Prediction of Vinyl Chloride Monomer Migration from Rigid PVC Pipe

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Data on the solubility and diffusion of vinyl chloride monomer (VCM) in PVC resin powders have been combined with published solutions of Fick's diffusion equation to yield predictions of the amount and rate of loss of residual VCM (RVCM) from rigid PVC pipe under storage and service conditions. The principal factors controlling VCM migration are the initial VCM content, thickness of the PVC section, temperature, and the age of the PVC product. Analytic solutions are presented for RVCM loss from freshly extruded pipe (uniform VCM concentration) into either the storage environment or the pipe contents. From these solutions, estimates are made for the real-world situation of closed-system service following variable storage periods. The validity of this approach for rigid PVC pipe in water-service is supported by reasonable agreement between its predictions and experimental laboratory data on the VCM content of water stored in PVC pipes. Both the predictive model and experimental data indicate that PVC pipe containing ≤1 mg/kg (1 part per million) residual VCM will result in VCM concentrations in water of less than 0.002 mg/kg under any expected service conditions.

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INTRODUCTION

A subject of continuing concern since the discovery of the potential toxic hazard of vinyl chloride monomer (VCM) has been the migration of residual VCM from finished PVC products into the environment or into liquids transported in PVC vessels. Many efforts have been made to investigate this problem by direct analysis for VCM in media in contact with PVC vessels. Early efforts in 1973 were questionable because of the imprecise analytical methods then available. As analytical procedures have been improved, the residual VCM levels in commercial PVC products have been sharply reduced, so the direct analysis for VCM migrating from today's PVC products remains a very difficult problem. Recent data (1) show that sensitivity in the thousandths of a milligram per kilogram range is needed to analyze for VCM in water contained in PVC pipe even at the residual VCM level of 20 mg per kilogram. A reliable model for predicting the amount and rate of VCM migration from available basic transport data and theory thus would be very useful.

Our approach to the development of a predictive model has been to combine the solubility and diffusion data we have obtained for VCM in uncompounded PVC resin powders (2, 3) with the solutions of the Fickean diffusion equations given by Crank (4). This report summarizes the assumptions and approximations involved in applying these diffusion equations to the VCM migration problem and illustrates the possible calculations with some numerical examples. The predictions of our model are compared with experimental data on VCM contents of water stored in PVC pipe.

CALCULATIONS OF VCM MIGRATION

Background and Assumptions

On the basic assumption that migration of VCM thru PVC is controlled by the diffusion of VCM in the PVC phase, this process may be treated by well-known theory. The basis of classical diffusion theory is the simple differential equation known as Fick's First law,

$$F = -D \frac{\partial c}{\partial x} \tag{1}$$

which states that the amount of diffusing substance crossing a unit plane area in unit time, F, is proportional to

the concentration gradient across the plane, $\frac{\partial c}{\partial x}$. The proportionality constant, D, is called the diffusion coefficient. The minus sign indicates that diffusion always occurs toward the region of lower concentration, i.e., "downhill". Net diffusive transport ceases when the concentration gradient becomes zero, i.e., when the concentration becomes uniform.

The use of Fick's law to calculate useful quantities, such as the rate at which a diffusing substance escapes from a solid object, or the concentration profile within the object, involves some very complicated mathematics. Exact mathematical solutions are generally possible only for geometrically simple shapes and for certain specified initial and boundary conditions. Many of the useful solutions are presented in Crank's text (4), and fortunately it seems that some of the most important problems in VCM migration from PVC can be handled with a few of these equations.

Our application of these equations and our diffusion data to VCM migration from PVC products involves several assumptions:

(1) The diffusion of VCM in PVC obeys Fick's law.

(2) The diffusion coefficient is independent of VCM concentration.

(3) The value of the diffusion coefficient in rigid PVC products is the same as we have determined for pure PVC resins.

(4) The diffusion coefficient is independent of the medium surrounding the PVC; i.e., values we have determined by vapor sorption/desorption also apply to migration into a liquid phase.

Assumptions (1) and (2) have been demonstrated to be very satisfactory approximations at quite low RVCM concentrations by our work on PVC powders (3). More limited experiments on thin, rigid PVC films also support assumption (3), although some variation of D might be expected for varying amounts and types of compounding additives. The use of assumption (4) should be considered a tentatively useful approximation; we shall see that it does seem justified by experimental data on VCM migration into water from PVC pipe.

To describe the diffusion of RVCM from PVC products through Crank's equations, three situations have been considered:

Case I: RVCM loss during storage of a freshly-manufactured PVC product.

Case II: RVCM loss from freshly formed PVC products into a closed medium.

Case III: RVCM loss into a closed medium from previously aged PVC products.

In both Cases I and II, the initial RVCM concentration is assumed to be uniform through the thickness of the PVC product; this is probably a valid assumption only at the time of extrusion, as the surface concentration of RVCM will quickly decrease upon exposure to a low-VCM environment. Cases I and II differ in the time-dependence of the surface concentration: In Case I, the surface concentration of VCM remains essentially zero, as any RVCM escaping is carried away in the environment; this case may represent storage or service in a continuously renewed environment, such as flowing water. In Case II, the VCM concentration in the medium builds up with time, and consequently so does the VCM concentration in the surface of the PVC. Case III is the general situation in a real-world application: VCM loss into a closed medium follows a variable storage period and thus proceeds from a product in which the surface VCM concentration is already depleted. We will see that the aging period between manufacture and closed-system service is quite important in determining the rate of VCM migration into the contents of a PVC pipe.

Now let us consider the details and some numerical examples of each of these three cases.

Case I—VCM Loss During Storage

Consider a freshly extruded PVC product, quickly cooled to ambient temperature and stored in an atmosphere of essentially zero VCM content. The initial RVCM concentration in the product is C_o and may be assumed to be uniform through the product. At the surface, equilibrium is quickly established with the environment and the RVCM concentration is zero. We assume that VCM leaving the PVC is carried away (e.g., good air circulation) so that the surface concentration remains zero. We want to calculate (a) the amount of VCM which leaves the PVC and (b) the concentration profile within the PVC, both as functions of time, temperature, and sample thickness.

Crank gives solutions to this problem for several simple geometries—plane sheets, solid and hollow cylinders and solid spheres. The predictions for hollow cylinders are virtually identical to those for plane sheets, provided the wall thickness is less than the inside diameter. Thus for all practical PVC products (pipes, bottles, sheets, films), we need consider only the mathematical solutions for plane sheets. Equations for the amount of VCM escaping from the sheet may be written in terms of M, the fraction of the original VCM which escapes in time t. The general expression, valid at all times, is

$$M = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-D(2n+1)^2 \pi^2 t/L^2} \qquad (2)$$

where n is the series of integers (0, 1, 2—), D the diffusion coefficient, and L the sheet thickness. For the late stages of the process ($M > \sim 0.6$), terms beyond $n = 0$ become insignificant, and *Eq 2* becomes

$$M = 1 - \frac{8}{\pi^2} e^{-D\pi^2 t/L^2} \qquad (3)$$

For $M < \sim 0.6$, a very good approximation is given by

$$M = 4\left(\frac{D}{\pi L^2}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \qquad (4)$$

Thus the initial loss of VCM is proportional to the square root of the storage time after extrusion. For numerical calculations, we need only the sheet thickness and the diffusion coefficient values. From our measurements on PVC resins (3), the value of D at various temperatures is given by

$$D = 3.7\exp\frac{-17{,}000}{RT} \qquad (5)$$

for D in cm²/sec, T in °K, and R = 1.987 cal/mol°K.

Equations 3, 4 and 5 permit prediction of the fractional loss of RVCM from rigid PVC products for different sheet thicknesses, times and storage temperatures. Examples of numerical results are given in *Figs.* 1 and 2 as plots of M vs $t^{\frac{1}{2}}$. *Figure* 1 shows such RVCM-loss curves for several sheet thicknesses at 30°C, where $D = 2 \times 10^{-12}$ cm²/sec = 1.73×10^{-7} cm²/day, and *Fig.* 2, for a 1 mm sheet thickness at several temperatures.

The concentration of RVCM remaining at time t at various distances from the sheet surface (i.e., the concentration profiles) can also be calculated from the same parameters. Crank gives the general solution as

$$\frac{C - C_o}{C_1 - C_o} = \sum_{n=0}^{\infty} (-1)^n \, erfc\left[\frac{(2n+1)\,l - x}{2(Dt)^{\frac{1}{2}}}\right] + \sum_{n=0}^{\infty} (-1)^n erfc\left[\frac{(2n+1)\,l + x}{2(Dt)^{\frac{1}{2}}}\right] \qquad (6)$$

where C is the concentration at time t at distance x from the center of the sheet, C_o is the initial (uniform) concentration, C_1 is the constant concentration at the surface (zero in our case), and l is the half-thickness of the sheet; "*erfc*" stands for error function complement, defined as

$$erfc\, z = 1 - erf\, z \qquad (7)$$

The error function, "*erf*", also called the probability integral, is tabulated in standard mathematical tables. For times short enough that the concentration at the center of the sheet does not decrease significantly below C_o, only the first term of *Eq* 6 is necessary; then, using *Eq* 7, we have simply

$$\frac{C}{C_o} = erf\left[\frac{l - x}{2(Dt)^{\frac{1}{2}}}\right] \qquad (8)$$

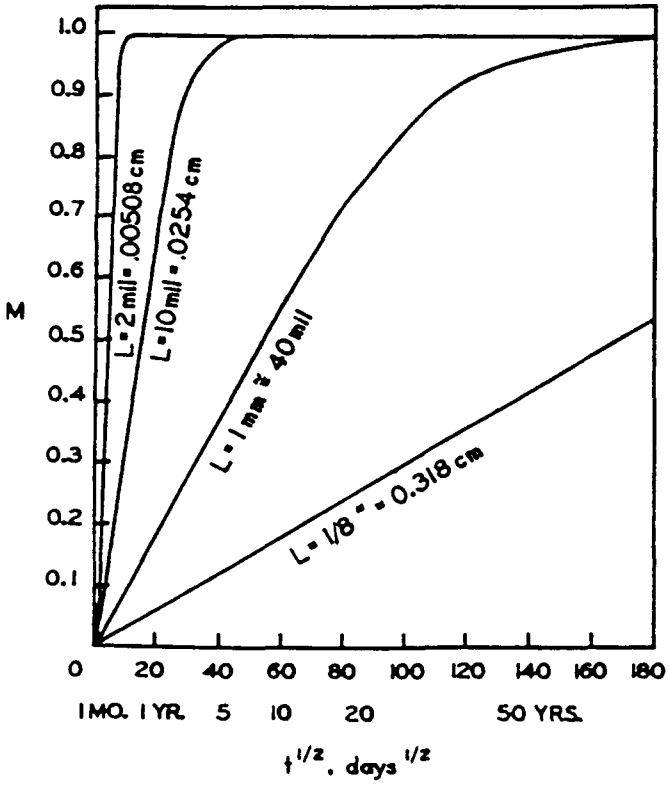

Fig. 1. Fraction of initial VCM content lost (M) vs square root of time ($t^{\frac{1}{2}}$) for PVC sheets of various thicknesses (L), calculated for 30°C ($D = 1.73 \times 10^{-7}$ cm²/day), Case I.

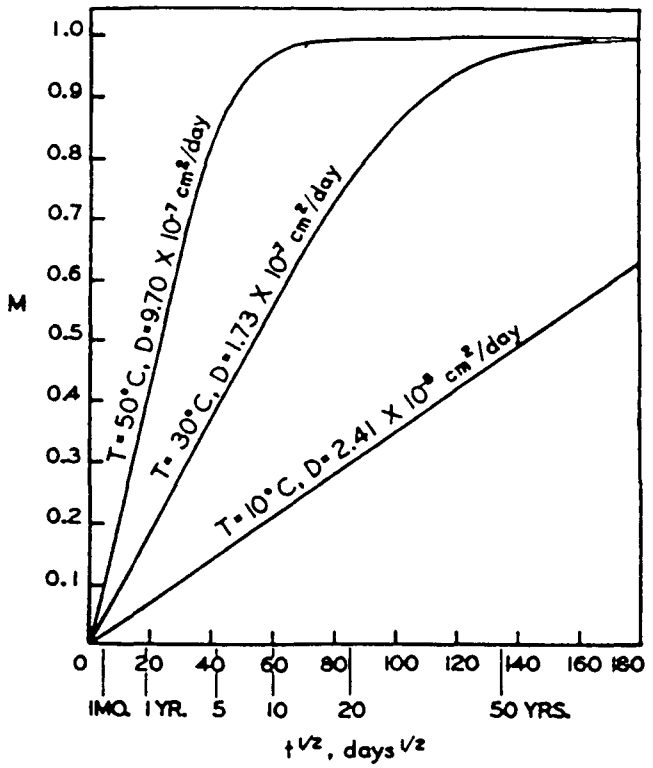

Fig. 2. Fraction of initial VCM content lost (M) vs square root of time ($t^{\frac{1}{2}}$) for PVC sheet 1 mm thick, calculated for various temperatures, Case I.

Using *Eq* 8, or *Eq* 6 where necessary, we have calculated concentration profiles at 30°C ($D = 1.73 \times 10^{-7}$ cm²/day) for a PVC sheet ⅛ in. thick (or pipe with ⅛ in. wall). The results at various times are plotted in *Fig.* 3. Note that the VCM lost in the first month comes only from the 100 microns of PVC near the surface. It takes over 20 years in this case for the VCM concentration near the center of the sheet to decrease appreciably.

CASE II—VCM MIGRATION FROM FRESHLY/FORMED PVC PIPE INTO CONTENTS

The Case I calculations may be applied whenever VCM leaving the PVC product is carried away by the environment (storage in circulating air, water-pipe service with flowing water, etc.), so that the surface concentration of RVCM remains essentially zero. For PVC pipes in ordinary service, the outer surface is generally exposed to a low-VCM environment, i.e., a Case I situation. On the inside of pipes with stagnant contents, on the other hand, VCM leaving the PVC builds up in concentration in the contents. Consequently, the inside surface concentration of RVCM in the PVC, assumed to remain in equilibrium with the contents, also increases with time. At very long times, RVCM in the inner half of the

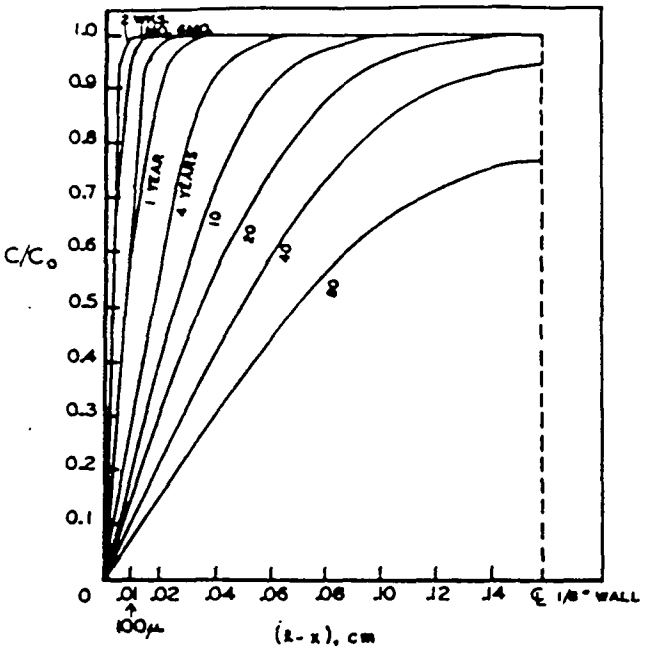

Fig. 3. Relative VCM concentration (C/C_o) vs depth below sheet surface ($l - x$) at various times, calculated for ⅛ in. thick PVC sheet at 30°C ($D = 1.73 \times 10^{-7}$ cm²/sec). Case I.

PVC wall and in the contents will diffuse outward to the environment. This net outward diffusion of VCM will only occur after the VCM concentration at the midline of the wall falls below its initial value; the time at which this occurs can be estimated from concentration profiles such as those in *Fig. 3*. Since this effect occurs at such long times for pipes of normal wall thickness, we have not considered it in our model, but instead have applied Case I and Case II calculations independently to the outer and inner halves of the PVC walls, respectively.

The rate and amount of VCM entering the pipe contents may be calculated through equations given by Crank. The maximum amount of VCM which will enter the contents is that required to establish equilibrium between PVC and contents, and is governed by the partition coefficient and the ratio of volumes of PVC and contents. The partition coefficient, K, is defined as the ratio of RVCM concentration in the PVC to that in the contents at equilibrium (both expressed in the same units, e.g., g/liter). The volume of PVC supplying VCM to the container contents, V_{PVC}, is one-half the total PVC volume, as RVCM in the outer half diffuses outward in the situation we are considering. It can be shown that the maximum VCM concentration, $C_{m,max}$ (ppm by weight) in the liquid contents of a PVC pipe originally containing C_o ppm VCM, is

$$C_{m,max} = \frac{C_o d_{PVC}}{(K + \frac{V_m}{V_{PVC}})d_m} \qquad (9)$$

where d_{PVC} and d_m are densities of the PVC and contents, and V_m is the volume of the contents.

From our data (2) on VCM solubility as a function of VCM pressure over PVC and water, we have estimated a value of $K = 49$ for the distribution coefficient of VCM between PVC and water at 30°C. It should be noted that this estimate of K assumes that the solubility of VCM in PVC is not affected by contact with water. It also involves a somewhat arbitrary selection of a value for VCM solubility in PVC, since we have shown (2) that this system shows non-ideal and history-dependent solubility. Using this value of K, *Eq 9* predicts that the maximum VCM concentration in water in a 1 in. I.D., ⅛ in. wall, PVC pipe containing 1 mg/kg residual VCM will be 0.027 mg/kg.

The rate of VCM desorption into the pipe contents may be obtained from another of Crank's equations:

$$M = \alpha[1 - e^{T\alpha^2} erfc(T/\alpha^2)^{\frac{1}{2}}] \qquad (10)$$

where $T = Dt/l^2$, M is the fraction of the original RVCM desorbed at time t, and $\alpha = V_m/KV_{PVC}$. To illustrate, we have applied *Eq 10* to the 1 in. I.D., ⅛ in. wall, PVC pipe filled with standing water. *Figure 4* shows the results, with scales showing both M, the fraction of original RVCM desorbed, and the VCM concentration in the water per original ppm RVCM. Also shown in *Fig. 4* is the M vs $t^{\frac{1}{2}}$ plot for Case I. Note that the initial rate of VCM desorption is the same for both Cases I and II, but the buildup of VCM in the water in Case II causes the desorption to slow down as equilibrium is approached.

Case III—VCM Migration in Closed-System Service from Previously Aged PVC Products

When a PVC product is put into closed-system service some time after manufacture, the RVCM distribution through the PVC at the time of filling and closing the container will not be uniform, as was assumed in the Case II calculations. Rather, RVCM will already be depleted near the surface, and VCM migration into the pipe contents will start from a VCM distribution as calculated in Case I (e.g., Figure 3). An analytical solution for this situation has been obtained by Daniels and Proctor (5), but a useful and simpler estimate of the rate

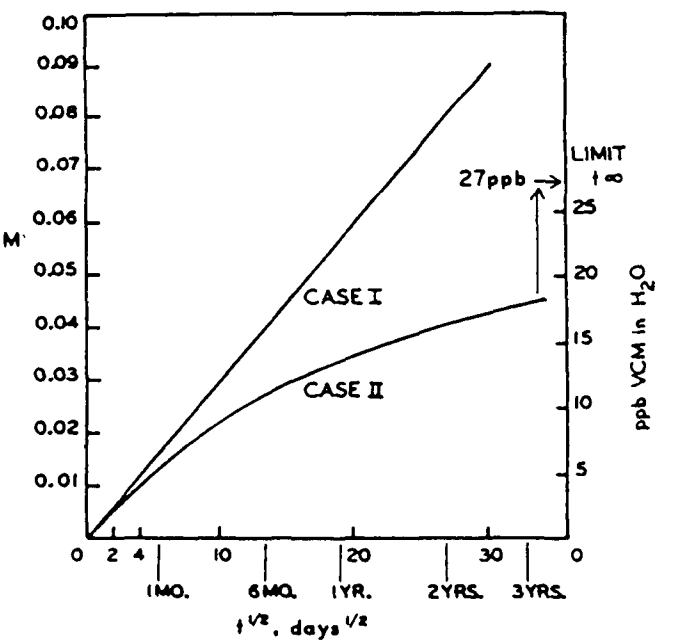

Fig. 4. Fraction of original VCM content lost (M) vs square root of time ($t^{\frac{1}{2}}$) for 1 in. I.D., ⅛ in. wall PVC pipe, calculated for 30°C ($D = 1.73 \times 10^{-7}$ cm²/day), Case I and Case II with water in pipe. Right-hand scale gives ppb VCM in water per ppm initial VCM in pipe.

of VCM migration can be made by combining results of our Case I and Case II equations. For Case I during desorption of the first 60% of the VCM, *Eq 4* shows that the amount of VCM desorbed is proportional to the square root of storage time. Differentiating *Eq 4* gives

$$\frac{dM}{dt} = 2\left(\frac{D}{\pi L^2}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \qquad (11)$$

Thus the *rate* of VCM loss is inversely proportional to the square root of storage time. For Case II, we saw that the *initial* rate of VCM migration into the medium in a closed system is the same as in Case I. Thus *Eq 11* also gives the initial rate of VCM migration into the closed system when t is the storage age of the PVC product at the start of closed-system service. Applying *Eq 11* to a PVC product with ⅛ in. wall thickness at 30°C ($D = 1.73 \times 10^{-7}$ cm²/day) gives the curve shown in *Fig. 5*. We see that the rate of RVCM desorption drops very sharply in the first few weeks of storage after manufacture.

It is also possible to estimate the amount of VCM which will migrate from a PVC product during a given period of a closed-system service following various Case I storage periods. This estimation may be explained with reference to *Fig. 6*, which illustrates the VCM-loss (M) vs $t^{\frac{1}{2}}$ curves for the three cases. Case III is approximated by shifting the origin of the Case II curve to point t_1 along the Case I line, where t_1 is the age of the PVC product at the start of closed-system service. Then the VCM lost from the PVC in the time interval a during continued open-system storage would be, from *Eq 4*

$$\Delta M = 4\left(\frac{D}{\pi L^2}\right)^{\frac{1}{2}} [(t_1 + a)^{\frac{1}{2}} - t_1^{\frac{1}{2}}] \qquad (12)$$

The VCM lost, and entering the contents of a PVC container, in Case III service, will be approximately equal to ΔM for relatively short service periods, and always less than ΔM. *Equation 12* thus is useful for calculating the maximum fraction of the original RVCM which will migrate into the contents of a PVC container during closed-system service for any time period as a function of the age of the container at the time of filling and closing. *Figure 7* illustrates results calculated from *Eq 12* for 7 and 30 day service periods for a ⅛ in. wall thickness at 30°C as functions of t_1. Again we see the important effect of a few weeks prior aging in reducing the amount of VCM migration into the contents.

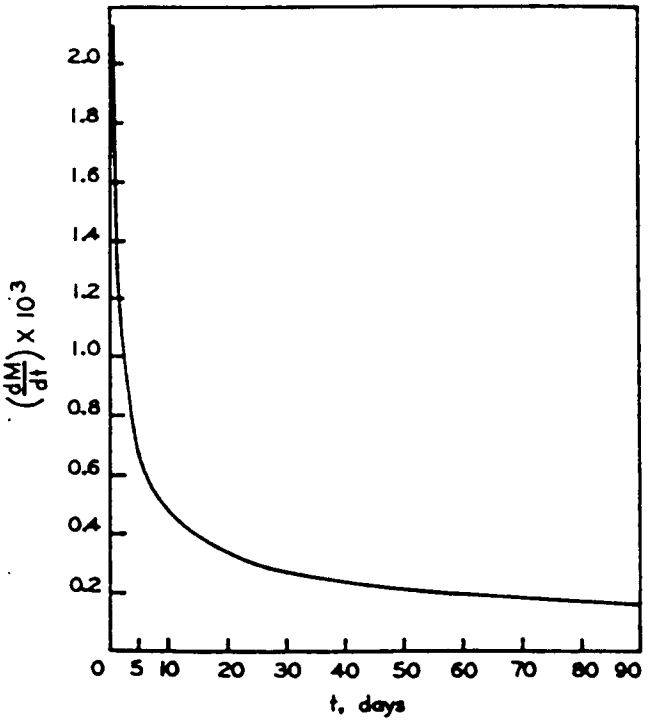

Fig. 5. Rate of VCM loss (dM/dt) vs time for ⅛ in. thick PVC sheet, calculated for 30°C, Case I.

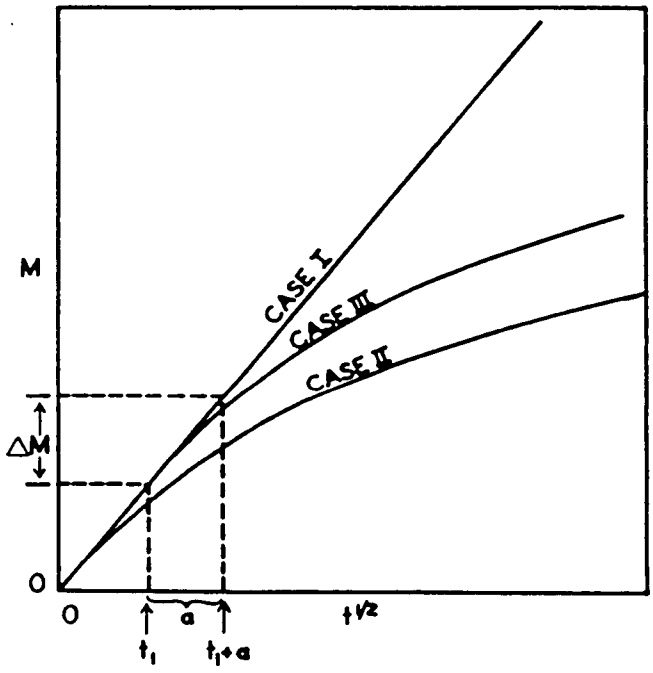

Fig. 6. Schematic comparison of fractional VCM loss (M) vs $t^{\frac{1}{2}}$ curves for Cases I, II, and III.

Comparison of Predictions with Experimental Data

The foregoing analysis clearly shows that the age of a PVC product at the start of an extraction test is an important factor in determining the amount of VCM extracted. Since this information is seldom available in reported extraction data, direct comparisons between our predictions and experimental data are possible for only a few cases.

For the data recently obtained by O'Mara and DeCapita (1) on the VCM content of water stored in 1 in. I.D. ⅛ in. wall PVC pipes at 23°C, the *approximate* age of the pipe samples, between extrusion and start of the extraction test, was known. A "headspace" GC analytical method was used to provide sensitivity to low VCM levels in the water (on the order of 1 or 2 thousandths of a milligram per kilogram). We have calculated the VCM content expected in the water, using *Eq 12* with the parameters appropriate to the experimental conditions; D was obtained from *Eq 5*. *Table I* compares the calculated and experimental results. The agreement must be considered quite satisfactory, especially in view of a) our application of D values obtained from resin powders to pipe compounds, b) the somewhat uncertain age and

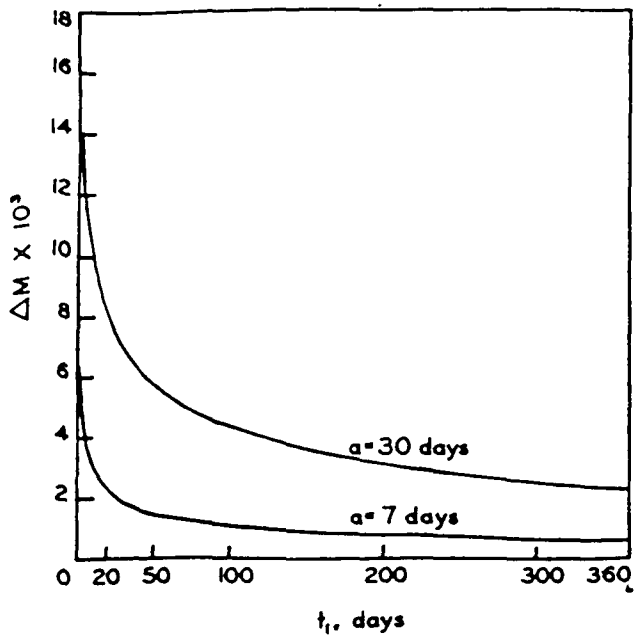

Fig. 7. Fraction of original VCM content entering pipe contents (ΔM) for 7 and 30-day extraction periods vs pipe age at start of extraction (t_1), calculated for ⅛ in. wall thickness and 30°C, Case III.

storage conditions of the pipe samples, and c) the difficulty of analysis of water for extremely low levels of VCM.

DISCUSSION

While further experimental verification would be desirable, it appears that the simple approach discussed above is quite adequate for describing and predicting the migration of RVCM from PVC pipe into water. The reasonable agreement between predicted and observed migration data for this application of rigid PVC supports the premises that, a) the diffusion coefficient determined for pure PVC resins is applicable to rigid PVC pipe compounds, and b) contact of PVC with water produces little change in the diffusivity of VCM compared to that measured by vapor sorption/desorption techniques. Further, for such relatively thick walled products as pipes, the diffusion into the environment from the outer half of the wall and into the contents from the inner half may be treated as independent processes over normal service lifetimes.

Our simple predictive model may thus be used with some confidence for estimating the concentrations of VCM in water which might arise during actual service of PVC water pipe systems. To illustrate, *Eq 12* has been used to calculate the VCM concentrations resulting from various stagnant exposure times of water in PVC pipes of 1 mg/kg original VCM content and varied diameter, warehouse age before installation and service age. Some results of such calculations are given in *Table* 2 for 2, 6 and 8 in. SDR21 pipes in service at room temperature (~23°C). While these data are presented as though they represent stagnant water situations, from known use conditions (flow rates, pipe dimensions and resultant residence time), these calculations can be shown to model dynamic flowing systems.

The figures in *Table* 2 clearly show that the highest VCM concentrations would be found in new installations of recently manufactured small diameter PVC pipe after long stagnation periods. Yet even for these most extreme conditions, the predicted VCM-in-water concentrations are well below the level of 0.002 mg VCM/kg H_2O when the original residual VCM content of the pipe is 1 mg/kg or less. In actual installations, stagnation times of more than a few days are rarely encountered. A typical residence time for water in PVC pipes is believed to be about 2 days (6-8) and in this situation, the predicted VCM-in-water concentration falls in the parts-per-trillion range. Thus we may conclude that PVC pipe containing ≤1 mg/kg residual VCM will result in VCM concentrations of less than 0.002 mg VCM/kg H_2O under any expected service conditions, and, therefore, non-detectable by present analytical methods.

Tabl 1. Comparison of Predicted and Experimental Extraction Results, Water-Filled 1 in. I.D. ⅛ in. Wall PVC Pipe Samples, 23°C

RVCM in pipe, mg/kg	Pipe age, t	Extraction Time, a,days	VCM in water, (mg/kg) Experimental	Calculated
292	~6 mo.	3	0.021	0.0257
292	~6 mo.	7	0.0414	0.0598
292	~6 mo.	14	0.113	0.118
177	~6 mo.	3	0.0173	0.0156
177	~6 mo.	7	0.0335	0.0362
177	~6 mo.	14	0.056	0.0717
22	~6 mo.	3	0.0006	0.0019
22	~6 mo.	7	0.0022	0.0045
22	~6 mo.	14	0.0046	0.0089
29	~1 yr.	14	0.0105	0.0084

Table 2. Calculated VCM in H_2O Concentrations for Stagnant Storage of Water in PVC Pipes of Varied Size and Ag and Original 1 mg/kg Residual VCM Content

Pipe size (SDR21)	Warehouse age, days	Service age, years	VCM in water after given storage times, mg/kg 2 days	2 weeks	1 month
2 in.	30	0(new)	.00007	.00044	.00087
	60	0	.00005	.00033	00067
	90	0	.00004	.00027	.00056
	90	1	0000180	.000125	000265
	90	2	.00001	.00009	000199
	90	5	.00001	.00006	00013
6 in.	30	0	00002	00015	00029
	60	0	.00002	.00011	.00022
	90	0	.00001	.00009	.00019
	90	1	.000006	.000042	.000088
	90	2	.000004	.00003	.000066
	90	5	.000003	.00002	00004
8 in.	30	0	.00002	.00011	00022
	60	0	.00001	.00008	.00016
	90	0	.00001	.00007	00014
	90	1	.0000045	.000031	000066
	90	2	.000003	.00002	000050
	90	5	.000002	.00001	.00003

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