GFRP erosion depth model under alkaline solution erosion

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Abstract. Based on the physical phenomenon of the fiber reinforced polymer material after the erosion of the liquid medium, the erosion law of the liquid medium on the FRP is analyzed. And considering the anisotropy of the FRP material, a FRP point source erosion depth model based on Fick's law is proposed. Taking the glass fiber reinforced polymer (GFRP) in alkali solution as an example, we carried out GFRP corrosion and aging test in alkaline solution, and the erosion depth of GFRP specimens was measured at 30, 90, 180, 360 and 720 days, respectively. At the same time, the water absorption rate of GFRP was used to calculate the erosion diffusion coefficient of solution medium. Through the comparison between the experimental value of erosion depth and the calculated value of erosion depth model, the error between the experimental data and the calculated data is within 10%, and the overall regularity is consistent. It shows that the erosion depth model of liquid medium proposed in this paper is reasonable and has high accuracy.

1. Introduction

Currently, FRP is being researched and applied more and more extensively in the field of civil engineering due to their excellent mechanical properties, good corrosion resistance and durability, designability of material properties, and thermal expansion coefficient similar to that of concrete [1-3]. In civil engineering, FRP structures are often subjected to various harsh environments, such as dry and wet alternating environment, hot and humid environment, ultraviolet radiation, freezing and thawing environment, acidic and saline environment, etc. One or more environmental factors affect the service life of FRP and thus the use of FRP is affected to different degrees, so the research on FRP durability is especially important [4-5]. According to different environmental factors, domestic and international scholars have made many achievements on the durability of FRP’s in aging environments.

The relationship between FRP ultimate strength, elastic modulus, elongation and aging time was studied to measure the durability performance of FRP sheets by the reduction of ultimate strength, and the aging model and material degradation law under different environments were established. Zhao Yan [6] and G.M. gunyaev [7] proposed a composite strength prediction equation based on the Gouniev median aging equation, and further established a mathematical relationship between the high confidence and high reliability natural aging life and residual strength of fiber composites by linear regression analysis using the aging test data at each moment. Based on William's [8] empirical model, Sun Bo et al. [9] conducted bending tests on fiber composites at different temperatures and different aging cycles through moist-heat aging, and the attenuation model of fiber composites under moist-heat aging was obtained through the test data and the introduction of interface parameters. On the basis of
Wiederhorn's \cite{10} empirical equation, Haibao Lu \cite{11}, Yang Zhao \cite{12} and Guanzheng Liu \cite{13} studied the effects of swelling and temperature on corrosion life, and proposed a corrosion life prediction model in relation to temperature, humidity, stress, swelling volume change rate and fiber composite factors. Guo Chunhong \cite{14}, Zhang Yanhong \cite{15}, and Yang Yongxin \cite{16} studied the decay of mechanical properties of fiber composites under various aging environments, and proposed to compare and analyze them with the existing results through bilinear model and parabolic-linear model, respectively, where the parabolic-linear model has higher accuracy and fewer computational parameters.

At present, most scholars evaluate the durability index of FRP by measuring the mechanical properties of FRP before and after environmental aging. They use the FRP strength index degradation model or elastic modulus index degradation model to reflect the change rule of FRP durability, and discuss and study the durability. In addition, in order to directly show the durability of FRP, the author team conducted many related FRP durability test, such as: through tensile nondestructive test and destructive test durability analysis \cite{17-19}, through the study of FRP corrosion degree test method \cite{20}, etc., on this basis, this paper studies the liquid medium FRP under erosion depth, the mathematical model for erosion depth as the evaluation index study provide a theoretical basis for the evaluation of the durability of the method.

2. Mechanisms of FRP erosion in liquid media

The corrosion of FRP includes physical and chemical aspects \cite{21}. Physical erosion is affected by environmental factors such as aging, UV radiation, or long time mechanical effects, such as penetration and diffusion of solution into FRP, which causes the material to absorb moisture and swell, resulting in the degradation of FRP performance; chemical erosion refers to the chemical reactions between FRP components and external environment or solution ions, including hydrolysis, oxidation, degradation, etc., which causes the polymer chains to break, and the large molecule chains to split into small molecule chains. This results in the degradation or even failure of FRP performance.

The erosive effect of the liquid medium on the resin: firstly, the solution enters the resin under the diffusion effect. The resin absorbs moisture and swells, the resin properties change, and due to the different expansion coefficients of the resin and fiber, resulting in the resin and fiber interface bonding deterioration. Different aging conditions, the same material moisture absorption rate and maximum moisture absorption of different; the same humidity conditions, the higher the temperature, the greater the moisture absorption rate, the higher the maximum moisture absorption \cite{22}. According to the theory of moisture absorption, as moisture absorption proceeds, the resin slowly reach moisture absorption equilibrium, the material reaches the maximum amount of moisture absorption, theoretically, the mechanical properties of materials gradually stabilized at a certain value, while the actual environment, the mechanical properties of materials will continue to decline at a slower rate, until the complete destruction. Second, the chemical reaction between the solution and the resin. The solution enters the resin through diffusion, and the chemically active groups contained in the resin react with the solution medium, resulting in the breakage of its polymer chain \cite{23-24}. When the solution medium is strong acid, strong base, the damage to the resin material is serious \cite{25-26}, such as:

1) Strong acid: If the base material contains ether bond, the ether bond reacts with chloride ion Cl(\(\text{HCl}\)) to hydrolyze ether bond, the reaction equation is as follows:

\[
\text{C} - \text{O} - \text{C} + \text{HCl} \rightarrow \text{C} - \text{OH} + \text{Cl}
\]

2) Strong alkali: If the base material contains ester bond, the saponification reaction between ester bond and hydroxide ion OH\(\) (\(\text{NaOH}\)) takes place, the reaction equation is as follows:

\[
\text{C} - \text{O} - \text{C} + \text{NaOH} \rightarrow \text{C} - \text{ONa} + \text{C} - \text{OH}
\]

The fiber is the supporting framework of the fiber reinforced polymer material and is the main
load-bearing part of the material. The fiber is wrapped by the resin, but the ionic solution can enter through pores and cracks and interact with the fiber in FRP, which leads to the deterioration of the bond between the fiber and the resin interface \cite{27}. Therefore, the durability of fiber is also a factor that can not be neglected in the durability of composite materials. Fibers in the production and processing process of surface undulation, uneven diameter, or a number of pores, notches, cracks and impurity particles, environmental solution medium permeate the material inside, it will spread rapidly along the cracks, and promote the formation and expansion of cracks, so that a series of physical and chemical changes in the fiber, the fiber surface blistering, holes, fiber dissolution and other erosion phenomena, thereby destroying the fiber structure, affecting the performance of the fiber, reducing its ability to effectively transfer the load. Carbon fiber due to the composition of a more stable, generally not easy to erode; and glass fiber, basalt fiber contains some Si, Mg, Al and other elements, when the solution is immersed in a chemical reaction with the solution, resulting in fiber destruction \cite{28-29}.

3. Liquid media erosion depth model for FRP

When FRP is eroded in the liquid medium, the liquid medium diffusion follows Fick's second law \cite{30}, from the external high concentration region to the internal low concentration region, the diffusion rate and concentration difference is related to the material's own diffusion coefficient, and during the erosion process, the internal deterioration due to physical hygroscopic swelling and chemical reaction of the medium accelerates the erosion rate of the liquid medium \cite{31-32}. For the erosion of FRP, the relevant erosion depth model is established based on Fick's second law and basic assumptions.

3.1. Basic assumption

In order to facilitate the study of the erosion depth model of FRP in liquid medium, the following basic assumptions are made for the model:

(1) Permeation of liquid media in FRP follows Fick's second law; and the diffusion coefficient at constant temperature does not vary with erosion time;

(2) The fibers in FRP are evenly distributed and the resin wraps around the fibers evenly to form a whole, with uniform performance at all points in the same direction;

(3) The boundary of FRP subjected to erosion is semi-elliptical.

Parallel to the fiber direction and perpendicular to the direction of erosion speed is different, according to the research achievements of the author team early \cite{20}, when we start erosion control from the point of sample with glass fiber reinforced plastic section (Figure 1), think erosion along the point to the glass fiber reinforced plastic internal development, erosion boundary for half the oval, vertical erosion depth of oval short half axis value, width of lateral erosion is the oval window axis value. The ratio of the long axis of the ellipse to the short axis of the point source erosion section remains unchanged.

(4) When the liquid medium diffuses into the interior of the FRP, we consider a point to have been eroded when the accumulated concentration at that point is just enough to chemically interact with the fiber or resin components of the FRP to reach a critical equilibrium concentration for the reaction, and the distance from that point to the outermost layer is the depth of erosion.

3.2. Erosion depth model

3.2.1. The basic form of the model

According to basic assumptions 2 and 3, the point source erosion depth model is semi-elliptical as shown in Fig. 1, and the erosion zone can be expressed as equation (1):

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1(x \in [-a,a], b \in [-b,0])$$

(1)
Fig.1. Point source corrosion depth model

The depth of erosion is the short axis radius b of the ellipse and the erosion transverse aperture is the long axis radius a of the ellipse.

Based on the results of previous studies \cite{20,33-34}, the main factors influencing the erosion depth of FRP in liquid media are the concentration of liquid media ($C_0$), diffusion coefficient ($D$), erosion time ($t$), and temperature ($T$). That is, the erosion depth ($Y$) can be expressed as a function of the concentration ($C_0$), diffusion coefficient ($D$), erosion time ($t$), and temperature ($T$) of the liquid medium.

Based on assumption 1, Fick's law is used to describe the macroscopic law of the phenomenon of diffusion of matter \cite{35-36}.

$$\frac{\partial C_0}{\partial t} = \frac{\partial}{\partial Y} (D \frac{\partial C_0}{\partial Y})$$

(2)

In the equation: $C_0$ is the concentration of the liquid medium ($mol/L$); $Y$ is the depth of the erosion point (mm); $t$ is the time of diffusion (d); $D$ is the diffusion coefficient of ions in the liquid medium ($mm^2/d$), which is related to the material properties, external environment and other factors.

$C_0$ is the liquid medium concentration, at any point $Y$ inside the FRP, there are corresponding initial and boundary conditions,

$$C(Y, t = 0) = 0, \quad C(Y = 0, t) = C_0.$$

Brought into the equation (2), then the concentration of the medium at this point at the moment ($t$) is related to it’s own material properties, external environmental concentration, temperature, time, etc., can be expressed by the equation (3).

$$C_{Y,t} = f(C_0, D, t, T \cdots) = C_0 [1 - erf\left(\frac{Y}{\sqrt{4D \cdot t}}\right)]$$

(3)

In the equation: $erf(\mu)$ is a Gaussian error function whose general expression is $erf(\mu) = \frac{2}{\sqrt{\pi}} \int_0^\mu e^{-\theta^2} d\theta$.

Based on assumption 4, we introduce a critical equilibrium concentration ($C'$), when a point is at a distance from the outermost layer $Y'$, the co-accumulated ion concentration at the moment $t'$ is just enough to reach the reaction equilibrium with the fiber or resin components in the FRP, and the depth of the point is considered to be the depth of erosion. Under the determined conditions, equation (3) can be inverted, then the erosion depth $Y'$ at the moment $t'$ can be obtained by calculating equation (4).

$$Y' = erf^{-1}(1 - \frac{C'}{C_0}) \cdot \sqrt{4D \cdot t}$$

(4)

In the equation: $Y'$ for the erosion depth (mm); $C_0$ for the concentration of the liquid medium ($mol/L$), $C'$ for the ion concentration at the value of the erosion depth $Y'$ at the time of $t'$ ($mol/L$); $D$ for the diffusion coefficient of ions in the liquid medium ($mm^2/d$); $t$ for the erosion time (d); $T$ for the ambient temperature, generally expressed in absolute temperature ($K$).

3.2.2. Critical equilibrium concentration $C'$

The erosion of FRP in liquid medium includes the erosion of fiber and resin. Due to the diversity of resin components, the degradation of resin in solution is a series of complex physical and chemical processes, the specific mechanism of degradation is not very clear, and physical aging is the main...
factor affecting the performance of resin \textsuperscript{[37-39]}. Based on the basic assumption (2), it can be known that the resin fiber is composed of a uniform whole, with the same performance at each point. Among them, the transformation or loss of a certain component can be manifested as the change of erosion depth. Therefore, the critical equilibrium concentration \((C')\) of FRP can be determined by the equilibrium constant \(K_c\) of the chemical reaction equation. The equilibrium constant \(K_c\) of the chemical reaction equation refers to the constant ratio obtained by dividing the product of the stoichiometric powers of the concentration of each product by the product of the stoichiometric powers of the concentration of each reactant under certain conditions when the reversible reaction finally reaches the equilibrium state (temperature, pressure, media concentration, material properties, etc.).

For example: the erosion of GFRP in alkali solution is mainly the reaction between glass fiber and \(OH^-\), when \(OH^-\) penetrates into GFRP, when the depth is \(Y'\), the \(OH^-\) ion concentration accumulates to \(C'\) just to satisfy the reaction equilibrium with \(SiO_2\) in GFRP. From the chemical reaction equation, when it is assumed that the \(OH^-\) ion concentration involved in the reaction at depth \(Y'\) is \(C_f\), and the concentration of \(SiO_3^{2-}\) generated is half of the \(OH^-\) ion concentration involved in the reaction \(C/C_2\), then the critical concentration \(C'\) can be solved by the equilibrium constant:

\[
K_c = \frac{[SiO_3^{2-}]}{[OH^-]^2} = \left(\frac{C_f}{2}\right)^2 \frac{C - C_f}{C'}^2 \tag{5}
\]

In the equation: \([SiO_3^{2-}]\) is the concentration of \(SiO_3^{2-}\) (mol/L); \([OH^-]\) is the concentration of \(OH^-\) (mol/L).

Transforming equation (5), the equation (6) for \(C'\) and \(C_f\) is:

\[
C_f = \frac{2C' + \frac{1}{2K_c} \pm \sqrt{(2C' + \frac{1}{2K_c})^2 - 4C'^2}}{2} \tag{6}
\]

By means of equation (6), the critical equilibrium concentration \(C'\) can be calculated.

3.2.3. Diffusion coefficient of liquid media \(D\)

The diffusion coefficient \(D\) is the mass or number of moles of a substance diffusing vertically through a unit area in the direction of diffusion per unit concentration gradient per unit time, depending on the type of diffusing substance and diffusion medium and its temperature and pressure.

For the diffusion coefficient of the liquid medium in FRP, its size mainly depends on the type of diffusion medium and FRP and the temperature and pressure of the environment. By measuring the hygroscopicity of FRP specimens, the diffusion coefficient of liquid medium in FRP can be calculated using equation (7) \textsuperscript{[40-41]} under the condition of determining the temperature, which has the advantages of convenience, speed and measurability.

\[
D = \pi \left(\frac{d}{4M_\infty}\right)^2 \left[\frac{M_{t_2}}{t_2} - \frac{M_{t_1}}{t_1}\right]^2 \tag{7}
\]

In the equation: \(D\) is the diffusion coefficient of ions in the FRP material (mm\(^2\)/s); \(M_\infty\) is the equilibrium hygroscopicity of the sample (%); \(d\) is the cross-sectional thickness (mm); \(M_{t_1}\) is the hygroscopicity of the sample at \(t_1\) (%); \(M_{t_2}\) is the hygroscopicity of the sample at \(t_2\) (%).

The critical equilibrium concentration of the reactants is calculated according to the chemical equilibrium constant after the equilibrium ion concentration of the products produced by the reaction between FRP and solution medium is determined by the test; Secondly, the moisture absorption rate of FRP in solution is used to solve the diffusion coefficient of the material under certain conditions; finally, the erosion depth model can be used to obtain the erosion depth of FRP under the erosion of liquid medium after determining each parameter.
4. Model validation

4.1. Experimental design

4.1.1. Test environment
Refer to the method recommended in ACI440.3R-12 \[42\] for the preparation of alkali solutions, with specific environmental factors: 3% mass fraction of \(\text{NaOH}\) solution, room temperature of \((25\pm2)\) ℃, and relative humidity \(\geq 50\%\).

4.1.2. Specimen fabrication
The specimen is designed as shown in Fig. 2, with dimensions of 200mm×100mm×35mm, prepared by GFRP, and a transverse notch is cut in 1/3 of the short side of the GFRP specimen, the depth of the notch is 2mm and the width is 4mm, the surface of the specimen is coated with protective layer to ensure that the alkali solution test program is designed to penetrate only in the notch area.

The specimens were immersed in 3% \(\text{NaOH}\) solution, the alkali solution erosion box was closed to reduce solvent evaporation, and the solution was replaced every month to ensure a constant concentration of solution \(\text{OH}^-\) ions. Test the erosion depth of the GFRP specimens in 3% \(\text{NaOH}\) solution for 0, 30, 90, 180, 360 and 720 days, respectively. When the specimens reached the erosion time point, the GFRP specimens were removed from the alkali solution environment, wiped and dried, and then cut by a cutting machine along the top of the specimens at the designed cutting position to obtain the slices of GFRP specimens with different erosion times.

![Fig.2. Specimen of GFRP](image)

4.1.3. Erosion depth observations
To observe and record the phenomenon of local variation in the observation area of the slice notch, with the initial moment serving as the original control. At the initial moment, the whole surface of GFRP section is light green, and as the GFRP specimen is immersed in alkali solution for a longer period of time, a whitening area gradually appears on the section. The size of the whitening part spreads from the notch to the interior of the specimen and increases with the increase of aging time, while the speed of development of the whitening part along the horizontal is faster than the vertical development, using 150x microscope to observe the local erosion region from the notch, the specific imaging situation is shown in Fig. 3.

![Fig.3. Erosion depth observations](image)
4.2. Analysis of results
Initially, we observed whether there was any obvious change in the sectioned notch area by visual inspection, took photos to record imaging, and the sectioned specimens are shown in Fig. 4. Then the slices were gridded, and eroded by AutoCAD at 30, 90, 180, 360 and 720 days. The erosion areas of the days, known to be 100mm×35mm in section area, divided the observation area into a grid composed of 0.2mm×0.2mm. Observe the area occupied by the chromatic aberration part of the notch part, estimate the proportional number of eroded area to the grid, convert to the corresponding size, and the result is shown in Table 1.

![Fig.3. 150 times magnification of the local area of the notch](image)

**Fig.4. Depth of cut surface erosion**

| Time / d | Left side erosion width / mm | Right side erosion width / mm | Depth of erosion / mm |
|----------|-----------------------------|-------------------------------|----------------------|
| 30       | 1.7                         | 1.6                           | 0.3                  |
| 90       | 2.6                         | 2.3                           | 0.5                  |
| 180      | 4.5                         | 4.2                           | 0.8                  |
| 360      | 5.8                         | 5.4                           | 1.0                  |
| 720      | 8.1                         | 7.8                           | 1.5                  |
4.3. Validation of results

According to the test in this paper, check the "Thermodynamic Data Book of Inorganic Materials" [43], when $T \leq 80^\circ C$, the reaction equilibrium constant $K_c$ does not change much, can be approximated as $K_c=0.015$. Through the test, it is determined that when the distance from the outermost $Y'$ at the $OH^-$ concentration involved in the reaction $C_f=1.0\times10^{-5}$(mol/L), the concentration of the generated $SiO_3^{2-}$ to reach $0.5\times10^{-5}$(mol/L). The relationship between $C'$ and $C_f$ is shown in Figure 5 by solving equation (6) to find the concentration of $OH^-$ ions $C'=0.0183$ (mol/L) at this point of the cumulative diffusion into the GFRP at the distance $Y'$ between the inner and outermost layers of the GFRP.

![Fig.5. Relationship between $C'$ and $C_f$](image)

The concentration of $OH^-$ in the external alkali solution of this test, $C_i=0.75$(mol/L), is brought into the equation, then there is $(1-\frac{C'}{C_0})=0.9756$, and the Gaussian error function is obtained:

$$erf^{-1}(1-\frac{C'}{C_0})=1.59$$

When predicting the corrosion depth of GFRP in alkali environment, the diffusion coefficient $D$ is taken as $D=2.794\times10^{-4}mm/d$, based on the durability safety consideration, and the change of diffusion coefficient $D$ with time is not taken into account under certain conditions such as temperature.

Through the equation (4) calculation, the depth of erosion of GFRP in 30, 90, 180, 360 and 720 days can be obtained, the test value and the equation calculation values are shown in Table 2.

| Time / d | Test value / mm | calculated value / mm | Error / % |
|----------|-----------------|-----------------------|-----------|
| 30       | 0.30            | 0.29                  | -3.33     |
| 90       | 0.50            | 0.50                  | 0.00      |
| 180      | 0.80            | 0.71                  | -11.25    |
| 360      | 1.00            | 1.01                  | 1.00      |
| 720      | 1.50            | 1.43                  | -4.67     |

The results of the test test and the calculation results of the model in this paper have a high consistency in the overall law, as shown in Fig.6, the equation to calculate the erosion depth value is slightly smaller, but the overall agreement is better, accurate calculation.
The $OH^-$ ion concentration of GFRP in the erosion test of alkali solution at 25℃ is in the range of 0.1~1.0mol/L. By analyzing the performance of GFRP under different concentrations of solution, we can get the depth change of GFRP under erosion of PH=13~14 solution with time as shown in Figure 7. After discussing and analyzing the erosion depth of GFRP under different concentrations of alkali solutions, the erosion depth model can provide a basis for predicting and analyzing the erosion depth value of GFRP with aging time.

5. Conclusion

(1) The erosion depth model of GFRP under the corrosion of alkali solution established in this paper comprehensively considers the effect of the concentration $C_0$, diffusion coefficient $D$, erosion time $t$ and temperature $T$ of liquid medium on the erosion results, which can directly express the erosion depth of FRP under the erosion of liquid medium.

(2) The experimental validation shows that the erosion depth model in this paper has good accuracy.

(3) Considering the similarity of the erosion laws of different media on FRP, the model in this paper can be used to calculate, analyze or evaluate the erosion degree of other kinds of FRP under different environmental effects, and provide the theoretical basis for the prediction and study of FRP durability.

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