# Accelerated Aging Studies and the Prediction of the Archival Lifetime of Optical Disk Media

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**Abstract**
Data archivists expect information storage media to have a lifetime greater than ten years. Furthermore they desire the ability to predict when the media will fail in order to plan for its replacement. Archival lifetime predictions are based on accelerated aging studies, where the media are subjected to conditions of high temperature and high humidity. The rate of failure is measured and the data extrapolated to obtain rates of failure under ambient conditions. This extrapolation is reasonable provided the degradation process is activated and the Arrhenius relationship holds. However this may not be the case for the complicated materials packages in optical data storage media. A primary concern for the polymeric materials is any phase transition, such a glass transition or a beta relaxation, that may occur at temperatures between ambient and the accelerated aging conditions. It is not clear how one extrapolates through those transitions. These phase transitions can give rise to large changes in the rates of diffusion for water, oxygen and other agents of degradation. Furthermore, for polymers, such as polycarbonate, the mode of failure is often hydrolysis and the degradation products can catalyze further hydrolysis, an autocatalytic degradation. The polymer degradation will change the phase transition temperatures. The degradation products may also plasticize the polymer, causing further changes in diffusion rates. We provide here a simple analysis of accelerated aging techniques and discuss other factors that may be involved.

**Optical Data Storage Media**
DVD is an emerging optical data storage technology that may find application in data archiving. DVD disks are complicated materials packages consisting of a 0.6 mm polycarbonate substrate coated with a recording layer or layers. For double-sided disks, two disks are laminated with a polymeric adhesive layer. In DVD-R the recording layer is a dyed-polymer with a gold reflective layer. The recording layer in DVD-RW is a phase change alloy surrounded by dielectric layers. These material packages are similar to the corresponding compact disk formats, CD-R and CD-RW, except the materials are tuned to red lasers rather than 780 nm lasers. We may draw on the experience for the CD formats to gain a sense for the reliability of the DVD formats. The block error rate was measured as a function of time for CD-R disks exposed to 8% relative humidity and either 60°C, 80°C or 100°C [1]. The rate of degradation of the block error rate under these conditions led to a prediction of a data storage lifetime of 100 years, comparable to the best CD-ROM disks. The materials package for DVD-R is different from CD-R. The substrate is thinner which would make it more sensitive to any mechanical changes arising from polycarbonate hydrolysis. The recording layer contains a different dye,

which absorbs the red laser instead of the 780 nm laser.  The chemistry of the degradation of the dyes used for DVD-R has not been systematically studied.  However accelerated aging studies of naphthalocyanine or cyanine dyes, sensitive to infrared lasers, suggested that the rate of degradation was reaction kinetics limited [2-3].  If the dyes for DVD-R are sensitive to degradation by oxygen or to moisture, it is expected that the degradation would be reaction kinetics limited.  However, for more aggressive penetrants, such as ozone, the degradation may very well be mass transport limited.  A systematic study of dye degradation by different penetrants would allow a rational accelerated aging strategy to be developed.

In DVD-RW the phase change alloys (In-Ag-Sb-Te) are sensitive to oxidation.  The penetrants must diffuse through the polycarbonate and through pinholes in the protective layer (ZnS-SiO$_2$) to get at the alloy.  Water would adsorb on the alloy surface, creating an electrolyte for the reduction of oxygen and the oxidation of the alloy [4].  This process disbonds the protective layer, exposing more of the alloy surface to corrosion.  The result would be random defects that would increase the bit error rate as the corrosion sites grow.  Clearly, this mode of degradation would be mass transport limited.


**Polycarbonate**
Under exposure to high temperature and high humidity conditions polycarbonate substrates hydrolyze to break the carbonate ester linkage, Eq. (1).  The products are carbon dioxide and two new phenol end groups.  Ester hydrolysis can be catalyzed by acids or by bases.  Although phenol and carbon dioxide are acids, they are very weak acids.  It is expected they would have a minimal effect on the rate of hydrolysis.  The kinetics for polycarbonate substrate hydrolysis under high temperature and high humidity conditions was reported earlier [5].  Plots of the degree of polymerization as a function of aging time were linear, indicating the degradation process was not autocatalytic.  The activation energy for hydrolysis was 70 ± 4 kJ/mol, which was close to the activation energy (59 kJ/mol) for the hydrolysis of diphenyl carbonate [6].  In the course of accelerated aging experiments, the polycarbonate was degrading.  There was no determination of the effect of this degradation on the physical properties on the substrate, such as the mechanical properties or the rate of diffusion of penetrant molecules.  There is a report that the bisphenol A monomer, liberated by hydrolysis, can diffuse to the surface [7].  The effect of bisphenol A on the degradation of optical disk recording layers is not understood.



$$\tag{1}$$
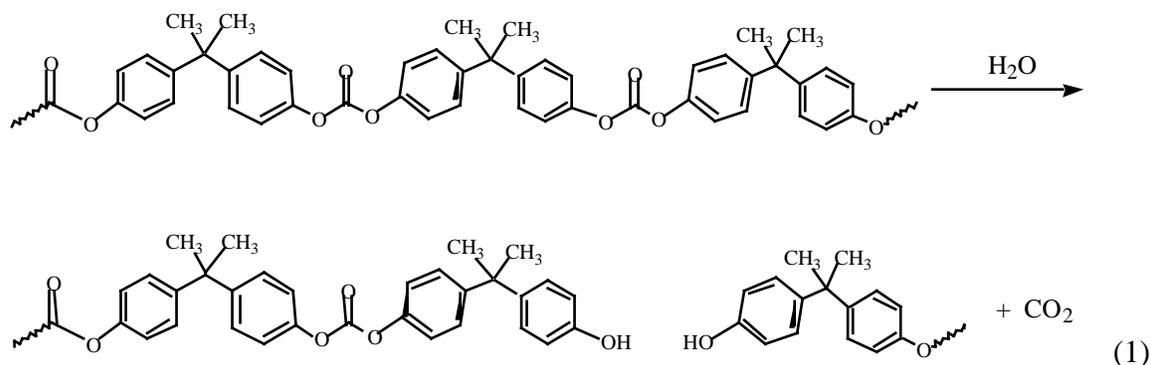
The diffusion of small molecule penetrants into polycarbonate has been studied [10]. At low partial pressure water shows a dual mode soption, consisting of Henry's law and Langmuir contributions. Eq. (2) [8]:

$$A = Kp + \frac{abp}{1+bp} \tag{2}$$

where $p$ is the partial pressure, $K$ is the Henry's law constant, $a$ is the Langmuir capacity and $b$ is the Langmuir affinity. The Henry's law contribution is temperature dependent as is the solubility of the penetrant in polycarbonate. The Langmuir contribution arises from occupation of excess volume. The excess volume depends on how the substrate was processed. At 25°C the solubility of water in polycarbonate is 0.35%, while the solubility of oxygen is 0.056%. The activation energy for diffusion of water is 26 kJ/mol, while the activation energy for oxygen diffusion is 32 kJ/mol. This information should be collected for other penetrant gases, such as ozone or the gases in the Battelle class II environment. Note that the activation energy for transport is significantly lower than the activation energy for the hydrolytic degradation. In extrapolating from high temperature conditions to ambient conditions, one wonders whether the mode of degradation may change from mass transport limited to reaction kinetics limited conditions.

**Aging Studies: Analysis**
Accelerated aging studies are used to predict the archival lifetime of information storage media. The strategy is to determine the rate of degradation at elevated temperatures or in environments containing elevated levels of potential degradants. Often the degradation is measured by a system metric, such as increase in bit error rate. The data are then extrapolated to ambient conditions. Typically, this involves a variety of assumptions such as an Arrhenius temperature dependence for the rates. However, these assumptions may be invalid depending on the underlying physical phenomena governing degradation or if the extrapolation passes through a phase transition, such as a glass transition in a polymeric component. Another problem is that many degradation processes, such as polymer hydrolysis or corrosion can be autocatalytic, *i.e.* the product of the degradation process can catalyze further degradation. A predictive model of archival lifetime must be based on an understanding of the chemical and physical processes leading to failure. This model must also account for the effect of these processes on the degradation of the system performance.

To demonstrate possibilities for analysis of accelerated aging strategies, we consider an example in two extreme limits: mass transfer limited degradation and kinetically limited degradation. The geometry that we examine consists of a large (effectively infinite in the lateral directions) plate or disc of the protective material of thickness $\delta$ (*i.e.*, the polycarbonate substrate, backed by the data storage material in a recording layer). We consider only degradation of the data storage materials as the results of reaction with a penetrant that must move through the substrate. In addition we make some general

assumptions: (1) The system is at steady state. (2) Mass transfer is one-dimensional. (3) The system can be treated as containing only two components: the penetrant and the substrate material and, therefore, adequately modeled with binary Fickian diffusion. (4) The substrate material is stationary (not diffusing). (6) Only a single degradation reaction occurs, and reaction products can by neglected in the analysis. (7) The degradation reaction occurs at the interface between the substrate and the data storage layer. The propriety of these assumptions is discussed below.

First we consider the case where degradation is kinetically limited. This means that there is always sufficient penetrant at the interface between the substrate and the data storage layer for the rate of degradation to be governed by reaction kinetics. Hence, we need only examine the kinetics of the degradation reaction. If we assume that the reaction exhibits Arrhenius temperature dependence, then the rate of degradation, $R$, shows the same temperature dependence, and we have:

$$R \propto e^{-E_r/T}$$
(3)

where $E_r$ is the activation energy for the reaction, and $T$ is the absolute temperature. This simple relation prescribes that accelerated aging tests at temperature $T_0$ can be used to predict the degradation rate at temperature $T$ via:

$$R(T) = R(T_0)\left\{\exp\left[E_r\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\right\}$$
(4)

If the penetrant concentration at the outer surface of the substrate, $c_p$, is varied in an accelerated aging test (*e.g.*, by varying the ambient humidity) in the kinetically limited system, then Eq. (4) will be modified simply by including the ratio of concentrations raised to the appropriate reaction order, $n$, on the right-hand side. That is:

$$R(T,c_p) = R(T_0,c_{p0})\left\{\left(\frac{c_p}{c_{p0}}\right)^n \exp\left[E_r\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\right\}$$
(5)

Hence, knowledge of the reaction order ($n$) and the activation energy for the degradation reaction ($E_r$) is all that is required for aging analysis.

If degradation is mass transfer limited, then the rate of degradation is governed by the rate at which penetrant can diffuse to the interface between the substrate and the data storage layer. The degradation reaction can be viewed as occurring spontaneously. The degradation rate is then equal to the mass transfer rate of penetrant. Therefore, under the assumptions given above we have [9]:

$$R = \frac{-D_{pc}}{\delta}\ln\left(1 - \chi_{ps}\right)$$
(6)

where $D_{pc}$ is the effective binary diffusivity of the penetrant and $\chi_{ps}$ is the ambient mole fraction of the penetrant at the outer surface of the substrate. The diffusivity in Eq. (5) is a relatively strong function of temperature. It is reasonable to assume that [10]:

$$D_{pc} \propto e^{-E_d/T} \tag{7}$$

where $E_d$ is the activation energy for diffusion. Hence, the analogue of Eq. (5) for predicting aging at temperature $T$ and ambient mole fraction $\chi_{ps}$ from data at $T_0$ and $\chi_{ps0}$ in this limiting case is:

$$R(T,\chi_{ps}) = R(T_0,\chi_{ps0}) \left\{ \frac{\ln(1-\chi_{ps})}{\ln(1-\chi_{ps0})} \exp\left[ E_d\left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \right\} \tag{8}$$

That is, knowledge of the activation energy for diffusion ($E_d$) is sufficient for the accelerated aging analysis. Eq. (8) also suggests the possibility of accelerated aging tests, valid under our fairly restrictive assumptions.

The dependencies on ambient penetrant concentration in Eqs. (5) and (8) are quite different indicating the importance of knowing which mode of transport and degradation dominates. The temperature dependencies in the two equations are very similar, although the difference in magnitudes of the two activation energies should make it possible to distinguish whether the process is mass transfer or reaction limited.

In reality, the degradation process probably occurs somewhere between the two extremes of mass transfer limitation and reaction kinetics limitation. In addition, it is important to examine the applicability of our general assumptions. The assumption that the system is at steady state and that transport is one-dimensional are acceptable for the case where the degradation is heterogeneous – occurring only at the interface between the substrate and the recording layer. The assumption that the system can be treated as containing only two components is clearly over-restrictive. Many species can diffuse through the substrate and cause degradation. The diffusion rates for each of these species will be different. In addition, the reaction products generated by the degradation reactions may actually promote further degradation. Including all of the possible degradation reactions and species involved would complicate the analysis considerably. The basic forms of the results (Eq. (5) and (8)) would be similar but with a spectrum of activation energies and reaction orders. Furthermore, it may be necessary to account for some movement of the substrate itself as it swells under the influence of the penetrant.

The assumption that the degradation occurs only at the interface between the substrate and the recording layer is also overly restrictive. Penetrants will diffuse into the recording layer and degradation will occur throughout the material. Furthermore, degradation of the substrate (*e.g.*, hydrolysis) will also occur. Including this homogeneous degradation will necessitate performing a non-steady state analysis of the process. That is, the analysis would require examination of the basic mass transfer

equation in the material. Under the assumptions listed above (*i.e.*, Fickian transport, constant diffusivity, binary system, stationary substrate) that is:

$$\frac{\partial c_p}{\partial t} = D_{pc}\nabla^2 c_p + r_p \tag{9}$$

where $r_p$ is the rate of reaction of the penetrant. However, it may be possible to include the diffusivity give by Eq. (7) in such a way as to provide a type of time-temperature superposition for aging studies. For example, if we assume that the rate of reaction of penetrant is first order in the concentration of the penetrant (*i.e.*, $r_p=-kc_p$), then the solution of Eq. (9) may be formally written as:

$$c_p = -k\int_0^t e^{kt'} f(\boldsymbol{r},t')dt' + e^{kt} f(\boldsymbol{r},t) \tag{10}$$

where we have assumed that there is no penetrant in the material initially, and $f(\boldsymbol{r},t)$ is the solution of:

$$\frac{\partial f}{\partial t} = D_{pc}\nabla^2 f \tag{11}$$

with boundary conditions as specified for $c_p$ and a homogeneous initial condition. That is, $f(\boldsymbol{r},t)$ is the solution of the mass transfer problem in the absence of reaction. Now we imagine conducting an aging experiment at a temperature $T_0$, with the goal of extracting information on the degradation that would occur at (lower) temperature $T$. The rate of degradation should be proportional to the concentration of penetrant in the sample, so we need to examine how the solution given by Eq. (10) varies with temperature. Temperature enters parametrically in this solution in two places: through the rate 'constant', $k$, and through the effective binary diffusivity, $D_{pc}$. For the former, it is reasonable to assume an Arrhenius dependence:

$$k(T) = k_0\left\{\exp\left[E_r\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\right\} \tag{12}$$

where $k_0$ is the rate constant at temperature $T_0$. For the diffusivity, we define a new time scale, $s$ through:

$$ds = \frac{D_{pc}(T)}{D_{pc}(T_0)}dt \tag{13}$$

This is a simple re-scaling of time if the temperature $T$ is constant, and Eq. (11) can be thought of as defining a material time, if $T$ is varying with time. From Eqs (11) and (13), we find:

$$f(\boldsymbol{r},t,T) = f(\boldsymbol{r},s,T_0) \tag{14}$$

That is, in the absence of reaction the mass transfer scales with temperature, so that we can conduct experiments on the accelerated time scale $s$ at temperature $T_0$ and extract information about degradation on (longer) time scale $t$ at temperature $T$. The relation between the time scales is given simply by Eq. (13) — requiring only knowledge of the temperature dependence of the effective diffusivity. Furthermore, the transformation remains valid irrespective of any phase changes that may occur in the material between $T$ and $T_0$; all that is required is that the mass transfer remain Fickian.

In the presence of reaction, we must combine Eqs. (11) through (14) to obtain:

$$c_p(r,t,T) = -k_0 \left\{ \exp\left[ E_r\left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \right\} \int_0^t e^{k_0\left\{\exp\left[E_r\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]\right\}t'} f(\boldsymbol{r},s',T_0)dt'$$

$$(15)$$

$$+ e^{k_0\left\{\exp\left[E_r\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]\right\}t} f(\boldsymbol{r},s,T_0)$$

where $s$ is given by Eq. (13). Unfortunately, the simple time re-scaling that we have for the no-reaction case does not apply here. That is, we cannot write the right-hand-side of Eq. (15) as a simple transformation of $c_p(\boldsymbol{r},t,T_0)$.

Finally, although our assumption that the mass transfer behavior is Fickian would at first seem to be innocuous and generally acceptable, mass transfer in polymeric materials is known to be anomalous — displaying a wide variety of nonlinear behaviors that are not described by Fick's law [11]. Incorporating nonlinear behavior into an accelerated aging analysis strategy presents many difficulties and possibilities for research. Given all of the above, it is clear that a more complete (and complicated) analysis is required.

**Aging Studies: Experimental Needs**

High temperature and high humidity accelerated aging studies are undertaken under the assumption that water and oxygen are the reactants that are causing failure. This may be true in many cases, however there are other trace substances in the atmosphere, particularly air pollutants, that may cause degradation. In response to this, Battelle has specified testing conditions to accelerate failure for the copper in electronics in an office environment — Battelle Class II Environment [12]. These conditions have been used in accelerated aging studies on metal particle magnetic tape [13]. The saturation magnetization was measured as a function of time exposed to Battelle Class II conditions. There was a concern that the iron particles in MP tape would be susceptible to corrosion and this would limit

Table 1. Battelle Class II Conditions [1]

| | |
|---|---|
| Temperature | 30°C |
| Humidity | 70% |
| $NO_2$ | 200 ppb |
| $Cl_2$ | 10 ppb |
| $H_2S$ | 10 ppb |

archival lifetime [14]. The corrosion problem has largely been solved by coating the particles with an amorphous aluminum oxide [15-17]. However tapes from different vendors can have vastly different rates of corrosion [18]. Furthermore, there was a concern about the reproducibility of this experiment [19]. Sides and Spratt used an impinging jet geometry that gave more control of the delivery of the corrosive gases to the tape samples [20]. However, no one has systematically determined the role of each component in the gas mixture plays in the degradation. Furthermore, these conditions do not include some of the more aggressive substances, *e.g.* ground level ozone, present in many urban environments. Similar studies should be performed on optical data storage media.

## Conclusions

A fundamental understanding of the chemical and physical processes that lead to failure in optical disks must underpin the accelerated aging studies used to predict the archival lifetime. Only with an understanding of the kinetics of degradation and mass transfer can rational models be developed for lifetime prediction.

## Acknowledgement

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