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Degradation of epoxy pipe coatings due to diffusion of chemicals

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Abstract

Concrete pipes are commonly protected by a coating of epoxy, or some other barrier. However, these coatings are subject to degradation by a variety of means. One important route is by diffusion of chemical species. This article reviews the state of knowledge on degradation of coatings due to diffusion, in order to provide an accessible context for recent publications on this topic. Specific caution must be taken in considering the model of diffusion to apply, implementation of the model, and the mode of failure. Solubilities should be estimated besides diffusivities: solubilities are especially important if the coating fails due to liquid pooling and blistering.

Introduction

Epoxy coatings are commonly used to protect pipe surfaces, such as used in water systems. Diffusion into epoxy coatings can degrade them, and eventually the underlying pipe. Diffusion of chemical species into and through solids has been well characterised by authors such as Barrer (1951) and Crank (1975). However, this does not mean that prediction of coating degradation is a simple matter of plugging a few numbers into a calculator.

Valix & Bustamante (2011) in a paper comparing commercial epoxy mortar coatings and the effect of fillers used a simplified treatment of diffusion of sulfuric acid into epoxy coatings. It is important to recognise that the situation may be more complicated in reality. The main points addressed herein are as follows:

- Analysis of typical experimental data using an approximate diffusion formula suitable for short times only will lead to substantial errors. A formula applicable for the complete process should be used.
- Care must be taken in preparing the specimen and defining its thickness.
- Degradation may occur by physical processes as well as chemical modes of attack.
- Solubility may be as important as, or even more important than, the diffusivity.

Evaluation of diffusivity

Diffusion in many materials can be described by Fick's law, which states that the flux of diffusing substance is proportional to the concentration gradient. The constant of proportionality is the diffusivity, D, in

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

where F is the permeation rate per unit cross-sectional area, C the concentration (or, strictly, activity), and x the space coordinate (Barrer, 1951; Crank, 1975).

It is known that 'glassy' materials — *i.e.* materials below their glass-transition temperatures, such as epoxy coatings at ambient conditions (Banks & Ellis, 1982; Barrie *et al.*, 1984; Liu *et al.*, 2004; Musto *et al.*, 2000) — often do not abide by Fick's law, but rather exhibit 'anomalous' diffusion (Alfrey *et al.*, 1966; Crank & Park, 1968; Legghe *et al.*, 2009; Vieth, 1991). (Sorption of *water* by *hydrophobic* glassy polymers typically exhibits the least deviation (Crank & Park, 1968).) Nevertheless, it is common practice to apply a Fickian analysis (Ivanova *et al.*, 2001; Legghe *et al.*, 2009; Liu *et al.*, 2008a), and so I will proceed on that basis, and return briefly to the topic of anomalous diffusion afterward.

A number of alternative techniques exist for estimation of the diffusivity of material through a solid. The first option is to measure the uptake of fluid or solute by the solid: a relatively small solid specimen is immersed in a much larger reservoir. This is a convenient technique, which requires simply the measurement of the mass of the specimen, as has been described in recent articles (*e.g.* Liu *et al.*, 2008a; Valix & Bustamante, 2011).
An alternative is to immerse a solid specimen in a small reservoir, and measure the change in concentration or volume of the fluid that has not been absorbed (Crank, 1975). This may be less precise, unless care is taken to avoid interferences such as evaporation. It also may be less representative of field exposure.
Another technique is to use a solid 'film' to separate two chambers, and measure the rate of transfer from one to the other, typically under the assumption of steady-state conditions (Crank, 1975; Huldén & Hansen, 1985). This represents a more difficult measurement, and again is more removed from field exposure. The advantage is that the steady-state analysis does not require assumption of Fickian behaviour (Crank & Park, 1968).
Finally, it is possible also to dissect a specimen that has been exposed to the penetrating fluid in order to find the profile of penetrant concentration through the thickness of the solid. The diffusivity could then be estimated by treating it as a curve-fitting parameter (Crank, 1975).
In the following I focus exclusively on the first technique, due to its convenience and popularity.

In the case of partially-filled pipes, part of the pipe coating would be in contact with a liquid phase, and part would be exposed to the vapours. Theoretically no difference is expected for diffusion above or below the waterline, if the vapour phase is saturated with the diffusing species (Crank & Park, 1968; Huldén & Hansen, 1985), which is a fair assumption in the pipes considered.

Theory of diffusion in solids

The basic theory of diffusion starts with an assumption that Fick's law holds, as in equation 1. Diffusion into a solid slab can then be described by (Barrer, 1951; Crank, 1975; Hill, 1928):

$$\frac{M}{M_\infty} = 1 - \frac{8}{\pi^2}\left(\mathrm{e}^{-\theta} + \frac{\mathrm{e}^{-9\theta}}{9} + \frac{\mathrm{e}^{-25\theta}}{25} + \frac{\mathrm{e}^{-49\theta}}{49} + \cdots \right), \tag{2}$$

in which

$$\theta \equiv \frac{\pi^2 D t}{4 l^2} . \tag{3}$$

M represents the uptake of penetrant mass at time t, while M_∞ is the corresponding value at equilibrium; D is the diffusivity, which has units of cm/s^2 or similar; l is half the thickness of the slab, both of whose faces are exposed to the fluid. A coating has only one face exposed to fluid, with the other bonded to the pipe; hence, l can also be taken as the thickness of a coating. Care must be taken, lest the wrong interpretation of l be used (*e.g.* Valix & Bustamante, 2011). The ellipsis indicates that the series continues indefinitely; however, for all but the shortest times the summation is sufficiently accurate when only a few terms in the series are retained.
A series of algebraic transformations to express the above equation in terms of the first integral of the complementary error function (see Crank, 1975) provides a more numerically tractable computation for the shorter times. In principle, that form of the equation can be used for all times, but at longer times it becomes impractical to evaluate, and at shorter times a simpler alternative can be employed (see below).

The foregoing equations make a number of assumptions. These include:

1. Diffusion occurs along one axis only. This means that the test specimen must be much thinner than it is wide or tall.

2. The material is uniform, chemically stable, and of constant dimensions.
3. The diffusivity is constant. An average effective diffusivity is readily defined, but may be difficult to evaluate from absorption measurements.
4. The rate-limiting process is the internal diffusion within the solid.
5. The concentration of the penetrating species at the surface is constant.
6. For a coating bonded to a substrate, and thus exposed on one face only, the mass of penetrant propagating into the substrate is negligible.

Simplifications

At small times the behaviour described above always simplifies to a power law, in which *M* is proportional to $\sqrt{t}$ (Hill, 1928). It is important to realise that "small" times is a relative concept. If the diffusion is a slow process (low diffusivity), then weeks might be considered small times. Conversely, if the diffusion proceeds quickly (high diffusivity), then even a minute might not be considered a small time.

For the first phase of the diffusion, when $M/M_\infty < 0.6$, the full equation can be well approximated by (Barrer, 1951; Crank, 1975):

$$\frac{M}{M_\infty} \approx 2\sqrt{\frac{Dt}{\pi l^2}}\ . \tag{4}$$

Then *M* is conveniently plotted as a straight line against $\sqrt{t}$, the gradient being proportional to $\sqrt{D}$. Despite what is sometimes seen in the literature (*e.g.* Legghe *et al.*, 2009; Valix & Bustamante, 2011), it is incorrect to apply this formula to the long-time response. When the diffusivity, *D*, is a function of concentration, the range of applicability of equation 4 may be either extended or curtailed from the default situation (Crank & Park, 1968).

The limiting behaviour for glassy polymers is found to be a direct proportionality between *M* and t, rather than $\sqrt{t}$ (Alfrey *et al.*, 1966). A combination of the two can also occur, as can powers intermediate to 0.1 and 1.0. Other 'anomalous' behaviours include power-law variation with indexes greater than 1.0 (Vieth, 1991), sigmoidal and two-stage uptake curves (Crank, 1975; Crank & Park, 1968; Ivanova *et al.*, 2001), and Langmuir adsorption (Liu *et al.*, 2008b).

An even simpler formula has been derived to relate the diffusivity to the normalised time at which half of the absorption has occurred, namely

$$D = \frac{0.19673\cdots}{T_{50\%}}\ , \tag{5}$$

in which $T_{50\%}$ is the value of t/l^2 at which $M/M_\infty = 0.5$ (*cf.* Crank, 1975). Again *l* is the half-width of a sheet exposed on both sides, or the full thickness of a lining exposed only on the outer face.

While this last formula is simpler, its estimates are more sensitive to any dependence of the diffusivity upon concentration than those of the initial-gradient method (Crank, 1975). The claims of remarkable accuracy associated with the $T_{50\%}$ formula (Crank, 1975) are not practically meaningful, as they ignore any kind of experimental error.

Application of the theory

The formulæ have been derived for coatings that are fulfilling their function, which means that they are applied to a substrate to protect it. One interface of the coating is bonded to the pipe, while the other is exposed to the fluids flowing through the pipe. This asymmetry is the reason for specifying *l* to be the thickness of a bonded coating, exposed at one face only. As mentioned, if the specimen is exposed on both faces, then its thickness is set equal to 2*l*.

In the formulæ, M_∞ is the mass uptake of the penetrant **at equilibrium**. Formally that means the value at infinite time. Fortunately, sufficient accuracy is maintained if one merely waits for long times.

How long is "long"? It means times that are long relative to the rate of diffusion. Hence, this can only really be determined by monitoring the mass uptake over time and ensuring that it has reached a **practically constant** value (assuming that no other transport mechanisms become important). In that case, any of the above formulæ could be used to estimate D with reasonable accuracy.

If the experiment has proceeded for a 'short' time only, then M_∞ is still unknown. Even though a "maximum" value of acid uptake will have been recorded in the experiment (*e.g.* Valix & Bustamante, 2011), this should not be confused with the asymptotic value, which could only be identified by continuing the observations. In this case, there is no possibility of correctly evaluating D. Cursory inspection of equation 4 might lead to the misapprehension that any arbitrary value of M_∞, such as the maximum value observed, can be used. Rearranging the equation demonstrates more clearly that D cannot be disentangled from M_∞, if M_∞ is unknown:

$$M \approx 2\sqrt{\frac{(M_\infty^2 D)\,t}{\pi l^2}}\,. \tag{6}$$

This is demonstrated in **Figure 1** and **Figure 2**. Even though the diffusivities vary by a factor of 16, the fourfold variation in solubility compensates, so that all three cases are described by the same curve at early times.

Finally, if the experiment has proceeded for an 'intermediate' length of time, then M_∞ is still unknown. However, it can be predicted by using the complete formula, consistent with equation 2. **Figure 3** presents an example in which only a few observations are available of the true underlying response, for which $D = 1$ and $M_\infty = 1$. In the scenario, the coating has unit thickness; equivalently, the horizontal axis could have been plotted as t/l^2 or $\sqrt{t}/l$, to obtain a 'reduced sorption plot' (Crank & Park, 1968). The observations were generated by taking the true uptake at times 0.1, 0.2, ..., 0.8, and rounding the uptake to two decimal places, in order to introduce a small experimental imprecision.

To employ the short-time formula, the obvious choice for M_∞ is the value of M at the last observation, namely $M_\infty \sim 0.89$. Applying the formula to all eight observations results in an 11 % overestimate of D. However, plotting this curve over the observations shows that it does not reflect the true initial uptake, as only the first few points closely approximate a $\sqrt{t}$ relation. Hence a revised fit is applied to only the first two observations. Interestingly, this results in a worse estimate of D, being 25 % larger than the true value. Evidently the error due to misspecification of M_∞ was partially compensated by an error of opposite sign due to the inappropriate curve fit when all observations were included. (This is a fortuitous circumstance, and not a recommended 'correction'.)

To use equation 5 it is necessary to first estimate a value of M for which $M/M_\infty = 0.5$. Taking $M_\infty \sim 0.89$ means that $T_{50\%}$ would occur at $M \sim 0.45$. The experimental data points in this example are fairly sparse, and so linear interpolation is applied to obtain an estimate $T_{50\%} \sim 0.161$, and hence $D \sim 1.22$. (Interpolation on $\sqrt{t}$ instead of t yields $T_{50\%} \sim 0.157$ and $D \sim 1.26$.) This estimate is as bad as the preceding one.

These estimates can be compared with application of equation 2. It might be considered easier to specify $M_\infty \sim 0.89$ again, so that only one parameter need be estimated. This expediency results in an unacceptable overestimation of D, by 39 %. It is seen that the prediction clearly reaches an asymptote at $M = 0.89$, and the estimate of D is very sensitive to this.

Finally, when both M_∞ and D are simultaneously estimated, by minimising the sum of squared errors, a good match is attained between the predicted curve and the real underlying response. (An exact match could not be expected, given the experimental errors introduced.) M_∞ has been almost perfectly estimated, and D is only underestimated by 3 %.

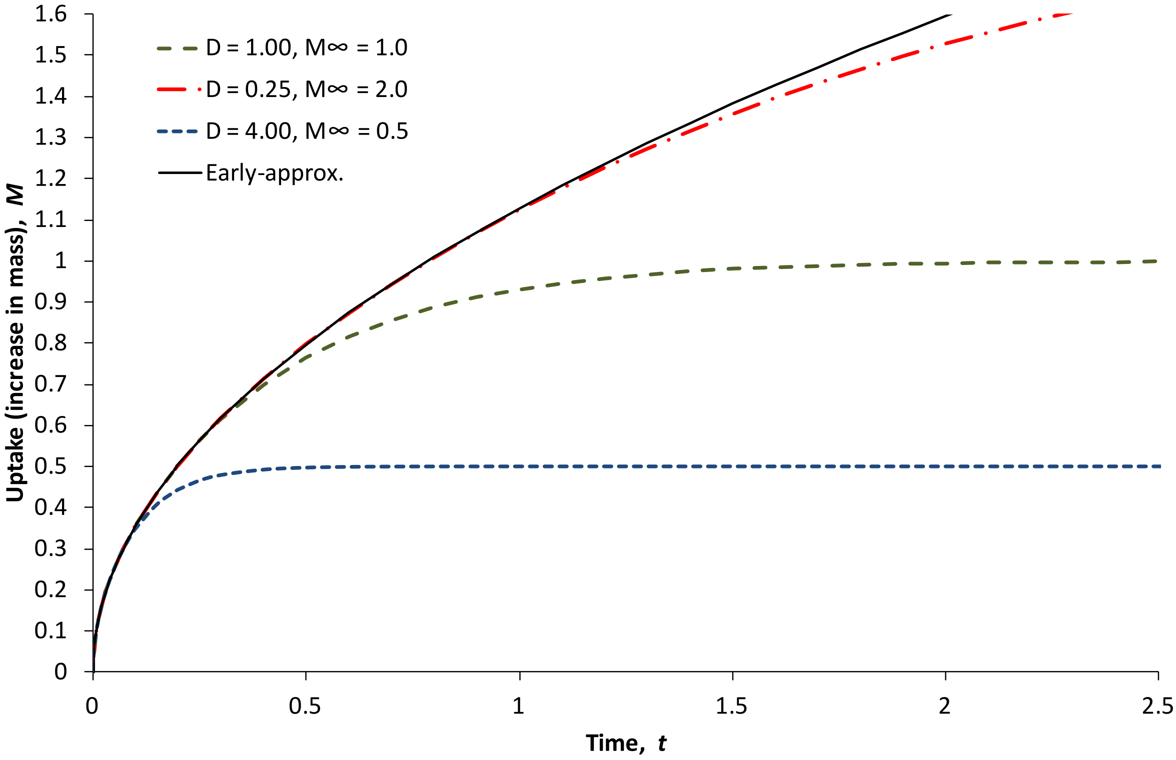

Figure 1: Uptake of penetrating species into coating of unit thickness for various combinations of diffusivity and equilibrium uptake, in comparison with the early-time approximation (which is the same for these three combinations). Plotted against time, so that the initial response follows a square-root profile.

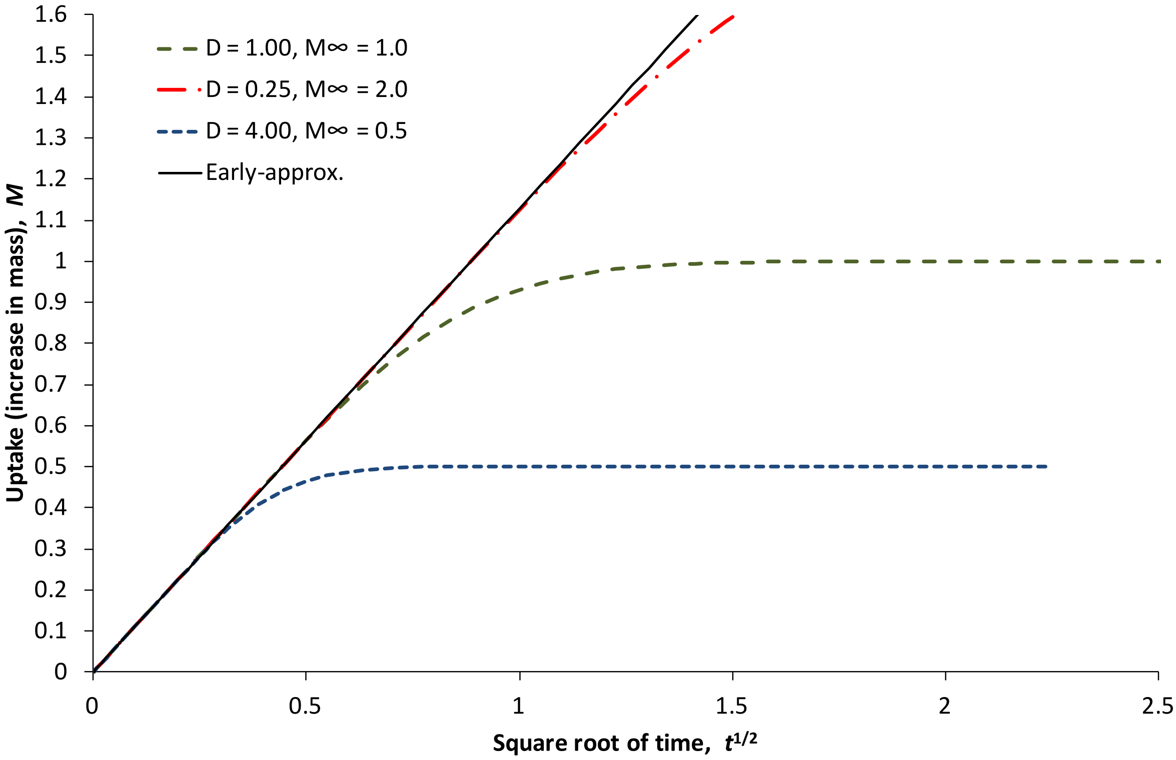

Figure 2: Same as Figure 1, but plotted against square root of time, so that the initial response is linear.

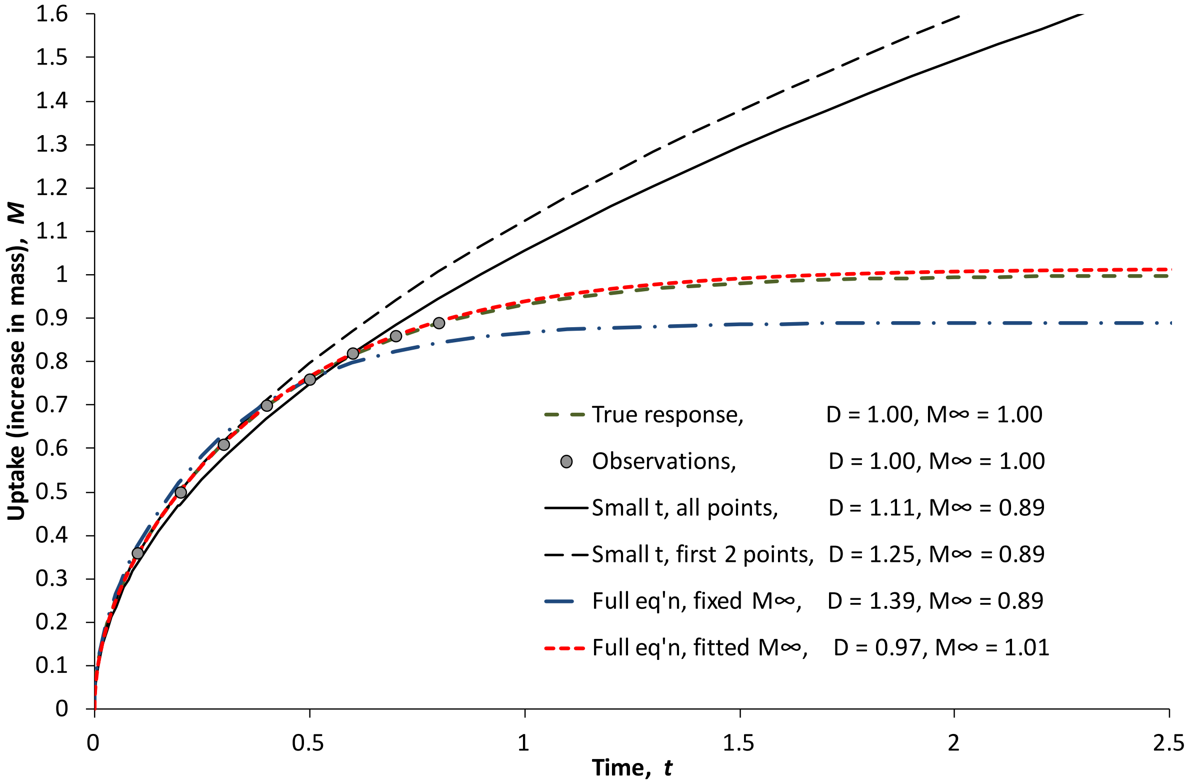

Figure 3: Comparison of uptake curves estimated by fitting 'observed' data with true underlying response. Unit thickness of coating.

Mechanism of degradation, and relevance of diffusivities

There are two important routes by which degradation might occur: physical, and chemical. One might also include microbiological processes as a third route, but it is convenient to describe these as chemical processes, because ultimately it will be secretions of an enzyme, acid, *etc*. from the microbes that react with the coating. Autogenous ageing is not considered. (While the emphasis of the present article is on degradation, certain chemical reactions may actually improve the stability of the coating (van den Brand *et al.*, 2004) (*cf.* Legghe *et al.*, 2009).)

The simplest models of chemical reaction consider that the rate of reaction is directly proportional to the concentration of reactant. If the diffusion kinetics are slower than the kinetics of reaction, then the highest concentrations will exist at the exposed surface of the coating, and it might be expected that this is where degradation will be worst. If the diffusion kinetics are faster than the kinetics of reaction, then the chemical will reach saturation levels throughout the coating, and degradation across the whole thickness will occur.

The coating likely has a very good resistance to a wide range of chemical agents, as it is designed to protect the substrate. (By the same argument, dissolution of the protective coating into the fluid is assumed negligible (*cf.* Crank & Park, 1968; Hansen, 2004).) It may be that even if the concentration of chemical that has penetrated the coating is much lower than the value in the bulk, this could still be the most critical region of degradation. Either the chemical may interfere with the bonding of the coating to the pipe, resulting in delamination, or the chemical may attack the substrate directly.

The *absolute* value of the chemical concentration within the affected region is the parameter of interest for chemical degradation. Hence, low solubility and low diffusivity can both be considered protective.

The most obvious and well-known physical mechanism of degradation may be abrasion. However, it is important to consider a more pernicious mechanism, due to liquid 'pooling' or 'blistering' within the coating (Hansen & Just, 2001, 2002). Although it is seldom recognised, this blistering phenomenon is very common, and has been seen specifically in numerous polymer films, including epoxy coatings (van den Brand *et al.*, 2004; Hansen, 2004). The pooling phenomenon is caused by prior supersaturation, and results in 'blistering' of the coating. In the dynamics of diffusion treated above, supersaturation would not have seemed possible, as the concentration is expected to approach an asymptote (the equilibrium value), and so at most is equal to the saturation concentration. To achieve supersaturation, it is necessary to recognise that in a real installation the temperature can fluctuate. If the coating were saturated with the chemical, either throughout or in some regions, then a decrease in temperature would (usually) lead to a decrease in solubility, and thus supersaturation. The supersaturated state is not stable, and some of the 'dissolved' species that have penetrated into the coating would tend to come out of solution (*i.e.* form a new phase within the solid matrix). Initially the liquid may form as extremely small droplets, but these quickly merge into larger pools or blisters within the solid matrix, especially at hydrophilic sites (Hansen, 2004) (*cf.* Musto *et al.*, 2000). In the sequence described, it is assumed that the timescale of temperature fluctuation — hours or days, say — is faster than the timescale of diffusion, which is the usual situation for the industrial coatings typically encountered. The physical forces involved can be tremendous, and can tear apart the coating, or cause catastrophic delamination from the substrate (Crank & Park, 1968).

In 'pooling' the parameter of interest is the chemical concentration *relative to* the saturation value, within the affected region. Hence, only low diffusivity can be considered protective for this degradation mechanism. Low solubility will not help, and in principle would be worse for this type of attack. It has been suggested that the application of coatings incorporating 'voids' would provide a means of relieving internal liquid pressure without mechanical degradation (Hansen & Just, 2001). However, this would create a lower permeation resistance.

A further potential mode of physical degradation is swelling upon liquid uptake (Alfrey *et al.*, 1966). Swelling of coatings on test coupons can result in catastrophic delamination, to relieve the shear stresses (van den Brand *et al.*, 2004). In the coupon coatings the shear stresses are generated because the swelling pressures are unbalanced at the edges. When the coating is applied to the inside of a pipe, the material cannot swell laterally, and so shearing stresses are minimised; however, tensile stresses may arise (*cf.* Alliband *et al.*, 2006). These stresses will be less evident in unbonded specimens.

It can reasonably be anticipated that the maximum swelling would be greater when the solubility is high, and would be attained more rapidly for higher diffusivities.

The foregoing discussion alerts us to the separate importance of both diffusivity and solubility in governing degradation by various chemical and physical mechanisms. This is illustrated also by **Figure 1** and **Figure 2**. For the combinations of D and M_∞ chosen in these Figures, the coating with the highest diffusivity (or highest permeability) can be expected to experience the least degradation by chemical attack — contrary to what might have been anticipated (*e.g.* Valix & Bustamante, 2011) — assuming the materials have the same susceptibility to given concentrations of the diffusing chemical. Of course, this could not be known unless observations were made for sufficiently long times.

Six assumptions were presented above. It is appropriate to test how reasonable those assumptions are.

1. **Planar diffusion (one dimensional)**. Although a pipe is curved, this does not affect the analysis, because coating thicknesses are typically much smaller than the pipe radius. It is important to ensure that the test coupons are suitably sized so that the additional penetration at the edges is small relative to the total ingress (Crank, 1975).
2. **Constant material**. In reality, a coating cannot be truly uniform. The most serious deviation from this ideality would be the presence of flaws in the coating such as pinholes or cracks (Vieth, 1991): an impermeable coating may be next to useless if the barrier is breached either in its initial state, or after some time in service (*e.g.* due to thermal expansion and contraction). Another deviation could occur by design, if the coating is a composite material, containing *e.g.* fibres, spherical fillers, or paracrystalline aggregates (Crank & Park, 1968; Huldén & Hansen, 1985; Liu *et al.*, 2008b; Vieth, 1991). The coatings discussed are chosen for their protective characteristics, but if we admit that diffusion may gradually occur in service, then we should also allow for the prospect of slow reaction. Lastly, the equations suppose that the coating does not change its shape, yet an intake of acid into epoxy of more than 30 % (Valix & Bustamante,

2011) suggests that these coatings could be subject to considerable swelling (Barrer, 1951). Strictly, swelling systems cannot be described by Fick's law as it is usually stated, and more generalised forms apply; however, the simpler version is still often employed for expedience (Barrer, 1951), with some theoretical justification (see Crank, 1975). (Swelling might also be expected to affect the diffusivity, beyond the simple change in geometry.)

3. **Constant diffusivity**. The diffusivity could vary with position in the coating. Solids are sometimes characterised as having a 'skin' (Crank, 1975; Hansen, 2004), *e.g.* due to more rapid curing of the epoxy at the exposed surface. Conversely, the coating properties may be affected by the presence of the substrate at the non-exposed face (van den Brand *et al.*, 2004; Crank & Park, 1968; Huldén & Hansen, 1985). The diffusivity can also vary as a function of concentration, which is common for a range of coatings (Barrer, 1951; Hansen, 2004); in this case an average effective diffusivity is obtained (Crank, 1975). Variation with temperature also occurs (Huldén & Hansen, 1985; Vieth, 1991).
4. **Diffusion in coating controlling**. Diffusion within the liquid phase is not likely to impose a constraint, especially with the flow present in typical installations. However, in some systems the resistance at the interface significantly affects the penetration rate (Barrer, 1951). The most problematic manifestation of this exhibits a false 'equilibrium' at intermediate times, which soon yields to further sorption (Crank, 1975); the plateau could easily be misinterpreted as the equilibrium state, which would underestimate the true final uptake that would apply in service.
5. **Constant concentration at surface**. Given a high diffusivity in the fluid phase, and continually replenished 'solution', this assumption would be met except for the obvious diurnal and seasonal variations. For design purposes a representative 'average' would be used. If coupons are to be exposed in the laboratory, it is important to ensure an adequate reservoir of acid, so that its concentration will not be appreciably diminished due to absorption into the specimen.
6. **Negligible efflux from coating**. The diffusivity and solubility in the pipe wall ought to be much less than that of the coating, suggesting flux out of the coating can be neglected. However, the possibility remains that the diffusing species could be consumed in a degradation reaction. As a first approximation, it would be assumed that any such reaction is slow, so that only diffusion in the coating need be considered, as in assumption 4. (Alternative equations can be derived for the case of fast reaction.)

It is not necessary for an assumption to exactly reflect the reality, it need only be an adequate approximation.

Discussion

The theory of diffusion based on Fick's law is very well known, and equations for this system have been available for around 100 years. They are readily implemented in commonly available software applications. Incorrect applications of the formulæ produce erroneous results, on which evaluations cannot be founded. Even though not all materials will obey Fick's law precisely, often it will be an adequate approximation. Correct application of the theory will at least allow recognition of exceptions, in which alternative models of 'anomalous' diffusion are required. Such models are detailed in the references provided.

To assess susceptibility to degradation, quantification of diffusivities is not sufficient. The solubility should also be estimated. This could be estimated from the diffusion experiment, from separate experiments, or perhaps from literature reports. The relative importance of the diffusivity and solubility depends on the mode and kinetics of degradation. In order to determine the mode of degradation, microscopic examination and chemical assays are valuable.

Conclusions

To assess coating stability, one should:

(i) know the **mechanism** of degradation of the coating or pipe;
(ii) identify **parameter(s)** to characterise the mechanism;
(iii) choose the correct theory, and correctly apply it, to **evaluate** parameter(s).

Of course, other factors will also weigh on the decision, such as the cost of the coating and ease of application.

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