

Last revised on September 15, 2014

This revision includes the effect of tensile strain on the diffusivity D .

Predicting the service life of corrosion barriers

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Abstract – The engineering community is well aware of the long service lives of composite equipment in a variety of harsh environments. It would take no more than a brief tour of any modern pulp bleaching facility to realize the importance of composites in applications where corrosion is an issue. However, a reliable method to predict the service life of such equipment is still lacking. The many studies and test methods that have been developed over the years, while certainly useful to establish suitability, are not adequate to predict durability. This is understandable in view of the overwhelming complexity of the problem. The many combinations of resin types, laminate constructions, processing variables, mechanical and thermal loadings, and the myriad of aggressive media, make the prediction of service lives a most daunting endeavor. This paper introduces a new method to predict the service life of composite equipment, herein defined as the durability of the corrosion barrier.

Keywords: durability of composites, corrosion barrier, service life of composites.

1 Introduction – The issue of durability depends on what is expected of the equipment. This study will focus on the durability of the corrosion barrier. As a rule this issue is addressed based on cosmetic, fitness for service and structural criteria.

- The cosmetic life is concerned with the loss of gloss or deterioration of any other feature that may be appealing to the eyes of the beholder. The cosmetic life is not relevant in industrial applications and will not be addressed in this paper.
- The structural life is defined by rupture, weeping, excessive deflection or any other structurally relevant criterion. The structural life of composites is addressed in references 1, 3, 4 and 5.
- The service life is determined by the durability of the corrosion barrier. The equipment is considered unfit for service when the aggressive chemicals reach the structural plies after penetrating the corrosion barrier. This paper will introduce a new method to predict the durability of corrosion barriers.

2 Two types of aggressive chemicals – We define as aggressive any chemical that lessens the ability of composites to perform. The damaging potential of the aggressive chemical is related to its ability to penetrate the laminates. Some species have low penetrating power and concentrate their damage on the surface plies of the composite. Others pervade the whole laminate and damage all layers. In this paper the aggressive chemicals are classified according to their ability to penetrate the laminates.

- **Non-penetrating.** This category includes the reactive chemicals used in industrial processes. These chemicals interact with the resin and this interaction delays their penetration. Their damage is limited to the plies that are located near the surface of the laminate. Examples of such media are all the reactive chemicals such as acids, oxidizers, etc. Also included in this category are UV radiation and abrasive materials, which erode away the outside surface of the composite while leaving the inner plies intact.
- **Penetrating.** This category includes the non reactive chemicals that do not interact with the resin and penetrate the whole laminate. The most important products in this category are water and some solvents. The penetrating chemicals do not interact chemically with the resin. Their penetration is fast and they saturate the entire laminate in a short period of time. The diffusion of solvents into the composite is so fast that the times they take to saturate all layers can be considered as short-term. Also included in this category

are agents like temperature and mechanical strains. The penetrating chemicals, together with temperature and mechanical strains, are the only agents that can affect the long-term structural life of composite structures.

The penetration of aggressive chemicals in polymers is very slow. This is due to the low solubility, low diffusivity and the high interactions that take place between the chemical and the resin. As a result, the rate of penetration is slowed down considerably and the reactive chemicals display a near flat advancing front as they enter the composite. Figure 1 shows some typical concentration profiles of non-penetrating chemicals plotted along the wall thickness of a composite. As the molecules enter the laminate, they react with the glass/resin and are slowed down in their advance. This produces a near flat advancing front such as the one shown in figure 1. The flatness of the advancing front is a characteristic of non-penetrating chemicals. Other things being equal, the higher the reactivity of the penetrating species, the flatter is the advancing front. The highly reactive chlorine dioxide, for instance, displays a very neat and distinct flat advancing front.

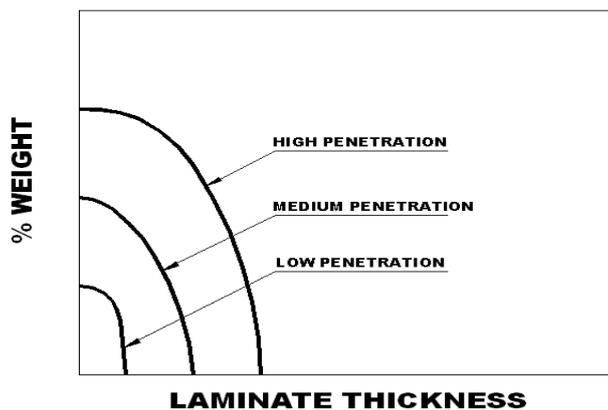


Figure 1 - Different species show different penetrating profiles. Note the flat front characteristic of the reactive low penetration chemicals.

As the reactive chemicals advance into the laminate, they deteriorate the resin and the fibers. It is reasonable to assume that the plies that are penetrated by the chemical lose their structural capability. It is the responsibility of the engineer to schedule regular shutdowns to check the depth of this penetration and, if necessary, replace the surface material that has been penetrated and damaged. The widespread practice of relining storage tanks would not be possible if the advancing front of the chemicals were not flat and well defined as shown in figure 1.

In applications where the relining is not possible, as in the case of small diameter pipes, the penetrating chemicals would continue their advance and eventually penetrate and destroy the structural layers. In such cases it is possible to have structural failure caused by non-penetrating products. Given enough time and no maintenance, the non-penetrating chemicals eventually pass the corrosion barrier and attack the structural plies. However, if the relining is done at the proper time, before the chemicals reach the structural layers, the corrosive media play no role in the long-term structural life of the composite. In other words, if proper maintenance is done, the damage caused by the chemical is limited to the sacrificial corrosion barrier.

The flatness of the advancing front is determined by the reactivity and the rate of diffusion of the chemical into the composite. This simple and obvious statement suggests that some resins may have better performance than others, not because of their superior resistance to chemical attack per se, but because of their lower permeability to the diffusing chemical. This statement explains the superior performance of the highly cross linked bisphenol polyesters and of the novolac vinyl esters. And it explains also the outstanding positive effect of post-cure.

The advancing front of the diffusing chemical divides the equipment wall in three zones (figure 2). The fully penetrated zone 1 is assumed destroyed by the chemical. The mechanical properties of the material in zone 1 are assumed to be zero. The material in zone 2, which has been partly penetrated, maintains some structural integrity. The material in zone 3, which has not yet been reached by the chemical, maintains its pristine state.

We assume that the ingress of the aggressive chemical destroys the structural capability of the penetrated plies. The penetrated plies will be assumed fully destroyed, while the non-penetrated remain intact. That is the way figure 2 should be interpreted. The classical interpretation, however, is the exact opposite. The conventional interpretation (a) assumes

full penetration of the entire laminate and (b) a partial reduction in the mechanical properties as a result of that penetration.

The current test method to assess the effect of chemicals on composites is based on the flawed assumptions of (a) full penetration and (b) uniform drop in the mechanical properties. We say this interpretation is not correct. The correct interpretation is that the composite in contact with chemicals (a) are partly penetrated and (b) only the penetrated plies lose mechanical properties.

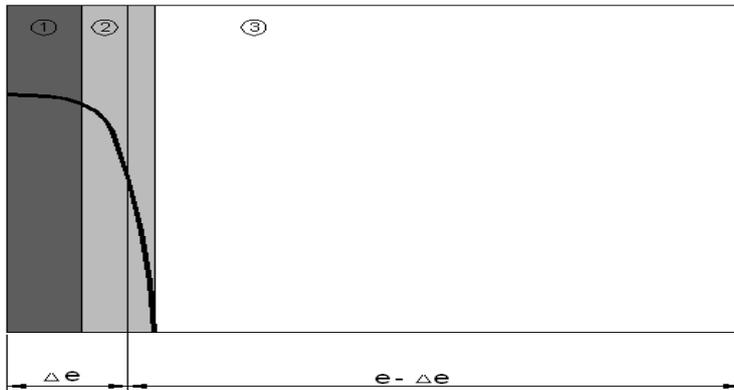


Figure 2 – The chemicals do not penetrate deep into laminates. The extent of penetration is measured by the effective penetrated depth indicated by “ Δe ”.

3 The effective depth of penetration “ Δe ” – In most cases the composite material that is penetrated by the chemical remains in place, preserving the original laminate thickness. This poses the problem of measuring the “effective” depth of penetration. The next section will present methods to measure the depth of penetration. The effective “penetrated” thickness is comprised of zone 1 and part of zone 2 as depicted in figure 2. The boundary between zone 2 and zone 3 defines the total depth of penetration. This boundary is too tenuous and possibly undetectable by optical means, which leads us to define the “penetrated” thickness as the “effective” depth of penetration “ Δe ” shown in figure 2. The effective “penetrated” thickness “ Δe ” is less than the actual depth of penetration. However, given the flatness of the advancing front, the effective depth “ Δe ” should differ little from the actual total depth of penetration.

4 Measuring “ Δe ” - The depth of penetration “ Δe ” can be measured directly by optical means or indirectly by tensile tests on specimens that have been immersed in the corrosive media.

The optical measurement of “ Δe ” is straightforward and needs no elaboration other than the comment that a contrasting dye would help identify the boundary separating the penetrated from the non-penetrated depth.

The tensile test method requires recognition of the distinct roles played by water and the corrosive chemical. Water is a penetrating chemical that reduces the strength of the entire specimen. This is in contrast with the non-penetrating nature of the chemical, which affects just a thin layer on the surface of the composite. The measurement of “ Δe ” by mechanical tensile testing requires that the effect of the penetrating water be accounted for separately from the attack by the chemical. This can be done by immersing a control coupon in water, to quantify its effect.

Figure 3 shows the cross-sections of coupons that have been removed from immersion in water and in the chemical solution. The control coupon - immersed in water - retains its original properties across the full thickness “ e ”. By contrast, the coupon immersed in the chemical retains the mechanical properties only on the non-penetrated thickness “ $e - 2\Delta e$ ”. The penetrated thickness “ Δe ” is counted twice to account for the two-sided exposure. Test specimens extracted from these coupons are submitted to tensile tests. Let the average measured tensile modulus be E_0 on the water exposed specimen and E_1 on the specimen that has been exposed to the chemical. It must be recognized that E_1 is an “apparent” modulus, calculated under the assumption that the chemical fully penetrates the test specimen. However, it is our contention that the chemical penetrates no further than the thickness “ $2\Delta e$ ”. The rest of the specimen thickness, $e - 2\Delta e$, is not penetrated and retains the original modulus E_0 . This new scenario leads to the following relation

$$\Delta e = \frac{e}{2} \times \left(1 - \frac{E_1}{E_0} \right) \quad (1)$$

Equation (1) calculates the penetrated depth “ Δe ” from the measured tensile moduli E_0 and E_1 and the known thickness “ e ”. The effective depth of penetration is calculated this way.

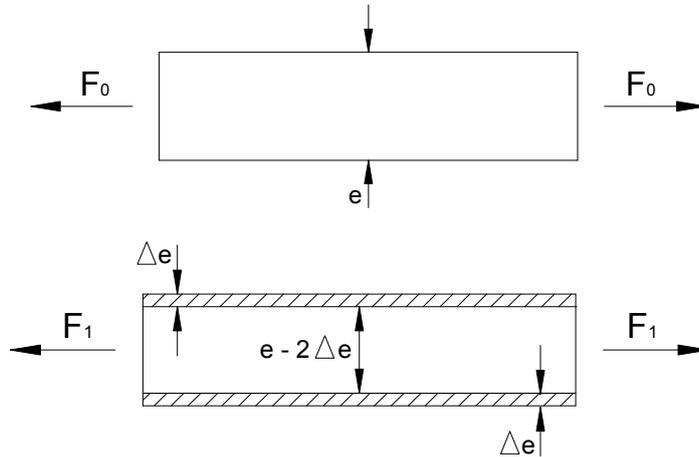


Figure 3 - Test coupons as they look prior to and after immersion in the corrosive chemical. The penetrated depth “ Δe ” is counted twice to account for the double exposure. The penetrated depth is assumed to lose all of its modulus. The non-penetrated depth retains the original modulus E_0 .

5 The governing equation – Having solved the problem of measurement of the depth of penetration, we next derive a mathematical relationship linking “ Δe ” to the aggressive chemical. The derivation will take into consideration the time and the temperature of exposure. It is assumed that the rate of change of “ Δe ” increases with the reactivity (r) and the concentration (c) of the chemical. Also, the rate of penetration decreases with the shielding effect from the penetrated material that remains on the laminate surface. Often times the penetrated material, of thickness “ Δe ”, remains on the surface of the composite and provides a shield against further penetration. These assumptions are expressed mathematically as

$$\frac{d(\Delta e)}{dt} = k \frac{D \times S \times r \times c^a}{(\Delta e)^s} \quad (2)$$

Where

- “ Δe ” is the penetrated depth.
- “ t ” is the time of exposure
- “ k ” is a factor to accommodate different units used to express time, thickness, etc.
- “ D ” is the coefficient of diffusion of the chemical into the corrosion barrier
- “ S ” is the solubility of the chemical in the resin
- “ r ” is the rate of attack by the chemical
- “ c ” is the concentration of the chemical
- “ a ” is a parameter related to the activity of the chemical in aqueous solution
- “ s ” accounts for the shielding effect of the corroded material that remains on the laminate.

Equation (2) can be amplified by recognizing the following relationships

$$D = D_0 \times e^{\left(\frac{-E_D + b\varepsilon}{RT} \right)}$$

The above expression recognizes the effects of the temperature and the tensile strain on the diffusivity of the composite. Both the temperature and the tensile strain affect the diffusivity of the corrosion barrier. Tensile strains above the infiltration threshold debond the fibers and create micro cracks that facilitate the penetration of the chemical. Both the temperature and the excessive tensile strain facilitate the ingress of chemical species into the composite. The tensile strain increases the diffusivity of the corrosion barrier, just like temperature. This effect is not to be confused with the phenomenon known as strain-corrosion. For details on strain-corrosion, please see reference 5.

$$S = S_0 \times e^{\left(\frac{-E_s}{RT}\right)}$$

$$r = r_0 \times e^{\left(\frac{-E_r}{RT}\right)}$$

Where

“E” is the Arrhenius energy of activation for each process

“R” is the gas constant

“T” is the absolute temperature

“ε” is the tensile strain

“b” is a parameter that depends on the glass-resin bonding

Entering the above in (2) we obtain

$$\frac{d(\Delta e)}{dt} = k \frac{D_0 \times S_0 \times r_0 \times c^a \times e^{b\varepsilon}}{(\Delta e)^s} \times e^{-\left(\frac{E_D + E_S + E_r}{RT}\right)}$$

Or

$$\frac{d(\Delta e)}{dt} = k \frac{D_0 \times S_0 \times r_0 \times c^a \times e^{b\varepsilon}}{(\Delta e)^s} \times e^{-\left(\frac{E}{RT}\right)} \quad (2a)$$

The coefficients “D₀”, “S₀” and “r₀” in equation (2a) take different values depending on the resin system and its interaction with the corrosive chemical. Although system dependent, these coefficients are independent of the temperature and of the time of exposure. Integrating (2a) we obtain

$$\Delta e = \left[k \times D_0 \times S_0 \times r_0 \times (s+1) \right]^{1/s+1} \times c^{a/s+1} \times e^{b\varepsilon/s+1} \times t^{1/s+1} \times e^{-\left(\frac{E}{RT(s+1)}\right)} \quad (3)$$

Equation (3) can be written on log-log space as

$$\log(\Delta e) = \left(\frac{1}{s+1}\right) \log[k \times D_0 \times S_0 \times r_0 (s+1)] + \left(\frac{a}{s+1}\right) \log(c) + \left(\frac{b\varepsilon}{s+1}\right) \log e + \left(\frac{1}{s+1}\right) \log(t) - \left(\frac{E}{RT(s+1)}\right) \log e$$

By definition, the permeability P of a given solvent-laminate system is the product of the coefficient of diffusion D times the solubility S. Since most engineers have an intuitive feel for permeability, as opposed to diffusion and solubility, we enter the permeability $P = D \times S$ into equation (3).

$$\log(\Delta e) = \left(\frac{1}{s+1}\right) \log[k \times P_0 \times r_0(s+1)] + \left(\frac{a}{s+1}\right) \log(c) + \left(\frac{b \times \log e}{s+1}\right) \times \varepsilon + \left(\frac{1}{s+1}\right) \log(t) - \left(\frac{E \times \log e}{R(s+1)}\right) \times \frac{1}{T}$$

or

$$\log(\Delta e) = A + B \log(c) + C \log(t) + \frac{D}{T} + E \varepsilon \quad (3a)$$

Where

$$A = \left(\frac{1}{s+1}\right) \log[k \times P_0 \times r_0(s+1)] \quad B = \frac{a}{s+1}$$

$$C = \frac{1}{s+1} \quad D = -\frac{E \times \log(e)}{R(s+1)} \quad E = \frac{b \times \log e}{s+1}$$

Equation (3a) can be used to predict the penetrated depth when the corrosion parameters “A”, “B”, “C”, “D” and “E” are known. We believe the reader will not confuse the parameters “D” and “E” in the above equations with the diffusivity D and the Arrhenius activation energy E.

6 Several scenarios. We next apply equation (3a) to a few limiting scenarios.

$r_0 = 0$. This situation occurs in environments that do not attack the corrosion barrier. In these environments the coefficient $A = -\infty$, “ Δe ” = 0 and the corrosion barrier is fully preserved. Water is a good example of such an environment.

$r_0 = \infty$. This case represents extremely aggressive environments. The rate of attack is very high and the corrosion barrier is destroyed rapidly. Combustion is a good example of this type of environment.

$s = 0$. This situation occurs when the penetrated thickness “ Δe ” is removed from the surface of the corrosion barrier, either by dissolution or by abrasion. In this scenario the shielding effect is lost, the laminate is exposed to direct attack at all times, and “ Δe ” increases linearly with time.

$s = \infty$. This scenario describes the cases where the corrosion barrier is fully insulated from the corrosive chemical. The penetration will not occur and “ Δe ” is zero.

$P_0 = 0$. This is the case where the corrosion barrier is not permeable to the chemical. Examples of real life situations approaching this case are found in corrosion barriers consisting of low permeability thermoplastic liners.

$a \neq 1$. The response of chemicals in water solution is not linear with respect to changes in concentration. Some systems show sharp increases while others show a flat response in activity as the concentration changes. The exponent “a” takes this non linearity into account, with $a > 1$ representing slow response and $a < 1$ representing fast response. The linear case occurs, of course, when $a = 1$.

The corrosion parameters A, B, C, D and E are determined by the usual least squares method used in multiple linear regression analysis. The next section describes this.

7 Measuring the corrosion parameters – There is no test method known at this time to predict the service life of corrosion barriers. The closest protocol available is ASTM C 581, which is a good predictor for the suitability – not for the durability – of corrosion barriers. In this section we propose a new test method to measure the corrosion parameters in equation (3).

The corrosion parameters can be obtained by measuring the depth of penetration “ Δe ” as a function of time when coupons representative of the corrosion barrier are immersed in test fluids at different concentrations and different temperatures. The penetrated thickness “ Δe ” can be measured directly by optical means or indirectly by the tensile modulus. The new test method departs from the ASTM C581 in the following:

- The test coupons used to measure the corrosion parameters are built to mimic the corrosion barrier and have no liner. The new method regards the liner as an “add-on” feature that may in some cases improve the equipment service life. However, since in most applications the liner is cracked and rendered ineffective after a short period in service, the corrosion parameters are measured on laminates made exclusively with chopped fibers and excluding the surface veil. The liner may increase the service life in some applications, but as a service life predictor, it is safer to ignore it.
- The penetrated depth “ Δe ” is measured as a function of the temperature, the exposure time and the concentration of the test fluid.
- The Barcol hardness and the visual appearance of the exposed coupons are irrelevant to the service life and are ignored in the new method.

The differences between the ASTM C581 protocol and the proposed new test method are summarized in table 1.

The data points corresponding to the penetrated depth “ Δe ”, the exposure time “ t ”, the concentration “ c ”, the tensile strain “ ϵ ” and the temperature “ T ” are annotated and processed by the usual least squares method to produce a statistical estimation of the corrosion parameters A, B, C, D and E. This is a typical multiple linear regression problem in which four independent variables (concentration, temperature, tensile strain and time) are used to estimate the mean value of the dependent variable “ Δe ”. The regression equation obtained this way is used to predict the service lives of corrosion barriers.

It is very difficult to include the elongation in the measurement of the corrosion parameters. Fortunately, the corrosion parameter E can be taken equal to zero for elongations less than the infiltration threshold. Since all composite equipment are designed to operate with strains less than the infiltration threshold, the parameter $E = 0$ in all cases.

	Current ASTM C 581 test method	New proposed test method
<i>Scope</i>	<i>Evaluates suitability</i>	<i>Predicts service life</i>
<i>Criteria</i>	<i>Hardness Appearance of the coupon Appearance of the medium Flexural strength retention.</i>	<i>Penetrated thickness “Δe” measured by optical means or tensile tests</i>
<i>Significance</i>	<i>Suggests suitability</i>	<i>Predicts durability</i>
<i>Coupons</i>	<i>Veil on both surfaces. Two 450 g/m² mats</i>	<i>Veils are not used. Coupon are made with chopped glass only</i>
<i>Procedure</i>	<i>Immersion of coupons. Specimens tested for flexural strength at regular intervals.</i>	<i>Immersion of coupons. Penetrated thickness “Δe” measured by optical means or tensile modulus retention at regular intervals.</i>
<i>Calculation</i>	<i>Tabulates/constructs graph of hardness as function of time. Tabulates/constructs graph of flexural strength as function of time.</i>	<i>The drop in tensile modulus is interpreted as penetrated depth. The penetrated depth is linked to the time of exposure by a log – log regression line.</i>
<i>Interpretation of results</i>	<i>Resin is suitable if flexural strength and hardness level off. Other indicators are the visual appearance of the laminate and of the media.</i>	<i>The log – log regression line predicts the service life. Visual appearances and hardness are irrelevant.</i>

Table1 - The two test methods side by side. Although similar in execution, they are fundamentally different in interpretation.

8 Worked examples – The following examples illustrates the application of the regression equation to a hypothetical situation. The equation used to predict the penetrated depth Δe in the corrosion barrier is:

$$\log(\Delta e) = A + B \log(c) + C \log(t) + \frac{D}{T} + E\epsilon \quad (3a)$$

We assume the following corrosion parameters for the corrosion barrier in this specific hypothetical case.

$$A = -0.219 \quad B = +0.206 \quad C = +0.321 \quad D = -133.760 \quad E = 0.600$$

8.1 Example 1 – The above hypothetical parameters are valid for “ Δe ” expressed in mm when the time of exposure “ t ” is expressed in months. The parameters A, B, C, D and E will be used to determine (a) the service life of a 2.5 mm corrosion barrier and (b) the required thickness of the corrosion barrier. The service life is assumed 25 years, meaning the corrosion barrier should not be replaced before 25 years of continuous use. In both cases we assume a residual corrosion barrier of 1.0 mm before the equipment is shut down for relining.

Estimating the service life of a 2,5 mm corrosion barrier – For a required residual corrosion barrier of 1.0 mm, the equipment is shut down for maintenance when the depth of penetration is $\Delta e = 2,5 - 1,0 = 1,5$ mm. The service life is obtained by entering this depth of penetration $\Delta e = 1.5$ mm and the given corrosion parameters in equation (3a). The service life will be estimated for a chemical of concentration $c = 0.5$, a tensile strain $\epsilon = 0.20\%$ and operating temperatures of 80C and 27C.

$$\log(1,5) = -0,219 + 0,206 \times \log(0,5) + 0,321 \times \log(t) - \frac{133,760}{273 + 27} + 0,600 \times 0,20$$

Solving for “ t ” we obtain $t \approx 273$ months (22 years) for the operating temperature of 27C.

$$\log(1,5) = -0,219 + 0,206 \times \log(0,5) + 0,321 \times \log(t) - \frac{133,760}{273 + 80} + 0,600 \times 0,20$$

Solving for “ t ” we obtain $t \approx 170$ months (14 years) if the operating temperature is raised to 80C.

The reader will note that we have made use of the parameter $E = 0,600$. That was done for illustrative purposes only, since in real life the tensile strain $\epsilon = 0.20\%$ is below the infiltration threshold and $E = 0$.

Designing the corrosion barrier for a service life of 25 years at 90C and $c = 0.3$. – We next determine the required thickness of the corrosion barrier to last 25 years when operating at a temperature of 90C and a concentration $c = 0.3$. Per equation (3a) the thickness that is penetrated in 25 years is

$$\log(\Delta e) = -0,219 + 0,206 \log(0,3) + 0,321 \log(25 \times 12) - \frac{133,760}{273 + 90} + 0,600 \times 0,20$$

$$\Delta e = 1.7 \text{ mm}$$

Assuming a residual corrosion barrier of 1.0mm, the original thickness of the corrosion barrier should be 1.7 mm + 1.0 mm = 2.7 mm.

Again, the tensile strain $\epsilon = 0.20\%$ is less than the infiltration threshold and the value of the parameter E should be taken as equal to zero.

8.2 example 2 - In 2001 Mark Greenwood published a remarkable paper (reference 2) showing the results of extensive creep-rupture tests performed on pultruded rods immersed in several aggressive media. The objective of the paper was to compare the effects of two types of glass fibers on the long-term structural lives of composites. The tested rods were identical in every respect except for the different compositions of the glass fibers. This worked example shows our interpretation of the test results.

The reported test results were taken from specimens under constant tension while immersed in the corrosive fluid. Creep tests such as these are good to assess the effect of the tensile strain on the durability.

It must be realized that creep tests performed in corrosive media combine the effects of two distinct modes of attack. For meaningful results, the investigator should judiciously separate the effects of the penetrating water from those of the non-penetrating chemical. Mark Greenwood, in his 2001 paper, did not separate these effects. Instead, he interpreted his results and based his conclusions on the classical (and incorrect) assumption that the reactive chemicals fully penetrated

the cylindrical rods and lowered their strength. The classical assumption that chemicals fully penetrate the entire laminate is not correct. As we know, reactive chemicals are non-penetrating and have their effect limited to a small depth “ Δe ”.

We will next use the test data published by Mark Greenwood in reference 2 to determine the depth of penetration “ Δe ”. The classical interpretation assumes the radius of the tested rods to remain unchanged throughout the test. This leads to the equations

$$\sigma_r^0 = \frac{F_r^0}{\pi R^2} \quad \sigma_r^t = \frac{F_r^t}{\pi R^2} \quad (4)$$

Where σ_r^0 and σ_r^t are the tensile strengths of the rods respectively prior to and after immersion. Note that the rod radius R remains unchanged in both cases and that the tensile strength σ_r^t drops in the same proportion as the measured rupture force F_r^t . That is the classical interpretation.

Our interpretation is quite different. We say that the tensile rupture force drops in response to (a) a decrease in the structural diameter equal to the depth that is penetrated and (b) a decrease in the tensile strength caused by water in the material that was not penetrated by the chemical. We repeat the argument for clarity.

We say that the non-penetrating reactive chemicals destroy the mechanical properties of the outer layer that is penetrated, while leaving the core of the rods intact. And we say also that the penetrating water attacks the glass fibers and cause a drop in the tensile strength of the core. These two modes of attack have different mechanisms and should be carefully separated.

The separation of the damage caused by the water on the core from the damage caused by the chemical on the surface involves a highly elaborate analysis that will not be shown here. The interested reader can email the authors requesting a proof of the derivations. The separation of the two effects produces equation (5).

Equation (5) predicts the thickness “ Δe ” that is penetrated by the chemical in the creep tests done by Mark Greenwood.

$$\Delta e = R \left\{ 1 - \left[(retention) \times \left(\frac{t_r}{t_0} \right)^{K_s} \right]^{\frac{1}{2}} \right\} \quad (5)$$

Where

“ Δe ” is the penetrated depth

“R” = 3,175 mm is the original radius of the rod

“Retention” designates the reported tensile strength retention for the rods after a time “ t_r ”

“ t_r ” is the reported time to rupture

“ t_0 ” = 0.1 hour is the time to rupture in short term tensile tests

$K_s = 0.0854$ is the slope of the static regression line for the rods made of E glass in water

$K_s = 0.0654$ is the slope of the static regression line for the rods made of boron-free glass in water

We illustrate the use of equation (5) for the rods tested in acid. According to Mark Greenwood, the strength retentions at 50 years for rods creep-tested in acid are 0.90% and 12.10% respectively for E glass and boron-free glass. The time to rupture to enter equation (5) is 50 years, or $t_r = 438000$ hours.

For E glass rods creep-tested in acid

$$\Delta e = 3,175 \left\{ 1 - \left[(0,009) \times \left(\frac{438000}{0,1} \right)^{0,0854} \right]^{\frac{1}{2}} \right\} = 2,60mm$$

For boron-free glass rods creep-tested in acid

$$\Delta e = 3,175 \left\{ 1 - \left[(0,121) \times \left(\frac{438000}{0,1} \right)^{0,0654} \right]^{\frac{1}{2}} \right\} = 1,35 \text{ mm}$$

The penetration depth, “ Δe ”, is small considering the exposure time of 50 years. The rods of E glass are penetrated 2.60 mm after 50 years of exposure in acid, versus 1.35 mm for the rods of boron-free glass. For equal performance after 50 years, the rods of E glass should be designed with diameters $2 \times (2,60 - 1,35) = 2,50$ mm larger than those of the rods made of boron-free glass. This does not seem like a big deal and supports the conclusion that the glass composition is not a driving factor in the durability of the corrosion barrier. Also, it should be noted that the rods tested had no corrosion barrier to slow down the penetration.

The classical interpretation of the tests performed by Mark Greenwood is not correct. It leads to the scary and incorrect conclusion that the E glass rods, regardless of their diameter, lose their strength (retention of 0.90%) after 50 years of immersion in acid. This conclusion is so unlikely that the great Mark Greenwood was forced to make the following apologetic comment in his 2001 paper:

“Considering the relatively good performance of isophthalic polyester laminates reinforced with traditional E glass, the results from this study appear to be excessively severe. However, the manufacturing method typically used for storage tanks that would hold a strong acid uses a liner or barrier layer that would significantly delay the adverse effects of the acid on the structural layers of the chemical storage tank.”

The above is implicit recognition that only the surface plies of the composite are subject to attack from reactive chemicals. The inner core remains intact. The classical assumption that the corrosive chemicals pervade the laminate and affect the mechanical properties of the core is wrong.

Table 2 summarizes our interpretation of the test results reported in reference 2 for other chemicals.

Corrosive medium @ 23C	Type of glass	Strength retention @ 50 years	“ Δe ” @ 50 years	Comments
5% salt solution	E glass	0,271	zero	Water does not affect the penetrated outer plies and “ Δe ” = 0. The results indicate that the hydrolytic stability of boron-free glass is superior to that of E glass.
	Boron-free glass	0,368	zero	
1,0N HCl acid	E glass	0,009	2,60 mm	After 50 years in acid the rods of E glass lose $2.60 - 1.35 = 1.45$ mm more thickness than those of boron-free glass.
	Boron-free glass	0,121	1,35 mm	
Cement extract	E glass	0,148	0,83 mm	After 50 years in cement extract the rods of E glass lose $0.83 - 0.57 = 0.26$ mm more thickness than those of boron-free glass.
	Boron-free glass	0,248	0,57 mm	

Table2 - A side by side comparison of stress-rupture tests on pultruded rods of E glass and boron-free glass. The depth of penetration “ Δe ” is small, given the time frame of 50 years and the absence of a corrosion barrier.

9 – Conclusion - This paper introduces a new method to quantify the service life of the corrosion barrier of composites. The basic assumptions underlying the new method lead to the following conclusions:

- 1 – The non-penetrating chemicals determine the service life of the corrosion barrier.
- 2 – Water is the only known chemical that fully penetrates the laminates and determines the long-term structural life.
- 3 - The current test method (ASTM C 581) is good to assess the suitability, not the durability, of composites in corrosive environments.

- 4 - The service lives of corrosion barriers made of boron-free and regular E glass are essentially the same.
- 5 - The durability of the corrosion barrier is determined primarily by the resin.
- 6 - The glass composition affects the structural life, not the service life.

References

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Acknowledgement: Antonio Carvalho is thankful to Mark Greenwood for his continuous advice and direction dating back to the distant year of 1973 when they first met at the Owens Corning's pipe and tank facility in Conroe, TX.

Biographies

Antonio Carvalho is an engineer with 40 years in composites. Past experience includes 30 years with Owens Corning and 15 years as a consultant.

Carlos Marques started his career as an engineer for Occidental Petroleum. Later experience includes 20 years with composites in industrial applications and sanitation. Carlos passed away in 2010 at the early age of 56.