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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 composites 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 the corrosion barrier of the composite in aggressive chemicals 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 durability of the corrosion barrier in aggressive environments.

Keywords: durability of composites, structural life of composites, service life of composites.

Introduction – The issue of durability depends on what is expected of the composite and is usually addressed based on cosmetic, fitness for service and structural criteria.

1 – The cosmetic life is concerned with the need to restore the gloss or any other feature that may be appealing to the eyes of the beholder. The cosmetic life will not be addressed in this paper.

2 – The structural life is defined by rupture, weeping, or any other structurally relevant criterion. The structural life of composites is addressed in references 1, 3, 4 and 5.

3 – The service life is determined by the durability of the corrosion barrier. The composite is considered unfit for service when the aggressive chemicals penetrate the corrosion barrier and reach the structural layers. This paper will introduce a new model to predict the durability of corrosion barriers.

Two types of aggressive media – We define as aggressive any medium that lessens the ability of composites to perform. The damaging potential of the aggressive medium is related to its ability to penetrate the laminates. Some media have no power of penetration and concentrate their damage on the surface. Others pervade the whole laminate and damage all layers. In this paper the aggressive media are classified according to their ability to penetrate the laminates.

1 - Non-penetrating. This category includes those agents that interact only with the plies located near the surface of the laminate. Examples of such media are combustion, UV radiation and abrasive materials, which erode away the outside surface of the composite while leaving the inner layers intact. Also included in this category are the chemical products used in industrial applications. The industrial chemicals interact with the resin/glass and do not penetrate very deep into the laminate. Their damage is therefore limited to the plies that are located near the surface.

2 - Penetrating. Some agents, like temperature, solvents and mechanical strains, penetrate all layers of the laminate. 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. Temperature saturation is also very fast. And the mechanical strains, of course, have instantaneous penetration. The penetrating media are characterized by fast action and pervasiveness. They are the only agents that can affect the long-term structural life of the composite.

The penetration of aggressive chemicals in polymers is very limited. This is due to several causes, such as low solubility, low diffusivity and interactions that occur between the chemical and the resin. This produces a near flat advancing front as the chemicals penetrate the composite. Figure 1 shows some typical concentration profiles of non-penetrating chemicals plotted along the wall thickness of a composite. As the molecules of the chemical products enter the laminate, they react with the glass/resin and are blocked in their advance. This produces a near flat advancing front such as shown in figure 1. The flatness of the advancing front is a characteristic of the 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 advancing flat front.

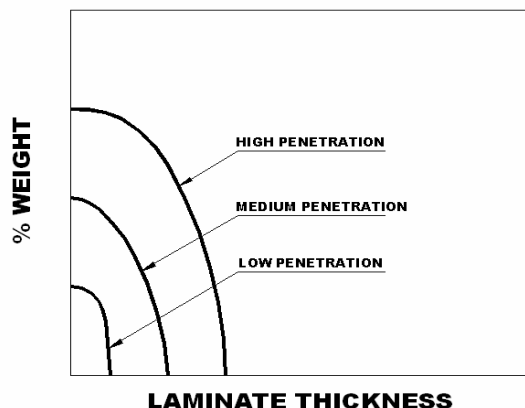


Figure 1 - Different species show different penetrating profiles. Note the flat front characteristic of the penetrating chemicals.

It is reasonable to assume that the resin material that is penetrated by the chemical loses its structural capability. It is the responsibility of the engineer to schedule regular shutdowns of the composite equipment to check 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 fronts of the chemicals were not flat and sharp as shown in figure 1.

In applications where the relining is not possible, like in small diameter pipes, the penetrating chemicals would continue on their advance and eventually penetrate and destroy the structural layers of the laminate. It is possible, then, to have structural failure caused by the penetration of non-penetrating environments. 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. If proper maintenance is done, the damage caused by the chemical is limited to the sacrificial corrosion barrier. In other words, the chemical products determine the service life of the equipment, but have no effect on its long-term structural life.

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 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 material in 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. The reader should understand that the ingress of the aggressive chemical destroys the structural capability of the penetrated plies. The part of the laminate that has been penetrated is assumed fully destroyed. And the part that has not been penetrated is left intact.

That is the way in which figure 2 should be interpreted. The conventional interpretation, however, is the exact opposite. According to the conventional interpretation (a) the composite is fully penetrated by the chemicals and (b) the mechanical properties are reduced 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 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) lose mechanical properties only in the penetrated plies.

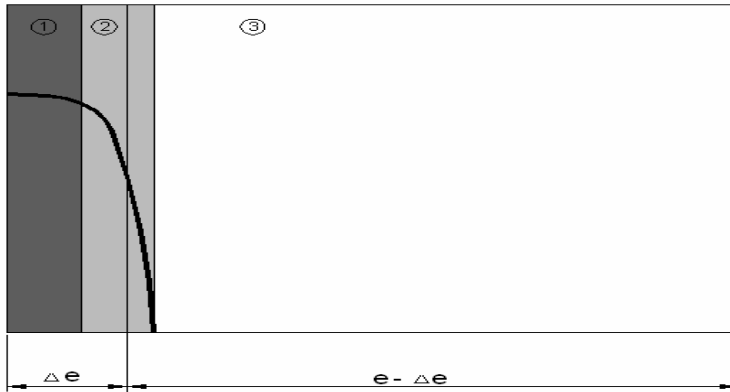


Figure 2 – The chemicals do not penetrate deep into laminates. The extent of penetration is measured by the effective penetrated depth indicated by “ Δe ”.

The effective depth of penetration “ Δe ” – In most cases the 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 shown in figure 2. The boundary between zones 2 and 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 represented by the combined zones 1 and 2. However, given the flatness of the advancing front, the effective depth “ Δe ” should differ little from the actual total depth of penetration.

Measuring “ Δe ” - The penetrated thickness “ Δe ” can be measured directly by optical means or indirectly by doing tensile tests on specimens removed from the corrosive media.

The optical measurement of “ Δe ” is straightforward and needs no elaboration other than the comment that a contrasting dye would help bring out 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 swells the resin and reduces the strength of the specimen. This is in contrast with the non-penetrating chemical that reduces the properties of a thin layer on the surface of the composite. The measurement of “ Δe ” by mechanical tensile testing requires that the swelling effect of the penetrating water be separated from the attack by the chemical. This can be done by immersing a control coupon in water, to cancel out the effect of water pick up on the mechanical properties of the test specimens.

Figure 3 shows the cross-sections of coupons after immersion in water and in the test solution. The control coupon - immersed in water - retains its original properties across the 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 chemical exposed specimen. 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 not of the whole laminate, but only the thickness “ $2\Delta e$ ”. The rest of the exposed laminate, $e - 2\Delta e$, retains its 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 “ 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.

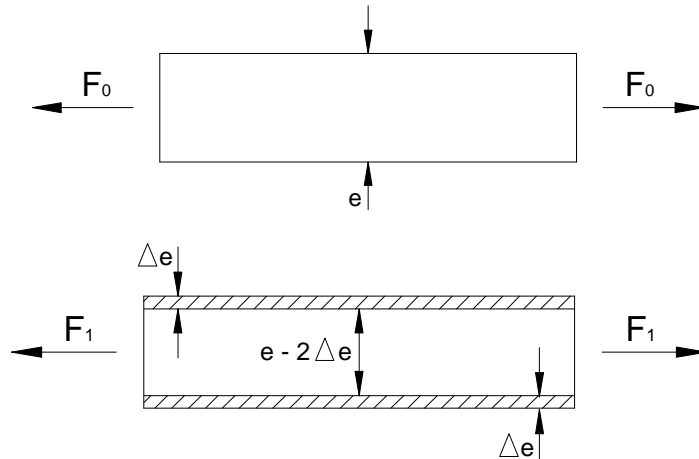


Figure 3- Test coupons as they look prior to and after immersion. The penetrated thickness “ Δe ” is counted twice to account for the double exposure.

The governing equation – Having solved the problem of measuring 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, while decreasing with the shielding effect from the “ Δe ” that remains on the laminate surface. Often times the damaged material of thickness “ Δe ” remains on the surface of the composite and provides a shield against further attack. 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 thickness of the corrosion barrier that is penetrated by the chemical

“ t ” is the time of exposure

“ k ” is a factor that accommodates the 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 into the resin

“ r ” is the rate of attack by the chemical

“ c ” is the concentration of the chemical solution

“ 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 surface.

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

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

The preceding expression recognizes the effects of temperature and tensile strain on the diffusivity. Temperature increases will increase the intermolecular spacing in the matrix. And tensile strains will debond the glass-resin interface. Both events facilitate the ingress of chemical species into the composite. The effect of the tensile strains in this context is to increase 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

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

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

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

By definition the permeability P of a given 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 thickness of the corrosion barrier that is penetrated 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 these equations with the diffusivity D and the Arrhenius activation energy E.

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 preserved. Water is a good example of an environment like this.

$r_0 = \infty$. 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 layer of 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 in this case and “ Δe ” is equal to 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 its 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 to increases in concentration. 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 how to do that.

Measuring the corrosion parameters – There is no test method known at this time to predict the service life of the corrosion barrier in aggressive media. The closest protocol currently used to do this is ASTM C 581, which is good to predict the suitability – not the durability – of corrosion barriers. In this section we describe 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 the test fluid at different concentrations and different

temperatures. The penetrated thickness “ Δe ” can be measured directly by optical means or indirectly by the tensile modulus of specimens cut from the test coupon. The new test method departs from the ASTM C581 in the following:

- The test coupons have no surface veil.
- 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 visual appearance of the coupons are ignored.

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

	Current ASTM C 581	New 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 loss of thickness. The loss of thickness 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.

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 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.

Worked example 1 – The following example illustrates the application of the regression equation to a hypothetical situation. The equation used to predict Δe 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 environment:

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

The above hypothetical parameters are valid for “ Δe ” expressed in mm when the time of exposure “ t ” is expressed in months. They 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 for a service life of 25 years. In both cases we will assume a margin of safety of 1.0 mm for the residual corrosion barrier

Estimating the service life of a 2,5 mm corrosion barrier – For a required residual margin of 1,0 mm, the composite equipment will be 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 the depth of penetration $\Delta e = 1.5$ mm and the given corrosion parameters in equation (3a). The service life will be estimated for a concentration $c = 0.5$, a tensile strain $\varepsilon = 0.20\%$ and 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) if the operating temperature is 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 temperature is raised to 80C.

Designing the corrosion barrier for a service life of 25 years at 90C and $c = 0.5$. – 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 (3b) 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 margin of 1,0mm, the thickness of the corrosion barrier should be $1.7 \text{ mm} + 1.0 \text{ mm} = 2.7 \text{ mm}$.

Worked 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 that were published in this 2001 paper.

The reported test results were taken from specimens under constant tension while immersed in the fluid. This differs from the method that we are proposing, which simply immerses the coupons with no applied tension. Creep tests are good to assess the structural life of composites in penetrating environments like water, but are useless to measure the effect of non-penetrating chemicals.

It could be argued that creep tests might capture the stress-corrosion effect of the chemical and therefore be “more realistic” than simple immersion. However, the strain corrosion effects are perceived only in bending situations and not in tensile tests like the ones conducted by Mark Greenwood. The tensile strains would affect the test results if the laminate were over-strained and cracked to allow the ingress of the chemical. This, however, is a non realistic situation that is not found in use. Therefore, the “more realistic” values from creep tests should not differ much from those obtained from simple immersion.

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 chemicals fully penetrated the rods and lowered their strength. The classical idea that chemicals fully penetrate the entire laminate, regardless of its thickness, is not correct.

We will next use the test data published by Mark Greenwood in reference 2 to determine the depth of penetration “ Δe ”. The classical line of interpretation assumes that the radius of the rods 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 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 old interpretation.

Our interpretation is quite different. We say that the tensile rupture force drops in response to (a) a decrease in the mechanical properties of the thickness that is penetrated and (b) a decrease in tensile strength caused by water on the non-penetrated material. We repeat the argument for clarity. We say that the chemicals penetrate and destroy the mechanical properties of 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 technical and 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 lead to equation (5), that 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 thickness

“ 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 reference 2 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 therefore 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 thickness that is penetrated, “ Δe ”, is small considering the exposure of 50 years. Also, it should be noted that the rods tested had no corrosion barrier to slow down the penetration. 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 corrosion barriers.

The classical interpretation, however, leads to the scary 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 the chemical attack takes place only in the outer layers of the laminate. 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 the other environments.

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 thickness. 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 penetrated thickness “ Δe ” is small, given the time frame of 50 years and the absence of a corrosion barrier.

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 - Non-penetrating environments determine the service life of the corrosion barrier.
- 2 - Water is a penetrating chemical that determines the long-term structural life.
- 3 - The current test method (ASTM C 581) to assess the suitability of composites in corrosive environments is inadequate and should be discarded.
- 4 - It is not necessary to conduct creep-tests in corrosive environments.
- 5 - The difference between boron-free and regular E glass in corrosive environments is less dramatic than reported in earlier studies.

6 – The durability of the corrosion barrier is determined primarily by the resin.

References

- (1) A new formula to predict the structural life of composite pipes, by Antonio Carvalho and Carlos Marques, in ACMA Composites Conference 2006.
- (2) Pultruded composites durability: A key value, by Mark Greenwood, in CFA (now ACMA) Composites Conference 2001.
- (3) Structural life of composite pipes. Part 1. Rupture/burst failure, by Antonio Carvalho in ACMA, Las Vegas, 2007
- (4) Structural life of composite pipes. Part 2. Weep failure, by Antonio Carvalho in ACMA, Las Vegas, 2009
- (5) Structural life of composite pipes. Part 3. Strain corrosion failure, by Antonio Carvalho in ACMA, Las Vegas 2011

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Biographies

Antonio Carvalho is an engineer with 40 years in composites. Past experience includes 30 years with Owens Corning and 10 years as a consultant. Current position is full time consultant for Reichhold do Brasil.

Carlos Marques started his career as an engineer for Occidental Petroleum. Later experience includes 20 years with composites in industrial applications and sanitation. Current position is commercial director for Ameron/Polyplaster in Latin America.