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Durability of GFRP Composites under Harsh Environments: Effect of pH and Temperature

Maria Martinez de Lahidalga de Lorenzo

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**Durability of GFRP composites under harsh environments:
Effect of pH and Temperature**

Maria Martinez de Lahidalga de Lorenzo

Thesis submitted to the
College of Engineering and Mineral Resources at
West Virginia University in
partial fulfillment of the requirements
for the degree of

**Master of Science
in
Civil Engineering**

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Keywords: Durability, Composites, FRP, Aging, pH, Temperature
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ABSTRACT

Durability of GFRP composites under harsh environment: Effect of pH and Temperature

Maria Martinez de Lahidalga de Lorenzo

In recent years, demand for Fiber Reinforced Polymer (FRP) Composites as a substitute of conventional materials has increased because of certain inherent advantages of FRPs over conventional materials such as concrete or steel. However, FRPs are also susceptible to degradation under both physical and chemical aging. To evaluate glass FRP composites aging behavior under harsh environments in a cost-effective manner, accelerated aging data are obtained under controlled lab environments, in short duration, to perform a correlation with data from naturally aged samples. Following the time-temperature superposition principle, the mechanical response in the field in a span of time of 75 to 100 years can be extrapolated to obtain the long-term degradation curves and strength reduction factors for design purposes.

In this work, a comprehensive literature review was performed to collect accelerated and natural aging data for glass fiber reinforced composites. Various methodologies were employed to normalize the data accounting for diversity in methods and materials so that the aging trends can be compared. To perform the aging correlation between the lab and field data, the Arrhenius type relationship was employed to extrapolate the data using the room temperature as reference temperature and to calculate activation energies.

Vinyl-ester was observed to have higher strength retention than Polyester in the majority of the scenarios evaluated in this study. In relation to mechanical properties, interlaminar shear strength yielded higher degradation in shorter periods of time and thus, it seems to be the controlling factor in determining the durability of GFRPs. Another dramatic strength reduction is noted in the lab under extreme alkaline environments in short duration which also shows much lower activation energy. Linear as well as nonlinear Arrhenius type relationships were evaluated and concluded that linear relationship provided more accuracy to determine the aging factors.

“Dame un punto de apoyo y moveré el mundo”
-Arquímedes

*A Mamá, Papá y Manu.
Gracias.*

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CHAPTER 1 INTRODUCTION

Fiber reinforced polymer (FRP) composites are susceptible to degradation under both physical and chemical aging. To encourage broader applications of FRP composites in infrastructure systems, an understanding of their chemo-thermo-mechanical responses, including durability (aging) under harsh environments and sustained load, is essential to ensure economical design. Implications of the aging factors are; reduced bonding between the fibers and matrix, oxidation, chain secessions, hydrolysis and possible total structural failure to a certain extent. Data collections in different research studies usually provide wide ranges of strength/ stiffness vs. time plots indicating a reduction trend in mechanical properties. For a wide variety of polymer composites accelerated aging tests have been performed by many researchers in the past to predict the durability behavior and service life, observing mostly asymptotic behaviors for the different mechanical properties.

The asymptotic behavior of strength with time essentially follows an Arrhenius type degradation. The Arrhenius approach uses activation energy as the focus of aging study, and is commonly observed in terms of number of years of service life of FRP materials; hence durability responses are correlated with an Arrhenius approach. This approach has certain limitations and needs some modification for service life predictions of polymer composites, especially under combined thermal, moisture, pH and sustained load effects. The main objective of this research is to arrive at resistance (knock-down) factors under several thermo-mechanical and environmental conditions varying pH and temperature.

1.1 Objectives

The basic conditions that any structural design must satisfy are the serviceability and ultimate strength/stiffness limit states. For a good design, the ultimate strength (forces/stresses) and deformation must be less than the design resistance values. Depending on the functionality of a FRP structure, any structural design must consider the effects of different chemical and environmental responses of the constituent materials with reference to pH, temperature, creep, fire, fatigue, impact, etc. To quantify these effects, the structural design should include factors affecting the strength/stiffness and deformations (i.e. deflections, rotations, twist, etc).

Following the Load and Resistance Factor Design (LRFD) based specifications, the nominal resistance and stiffness values for design are obtained by multiplying the initial values with knock-down factors (which are generally <1) in order to consider the effects of the surrounding field environment, as presented in Equation 1-1.

$$R_n = \varphi \cdot R \quad (1-1)$$

The absence of knock-down factors for pH, creep, fatigue, temperature and others is holding back further implementation of FRP composites in civil infrastructure. These factors are established through several laboratory based test responses of structural components and corresponding field evaluations with references to service life. It is the objective of the research herein, to obtain these factors based on the effect of pH and temperature values for Glass Fiber Reinforced Polymer (GFRP) composites.

1.2 Followed procedure and structure of the document

In order to achieve the objective of this research project, the process is as follows:

- 1st. Data collection under different environments
- 2nd. Data correlation & standardization of accelerated aged data
- 3rd. Development of Arrhenius plots & Time Shift Factors
- 4th. Shift of the accelerating aging data
- 5th. Calibration of Accelerated vs. Natural aging data
- 6th. Development of formulas for degradation factors & Strength Resistance Factors

Following this introductory chapter, a critical review of the literature is presented in Chapter 2. In Chapter 3, the data collection and correlation for the different environments is presented in detail together with the Arrhenius plots. Followed by the development of the methodology employed to correlate the accelerated and naturally aged data in Chapter 4. The Time-Temperature Superposition principle and the concept and meaning of Activation Energy are presented in Chapter 5, as well as the shift of the accelerated data and the longer degradation trends. Chapter 6 showcases the calibration of accelerated and natural aging data, and the determination of knock-down factors.

1.3 Need for accelerated aging research

Contemporary civil engineering structures are designed to be both durable and sustainable, lasting for long periods of time ranging from 75 to 100 years of service life. To obtain the strength reduction factors for design purposes, the performance behavior of constituent materials and their

bond behavior over the long term is required. The same can be said for GFRP composites. The primary difference between new materials, such as composites, compared to conventional ones, i.e. concrete or steel, is the lack of information related to their performance over 75 to 100 year period.

In order to promote the implementation and subsequently increase the appeal of these new and advanced materials in civil engineering, their behavior when exposed to different environments is required. Obtaining natural degradation data involves considerable investment in both time and capital. To reduce costs and obtain an accurate approximation of the real behavior of FRP materials in the field, several experiments are conducted in controlled lab environments. These lab environments are harsher than the field environments inducing structural/material degradations, i.e. higher temperatures, different pH values and others. As a result, higher degradations in a shorter period of time are exhibited in comparison to naturally aged specimens, allowing for a posterior correlation between lab and field data. Applying this durability evaluation method allows for cost-effective research as the data of several months of acceleratedly aged samples and several years of naturally aged samples are recorded, for correlation. The central idea of this approach is that a good approximation of the performance of FRP composites under different environments may be obtained so that degradation rates can be established and design knock-down factors accurately evaluated from field data.

CHAPTER 2 LITERATURE REVIEW

The durability of a material is defined as “its ability to resist cracking, oxidation, chemical degradation, delamination, wear, and/or the effects of foreign object damage for a specified period of time under specified environmental conditions” (Dutta, 2001). How the fiber-reinforced polymers (FRP) experience degradation has become an important issue for the applications of these materials in the civil infrastructure system.

The application of GFRPs in civil engineering structures is gradually being taken as a good alternative to conventional materials, especially in harsh environments. This becomes apparent when using steel as reinforcement of concrete structures as it is subjected to a high alkaline environment of pH values around 13 stemming from the cement. For this reason, loss of strengths in steel can be major concern when determining the service life of a structures' reinforcement (Almusallam, 2001).

FRP composites are based on high strength fibers in a matrix that provides favorable bonding between the fibers. “Both fibers and matrix retain their physical and chemical identities, yet they produce a combination of properties that cannot be achieved with either of the constituents acting alone” (Mallick, 2007). In general, the fibers carry the load applied on the material whereas the resins dissipate loads to the fiber network thru interlaminar shear. This maintains the bonding between the two components of the material, maintains the fibers orientation, softens the fiber, and most importantly protects the fibers from damaging environmental conditions such as humidity and high temperature (Mallick, 2007).

Having the matrix act as a protective core and also as a binder to fibers ensures that fibers are less exposed to external environments and therefore their degradation less severe. This makes the rate of degradation of FRP components less likely compared to the degradation rates of reinforcing steel (Park, 2012). As fibers do not degrade under the infrastructure service environments, the FRP materials would be able to carry mechanical load since the properties are controlled by the fibers (440.1R-06, 2006). The different degradations of the materials under several environments are developed later in the chapter.

2.1 Constituent materials of FRP specimens

2.1.1 Glass fibers

Glass fiber reinforcements are the component of the material that provide the strength and stiffness to the FRP elements. In addition, glass fibers are used as reinforcements in composites due to their low electrical and thermal conductivity, magnetic neutrality, hardness and non-corrosive properties. However, their elastic modulus is usually lower than the modulus presented by conventional reinforcements such as steel. In comparison with steel, the glass fibers are more flexible, lighter and inexpensive (Chen, 2007) (Barbero, 1998). The commonly used glass fibers are E-, S- and AR- fibers. All the fibers are similar in stiffness, but present a huge variability in their strength and degradation rates under the different environments.

2.1.2 Thermoset matrices

The matrix, binding reinforcement in a composite creates the load transfer thru shear within the structural element. Matrices protect fibers from environmental conditioning and reduce the abrasion of fibers, and also for processing convenience. Polymers are the most widely used

matrices because they offer many benefits in terms of manufacturing and are cost-effective, as they do not require complex tools. Other properties such as the low viscosity of the thermoset resins grants the manufacturer relative freedom with regards to shape, allowing for a wide variety of aesthetic designs.

The mechanical properties of the polymers vary substantially in terms of the temperature to which they are subjected and the loading rate. It is important to note that the temperature at which polymers change from hard and brittle nature to soft and tough and such phase change, is referred to as glass transition temperature (T_g). Accordingly, the temperatures at which the structural elements are exposed should be far from this magnitude as the strength within this temperature decreases about five times lower than that experienced at lower temperatures (Chen, 2007). With this in mind, selecting the appropriate resin is a crucial step for processing and also for attaining certain design levels of thermo-mechanical properties. Conventional thermoset resins used in civil infrastructures are polyester, vinyl-ester and epoxy resins.

2.2 Aging factors over FRP composites

When studying the durability of FRP composites, many different environmental agents affecting the material can be studied; moisture uptake, sustained stress, pH and temperature variations and UV radiation are the most common. For the purpose of this study only pH and temperature variations will be analyzed.

2.2.1 pH

The variation in pH exposure of a FRP composite severely affects the interfacial bonding strength between the fiber and the matrix (Kajorncheappunngam, 1999). The lowest amount of

susceptible linkages in the matrix-fiber interface is desired when GFRP composites are exposed to reactive environments. If partial linkage collapse is unavoidable, then a higher concentration of linkages are preferred. For example, by analyzing two types of chemical bonds in GFRP's Vijay 1999 indicates how siloxane linkages between glass and a coupling agent, and within the coupling agent ester linkages between polymer resins and anhydride-hardened epoxies, are susceptible to bond breakage and therefore lead to higher rate of bond degradation (Vijay, 1999; Kajorncheappunngam, Gupta, & GangaRao, 2002).

2.2.1.1 Acidic solutions

FRP composite specimens subjected to acidic environments usually present multiple cracks in the matrix, resulting in resin flaking and fiber damage. Several researchers have shown that fiber reinforced polymers under an extremely acidic solution present a higher degradation rate than the one under extremely alkaline environments (Figure 2-1) (Wang, GangaRao, Liang, & Liu, 2015).

However, in composites for civil engineering applications, it is less likely to find an extreme acidic environment, but more probable to find materials subjected to marine environments in which pH values range from 4 to 6. In cases of composites under saline water, the degradation is less severe than in acidic or alkaline mediums, as presented in Figure 2-1 (Kajorncheappunngam S. , 1999; Kajorncheappunngam, Gupta, & GangaRao, 2002).

Figure 2-1- Comparison of percent retention of tensile strength of composite aged in different solutions at RT
(Kajorncheappunngam, 1999)

2.2.1.2 Alkaline solutions

Alkaline environments not only attack the matrix but also the glass fibers (Wang, GangaRao, Liang, & Liu, 2015). Due to the non-metallic nature of the glass fibers, they do not corrode under chloride environments. Therefore, when discussing the degradation of fibers, the focus lies on alkaline or acidic solutions and high moisture environments with the most critical degradation witnessed under alkaline solutions (Nkurunziza, Debaiky, Cousin, & Benmokrane, 2005)

One of the principal degradation processes that glass fibers suffer is the Alkali Silica Reaction (ASR); the attack of the fibers is a product of the dissolution of silica (SiO_2) by the alkaline ion (OH^-). The reaction of silica in glass and alkali solution causes hydrolysis, dissolution and leaching. Alkaline hydrolysis occurs when the OH^- ions react with ester bonds which are the

weakest component of the polymer's chemical structure (Wang, GangaRao, Liang, & Liu, 2015; Yilmaz & Glasser, 1991; Nkurunziza, Debaiky, Cousin, & Benmokrane, 2005).

Under alkaline environments, the bond in between the coupling agent and the fiber's surface is weakened and destabilized. With the diffusion of moisture and alkalis through the material, the bond is gradually destroyed. This loss of bonding causes serious damage to the interface as its strength is directly related to the amount of coupling agent remaining in the material (Nkurunziza, Debaiky, Cousin, & Benmokrane, 2005).

Many researchers have demonstrated that the different strengths of materials (i.e. tensile, flexure and shear) decreased dramatically over time when subjected to high concentrations of alkaline solution, whereas the modulus of elasticity of GFRP specimens maintains practically constant (Wang, GangaRao, Liang, & Liu, 2015). As a result, the behavior under alkaline environments is worse than that under acidic environments. The degradation of different mechanical properties of materials under pH variations mainly focused on alkaline environments. This is a critical point of study in the area of civil engineering and the application of FRP's, as alkaline environments experience the greatest degradation around its reinforcing structural elements. For example, the pores on the concrete – with pH values ranging from 11 to 13.5, accumulate bleeding water while curing and this constituted a flow of interstitial alkaline solution.

2.2.2 Temperature

The different components of GFRP composites exhibit distinctive behaviors under the effect of temperature.

2.2.2.1 High Temperatures

Even though fibers are known to be temperature resistant and can retain most of their strength and stiffness at high temperatures, most polymer matrices are susceptible to these environments. When temperatures surpass or border around 20°C below the glass transition temperature (T_g), the strength of the resin drastically decreases. At these temperatures, matrices can arrive to plasticization, melting or pyrolysis. The loss of strength in the matrix leads to a more susceptible material as the load transfer could be affected, causing an increase in the degradation rate. In the case of the temperature of exposure exceeding the ignition point of the resin, the bonding element may no longer provide protection to the fiber surfaces, leading to a major decrease in the mechanical behavior of the material and a shortening of its service life (Bank, Gentry, Thompson, & Russell, 2003; Wang, GangaRao, Liang, & Liu, 2015).

Park 2012 presented that in uniaxial specimens, axial mechanical properties do not show huge changes with the increase of temperature, whereas the transverse properties show a loss of strength under the same conditions. As shown in Figure 2-2, i.e. Alsayed 2012, when the influence of elevated temperatures over GFRP composites was studied and presented that under temperatures of 100°, 200° and 300°C, the variation of tensile modulus was practically null; whereas the tensile strength and failure strain presented a gradual decrease as the temperature levels and time of exposure increased.

Figure 2-2-Performance of GFRP bars under elevated temperatures. (a) Tensile strength, (b) Failure strain and (c) Tensile modulus (Alsayed, 2012).

2.2.2.2 Low temperatures and freeze-thaw cycles

Degradation rates of FRP composites under low temperatures are less than those under high temperature environments. Nonetheless, cold temperatures and freeze-thaw (FT) cycling can affect FRP composites due to a differential thermal expansion between the polymeric matrix and the fiber reinforcements, possibly resulting in a deterioration of the fiber-matrix interface (Wang, GangaRao, Liang, & Liu, 2015).

Robert et al. 2010 test data showcased increased values in their mechanical properties (tensile, shear and flexural strengths) when the temperature decreased, as presented in Figure 2-3. This phenomenon occurred due to the increase of stiffness in the amorphous polymer matrix under low temperatures. The flexural modulus of elasticity appeared to be stable in temperatures between -40° to $+50^{\circ}\text{C}$.

(a)

(b)

(c)

(d)

Figure 2-3-Average mechanical properties of GFRP bar specimens tested under different temperatures:

(a)Tensile strength, (b)Shear strength, (c) Flexural strength and (d) Tensile Modulus (Robert, Wang, Cousin, & Benmokrane, 2010)

When FRPs are subjected to freezing temperatures along with mechanical properties variations, additional micro-cracks are appreciated in the specimens. This can lead to an increase in water absorption when temperatures raise. Also, the expansion of water, present in the FRP structure when subjected to freezing temperatures, can cause the growth of cracks and finally lead to debonding in the fiber-matrix interface (Wang, GangaRao, Liang, & Liu, 2015).

2.3 Aging prediction models of FRP composites

As stated in GangaRao et al. 2006 and presented in previous sections of this chapter, the rate of degradation in polymer composites depends on various factors such as:

- The chemical and physical structure of polymers
- Additives and modifiers
- Moisture
- Sustained stress or pressure
- Temperature
- Physical and chemical aging
- Etc.

Different environmental exposures as well as the combination of factors mentioned above show different degradation models. Several degradation models are presented in the literature, but for the purpose of this research only two have been studied. Both of them are presented in the following sections and results from following the Arrhenius equation (2-1).

2.3.1 Arrhenius Principle

The fundamental assumption behind using the Arrhenius principle is that degradation is dominated by a mechanism that does not change with time, but degradation rates vary by temperature. Whereas the degradation mechanism does not change during exposure with neither time nor temperature. This principle is used to obtain or extrapolate the long-term behavior and service life prediction of a material following the Arrhenius Equation (2-1), by using the temperature dependence of the polymer subjected to environmental aging at different temperature levels (Celina, Gillen, & Assink, 2005) (GangaRao, 2006) (Silva, da Fonseca, & Biscaia, 2014).

$$k = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad \text{or} \quad \ln k = \ln A + \frac{-E_a}{R \cdot T} \quad (2-1)$$

In relation to Equation 2-1, the Arrhenius extrapolations are based on the assumption that the reaction rate k controls the degradation process which is proportional to $\exp\left(\frac{-E_a}{R \cdot T}\right)$, where E_a is the Arrhenius activation energy, R the gas constant (8.314 J/mol-K), T the absolute temperature and A the pre exponential factor. Consequently, a plot in a log scale of the reaction rate (k) or the degradation times ($1/k$) is expected to show a straight line variation as shown in Figure 2-4 (Celina, Gillen, & Assink, 2005).

Figure 2-4- Example of an Arrhenius plot for temperature- and time-dependent strength retention.

(GangaRao, 2006)

For the extrapolation of long-term behavior, assuming that the Arrhenius time-temperature relationship is valid for all the temperatures of the tested range, the determination of a time shift factor (TSF) is needed, as presented in Equation 2-2 where T_1 is the temperature chosen as reference and the T_0 the aging temperature of the data which is being shifted.

$$TSF = \exp \left[\frac{Ea}{R} \left(\frac{1}{T_0} - \frac{1}{T_1} \right) \right] \quad (2-2)$$

Although the TSF presented in Equation 2-2 is the most common form in which Arrhenius type relationships are found, other research studies (i.e. Zou et al. 2011) have presented a variation of the Arrhenius type relationship in which the TSF variation is presented in terms of the pH of the solution, as shown in Equation 2-3, where pH_r is the pH taken as reference and pH is the pH

of the environment of the aged data that is being shifted. Further details on the Time-Superposition Principle and the shifts for long term performance will be developed in Chapters 4, 5 and 6.

$$TSF = \exp[A \cdot (10^{-pH} - 10^{-pH_r})] \quad (2-3)$$

2.3.2 Non-Arrhenius behavior

The accelerated data prevalent in the literature ranges from several months up to a year, with instances stretching over several years, but a longer extrapolation is needed to obtain actual degradation formulas. This limited availability of experimental data is the key weakness in the Arrhenius principle (Celina, Gillen, & Assink, 2005). Optimal data would include curves that showcase degradations during several decades of a material's service-life, highlighting the limitations within the Arrhenius procedure and its applicability to various projects. This argument is strengthened when several instances of the linear approximation of the Arrhenius plot (Figure 2-4) showed a tendency to produce a curvature in the degradation plot. This occurs when subjected to several aging agents when different E_a 's, or a variation of the activation energy to create degradation reactions comes into picture in the degradation process (Celina, Gillen, & Assink, 2005).

The non-Arrhenius behavior is shown as a combination of two or more independent reactions with individual and independent degradation rates. The different degradation rates are presented as a curvature change as a function of different reactions from pH, temperature, etc. This effect is shown as a change in the constant A on the Arrhenius equation to a function of the simultaneous process taking place (Equation 2-4). The problem when establishing the non-

Arrhenius type relationship, is to determine the exact point of curvature change; as well as determining the function followed by the changing of the constant A.

$$k = f(x) \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad \text{or} \quad \ln k = g(x) + \frac{-E_a}{R \cdot T} \quad (2-4)$$

As presented in Equation 2-5, the variation of the Arrhenius type relationship could also be represented by establishing a function of the various external agents for the activation energy. Maintaining A as a constant, as presented in the original Arrhenius equation.

$$k = A \cdot \exp\left(\frac{-E_a(x)}{R \cdot T}\right) \quad \text{or} \quad \ln k = A + \frac{-E_a(x)}{R \cdot T} \quad (2-5)$$

In Figure 2-5, an example presented in Celina et al. (2005) is shown, it can be observed the double curvature presented coming from two different degradation processes.

Figure 2-5 Example of curve fitting with two degradation process following a non-Arrhenius type relationship
(Celina, Gillen, & Assink, 2005)

2.4 Strength reduction factors “ ϕ ” for environmental conditions

Civil engineering structures are generally designed for service life of 75 to 100 years. However, any material used in the design does not maintain the same mechanical properties during the service life; therefore, it is important to know the degradation rate of materials with time and the performance rate of the different elements. For FRP elements, determination of degradation rate becomes a problem as the knowledge on degradation is limited.

The initial characteristics of a material's properties and specifications are given by manufacturers without taking into account the long-term effects from environmental exposure. Due to degradation, the properties of the composite materials must be modified (reduced) to factors in different types and levels of environmental effect; these factors are referred as knock down or strength reduction factors, showcasing the retained strength of the specimens for the service life period.

Obtaining the strength reduction factors is one of the main efforts of ongoing durability research. The primary issue is gathering data from all the different experimental studies and categorizing them by design specifications as every researcher applies different test methodologies due to a lack of durability test standards. When using the same test methodologies, there are huge variations in the resin type, fiber type, fiber architecture or manufacturing process; characteristics that may create variations in the strength of the tested specimens (Wang, GangaRao, Liang, & Liu, 2015).

For example, as presented in ACI440.1R-06 the design equation for tensile strength is:

$$f_{fu} = C_E f_{fu}^* \quad (2-6)$$

where

f_{fu} = design tensile strength of FRP, considering reductions for service environment

C_E = environmental reduction factor, given in Table 2-1 for various fiber type and exposure conditions

f_{fu}^* = guaranteed tensile strength of an FRP bar defined as the mean tensile strength of a sample of test specimens minus three times the standard deviation ($f_{fu}^* = f_{u,ave} - 3\sigma$).

Table 2-1 Environmental reduction factor for various fibers and exposure conditions (440.1R-06, 2006)

Exposure condition	Fiber type	Environmental reduction factor C_E
Concrete not exposed to earth and weather	Carbon	1.0
	Glass	0.8
	Aramid	0.9
Concrete exposed to earth and weather	Carbon	0.9
	Glass	0.7
	Aramid	0.8

The design modulus of elasticity as well as that given by the manufacturer is assumed to be constant. Usually the reduction factors, C_E , are conservative values adopted as a consensus of the American Concrete Institute (ACI) Committee. The temperature is considered in these values, but under the assumption that the FRP composite elements are not subjected to a temperature higher than the glass transition temperature (T_g).

Many experts on the subject consider the current codes and values to be conservative, and therefore consider it necessary that further research adopts a more accurate approach to evaluate the degradation of the materials.

2.5 Conclusion

The Arrhenius principle was assumed to be the right path to follow when studying the degradation and durability of FRP composites as the behavior presented by specimens is generally a logarithmic decay. In this research study, glass reinforced thermosets are studied under different environments of pH and temperature.

The degradation sets collected from the literature are presented partially in Chapter 3 and completely in Appendix A and B. In the sets of data, this study will show how the different temperature and pH levels affect the degradation to the studied materials for tensile, flexure and interlaminar shear strengths. Highly alkaline environments ($\text{pH} \approx 13$) are the pH environments of extreme concern due to the exposure of composites to concrete environments when applied in civil infrastructure.

CHAPTER 3 DATA COLLECTION

In this chapter, the procedure for existing data collection is developed. In addition, different data correlations are suggested for a more homogeneous source of information. Data collection is fundamental to this study. The author lacked adequate time to obtain the data of her own in the lab, therefore the data presented, stems from data available in the literature.

Most of the data comes from previous research studies on durability at West Virginia University (WVU), as well as other external sources. The only restriction being that the test data would not be influenced by any external agent other than pH and Temperature.

3.1 Accelerated aging data

3.1.1 Organization of the database

All the accelerated data collected for this study was gathered and organized in a database for all the different evaluated environments. The general data collection is formed by 196 sets of degradation curves lasting up to a time period of 18 months. Each of these sets represents 1 to 7 replications and the majority represent asymptotic behavior.

Given the various sources from which the data was obtained, and the many ways in which the raw content was presented, all the data gathered in this study was converted to percentage of strength retention of the tested samples. Several test samples witnessed an increase of strength in the beginning of the aging process. This increase of strength in the initial months has been assumed to be a result of post curing issues; the correction for these cases is presented in section 3.1.2.

Due to the lack of homogeneity in the data collected, different groups for temperature and pH were established in order to create representative data groups. For this particular case, five different categories were presented for both environmental agents, as exhibited in Table 3-1.

Table 3-1- Organization of database

Temperature groups:	pH groups:
– T1: -10 to 15 °C	– P1: acidic pHs between 0 and 4
– T2: 15 to 40 °C	– P2: Saline environment: pHs between 4 and 6
– T3: 40 to 60 °C	– P3: neutral pHs from 6 to 8
– T4: above 60 °C	– P4: pHs between 8 and 10
– FT: Freeze-Thaw cycles	– P5: Alkaline environments between 10 and 14

This distribution was made at the beginning of the data collection as some of the data present in the group was not enough to make a fair statistical representation. Thus, for those cases the data was not used for further data analysis.

The primary pH environment represented were P2; marine environments in which the pH is slightly below neutral. P3, neutral pH, and P5 which represents alkaline environments, which proved especially interesting for the application of composites in civil infrastructure as concrete environments result in extremely high pH of up to 13.7. In the case of temperature, the data group representative of temperatures ranging from room temperature up to 65 °C (T2, T3 and T4) were most prevalent, whereas freezing temperatures or freeze-thaw cycles (FT), provided insufficient

data for the use of this study. The data sets of special concern are presented at the end of this chapter, but all the collected data is presented in Appendix A.

3.1.2 Correction for post-curing

Curing of resin plays a critical role in the determination of mechanical and chemical properties of the material. For thermosets, the curing process is an irreversible reaction which is initiated by heat. In this reaction, the formation of cross links results in a material that is thermally and mechanically stable (Kumar, et al., 2015).

Since the maximum mechanical properties are achieved when the material has completely cured, it is possible for the mechanical properties to increase while aging. This is due to the fact that specimens are not always completely cured at the onset of aging. This test procedure requires data exhibiting post-curing to be corrected. If the mechanical properties are observed to increase during aging, this is an indication that the sample has not yet fully cured. The aging process does not cause these properties to improve. Therefore, data for samples demonstrating increased strength during aging were adjusted to account for post-curing effects.

In order to make the correction, the maximum strength was determined. The time of the maximum strength was then established as t_0 . The data prior to time t_0 was then neglected. This correction is based on the assumption that the aging process does not affect the continuation of curing up to time t_0 , at which maximum strength is achieved. An example of a correction in a sample showing post-curing can be seen in Figure 3-1. Where the max strength was determined to be 102.5 percent of the initial strength. This strength was achieved after 3 weeks of aging. Thus, the 3 week time period is taken as t_0 , and 102.5 percent is taken as the actual 100 percent.

Figure 3-1- Example of Post curing correction

3.2 *Natural aging data*

The collection of naturally aged data was one of the biggest concerns in achieving the objective of this project. The main limitation when collecting the data, as mentioned before, was the fact that the samples could not be subjected to any other environmental agent apart from pH and/or temperature. Within the literature, the bulk of the data available was affected by other environmental effects, mainly sustained stress as they were samples coming from structures that had been in service for several years.

The leading source of data for this section stemmed from a previous research conducted at the Constructed Facilities Center (CFC) at WVU, Dittenber, Gangarao, & Liang, (2016). The problem with this being that when trying to obtain the strength retention percentages, several sources (mainly sources external to WVU) did not indicate the initial strength of the material. The data for which the initial strength was not provided was neglected for the posterior correlation with the data obtained from lab controlled environments.

Another issue emerged when some of the samples showed an increase in the strength of the aged data, presumably stemming from post-curing problems, as commented before. Considering the fact that only two points of degradation trends were indicated in the source, there was not an option to calculate when the post curing reached its maximum and thus, the post-curing correction presented in section 3.1.2 cannot be applied.

The collected field data is presented in Appendix B and as summary of the obtained data the degradation curves in Table 3-2.

Table 3-2 Field aging degradation curves

	Field degradation curve
Flexural strength	$y = -3.458\ln(x) + 104.14$
Tensile strength	$y = -2.52\ln(x) + 102.66$
Interlaminar Shear strength	$y = -4.762\ln(x) + 100.39$

3.3 Normalization of the accelerated aging data

The data collected lacks homogeneity in terms of the physical characteristics of the specimens tested. To make up for this inconvenience, a correction on the data obtained in the lab tests is required. Different corrections could be done in terms of different characteristics of the manufactured coupons, however in this study only two corrections were made. On the one hand, different equations were developed for the effect of thickness of the samples and the main mechanical properties while on the other hand, the effect of the Fiber Volume Fraction (FVF). Both are extensively developed in sections 3.3.1 and 3.3.2.

For the collected data, the prorating made with a thickness of 1 cm (0.4”) and a FVF of 50 percent.

3.3.1 The effect of Fiber Volume Fraction on the strength of the FRP samples

Fiber volume fraction (FVF) is defined as the percentage of the total volume taken by fibers in a cured fiber reinforced polymer composite. This is a fundamental factor when calculating the mechanical properties of the material, such as strength or stiffness. An increase of these properties usually improves the mechanical behavior up to a certain maximum percentage of FVF. Beyond the max FVF percentage, properties degrade due to inadequate bonding between the fibers and the polymeric matrix (Siva, 2013).

As stated earlier, the fibers of the FRP composites are assumed to be the major carrier of its strength, whereas the resin keeps fibers bonded together and provides continuity to the finished composite. The increase of fiber volume fraction in a composite improves its stiffness and FVF percent variation changes thermo-mechanical properties. In Figure 3-2, it can be seen how stiffness keeps increasing as the FVF increases up to certain limit. This increase is approximately linear until a maximum threshold is reached where it can be seen that the material does not get stiffer regardless of a higher FVF. However, decrease in the stiffness is found with an increase of the fiber volume fraction due to inadequate fiber wet-out and lack of adequate shear transfer. This decrease can be related to a reduction in the bond strength between the resin and fibers (Mini, Lakshmanan, Mathew, & Mukundan, 2012).

Figure 3-2- Variation of Young's Modulus with volume fraction (Mini, Lakshmanan, Mathew, & Mukundan, 2012).

The strength prediction and correlation with the FVF results were more complicated than the stiffness (modulus) prediction. Different sources had different statements for the effect of FVF within the various mechanical properties, and thus the information available was not consistent in terms of the conditions or characteristics of the samples. In Siva, (2013) ILSS and TS were shown to increase practically linearly up to 42 percent of FVF. In this research project the strength of the material was assumed to increase linearly with the FVF. As in Mallick, 2007, assuming that the fibers in the composite lamina are arranged in a square array, the maximum fiber volume fraction that can be packed in the arrangement is 78.5%. The maximum FVF presented in the collected data is a 72%, therefore all the correlated specimens were under the limit at which the mechanical properties start to decrease.

The correction of the data sets in terms of FVF was made as in Equation 3-1.

$$\sigma_{cor} = \sigma_{given} \cdot \frac{FVF_{cor}}{FVF_{given}} \quad (3-1)$$

Represented in the formula above:

σ_{cor} : Strength resulting from prorated conditions

σ_{given} : Strength given from test results

FVF_{cor} : Fiber volume fraction to which the correlation needs to be done

FVF_{given} : Fiber volume fraction of the tested samples

3.3.2 The effect of the coupon thickness on the strength of the FRP samples

The theories proposed by Wei-Pin, (1990) have been used for obtaining the influence of composite thickness on the coupons or bars with both the tensile and bending strengths of the specimens. A theory has been created for interlaminar shear strength based on the principles mentioned above with special emphasis on shear lag phenomenon.

It is necessary to clarify that the behavior and responses of composites are complicated to compute because of different failure modes that the samples may experience under different loads. Hence a large body of experimental data is needed to validate assumptions and to develop an accurate prediction theory, as well as for evaluating the process response.

3.3.2.1 Tensile strength

Wei-Pin, (1990) developed a simple relationship between the specimen diameter and the ultimate tensile strength. The mechanics of materials approach was used in his proposed model, using three assumptions, given as follows:

- i. FRP composite fails when the tensile strain reaches the ultimate fiber strain.
- ii. First fiber failure is treated as global failure for design purposes.

- iii. Strain distribution is parabolic and axisymmetric across the cross-section. The distribution varies depending on the values of two constants “a” and “b” to be determined with boundary conditions and experimental data.

$$\varepsilon_t = a \cdot r^2 + b \quad (3-2)$$

Figure 3-3- Parabolic tensile stress-strain relations assumed. (Wei-Pin, 1990)

Assuming a constant transverse Young's Modulus along the specimen and that the maximum value of strain happens in the extreme fibers of a specimen. The tensile strength distribution ends up being:

$$\sigma_z = \frac{E_t}{2} (aR^2 + 2b) \quad (3-3)$$

$$a = \frac{(\varepsilon_u - b)}{R^2} \quad (3-4)$$

$$\sigma_z = \frac{E_t}{2} (\varepsilon_u + b) \quad (3-5)$$

As shown in the equations above, the tensile strength for both circular and rectangular section coupons result in a linear relationship in terms of the thicknesses of the sample. Leaving the tensile strengths of the FRP composite to be calculated in terms of “b”. Further details of this derivation can be found in Wei-Pin’s dissertation (Wei-Pin, 1990).

3.3.2.2 Flexural strength

The development for the effect of thickness for flexural strength results simply by following the distribution of bending stresses along any section. The equations presented below show the effect of the size of the sample in the strength by varying the basic stress equation with the moment of inertia value for a determined section.

Figure 3-4-Distribution of bending stress along the section of a specimen

RECTANGULAR SECTION**CIRCULAR SECTION**

$$\sigma = \frac{M \cdot y}{I} = \frac{6 \cdot M}{b \cdot h^2}$$

$$y = \frac{h}{2} ; I = \frac{b \cdot h^3}{12}$$

(3-6)

$$\sigma = \frac{M \cdot y}{I} = \frac{4 \cdot M}{\pi \cdot r^3}$$

$$y = r ; I = \frac{\pi \cdot r^4}{4}$$

(3-7)

In the equations above it is shown how the rectangular section has a parabolic relation (h^2), whereas for the circular section a cubic correction is made.

3.3.2.3 Interlaminar shear strength

For the case of interlaminar shear strength, the three assumptions made for tensile strength will be taken into account, assuming the FRP composites are transversally isotropic or orthotropic materials.

$$\begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \tau_{xy} \\ \tau_{xz} \\ \tau_{yz} \end{Bmatrix} = \begin{bmatrix} \bar{C}_{11} & \bar{C}_{12} & \bar{C}_{13} & \bar{C}_{14} & \bar{C}_{15} & \bar{C}_{16} \\ \bar{C}_{21} & \bar{C}_{22} & \bar{C}_{23} & \bar{C}_{24} & \bar{C}_{25} & \bar{C}_{26} \\ \bar{C}_{31} & \bar{C}_{32} & \bar{C}_{33} & \bar{C}_{34} & \bar{C}_{35} & \bar{C}_{36} \\ \bar{C}_{41} & \bar{C}_{42} & \bar{C}_{43} & \bar{C}_{44} & \bar{C}_{45} & \bar{C}_{46} \\ \bar{C}_{51} & \bar{C}_{52} & \bar{C}_{53} & \bar{C}_{45} & \bar{C}_{55} & \bar{C}_{56} \\ \bar{C}_{61} & \bar{C}_{62} & \bar{C}_{63} & \bar{C}_{46} & \bar{C}_{65} & \bar{C}_{66} \end{bmatrix} \begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \gamma_{xy} \\ \gamma_{xz} \\ \gamma_{yz} \end{Bmatrix} \quad (3-8)$$

$$ILSS = \tau_{xz} = \bar{C}_{15} \cdot \varepsilon_{xx} + \bar{C}_{52} \cdot \varepsilon_{yy} + \bar{C}_{53} \cdot \varepsilon_{zz} + \bar{C}_{45} \cdot \gamma_{xy} + \bar{C}_{55} \cdot \gamma_{xz} + \bar{C}_{56} \cdot \gamma_{yz} \quad (3-9)$$

From the transversely isotropic condition: $\bar{C}_{15} = \bar{C}_{52} = \bar{C}_{53} = \bar{C}_{45} = \bar{C}_{56} = 0$

$$\bar{C}_{55} = G_{12} = \frac{E_1}{2 \cdot (1 + \vartheta_{12})} \quad (3-10)$$

$$\tau_{xz} = \frac{E_1}{2 \cdot (1 + \vartheta_{12})} \cdot \gamma_{xz} \quad (3-11)$$

The distribution of the shear stresses are parabolically distributed along the section of the specimen.

$$\gamma_{xz} = a \cdot r^2 + b \cdot r + c \quad (3-12)$$

Figure 3-5- Shear stress distribution on a rectangular section.

Mallick, (2007), indicates what the maximum shear stress value achieved in the center of a cross section under bending is:

$$\tau_{xz} = \frac{3 \cdot P}{4 \cdot b \cdot h} \quad (3-13)$$

The equation above shows a linear relation between the maximum strength of the specimen and the thickness.

Figure 3-6- Shear stress distribution in a circular section.

$$\tau = \frac{4 \cdot \pi}{3 \cdot \pi \cdot R^2} \quad (3-14)$$

On the other hand, and as shown in Figure 3-6, the relation between the maximum strength of the specimen and the bar diameter is parabolic.

3.3.2.4 Summary

In Table 3-3, the equations to account for the effect of the thickness of the tested specimens in the strength of the materials are presented.

Table 3-3- Effect of the thickness of the sample in the strength of the material

	Tensile	Flexure	Interlaminar Shear
Circular Section (Bars)	$\sigma_{corr} = \sigma_{given} \frac{r_{corr}}{r_{given}}$	$\sigma_{corr} = \sigma_{given} \left(\frac{r_{given}}{r_{corr}} \right)^3$	$\tau_{corr} = \tau_{given} \left(\frac{r_{given}}{r_{corr}} \right)^2$
Rectangular Section	$\sigma_{corr} = \sigma_{given} \frac{t_{corr}}{t_{given}}$	$\sigma_{corr} = \sigma_{given} \left(\frac{t_{given}}{t_{corr}} \right)^2$	$\tau_{corr} = \tau_{given} \frac{t_{given}}{t_{corr}}$

3.4 Presentation of the prorated data

After the post-curing, thickness and Fiber Volume Fraction corrections were made to all data sets, the average of the prorated data for the different degradation times was plotted as shown in the Figures 3-7 and 3-8. In these plots the degradation under different temperatures for a certain material, mechanical property and pH group can be seen. All the plots are presented in Appendix A, at this point only the most relevant plots are presented in Figures 3-7 and 3-8. In these figures, the degradation plots of Interlaminar Shear Strength for Vinyl-ester and Polyester under alkaline environments are presented. From all the cases studied these two are the ones showing the most concerning behavior as they present an early dramatic decrease of the materials' interlaminar shear strength under the alkaline environment.

It may be noted that these plots display varying degradation patterns, but as in many other research studies the polyester shows a higher degradation than vinyl-ester. Also, it can be seen in the figures below that the higher the temperature to which the samples are subjected the higher the degradation is; a behavior exhibited in the majority of all studies in degradation.

The main concern when achieving this result is the fact that the most common use of GFRPs in civil infrastructure is reinforcing bars embedded in concrete (which produces a strong alkaline environment), many of these bars are to a certain extent subjected to shear forces, which lab tests indicate that under room temperature, the FRP composites experience a reduction of approximately 50-60% in strength for the first 3-4 months of accelerated aging.

In following chapters, how this behavior translates to a longer period of time will be evaluated by using the time-temperature superposition principle. Correlating with the natural aged specimens data, the strength reduction factors are obtained following the procedure presented in Chapter 4.

Figure 3-7- Degradation of Interlaminar Shear Strength for Vinyl-ester under alkaline environments

Figure 3-8-Degradation of Interlaminar Shear Strength for Polyester under alkaline environments

CHAPTER 4 METHODOLOGY FOR CORRELATION BETWEEN ACCELERATED AND NATURAL AGING

In previous chapters, the need for accelerated aging data was addressed and the data available in the literature was presented. To increase the implementation of new materials, it is necessary to know the service and aging behavior in the field. For performance durability understanding, accelerated aging tests were performed under controlled lab environments by many researches. In this chapter, a methodology is presented to correlate the different environments created in the lab and the limited data obtained from the field. The correlation is made by applying the Arrhenius type relationship and following the Time-Temperature superposition principle, and a set procedure developed herein presented in Chapter 5.

In this research, time dependent stresses at different temperatures for different pH environments (Saline, Neutral and Alkaline environments) were taken in order to correlate the accelerated aging data to that of the naturally aged data. The process followed is outlined in Section 4.1.

4.1 Accelerated aging methodology

In addition to recording material behavior under varying chemical and environmental conditions, resistance factors and degradation curves of different materials are needed as the composite age under service conditions. It is crucial to understand long-term aging trends and a range of values of the strength of a material under different conditions. The service life of a structural element fundamentally determines the service life and performance of a structure.

Furthermore, the service life based conditions should be closely examined as they impact the structural performance. However, as FRP composites are relatively new, a vast amount of data which covers long term field performance are not yet available in order to establish the strength reduction factors. To overcome this limitation, an approximate simulation of the lifetime of the material was established by using lab based accelerated aging techniques. By evaluation of the lab based simulation, it is possible to simulate field (longer-term) performance of GFRP composites.

The accelerated aging tests mentioned above consist of subjecting the different structural elements to different levels of temperature and pH solutions for establishing material property degradation under different conditions. Several lab tests run by other researches [Cabral-Fonseca, Correia, Rodrigues, & Branco, 2012; Chen, Davalos, & Ray, 2006; Chin, 2001; Dejke & Tepfers, 2001; Grammatikos, et al., 2016; Hammami & Al-Ghuilani, 2004; Kajorncheappunngam, 1999; Karbhari, 2004; Kim, Park, You, & Moon, 2008; Maru, et al., 2014; Rivera, 2002; Robert, Wang, Cousin, & Benmokrane, 2010; Sen, Mullins, & Salem, 2002; Shi, Zhu, & Wu, 2011; Sonawala, 1996; Vijay P. , 1999; Wang, GangaRao, Liang, & Liu, 2015; Won, Lee, Kim, Jang, & Lee, 2008] at different time periods measuring the desired mechanical properties and obtaining the degradation curves for different environments are evaluated. The accelerated aging data is processed and correlated to naturally aged data. This complete process is done by following the principles established by Litherland, 1981 and Vijay, 1999 whose principles are summarized in the steps below:

1. Test specimens need to be prepared for different environments from where the accelerated aging data is going to be extracted after lab based aging of FRP composites. Usually these environments are more aggressive compared to in-service structural elements. The factors

considered for this research are different variations in pH values, temperature and their combinations.

2. The prepared specimens are tested and evaluated for different mechanical properties. Typically, testing is done in previously established time intervals, the time periods in between each testing should be more frequent at the beginning and could be expanded in time in later experiments.

This research is based on data available in the literature. Therefore, as presented in Chapter 3, the data was collected and prorated to meet an arbitrary sample.

3. After collecting the data from literature, the degradation curves for different environments are created. For these degradation curves, the strength loss has been presented in percentage of ratio of stress to failure of aged sample to the original stress to failure (strength retention) versus the time for the different environments. Plots are usually non-linear, typically presented as logarithmic or asymptotic degradation with the time, as shown in Figure 4-1. In addition, it is exhibited that the degradation is faster and more severe as the temperature increases (GangaRao, Taly, & Vijay, 2006).

These plots are obtained after following the process presented in chapter 3. Different degradation sets after corrections were made (post curing, effect of FVF and the thickness of the specimen) and are presented in Appendix A, in which it can be seen that the majority of data sets displayed asymptotic behavior.

Figure 4-1- Strength retention of aged FRP at different temperatures

4. Following an Arrhenius type relationship, a replot of the degradation curves is required. This replotting method transforms the logarithmic curves into linear curves. For each of the strength retention values (90%, 80%, 70%, etc.), a straight line was fitted for the logarithm of the time needed to reach that particular strength retention versus the inverse of temperature. Normalization of Arrhenius plots provides an overall image of the relative acceleration of the loss of mechanical properties at different temperatures/degradation rate (GangaRao, Taly, & Vijay, 2006). Lines are, generally, parallel for a perfect strength degradation-temperature relationship but that may not be the case in normal practice.
 - As presented in Figure 4-2, the data is plotted with time on the vertical-axis and the inverse of temperature on the horizontal-axis.

Figure 4-2-An Arrhenius plot for temperature- and time-dependent strength retention

Normalization of the curves plotted in

5. Figure 4-2 Normalization of the curves plotted in Figure 4-2, into a single curve. The normalization is made along the vertical axis relative to a reference temperature. The normalization procedure starts by selecting the reference temperature (t_0). In this research, room temperature ($RT=25^\circ\text{C}$) was chosen as the reference temperature.

Once the reference temperature is chosen, the time shift factors are obtained to create the normalized time displacement curve relative to the reference temperature as shown in Figure 4-3, resulting in longer-term degradation curves of the data obtained from the lab. Following Equation 4-1, the Time Shift Factors (TSF) are obtained as a ratio of the degradation time under certain temperatures over the degradation time (up to the same Strength Retention) under the temperature of reference (Silva, da Fonseca, & Biscaia, 2014; GangaRao H. V., 2006).

The degradation times for each of the strength retention levels (90%, 80%, 70%, etc.), are obtained from the degradation curves presented in Figure 4-1. TSF can also be obtained as a ratio of the slopes presented by Arrhenius plots, resulting in a more tedious process and less accurate approximation the curves obtained from the lab data are, generally, not exactly parallel so the variation of the variable “A” in the Arrhenius equation would need to be taken into account, leading to a slight variation of the results.

$$TSF = \frac{t_1}{t_2} = e^{\frac{Ea}{R}(\frac{1}{T_2} - \frac{1}{T_1})} \quad (4-1)$$

Figure 4-3- Normalized time displacement curve (Arrhenius plot) relative to a reference temperature

After arriving to this stage and obtaining the normalized time-displacement curves relative to the temperature of reference (also referred to as the longer term degradation curve for the accelerated aging data under the reference temperature), the work of the accelerated aging data is completed and ready to correlate with the field data, as presented below.

6. Finally, with the shifted plots obtained previously, the natural aging data correlation can be made. A similar normalization to that in the various temperatures presented in steps 4 through 6 is made between the accelerated aging data at room temperature and the naturally aged samples. A good example is presented in Figure 4-4. It should be noted that not enough data points may be available for naturally aged data under various temperatures. A calibration with naturally aged data will be necessary to accurately predict strength reduction under long-term field conditioning.

Figure 4-4-Normalized time displacement curve (Arrhenius plot) with natural weathering data (GangaRao, Taly, & Vijay, 2006).

Using the normalized/calibrated plots, the objective is to predict the loss of mechanical properties over the natural weathering process. Ideally, prediction for a range in between 10 and 100 years of natural aging is desired to obtain a reliable degradation plot and strength reduction factors for design purposes. Having such a long period of degradation time from a field degradation is neither practical nor cost-effective. By following the procedure above, having a shorter field

degradation data and correlating it with the data aged in the lab, the long term degradation can be extrapolated cost-effectively and with less time constraints.

4.1.1 Limitations of the approach

The limitation of this method, is the fact that only one environmental effect is taken into account to correlate the data. This temperature is taken as the basis of the normalization process setting aside other effects such as the pH of the solution used for, accelerated aging moisture absorption, sustained stress to which the structural components could be subjected to or any other agent that could age a GFRP element (Vijay, 1999).

4.2 Arrhenius plots

Normalize Arrhenius plot provides an overall curve of relative loss of accelerated strength or stiffness at different temperatures, as shown in Figure 4-2. As noted earlier, the principal assumption when applying the Arrhenius principle is the degradation mechanism of the materials which does not change with time, but changes with temperature only. In other words, the behavior of materials in the long term has one dominant degradation mechanism, i.e. temperature in this case. Due to this assumption, all temperature regression curves should be presented approximately parallel, with similar slopes. Otherwise the degradation mechanism is also temperature dependent (Silva, da Fonseca, & Biscaia, 2014).

As presented in Appendix C, most plots present a good parallel behavior with reference to temperature. But a few cases have been exhibiting deviation from linear and parallel behavior, which could be related to the fact that there is pH acting on the temperature exposure (sole variation as assumed originally), causing deviation to ideal (linear) degradation response to temperature. Such effect is shown with an example in Figure 4-5, where it is seen that the fit to parallel lines to

the neutral pH is consistent whereas for alkaline environments at lower degradations, the strength retention curves are parallel. At higher degradations however a slight increase in slopes of these curves are observed.

Figure 4-5-Example of pH effect in the deviation of the Arrhenius plots

4.3 Activation energy

Activation Energy (E_a) is known as the difference between the reactant and the transition state. In other words, the energy level that the reactants need in order for a reaction to occur.

Figure 4-6- Activation Energy of a reaction

The transition state is the highest energy state of a reaction, the higher the Activation Energy the more complicated is the reaction to occur (Figure 4-6). As mentioned earlier, the Arrhenius Equation (4-2) is used to obtain the activation energy for the reaction by relating the rate constant with the temperature applied to the system.

$$k = A e^{\frac{-E_a}{RT}} ; \ln k = \ln A - \frac{E_a}{RT} \quad (4-2)$$

Where A is a constant referred as the pre-exponential factor, E_a is the activation energy, R the gas constant and T the aging temperature.

Figure 4-7-Activation energy in the Arrhenius plot

Mentioned earlier in this chapter and shown in Equation 4-2 and Figure 4-7 the activation energy is shown as the slope of the Arrhenius curve when plotting the $\ln k$ versus $1/T$. The steeper this slope is the more susceptible the material's behavior is to temperature changes. In Appendix C the different Arrhenius plots are presented with the respective slope represented in them. In Table 4-1 this slope or activation energy over the gas constant (R) for the different degradation environments is presented. The higher the value shown in the table the higher the activation energy is; thus, the more susceptible the material is to temperature changes under certain strength and pH conditions.

Table 4-1- Activation Energy values for the different aging processed

Resin	Strength	pH	-Ea/R
VE	Tensile Strength	Neutral pH	-0.241
		Saline pH (4-6)	-0.636
		Alkaline (pH=13)	1.301
PE	Tensile Strength	Neutral pH	-1.247
		Saline pH (4-6)	1.049
		Alkaline (pH=13)	-
VE	Flexure Strength	Neutral pH	-1.139
		Saline pH (4-6)	5.178
		Alkaline (pH=13)	-
PE	Flexure Strength	Neutral pH	0.062
		Saline pH (4-6)	2.414
		Alkaline (pH=13)	-
VE	Interlaminar Shear Strength	Neutral pH	4.583
		Saline pH (4-6)	5.327
		Alkaline (pH=13)	1.983
PE	Interlaminar Shear Strength	Neutral pH	2.637
		Saline pH (4-6)	0.414
		Alkaline (pH=13)	0.964

The lower the activation energy values are, lower temperature is needed for the degradation to occur, wherein the time shift factor is less dependent on temperature. For higher activation energy values the time shift factors are more dependent on temperature and the temperature required for degradation is higher than that at lower values of Ea. The results presented in Table 4-1 are not totally consistent with the theory behind. The results for Interlaminar Shear Strength (ILSS) are presenting the most accurate fit to the theory, being neutral pH the environment at

which the highest activation energy is presented. Thus, for developing the degradation under neutral environment, the temperature required is the highest between the studied environments (saline, alkaline and neutral pHs). On the other hand, for alkaline environments it is observed that half the activation energy is required compared to the neutral environments, showing that the presence of the alkalinity in the environment could be helping the degradation to happen at lower temperatures.

When comparing between the behavior of Vinyl-ester (VE) and Polyester (PE) in ILSS, VE showcases higher values of activation energy than PE. Meaning that, at same temperature, the degradation is less likely to happen in VE than in PE, consistent results with those presented in Chapter 3 and Appendix A.

The values for activation energy can be used to determine predominant failure mechanisms under various environments. While models for these predictions have not yet been employed, these failure modes can be determined through comparison of the durability behavior between neat resin coupons and reinforced polymers. This comparison is needed under the assumption of the degradation of GFRP composites being predominantly due to degradation of the matrix or the fiber-matrix interface and not due to degradation of the reinforcing fibers.

4.4Conclusions

The methodology adopted in the research has been presented. The different steps are presented for obtaining long term extrapolation of the behavior of FRP materials in the field by correlating the acceleratedly aged data obtained in the lab in several months, with the sparsely available data from the field over several years. This full process is developed in more detail with the data obtained from the literature in Chapters 5, 6 and Appendices C and E .

In the following chapter, a relationship is obtained between temperature and pH to which the materials were exposed and the Time Shift Factors, closely related to the activation energy. By establishing this relationship in case of having other test data, a quick shift of the new data could be made, avoiding the tedious process presented in Chapter 4.

CHAPTER 5 TIME-TEMPERATURE SUPERPOSITION

Most durability studies take place in controlled laboratory environments where the specimens are subjected to different controlled temperatures, allowing researchers to obtain a long-term degradation of subjected specimens in a relatively short period of time by using the Time-Temperature Superposition (TTS) principle. Such a principle, developed earlier by many authors (i.e. Van Gurp, 1998; GangaRao et al, 2006) has been elaborated in this chapter.

5.1 Time-temperature stress superposition principle

The Time-Temperature Superposition (TTS) principle is predominantly used to establish the behavior of materials under different mechanical properties for longer periods of time than the time used to obtain the original data obtained from the lab. By shifting the behavior of the samples at different temperatures to a referenced temperature, an extrapolation of the degradation plots can be obtained (Van Gurp, 1998). For example, by performing accelerated aging test in the span of 18 months in the lab under different environments and applying the TTS principle, up to 45 years of degradation in the field can be extrapolated.

The strength retention and other properties, i.e. stress relaxation modulus (Figure 5-1), of a polymer composite measured over time under a certain temperature, may be used to relate approximately the behavior of a material's properties under other temperatures. This principle is generally known as the Time-Temperature Superposition principle and is employed to correlate or calibrate naturally aged results of FRPs at ambient temperatures with results from acceleratedly aged specimens (GangaRao, Taly, & Vijay, 2006), implying that the behavior at one temperature can be related to that at another temperature by a change in the time-scale only (Ward, 2004).

This principle is only applicable under the conditions in which the materials are stable and those that do not change the rheological measurements. For example, the TTS is not applicable for temperatures around the glass transition temperature of the polymers (Van Gurp, 1998).

Figure 5-1- Construction of a master curve for the stress relaxation modulus at 25°C reference temperature (Strobl, 1997)

5.2 Time shift factors

Time shift factors (TSF) allow one to normalize the degradation rates of specimens under different environmental into a single time-scale. After the TSF is obtained, the activation energy is calculated and the regression curves can be applied to predict strength retention for natural aging conditions.

5.2.1 Time shift factors vs. temperature

By using an Arrhenius type relationship in the degradation trends in terms of temperature, and as found in Silva et al. 2014 “the time shift factor (TSF) is defined as the ratio between the

times required for a certain decrease in a mechanical property at two different temperatures”, as shown in Equation 5-1.

$$TSF = \frac{t_1}{t_2} = \frac{A \cdot e^{\frac{Ea}{R}(\frac{1}{T_2})}}{A \cdot e^{\frac{Ea}{R}(\frac{1}{T_1})}} = e^{\frac{Ea}{R}(\frac{1}{T_2} - \frac{1}{T_1})} \quad (5-1)$$

Represented in the equation above, t_1 is the time it takes to achieve certain degradation at temperature T_1 , and t_2 is the time to arrive to that same degradation at T_2 (where T_2 is the temperature of reference).

Table 5-1 Example to obtain Time Shift Factors for Vinyl-ester under Interlaminar Shear Strength and Alkaline pH (T2: 25°C-temperature of reference, T3:45°C, T4:60°C)

Degradation times (days)				Time shift factors			
	T2	T3	T4		T2	T3	T4
90%	20	12	11.25	TSF 90%	1	1.67	1.78
80%	40	20	22.5	TSF 80%	1	2	1.78
70%	60	35	33.75	TSF 70%	1	1.71	1.78
60%	85	50	45	TSF 60%	1	1.7	1.89
50%	150	60	56.25	TSF 50%	1	2.5	2.67
40%	300	75	67.5	TSF 40%	1	4	4.44
				TSF (Average)	1	2.263	2.389

In Table 5-1, an example to explain how to obtain the TSF is presented using Equation 5-1. Firstly, the time of degradation for each strength retention level (90%, 80%, 70%, etc.) is extracted from the degradation plots (Appendix A). Using Equation 5-1, TSF for each strength retention level is defined by the ratios of time “ t_1 ” at certain temperature to achieve the strength retention level over that time “ t_2 ” at the temperature of reference to arrive to that same strength retention level (i.e. 90% ,80% ,70% , etc.). The TSF values presented in Table 5-2 are the averages

of the TSF for all the different strength retention levels for acceleratedly aged specimens. The average TSF value shown as TSF (Average) is used to extrapolate plots for another temperature to the reference temperature.

The room temperature (25°C) was taken as reference of temperature for this research, therefore the TSF for that temperature remains constant in every case, as unity. Given that at higher temperatures (always remaining under the glass transition temperature to apply the TTS principle) the degradation rates are higher, the TSF theoretically increase with temperature. The fact that degradation increases with temperature leads to TSFs greater than one (>1) when temperature is higher than the reference. However, the results obtained are not always consistent with this TTS theory. In some of the TSFs presented in Table 5-2 it can be observed that certain values are below unity which means that the degradation at that temperature is less than at the temperature of reference. Given that the temperature of reference is the lowest temperature presented the fact that the degradation is faster under 25°C would not follow the theory behind. Varied reasonings could explain the numbers exhibited in Table 5-2. For example, the effect of pH is not taken into account when applying the Time-Temperature Superposition principle. However, the aging effect of pH levels (to which the samples are subjected to) could explain the disparity of results to some extent. In addition, variations in the manufacturing processes may also affect the test data. Studies used in this report did not provide enough details about the manufacturing process employed, which also led to a wide-spread variation of the strength retention during the accelerated aging process.

Table 5-2- Time Shift Factors for acceleratedly aged samples coming from lab controlled environments

Resin	Strength	pH	Time Shift Factors		
			T=298°K	T=318°K	T=333°K
VE	Tensile Strength	Neutral pH	1.0	0.3	0.9
		Saline pH (4-6)	1.0	-	0.9
		Alkaline(pH=13)	1.0	-	10.4
PE	Tensile Strength	Neutral pH	1.0	1.2	1.4
		Saline pH (4-6)	1.0	1.4	0.6
		Alkaline(pH=13)	-	-	-
EX	Tensile Strength	Neutral pH	-	-	-
		Saline pH (4-6))	1.0	1.2	1.7
		Alkaline(pH=13)	1.0	1.2	3.0
VE	Flexural Strength	Neutral pH	1.0	2.4	6.5
		Saline pH (4-6)	1.0	1.3	0.6
		Alkaline(pH=13)	-	-	-
PE	Flexural Strength	Neutral pH	1.0	1.0	0.8
		Saline pH (4-6)	1.0	2.2	0.9
		Alkaline(pH=13)	-	-	-
VE	Interlaminar	Neutral pH	1.0	3.5	6.6
	Shear Strength	Saline pH (4-6)	1.0	2.4	5.1
		Alkaline(pH=13)	1.0	2.3	2.4
PE	Interlaminar	Neutral pH	1.0	1.1	1.2
	Shear Strength	Saline pH (4-6)	1.0	1.9	2.6
		Alkaline(pH=13)	1.0	1.5	1.7

5.2.2 TSF -temperature relationship

It is important to obtain the relationships between TSF and temperature in order to obtain time shift factors to avoid the tedious process of obtaining Arrhenius plots. It is observed that the relationship between the TSF and the inverse of temperature ($1/T$) should fit in an exponential relationship. The obtained equations for the TSF versus Temperature relationships are presented in Table 5-3 and the plots shown in Appendix D. In these plots, it is noticed that the R^2 values exist as two extremes: either values above 90 percent (i.e. polyester under tensile strength and neutral pH, vinyl-ester under flexure and neutral pH, and both vinyl-ester and polyester under shear and all pH variations) or almost null values (i.e. vinyl-ester under tensile strength and both neutral and saline pHs or polyester under flexural strength and saline pH). Showing that the relationship between TSF and Temperature is either highly accurate fitting in an exponential curve or highly inaccurate. Correcting these values is difficult due to the narrow range of data available for obtaining these relationships.

Overall the best fits were obtained for Interlaminar Shear Strength (ILSS) related time shift factors, as presented in Figures 5-2 and 5-3 .

Figure 5-2 TSF versus temperature relationship for Vinyl-ester under interlaminar shear strength

Figure 5-3 TSF versus temperature relationship for Polyester under interlaminar shear strength

Table 5-3- TSF vs Temperature Relationship for samples coming from lab controlled environments

Resin	Strength	pH	TSF vs T relationship (y=TSF & x=1/T*1000)
VE	Tensile Strength	Neutral pH	$y = 0.055e0.7733x$ $R^2 = 0.0409$
		Saline pH (4-6)	$y = 0.3068e0.3177x$ $R^2 = 0.0482$
		Alkaline (pH=13)	$y = 5E+09e-6.644x$ $R^2 = 1$ (only two data points)
PE	Tensile Strength	Neutral pH	$y = 24.987e-0.964x$ $R^2 = 0.9562$
		Saline pH (4-6)	$y = 0.0181e1.2449x$ $R^2 = 0.2721$
		Alkaline (pH=13)	-
VE	Flexural Strength	Neutral pH	$y = 4E+07e-5.224x$ $R^2 = 0.9806$
		Saline pH (4-6)	$y = 0.0323e1.0634x$ $R^2 = 0.2893$
		Alkaline (pH=13)	-
PE	Flexural Strength	Neutral pH	$y = 0.1251e0.6308x$ $R^2 = 0.6465$
		Saline pH (4-6)	$y = -0.2227x + 2.0776$ $R^2 = 0.003$
		Alkaline (pH=13)	-
VE	Interlaminar Shear Strength	Neutral pH	$y = 8E+07e-5.413x$ $R^2 = 0.9953$
		Saline pH (4-6)	$y = 5E+06e-4.597x$ $R^2 = 0.9943$
		Alkaline (pH=13)	$y = 6173.4e-2.578x$ $R^2 = 0.879$
PE	Interlaminar Shear Strength	Neutral pH	$y = 3.9678e-0.409x$ $R^2 = 0.9623$
		Saline pH (4-6)	$y = 9903.6e-2.736x$ $R^2 = 0.9936$
		Alkaline (pH=13)	$y = -1.8945x + 7.3915$ $R^2 = 0.9537$

5.2.3 Time Shift Factors vs. pH

As presented in section 5.2.1, the effect of pH is perceived to have certain influence when obtaining the relationship between time shift factor and temperature. However, this influence is complicated to formulate because of the overlapping influences of different temperatures and acidity/alkalinity of solutions.

For this study, the shift in terms of pH was not performed as the degradation under saline, alkaline and neutral environments were studied, separately. In the case where the accelerated data needs to be shifted in terms of pH effect, Equation (5-2) may be helpful which uses neutral pH (=7) as a reference.

$$a_{pH} = a_{0T} \left[1 - \frac{abs|7 - pH|}{7} \right] \exp \left[\frac{-\frac{\Delta E}{R} \left(1 - \frac{abs|7 - pH|}{7} \right)}{T} \right] \quad (5-2)$$

5.3 Shift of the accelerated aging data for long term degradation trends

Using the time-temperature superposition principle, the prorated data presented in Chapter 3 was shifted (normalized) to obtain a longer time base as compared to those obtained from the lab. The increase of the duration of the new degradation trends is computed as a multiplication of TSF with the original data sets (Equation 5-3).

$$t_{shift} = t_{original} \cdot TSF \quad (5-3)$$

All shifted data sets are presented in Appendix E, representing the degradation curves as shown in Table 5-4. These degradation curves indicate a logarithmic degradation showing different

values for the coefficient of determination (R^2). Maximum values of R^2 are desired for the degradation curves, though originally some of the values presented were as low as 20 percent. After in depth evaluation of the degradation data, some of the points were assumed to be bad test data. After neglecting the defective data, a minimum R^2 value of 43 percent was found, with an average R^2 value of 68 percent.

In Figures 5-4 and 5-5, the plots of degradation curves are presented for vinyl-ester and polyester respectively. Both polyester and vinyl-ester show similar behavior under normal condition. With regards to the extreme environments (dramatic degradation), the strength retention of Vinyl-ester is higher. As previously stated in this report, Interlaminar Shear Strength (ILSS) is showing the highest degradation rate; as can be noted in the degradation plots presented in Table 5-4 and Figures 5-4 and 5-5. In Figures 5-4 and 5-5 the graphic representation of the degradation curves is presented, to have the whole scatter of obtained data refer to Appendix E. For vinyl-ester, the most detrimental values of ILSS degradation under alkaline environment, indicating a strength retention as low as 26 percent after conditioning for 1.5 years in the lab. Similarly, ILSS degradation for polyester under alkaline environment has the most dramatic strength reduction - presenting a strength retention of 17 percent after conditioning for 1.5 years in the lab.

The results presented may seem dramatic, but it is important to note that accelerated aging is not a direct representation of the behavior of the material in the field. Without a correlation (as given in Chapter 6) between the acceleratedly and naturally aged data, it is difficult to have a good grasp of aging behavior in the field applications.

Table 5-4- Degradation curves for accelerated aging data coming from lab controlled environments, for different resins, mechanical properties and pH environments

Resin, Mechanical Property & Environment		Degradation curve
VE-FS	Saline Env.	$y = -2.398\ln(x) + 89.67$ $R^2 = 0.6544$
	Neutral Env.	$y = -3.088\ln(x) + 96.623$ $R^2 = 0.6682$
	Alkaline Env.	$y = -5.183\ln(x) + 95.696$ $R^2 = 0.9099$
PE-FS	Saline Env.	$y = -2.411\ln(x) + 98.388$ $R^2 = 0.7599$
	Neutral Env.	$y = -3.024\ln(x) + 91.418$ $R^2 = 0.5147$
	Alkaline Env.	$y = -10.99\ln(x) + 95.82$ $R^2 = 0.7949$
VE-ILSS	Saline Env.	$y = -3.218\ln(x) + 95.007$ $R^2 = 0.453$
	Neutral Env.	$y = -3.075\ln(x) + 93.477$ $R^2 = 0.4599$
	Alkaline Env.	$y = -15.24\ln(x) + 122.38$ $R^2 = 0.8978$
PE-ILSS	Saline Env.	$y = -5.021\ln(x) + 95.084$ $R^2 = 0.4324$
	Neutral Env.	$y = -6.992\ln(x) + 83.9$ $R^2 = 0.654$
	Alkaline Env.	$y = -11.4\ln(x) + 89.288$ $R^2 = 0.9389$
VE-TS	Saline Env.	$y = -5.243\ln(x) + 94.317$ $R^2 = 0.7358$
	Neutral Env.	$y = -3.485\ln(x) + 87.566$ $R^2 = 0.6805$
	pH:8-10	$y = -4.292\ln(x) + 101.69$ $R^2 = 0.8403$
	Alkaline Env.	$y = -5.435\ln(x) + 93.573$ $R^2 = 0.6142$
PE-TS	Saline Env.	$y = -3.094\ln(x) + 94.634$ $R^2 = 0.5934$
	Neutral Env.	$y = -3.704\ln(x) + 90.273$ $R^2 = 0.6149$

Figure 5-4-Degradation curves for accelerated aging data related to Vinyl-Ester

Figure 5-5-Degradation curves for accelerated aging data related to Polyester

CHAPTER 6 ANALYSIS OF THE CORRELATION BETWEEN FIELD AND ACCELERATED AGING DATA

Ideally, one would like to use aging data of FRP composites obtained from accelerated aging experiments to predict degradation behavior of naturally aged components because of time and cost factors. Validity of this approach can be examined by comparing data obtained from testing the field samples with the predictions made from accelerated aging experiments and analysis.

Though plenty of accelerated aging data is available as presented in previous chapters, obtaining the field or naturally aged data are the major issues, as majority of the field aged samples stem from structures in service. As one can imagine, aging conditions for in-service structures can be significantly different from accelerated aging conditions. For example, in-service structures are subjected to certain amount of sustained stress and occasionally, UV radiation as a result of exposure to the Sun and undergo temperature and humidity cycling with the changes in weather. In contrast, for accelerated aging tests reported here, temperature, pH and humidity were carefully controlled and kept constant while sustained stress and UV exposure were absent. Therefore, most of the data available in the literature could not be used to correlate field data with lab data for this study. Only useful field data was obtained from Dittenber et al., 2016 where mechanical properties were evaluated after 5 to 22 years of aging. These data are exclusively for glass reinforced vinyl-ester under an environment with neutral pH and room temperature. Furthermore, only two points of data on time scale - one fresh samples and other after several years of aging are available as shown in Appendix B. Data during the early part of aging process are not available which are most useful for performing time-temperature shift analysis. Nonetheless, this data was used to develop degradation curves for naturally aged composite samples. Figure 6-1 shows degradation curves for

lab and field data. Table 6-1 shows corresponding logarithmic expressions relating % retention to aging time in days. As one can see that there is poor correspondence between the accelerated and naturally aged behavior. This can be expected since the data under field aging (natural) is extremely limited and as has been shown in previous chapters, the accelerated aging data has lot of spread in values particularly under longer time exposures.

Table 6-1 Field and Accelerated aging degradation curves for Glass reinforced Vinyl-ester in Neutral pH and Room Temperature conditions

	Field degradation curve*	Accelerated aging curves
Flexural strength	$y = -3.458\ln(x) + 104.14$	$y = -3.088\ln(x) + 96.623$
Tensile strength	$y = -2.52\ln(x) + 102.66$	$y = -3.485\ln(x) + 87.566$
Interlaminar Shear strength	$y = -4.762\ln(x) + 100.39$	$y = -3.075\ln(x) + 93.477$

*only two data points are used

However, to correlate the accelerated and field aging presented above, a similar procedure as that used to correlate the accelerated aging data based on Time-Temperature Superposition (TTS) principle can be utilized. As presented in Table 6-1, the degradation curves can be represented by semi-logarithmic expressions relating % retention with aging times in days. Thus, it can be proposed that similar expressions as represented by Equations 6-1 and 6-3 can be used to express degradation curves for field and lab environments, respectively, assuming that theoretically at the beginning of aging ($t = 0$ days) the strength retained by the GFRP samples is total ($\sigma_{retention} = 100\%$). Then in Equation 6-5, the TSF for these correlations is defined as the time taken by a specimen in the field to achieve a determined strength retention level (Equation 6-2), over the time

it would take the same sample to arrive to that same strength retention level under accelerated aging (Equation 6-4).

For naturally aged data:

$$\sigma_{nat} = a \ln(time_{nat}) + b \ln(time) + b \quad (6-1)$$

$$\text{or,} \quad time_{nat} = A \exp\left(\frac{\sigma_{nat}-b}{a}\right) \quad (6-2)$$

For acceleratedly aged data:

$$\sigma_{acc} = c \ln(time_{acc}) + d \ln(time) + d \quad (6-3)$$

$$\text{or,} \quad time_{acc} = A \exp\left(\frac{\sigma_{acc}-d}{c}\right) \quad (6-4)$$

$$TSF = \frac{t_{natural}}{t_{accelerated}} \quad (6-5)$$

Now two different approaches are presented to obtain the TSF to correlate accelerated with naturally aging of GFRP specimens. In the first approach the exact values retrieved from the degradation equations are used. In the equation presented in Table 6-1 “*b*” and “*d*” (constants of the logarithmic equation for the natural and accelerated aging curves, respectively) are not 100, but suffered a slight variation due to the data obtained from the literature and the applied corrections. In second approach, an approximation where the theoretical values of “*b*” and “*d*” ($b = d = 100 \%$) are taken. An expression for TSF can be obtained by combining equations 6-

1 to 6-5 which is given as Equation 6-6. Equation 6-6 can be further simplified to Equation 6-7 if b and d are taken to be 100. The comparison between the TSF for the two approximations is presented in Table 6-2. It can be seen that the approximation is reasonably close to the exact values, with a maximum variation of 9.6 percent.

$$TSF = \frac{t_{natural}}{t_{accelerated}} = \frac{\exp\left(\frac{y-b}{a}\right)}{\exp\left(\frac{y-d}{c}\right)} = \exp\left(\frac{ad - cb + y(c-a)}{ac}\right) \quad (6-6)$$

$$TSF \cong \exp\left(\frac{(y-b)(c-a)}{ac}\right) \quad (6-7)$$

Table 6-2 TSF for the accelerated aged and field data correlation

		Approximation			Exact		
Strength Retention (%)		ILSS	FS	TS	ILSS	FS	TS
Time Shift Factors	100	1.0	1.0	1.0	1.1	1.0	1.0
	90	3.2	1.4	3.0	3.5	1.4	3.1
	80	10.0	2.0	9.0	11.1	2.0	9.2
	70		2.8			2.9	
	Average	4.7	1.8	4.3	5.2	1.8	4.4

Figure 6-1 Accelerated and natural aged samples degradation plots for vinyl-ester under neutral pH

Figure 6-2 Predictions for naturally aged data using accelerated aging data and time shift factors for vinyl-ester under neutral pH

Degradation vs time curves using the approach previously presented are shown in Figure 6-2 by correlating natural aging data with acceleratedly aged data, previously presented in Table 6-1 and Figure 6-1. It should be noted that this data is applicable only for long-term degradation of glass reinforced vinyl-ester composites under neutral pH and room temperature and must be used as an example of applicability of the proposed approach.

Equations 6-1 and 6-4 can be combined to obtain Equation 6-8 which shows that the strength retention under natural aging follows the same trend with respect to time as the accelerated aging samples but at a different time scale, where the time under natural degradation equals to TSF multiplied by accelerated aging time as expressed in Equation 6-9.

$$\sigma_{nat} = a_{acc} \ln(TSF \text{ time}_{acc}) + b_{acc} = a_{acc} \ln(TSF \text{ time}_{acc}) + 100 \quad (6-8)$$

$$t_{nat} = TSF t_{acc} \quad (6-9)$$

However, it can be noted that the TSF obtained and presented in Table 6-2 appear to be smaller than the values normally presented in literature for the correlation between acceleratedly and naturally aged samples. From the TSF values obtained, it may be said that a day of accelerated aging in the lab corresponds to 1.8 to 4.7 days of degradation in the field. In some research studies (for example, Vijay, 1999) TSF values as high as 30 are exhibited. This implies that undergoing 18 months of exposure in lab under controlled environments (as the ones presented in this research) would lead to an extrapolation of 85 months (7 years) of degradation in the field for a TSF of 4.7. Whereas using TSFs ≈ 30 , 540 months (45 years) of degradation in the field could be extrapolated with the same amount of data from the lab.

The major limitation in relating the long term natural degradation from field data to accelerated aging laboratory data is that: accuracy in obtaining the time shift factors at early periods of exposure to pH or temperature and consequent degradation cannot be obtained due to the lack of detailed data available from the naturally aged samples in their early service life. For example, the field data obtained from the tested samples in the study by Dittenber et al 2016, the second data point was recorded after 12 years of aging where the specimens would have arrived at the plateau zone of the semi-logarithmic curve, but the degradation curve during the early years is missing but which is most crucial for determining the time shift factors for the correlation. For more accurate results, property measurements during natural aging tests should be conducted more often during the initial aging stage as the degradation rates are generally higher and the degradation rates plateau out as time advances. A recommended testing procedure is presented in section 7.5 showing recommended testing times. Having the data of the degradation at early aging in a natural environment will allow us to obtain a better correlation with the accelerated aging data so that better prediction about the TSF can be made.

With only two data points for natural aging and the correlation presented in this chapter, the strength retentions obtained for the long-term field data are as presented in Table 6-3. For a 100 year design service life, the strength retention presented by vinyl-ester samples under neutral pH is of 66 percent for flexural strength, 63 percent for interlaminar shear strength and 58 percent for tensile strength. Without taking into account the statistical variability of the data and the fact that the correlation is made only from two data points of natural aging, the strength reduction factors to calculate the design nominal strength (Equation 6-10) are presented in Table 6-4.

$$\phi \cdot R \geq \gamma \cdot Q \quad (6-10)$$

Table 6-3 Estimated strength retention in the field for Vinyl-ester and neutral pH after correlation between acceleratedly and naturally aged data

Strength retention in the field (%)			
time (years)	VE-FS	VE-ILSS	VE-TS
5	75	72	69
10	73	70	66
25	70	67	63
50	68	65	61
75	67	63	59
100	66	63	58

Table 6-4 Estimated strength reduction factors for Vinyl-ester under neutral pH and a 100 year design service life

Strength Reduction Factor “ϕ”	
Flexural Strength	0.65
Interlaminar Shear Strength	0.60
Tensile Strength	0.58

From the analysis above it can be concluded that there is a critical need for the collection of more natural aging data particularly during the early stages of aging to develop better correlations and validate the TSF approach. Additional limitations and needs are identified in Chapter 7.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 *Summary*

With the constant evolution of technology, new and advanced materials such as Fiber Reinforced Polymer (FRP) composites are continuously being developed as structural materials and systems. In recent years, the demand to substitute conventional construction materials such as steel or concrete with more advances in materials has grown, for both the new construction and rehabilitation. This growth is a product of the improved thermomechanical characteristics that composite materials offer compared to conventional counterparts. Nonetheless, FRP composites are also susceptible to degradation under both physical and chemical aging. For the increased implementation of these materials in design, it is important to enhance knowledge base (behavior, aging, design, etc.) of FRP composites so that they withstand at least 75 to 100 years of service life.

For a more optimal research of the behavior of FRPs under harsh environments, several tests were conducted after weathering in lab controlled environments under different temperatures and pH solutions. Following the proposed correlation between the acceleratedly aged samples in the lab with data originating from field conditioned samples, a procedure to establish long-term degradation trend(s) is suggested. The method employed to obtain the correlation proposed in this thesis was presented first in Litherland et al. (1981) and Vijay (1999).

Firstly, the data was collected for both acceleratedly and naturally aged samples. In the case of this research due to time constraints, data was extracted from the literature, corrections were applied (post-curing issues, effect of the Fiber Volume Fraction (FVF) and thickness of the coupon on strength retention of the tested specimens) and data was prorated to a 50% FVF and a 0.5 cm

thick sample. Data was collected for vinyl-ester and polyester resins reinforced with glass fibers and under tensile strength (TS), flexural strength (FS) and interlaminar shear strength (ILSS). ILSS was shown to be the most dramatic mechanical property of degradation under aging. In terms of environments, the extreme alkaline environment showed the biggest decrease in strength at early ages between the pH environments (saline, neutral and alkaline solutions) that have been evaluated under this study. The drastic loss in strength produced under alkaline environment creates concerning results as concrete is commonly used in civil structures. The pore water present in concrete while curing may give pH values up to 13.5 weakening the composites used as reinforcement within concrete structures.

With respect to field data, collecting naturally aged data proved a major issue due to limitations of the research. The primary limitation imposed by the research when collecting naturally aged data was the samples not to be subjected to effects other than pH and/or temperature. Most of the available data in the literature for naturally aged specimens presented were of structures in service, thus involving sustained stress; which became a burden when gathering data from the field.

After all the data was collected and evaluated, the acceleratedly aged data was correlated in terms of the temperature of reference in order to obtain a longer-term degradation plot. This correlation was made by the Time-Temperature Superposition principle following the Arrhenius equation, obtaining Time Shift Factors and shifting the acceleratedly aged data according to the room temperature (25°C) chosen as temperature of reference.

A similar process was employed to correlate the field and lab data. Using the field data as reference, the data from the lab resulted in an extrapolation of the long-term behavior of the studied materials in the field. Lack of data for the short-term naturally aged samples led to an inaccurate

result of the Time Shift Factors for the correlation between the data from the field and data coming from lab tests.

A main consideration for future studies, is the collection of natural data as it is needed to acquire an accurate view of the extrapolation of the lab data in relation to the real behavior in the field. In addition, the determination of the strength reduction ϕ factors include the statistical variability of the results in order to make this research applicable in the design codes and standards.

7.2 Conclusions

Upon studying the durability behaviors of GFRP composites under harsh environments (pH and Temperature) for their broader application in civil infrastructure, following conclusions are drawn:

1. The Arrhenius type relationship is chosen as the best model to represent the degradation behavior of GFRP composites, as their degradation curves exhibit an asymptotical shapes with time.
2. Non-Arrhenius type relationships is not observed. When making the shifting in terms of pH groups, a slight tendency to a variation from the linear Arrhenius might be observed. This trend was not developed further or established to evaluate the fit to a non-Arrhenius relationship.
3. In the available acceleratedly aged data, vinylester is shown to retain its original strength better than polyester under harsh environments.
4. Interlaminar shear strength presents the most dramatic decrease in strength retention from all mechanical properties observed.

5. For the majority of accelerated aging specimens, extreme alkaline pH solutions are shown to be the most concerning environments when conditioning GFRP composites.
6. For all the conditionings, stiffness was assumed to stay nearly constant over the aging periods.
7. Good parallel fits were shown for the Arrhenius plots, witnessing a slight deviation of this parallel behavior at higher degradations for high pHs. Representing a possible influence of pH apart from the influence of temperature at higher degradations and end of the aging process.
8. To obtain the failure mechanism of the GFRP composites under various environments, following the assumption that failure corresponds to degradation of the matrix and/or the fiber-matrix interface, the activation energy values obtained and presented in Chapter 4 would need to be compared to activation energy values of neat polymers under the same circumstances.
9. Room temperature (25°C) was adopted as the reference temperature to the accelerated aging superposition and extrapolation of longer degradation curves.
10. Time shift factors (TSF) show an increase with an elevation of the conditioning temperature. TSF values as high as 10 were observed for acceleratedly aged data correlations.
11. With the narrow data available in the literature for natural aging, only the correlation for Vinyl-ester under neutral pH was conducted. This correlation held maximum TSF values of approximately five, which was considered to be an extremely low value. The lack of natural weathering at early degradation renders the obtained values as inaccurate.

12. Further data collection is needed for a successful completion of obtaining the strength reduction factors for design purposes.
13. The procedure presented in Chapter 4 resulted in a good approximation to develop the longer-term degradation for accelerated aging data, obtaining up to ten times longer degradations for the accelerated aged specimens by the exposure to higher temperatures. On the other hand, the methodology to correlate the field and the lab data did not work as expected due to the limitations of field data. Regardless of the quality of the field data the procedure produces a good simulation of the long-term behavior of the GFRP composites in the field.
14. Under the strong limitations (Section 7.3) under which this research was conducted, the confidence level of the results is strong for not having performed the lab testing. With all the data collected from the literature, the long term accelerated degradation curves fit to a logarithmic equation to R^2 from 43% up to 94%.
15. Considering only two data points for the field behavior and after correlating them to the data obtained in the lab, the strength reduction factors obtained for glass reinforced Vinyl-ester under neutral pH are presented in Table 7-1.

Table 7-1 Strength reduction factors for Vinyl-ester under neutral pH and a 100 year design service life

	Strength Reduction Factor “ϕ”
Flexural Strength	0.65
Interlaminar Shear Strength	0.60
Tensile Strength	0.58

16. The confidence level presented for the obtained strength reduction factors is not as good as it would be desired to be presented in design codes and standards. To improve the reliability of these values higher volume of naturally aged data is required.

7.3 Limitations of the research

The major limitation for this study was the time constraints which necessitated conducting the study with data collected from the literature. In certain instances, the reporting of all the testing conditions, geometry or characteristics of the specimens were not as complete as they would have been if directly obtained by the interested party or the author in this case.

With the data collected primarily from external sources to WVU, this narrowed the information available about the tested specimens from majority of the studies. There were also gaps in information relating to the manufacturing of the samples. Because of this, the influence of the manufacturing process on the specimens was not considered for the degradation study, which could have led to instances of data variability found in some of the results.

A similar issue to the manufacturing is founded in relation to stiffness. Due to a lack of information in the majority of the sources on documenting the stiffness of the samples tested, the influence of the stiffness variable has not been taken into account.

All of the above presented issues, may lead to non-exact representation of the true values and could be one of the reasons as to why some of the results obtained, present slight deviations of the expected values.

7.4 Recommendations

With the objective of achieving a complete analysis on the durability of FRP composite research, special attention should be placed on the gathering of more naturally aged data. As noted previously, the lack of field data concerning the implementation of composites without sustained stress, exposes on of the weaknesses in this research study.

Several in progress studies at West Virginia University aim to provide a complete view of the durability of composites and their application in civil infrastructure, improving the overall implementation of FRPs. For broader understanding of material aging, different environmental factors (i.e. freeze-thaw cycles, moisture absorption, UV radiation, sustained stress, etc.) and their effect on aging should be accounted for both the experimental and theoretical studies. Together with the different environmental effects, also other materials should be taken to study. In this research, two types of thermoset matrices (vinyl-ester and polyester) reinforced with glass fibers were evaluated. However, all thermoset materials should be investigated, ranging from thermosets to thermoplastics and the behavior of other fiber reinforcements such as carbon or natural fibers.

Strength reduction Phi “ ϕ ” factors need to be determined to ensure reliability of design of fiber reinforced polymer composite materials in civil structures. The procedure to obtain these “ ϕ ” factors is presented in Appendix F.

7.5 Recommendation for test procedures

As addressed along the document, non-consistency in the elaboration of the tests has been a burden all along the process of the durability study. For both, the lab controlled and the testing for naturally aged samples, frequency at which tests are made needs to be higher in the early

degradation and can be slowed at later stages of the aging process. Different testing rates are recommended for the two aging methods as presented in the subsections 7.5.1 and 7.5.2.

7.5.1 Recommendation for accelerated aging testing

In the results presented in Appendix A it is observed that the accelerated aged specimens exhibit a substantial decrease of strength in the first 30 to 60 days of aging, achieving at that time the plateau zone for the degradation rate. Under this case scenario, the testing timing does not necessarily need to be extended as much as 18 months, but it would be preferable to concentrate the testing efforts in the initial period of aging while the variability on the degradation rate is relatively high.

That said the testing times recommended during the aging process are as follows:

- Controlled samples at 0 days of aging to establish the reference of 100% of strength retention of the tested specimens.
- To have a close follow up of the high drop in strength retention in the beginning of degradation process the testing times recommended are 1, 4, 7, 14, 21, 30, 45 and 60 days of aging.
- After arriving to the plateau zone of degradation rate it is convenient to have some test to ensure that the strength retention of the tested specimens remains relatively constant. Test at 90, 150, 210 and 300 days of aging are recommended. If the behavior is showing a clear constant strength retention at 150 days of aging, the last two testing times could be disregarded.

WVU-CFC is currently taking this testing procedure to ensure that with a close monitoring of the initial 30 to 60 days of degradation, a good grasp of the degradation behavior of GFRP composites can be obtained.

7.5.2 Recommendation for natural aging testing

For the case of naturally aged samples, the process is similar but with the testing expanded in longer periods of time. The main difference with the lab controlled environment is that the knowledge of the behavior of the degradation pattern presented by GFRP specimens under natural aging is basic, therefore it is complicated to determine the approximate time at which the plateau zone of degradation rates is achieved.

Given that the point at which the degradation rates slows down is not accurately known, the testing for naturally aged specimens needs to be performed at a more constant frequency. The recommended testing timings are as follows:

- Controlled samples at 0 days of aging to establish the reference of 100% of strength retention of the tested specimens.
- As previously presented for the specimens aged in lab controlled environments, the testing frequency needs to be higher at initial stages of degradation and slowed down when the recorded strength retention values are approximately constant. During the first months of aging the recommendation would be to test after 1, 3, 6, 10, 14, 20, 30, 50 and 70 weeks of aging, obtaining a track of the strength retention over the first 1.5 years.
- Following the high testing frequency of the initial degradation, the testing rate can be slowed down to get strength retention values after 3, 6, 10, 15 and 20 years of aging. If further data is considered to be needed every 10 years a control test can be performed to ensure the arrival to the plateau zone of the degradation rates.

For the case of specimens aged under natural environment conditions, the determination of the time at which the plateau zone of degradation rates needs to be closely followed to ensure that

after 1.5 years this behavior has already been adopted. The testing timing can vary if the researcher considers that further information is needed to determine the arrival to the constant strength retention.

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APPENDIX A. PRORATED DATA

The collected data from the literature is presented in this appendix. The presented data has been previously corrected in terms of post-curing, effect on strength on FVF and thickness of the samples, as indicated in Chapter 3. The data available in the literature was prorated to a sample of 50% FVF and 0.5 cm thick. The presented plots are a result for the different collected samples under the conditions specified in the title of each Figure. The plots are presented in function of different temperatures for a certain matrix, mechanic property and pH.

The terms used in the Figures presented are described in Table A- 1, for referring the resin type used in each graph, Vinyl-ester is referred as “VE” and Polyester as “PE”.

Table A- 1 Notation for terms presented in the degradation plots

Mechanical Property notation	Temperature notation	pH notation
		– P1: acidic pHs between 0 and 4
		– P2: Saline environments, pHs between 4 and 6
– ILSS: Interlaminar Shear Strength	– T1: -10 to 15 °C	– P3: neutral pHs from 6 to 8
– TS: Tensile Strength	– T2: 15 to 40 °C	– P4: pHs between 8 and 10
– FS: Flexure Strength	– T3: 40 to 60 °C	– P5: Alkaline environments between 10 and 14
	– T4: above 60 °C	

The sources from which the data have been obtained are as follows:

1. (Cabral-Fonseca, Correia, Rodrigues, & Branco, 2012)
2. (Chen, Davalos, & Ray, 2006)
3. (Chin, Hughes, & Signor, 2001)
4. (Dejke & Tepfers, 2001)

5. (Grammatikos, et al., 2016)
6. (Hammami & Al-Ghuilani, 2004)
7. (Kajorncheappunngam, 1999)
8. (Karbhari, 2004)
9. (Kim, Park, You, & Moon, 2008)
10. (Maru, et al., 2014)
11. (Rivera, 2002)
12. (Robert, Wang, Cousin, & Benmokrane, 2010)
13. (Sen, Mullins, & Salem, 2002)
14. (Shi, Zhu, & Wu, 2011)
15. (Sonawala, 1996)
16. (Vijay, 1999)
17. (Wang, GangaRao, Liang, & Liu, 2015)
18. (Won, Lee, Kim, Jang, & Lee, 2008)

A.1 Vinyl-Ester

A.1.1 Interlaminar shear strength

A.1.2 Tensile strength

A.1.3 Flexural strength

A.2 Polyester

A.2.1 Interlaminar shear strength

A.2.2 Tensile strength

A.2.3 Flexural strength

APPENDIX B FIELD DATA

The available data for naturally aged data is presented in this Appendix. Under the limitations presented by the research for this research, the narrow data for field weathering samples resulted for Vinyl-ester under neutral pH.

#SAMPLE	THICKNESS (in)	YEAR OF MANUFACTURING	AGE (years)	AGE (months)
1	0.212	1993	21	252
2	0.252	1992	22	264
3	0.254	2004	10	120
4	0.26	2002	12	144
5	0.374	2002	12	144
6	0.22	2002	12	144
7	0.126	2005	9	108
8	0.219	2002	12	144
9	0.246	2005	9	108
10	0.375	1995	19	228
11	0.431	2004	10	120
12	0.143	2003	11	132
13	0.308	2009	5	60
14	0.375	2009	5	60

B.1 Flexural data

Sample #	FVF	t0	TIME (months)	Original strength	Aged strength	%Original	%Aged	Notes
1	38.2	0	252		39.29			Missing original str
2	45.4	0	264		55.06			Missing original str
2 web	38.7	0	264		53.48			Missing original str
3	45.2	0	120		54.5			Missing original str
3 web	49.1	0	120	66.1	60.96	100	92.223	
3 web/trans	49.1	0	120		17.65			Missing original str
4	44.4	0	144	59.9	61.83	100	103.22	Post Curing. Data neglected
4 web/trans	40.7	0	144	21.9	22.16	100	101.18	Post Curing. Data neglected
5	52.7	0	144	51.61	47.37	100	91.784	

5 web	45.7	0	144	43.69	45.44	100	104.00	Post Curing. Data neglected
6	43.3	0	144	81.7	40.54	100	49.620	
7	47.6	0	108		57.54			Missing original str
8	39.4	0	144	53.86	39.77	100	73.839584	
9	44.8	0	108	67.5	70.05	100	103.77	Post Curing. Data neglected
9 web	49.7	0	108	72.2	84.77	100	117.40	Post Curing. Data neglected
10	37.8	0	228		46.63			Missing original str
10 web	37.9	0	228		47.08			Missing original str
10 web /trans	37.9	0	228		14.01			Missing original str
11	53.9	0	120	38.2	45.14	100	118.16	Post Curing. Data neglected
12 sun side	43.9	0	132	66.82	49.05	100	73.406	
12 earth side	43.9	0	132	66.82	48.02	100	71.864	
13	46.3	0	60		55.82			Missing original str
13 trans	46.3	0	60		9.53			Missing original str
14	38.7	0	60		28.27			Missing original str
14 web	39.6	0	60		229.31			Missing original str
14web /trans	39.6	0	60		14.42			Missing original str
15	43.3				51.27			Missing original str

B.2 Tensile strength

Sample #	FVF	t0	TIME (months)	Original strength	Aged strength	%Original	%Aged	Notes
1	38.2	0	264	36.11	59.64	100	165	Post Curing. Data neglected
2	45.4	0	120	37.78	59.18	100	157	Post Curing. Data neglected
2 web	38.7	0	120	34.15	39.49	100	116	Post Curing. Data neglected
3	45.2	0	144	53.7	40.48	100	75	
3 web	49.1	0	144	53.7	47.75	100	89	
4	44.4	0	144	41.7	42.81	100	103	Post Curing. Data neglected
5 web	45.7	0	144	39.38	35.03	100	89	
6	43.3	0	144	63.41	52.69	100	83	
7	47.6	0	108	-	65.31			Missing original str
8	39.4	0	144	59.98	48.3	100	81	
9	44.8	0	108	54.8	67.84	100	124	Post Curing. Data neglected
9 web	49.7	0	108	60	72.41	100	121	Post Curing. Data neglected
10	37.8	0	228	-	36.87			Missing original str
10 web	37.9	0	228	-	33.14			Missing original str
11	53.9	0	120	38.4	40.54	100	106	Post Curing. Data neglected
12 sun side	43.9	0	132	45.6	36.26	100	80	
12 earth side	43.9	0	132	45.6	34.15	100	75	
13	46.3	0	60	-	56.08			Missing original str
13 trans	46.3	0	60	-	4.78			Missing original str
14	38.7	0	60	-	30.45			Missing original str
14 web	39.6	0	60	-	29.35			Missing original str
14web/trans	39.6	0	60	-	38.6			Missing original str

B.3 Interlaminar Shear Strength

Sample #	FVF	t0	TIME (months)	Original strength	Aged strength	%Original	%Aged	Notes
1	38.2	0	264	-	4237			Missing original str
1 transverse	38.2	0	264	-	1859			Missing original str
2	45.4	0	120	-	3330			Missing original str
2 web	38.7	0	120	-	2615			Missing original str
2 web/trans				-	1946			Missing original str
3	45.2	0	144	8177	5049	100	61.74	
3 web	49.1	0	144	8177	5003	100	61.18	
3 web/trans	49.1	0	144	-	2829			Missing original str
4	44.4	0	144	5230	4339	100	82.96	*
4 transverse				-	2814			Missing original str
4 web/trans	40.7	0	144	-	2389			Missing original str
5	52.7	0	144	8366	3778	100	45.15	
5 web	45.7	0	144	5284	3335	100	63.11	
5 web/trans				-	3084			Missing original str
6	43.3	0	108	5509	4172	100	75.73	
6 trans				-	2417			Missing original str
7	47.6	0	144	-	5148			Missing original str
7 trans				-	1939			Missing original str
8	39.4	0	108	7310	4338	100	59.34	
8 trans				-	2172			Missing original str
9	44.8	0	228	5040	4502	100	89.32	*,

9 web	49.7	0	228	4690	4950	100	105.54371	Post Curing. Data neglected
9 web/ trans				-	2507			Missing original str
10	37.8	0	120	-	4239			Missing original str
10 web	37.9	0	120	-	2638			Missing original str
10 web/trans	37.9	0	120	-	19331			Missing original str
11	53.9	0	132	4287	3906	100	91.11	*
11 trans				-	3118			Missing original str
12 sun side	43.9	0	60	-	4176			Missing original str
12 sun trans				-	4029			Missing original str
12 earth side	43.9	0	60	-	3661			Missing original str
12 earth trans				-	4498			Missing original str
13	46.3	0	60	-	3205			Missing original str
13 transverse	46.3	0	60	-	1409			Missing original str
14	38.7	0	0	-	2551			Missing original str
14 web	39.6	0	0	-	2677			Missing original str
14web/trans	39.6	0	0	-	1736			Missing original str
15	43.3			-	4332			Missing original str

* Post curing could be assumed as the data is out of average and in the rest of strength post curing happened

APPENDIX C ARRHENIUS PLOTS

As mentioned in Chapter 4, the Arrhenius plots obtained from the previously presented degradation plots is shown in this Appendix.

C.1 Vinyl-ester Arrhenius plots

C.1.1 Tensile Strength (TS)

C.1.2 Flexural Strength (FS)

C.1.3 Interlaminar Shear Strength (ILSS)

C.2 Polyester Arrhenius plots

C.2.1 Tensile Strength (TS)

C.2.2 Flexural Strength (FS)

C.2.3 Interlaminar Shear Strength (ILSS)

APPENDIX D TIME SHIFT FACTOR-TEMPERATURE RELATIONSHIPS

To be able to get time shift factors to different temperatures and be able to extrapolate the TSF related to different temperatures the relationship between TSF and temperature was obtained and presented as can be seen in the figures below.

APPENDIX E ACCELERATED SHIFTED DATA FOR LONG TERM DEGRADATION TRENDS

After obtaining the Time Shift Factors for the different cases presented in Chapter 5, a longer-term degradation curves are extrapolated for the acceleratedly aged samples and presented in this Appendix.

APPENDIX F .DETERMINATION OF STRENGTH REDUCTION FACTORS “ ϕ ”

Ongoing research at West Virginia University (WVU) indicates the process used to determine the strength reduction factors Phi “ ϕ ” in design codes, which is based on reliability indices of probabilistic approaches. Determining these factors involves the adoption of the “probability of failure” criterion under the different circumstances.

The “probability of failure” criterion suggests that in practice, the occurrence and consequences of accident can be associated with certain risk level, which is established in the design codes and standards. A zero-risk level is unlikely to be reached, thus a residual risk level needs to be determined by a combination of cost, safety and public reaction resulting from failures (CEN, 2004).

In previous codes, the deterministic methods were used to compute the different factors of safety which often resulted in non-uniform probability of failures.

The structural reliability method attempts to select a ϕ factor for the structural design strength “ R ” that will provide an appropriate and uniform probability of failure when the structural element is subjected to the Q load effect, as can be seen in Equation F-1.

$$\phi \cdot R \geq \gamma \cdot Q \quad (F-1)$$

The modification factor, γ , has already been tabulated in most of the Load and Resistance Factor Design (LRFD) codes, so the main interest falls back onto obtaining the ϕ factor for structural components made of materials different from the conventional, as FRP composites.

The method to determine the ϕ factors is as follows:

1. Select the reliability index β . Most of the codes in the United States and Canada have adopted an acceptable reliability index of 3.5 or higher. This index is a theoretical value for probability of failure of approximately 1 in 5,000.
2. Develop probability density functions of the material properties used to compute “R” using the data from lab tests or the given by the manufacturer. Instead of developing the probability density functions for each design parameters, mean values, bias factors and standard deviation are used.
3. Select the common design situation (span length, loading, environment, member size, etc.) in which ϕ factor will be used. Some parameters are assumed to be constant, whereas others could be variable in the probability density functions. For example, the span length of the structure is assumed to be a precise parameter whereas the yield strength (F_y) or a distributed load (w) are assumed to be variable.
4. Write the reduced limit state design equation in terms of the variables. Compute mean values and standard deviations for the variables. For example:

$$G(w, F_y) = \phi \cdot R - \gamma \cdot Q \quad (\text{F-2})$$

5. Select a trial value for ϕ . 1.0 is a good reference point to be able to compute a nominal value of β , leaving the reduced limit state equation in terms of the variables. Continuing with the previous example, where a_1 and a_2 are computed constants:

$$G(w, F_y) = a_1 \cdot F_y - a_2 \cdot w \quad (\text{F-3})$$

6. Having obtained the mean value (μ) and standard deviation (σ) of the different parameters, compute the nominal β and compare it to the target value. In simplistic form, it can be computed as:

$$\beta = \frac{a_1 \cdot \mu(F_y) - a_2 \cdot \mu(w)}{\sqrt{a_1 \cdot \sigma(F_y)^2 - a_2 \cdot \sigma(w)^2}} \quad (\text{F-4})$$

7. Adjust φ doing an iterative process of steps 5 and 6 until obtaining a β close to the objective.
8. For the different cases repeat steps 3 to 7 and obtain the corresponding values of φ for each one.
9. Select a conservative value of φ .

The obtained strength reduction “ φ ” factors account for the statistical variability of the strength values along the designed service life, or 75 to 100 years. The available values for the φ factors are considered to be conservative by many experts. By following the process presented in this thesis, an overall view of the different durability researches is given in order to obtain more rational values for the strength reduction factors for design purposes. To have the most accurate approximation to the optimal *phi* factors the maximum available data is needed, either of accelerated data or naturally aged samples.