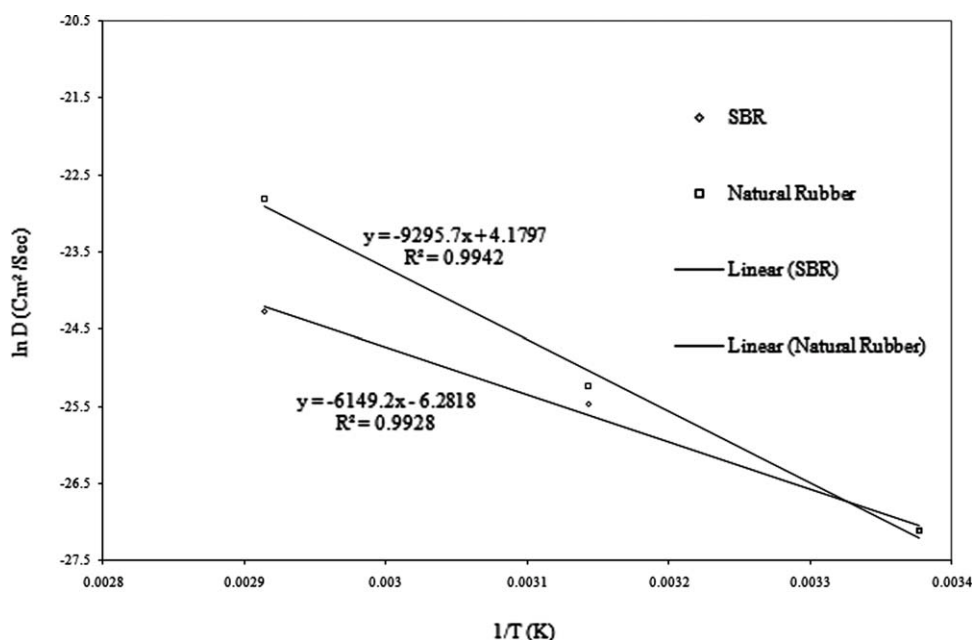


Figure 6 Arrhenius activation energy plot for SBR and NR.

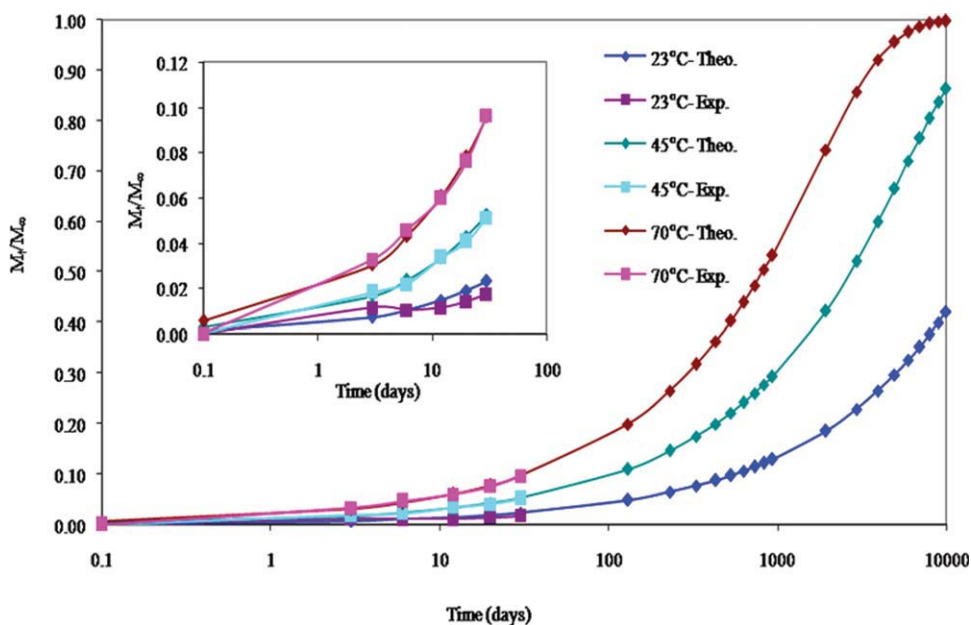


Figure 7 Long-term mass intake curve for SBR (1 mg/L chloramine concentration). Inset graph shows the experimental and theoretical data fit. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TTS master degradation curves were not developed for 30-day mass intake data, as the $1/\log(a_t)$ vs. $1/(T-T_0)$ plot R^2 value was low. When TTS was attempted to obtain one final composite curve for three chloramine concentration long-term performance curves (Figs. 7 and 8), the R^2 value remained low. However, long-term performance curves devel-

oped using diffusion theory (Figs. 9 and 10) for different temperatures produced an acceptable R^2 value. Figures 11 and 12 show (a) theoretical long-term performance curve computed from diffusion theory and (b) TTS curve obtained by shifting higher temperature data to service conditions. Even though it was possible to develop TTS curve, the final curve

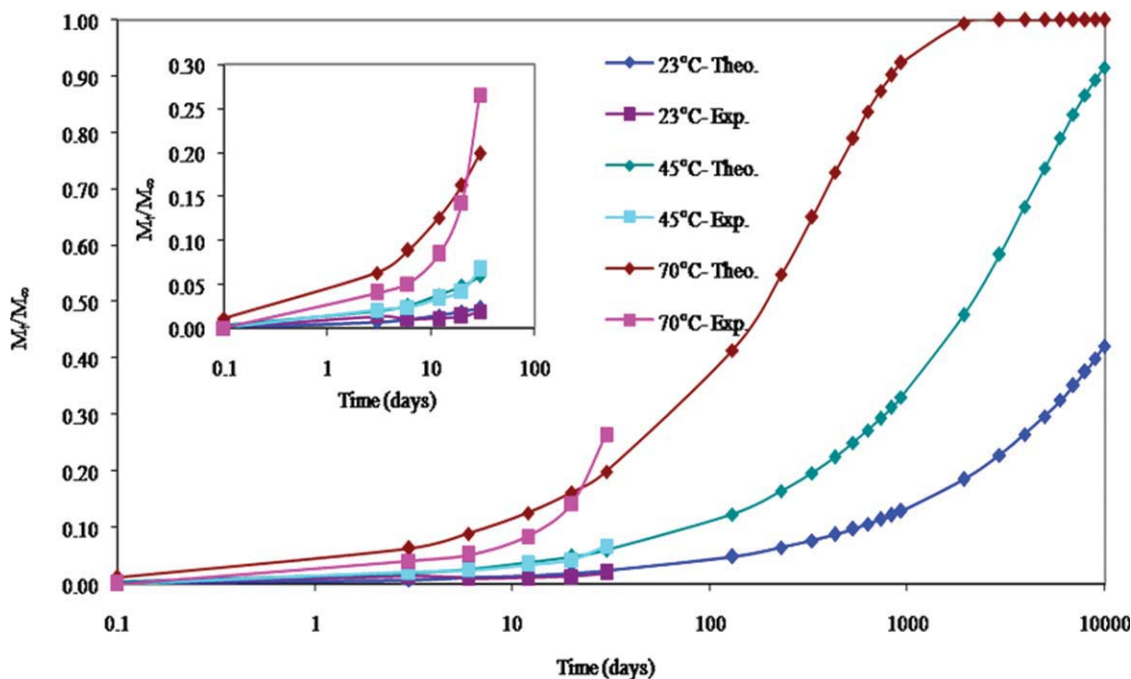


Figure 8 Long-term mass intake curve for NR (1 mg/L chloramine concentration). Inset graph shows the experimental and theoretical data fit. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

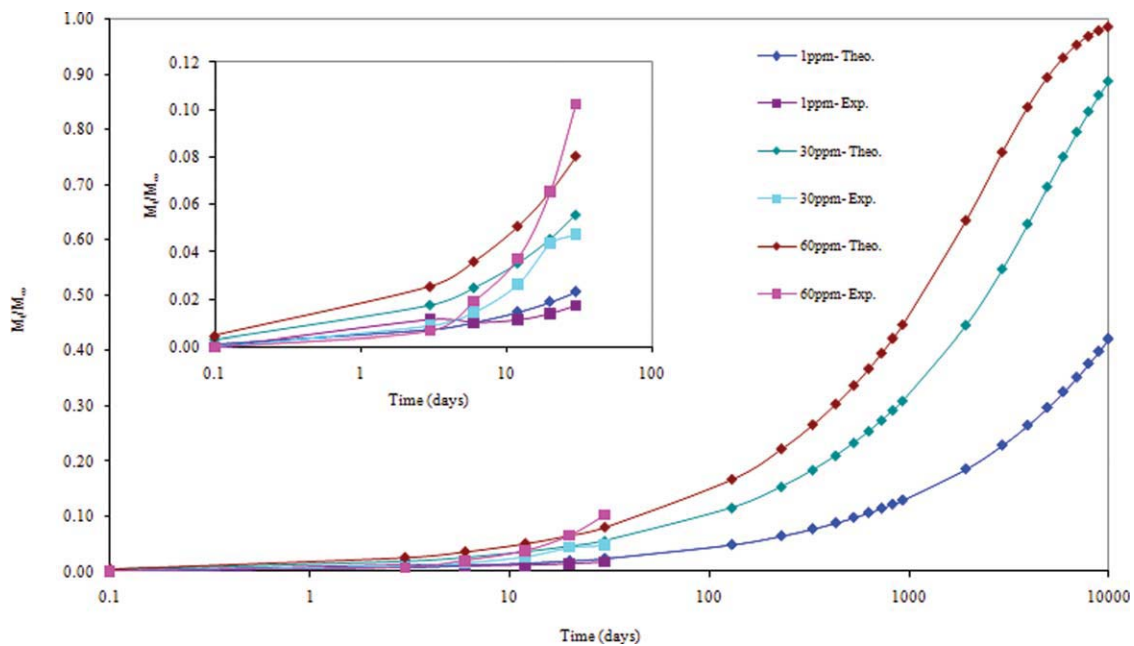


Figure 9 Long-term mass intake curve for SBR (23°C). Inset graph shows the experimental and theoretical data fit. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

developed did not show the trends as expected (transition from Type I to Type II to Type III).

In the absence of a better technique to develop a composite curve, it is the conclusion of this research that the long-term performance curve developed using diffusion theory at 1 ppm, 23°C, is better representative than TTS curves. This conclusion was

verified with 70-day mass intake experiment data of 32-inch elastomeric coupons. As shown in Figures 11 and 12, the data were much closer to diffusion theory curve than TTS. It should be noted here that the mass intake data of 0.32-inch sample is expected to be slightly lower than 0.08-inch samples because of the higher initial volume of 0.32-inch samples.

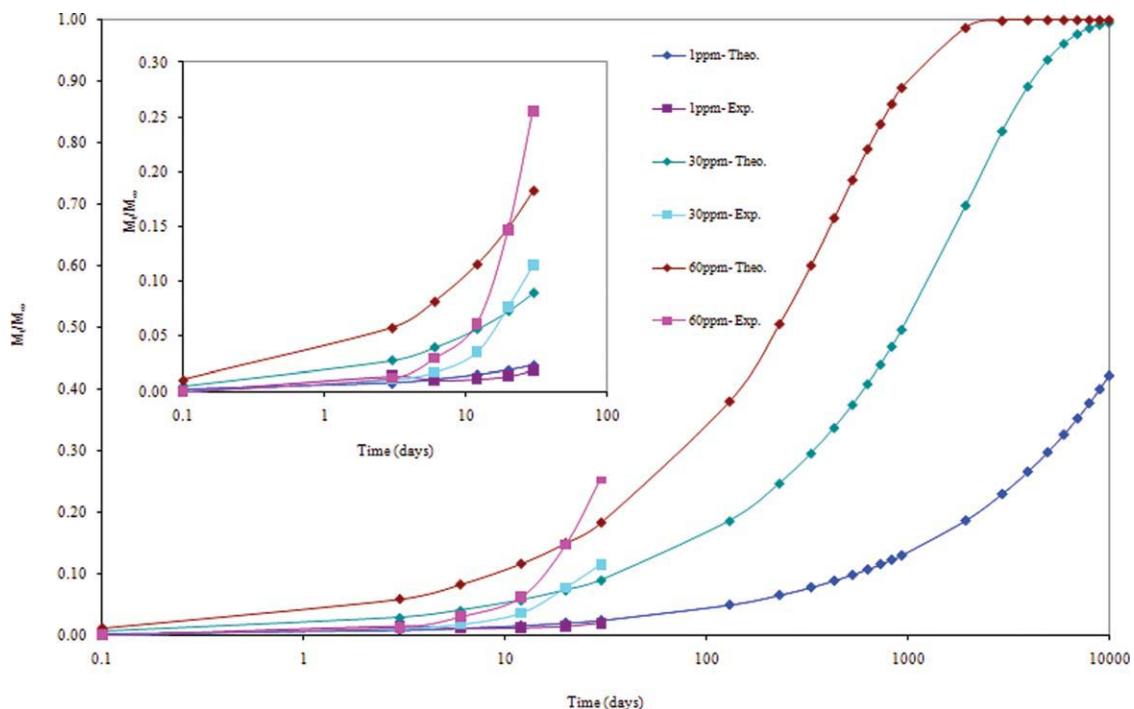


Figure 10 Long-term mass intake curve for NR (23°C). Inset graph shows the experimental and theoretical data fit. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

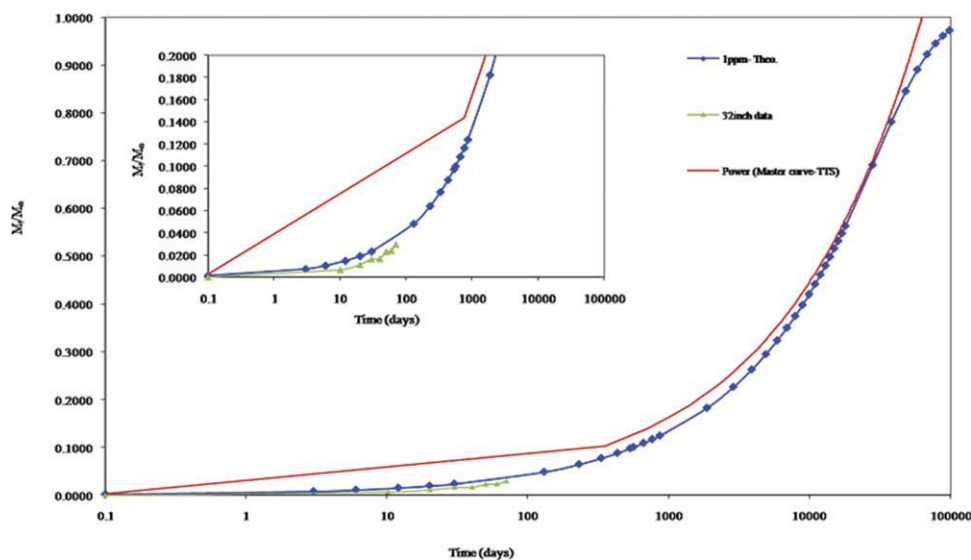


Figure 11 Long-term mass intake curves (diffusion theory and TTS) for SBR (1 ppm, 23°C). Inset graph shows the experimental data and theoretical data fit for the 30-inch sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Concentration profiles

It is noted that the sample would not be uniformly saturated across its profile as the aqueous chloramine solution penetrates the elastomer along a “wetting front.” Thus, the degree of saturation within the sample is dependent upon the specific location of interest with the outer surfaces achieving higher saturations than interior locations within the same time period. The extent of penetration with respect to time can be obtained by solving Fick’s second law of diffusion [eq. (2)] with appropriate boundary condi-

tions using a finite-difference method approximate solution^{19,25} as explained in the Numerical Solution section.

Computed concentration profiles for SBR and NR after 30 days of exposure were presented in Figures 13 and 14. Each figure contains a unique concentration profile for each of the temperatures investigated for 1 mg/L chloramine concentration. As expected, the distance traveled by the aqueous chloramine into elastomer is higher at higher temperatures for both elastomer materials.

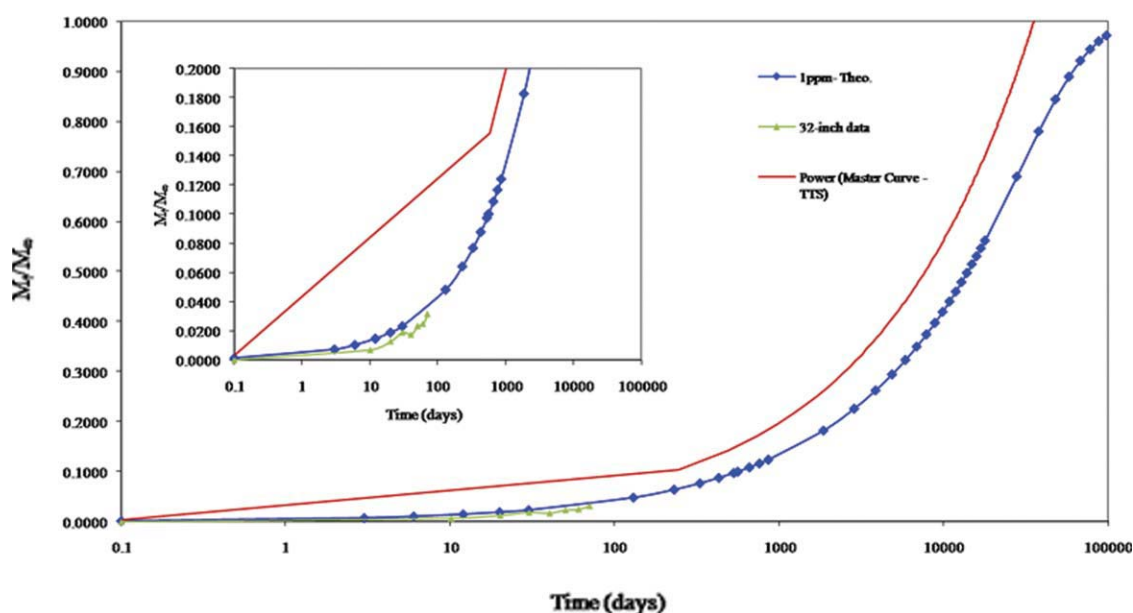


Figure 12 Long-term mass intake curves (diffusion theory and TTS) for NR (1 ppm, 23°C). Inset graph shows the experimental data and theoretical data fit for the 30-inch sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

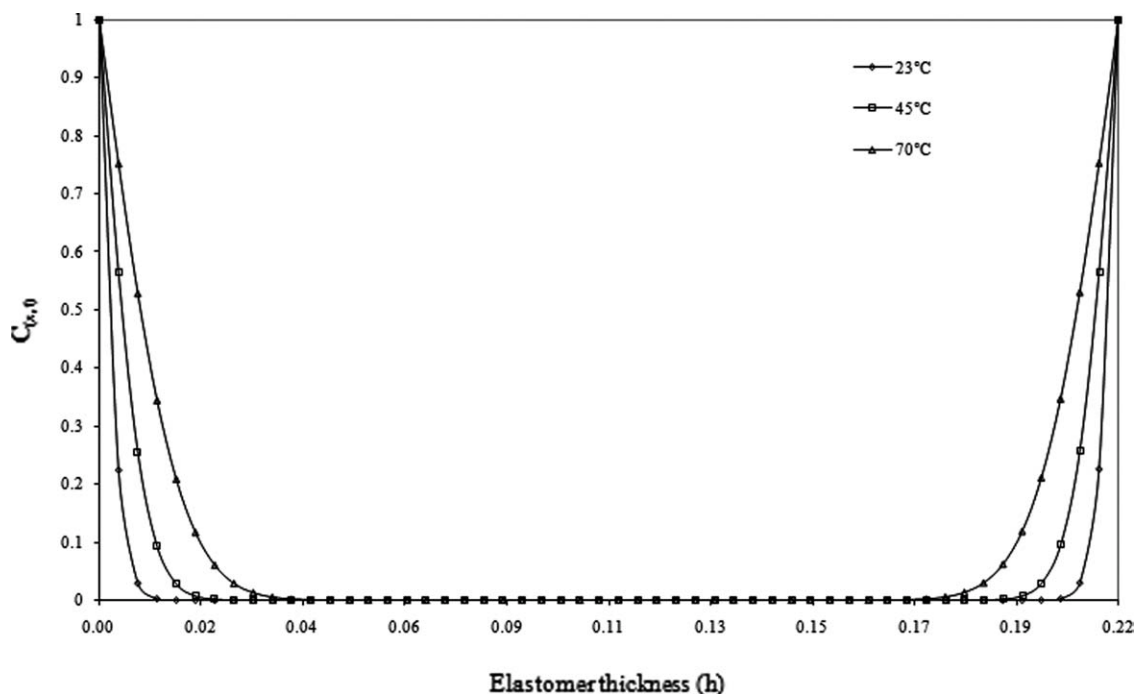


Figure 13 Aqueous chloramines concentration profile (30-day exposure) along elastomer thickness for SBR.

DISCUSSION

It is well documented in the literature that increasing the temperature will accelerate the diffusion process of elastomers, and the diffusion coefficients increase on an exponential scale as temperature increases. It is a common practice to study accelerated diffusion by increasing the temperature, to get the information on long-term diffusion rates. How-

ever, in the long-term mass intake prediction studies on elastomers, it is thought that temperature-accelerated diffusion does not quite duplicate the service condition's diffusion mechanism.

At higher temperatures, the elastomer degradation can be thought of as a three-component process, i.e., rubber molecular activity, reaction rate, and diffusion, which happens simultaneously aiding one another. All these processes increase as the

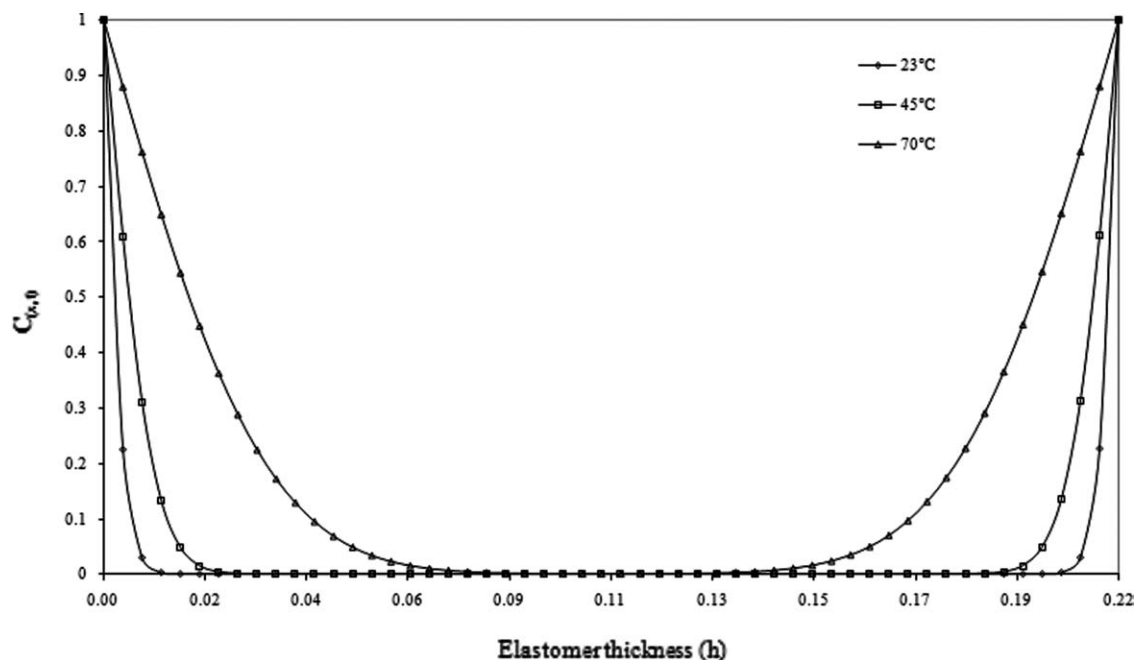


Figure 14 Aqueous chloramines concentration profile (30-day exposure) along elastomer thickness for NR.

temperature increases, resulting in an accelerated elastomer degradation. At higher temperatures, the elastomer matrix opens up quickly throughout because of the increased heat energy of molecules and high reaction rate, allowing more aqueous chloramine mass intake. This increased aqueous chloramine mass intake would accelerate the oxidation process of the elastomer matrix, which further opens up the elastomer matrix, increasing the mass intake.

At service conditions, the elastomer degradation would only be a two-component process i.e., reaction rate and mass intake. At the service conditions, diffusion would be primarily because of aqueous chloramine concentration gradient through the elastomer matrix free volume. The aqueous chloramine oxidation attack would be predominantly focused on the exposed surface. Since diffusion at service conditions is very slow processes, it would take long time for aqueous chloramine to diffuse into and then oxidize the elastomer matrix.

This service condition diffusion can better be duplicated and accelerated by increasing chloramine concentrations. Increasing the chloramine concentration would increase the reaction rate, which increases the oxidation attack. In this case, the oxidation attack would be predominantly at the elastomeric surface. The diffusion would be mainly due to concentration gradient, and a little extra diffusion would result from the opening of elastomer matrix network near surface because of oxidation. In short, increasing the aqueous chloramine concentration would principally accelerate the oxidative attacks of the aqueous chloramine on the elastomeric surface. Figures 3 and 4 present the increase of diffusion coefficients based on temperature and chloramine concentration. Based on the above reasoning, it can be said that the diffusion coefficients computed for higher chloramine concentration data would be a better representative of long-term diffusion rate than the ones computed with higher temperature data.

CONCLUSIONS

The aqueous chloramine mass intake into six most commonly found elastomers in the water utility industry, i.e., NR, SBR, NBR, neoprene rubber, EPDM(S), and EPDM(P), were analyzed. Of the elastomers considered, EPDM compounds showed least amount of degradation followed by NBR, SBR, NR, and neoprene rubber. For SBR and NR, diffusion coefficients and long-term mass intake curves were developed using Fick's second law of diffusion. It has been noted that as the degradation progresses, the diffusion process changes from Fickian to non-Fickian. Activation energies were computed to be 51.13 and 77.29 kJ/mol, respectively, for SBR and NR in 1 mg/L aqueous chloramine solutions. Con-

centration profiles were developed to understand the saturation progression along the elastomer thickness. For long-term performance prediction of elastomeric compounds in drinking water systems, accelerating the degradation by increased chloramine concentration is thought to be a better service condition degradation representative than the increased temperature acceleration.

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