Experimental Study on Durability of FRP Tendon under Acid - Base Erosion in Civil Engineering

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The use of new corrosion resistant materials can improve the durability of the structure. This material can solve the serious problem of steel corrosion, and can effectively extend the useful life of the project, thereby saving resources. This paper studies the durability of CFRP tendon under acid and alkali corrosion, and reveals the variation of CFRP tendon under the action of corrosion, so as to provide theoretical basis for the durability design of CFRP tendon. In this case, reasonable structural durability theory and design can be determined, and work efficiency of FRP tendon in harsh conditions can be guaranteed. This paper studies the durability of CFRP tendon, analyses the durability of CFRP tendon in acid and alkali conditions, and proposes effective schemes to carry out reliable test process. Firstly, under room temperature, the corrosion test was carried out in the NaOH solution (0.2mol/L, 0.1mol/L, and 0.05mol/L). The water absorption and mass loss of the CFRP tendon were measured. Based on the data extraction and analysis, the corrosion mechanism of FRP tendon under alkaline erosion was found. Secondly, under room temperature, the corrosion test was carried out in the HCL solution (0.2mol/L, 0.1mol/L, and 0.05mol/L). The water absorption and mass loss of the CFRP tendon were measured. Based on the data extraction and analysis, the corrosion mechanism of FRP tendon under alkaline erosion was found. Finally, under room temperature, the corrosion test was carried out in the chemical medium HCl solution and NaOH solution, and the tensile strength of the CFRP tendon was measured at 60d and 120d respectively. The law of corrosion of CFRP tendon can be obtained under the data collected by the test.

1. Introduction

The current steel consumption is about 430 million tons. There is a huge loss of corrosion behind the demand, it is estimated that the world every year due to corrosion scrap steel equipment equivalent of 30% of steel production. In 1969, the British "Hoar" reported that annual corrosion caused at least £ 1,365 million in losses to the UK. In 1975, the US National Bureau of Standards (NBS) survey announced that the United States the loss of steel corrosion reached to 70 billion US dollars (Choi and Souri, 2015). China's annual economic loss caused by corrosion is also very alarming. China's steel corrosion losses accounted for 3% to 4% of the national economic net output (GDP).

As we all know, materials, energy and information are the three pillars of modern civilization. Corrosion is an important part of material research. In order to solve the problem of reinforced concrete structure caused by corrosion, domestic and foreign scholars have carried out a lot of experimental research, and take a variety of forms to make up for this defect. Fiber reinforced polymer has been produced as a new type of composite material. FRP tendon is made up of tens of thousands of fibers and resins (Ghosh et al., 2015). The fiber diameter is between 6 and 15 μm. In the civil engineering structure, the FRP tendon includes carbon fiber reinforced polymer (CFRP), glass fiber reinforced polymer (GFRP), and aramid fiber reinforced polymer (AFRP). When the FRP tendon are subjected to external loads, due to their mechanical properties, the fibers and resins will transfer the load pressure to the adjacent fibers to achieve the common load. Compared with steel, FRP tendon has a high strength - mass ratio, small elastic modulus, good fatigue, small stress relaxation, and good corrosion resistance. In addition, FRP tendon has a non-magnetic, and it can greatly reduce the formation of electrochemical environment. For the corrosion of alternative steel bars, it provides a great help (Xie and Ozbakkaloglu, 2015).

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2. Analysis of FRP tendon composite properties

2.1 Analysis of FRP tendon fiber properties

(1) Carbon fiber material
Carbon Fiber Reinforced Polymer is also called CFRP tendon. According to the precursor fiber raw materials classification, CFRP can be divided into polyacrylonitrile-based carbon fiber, asphalt-based carbon fiber, twist-based carbon fiber and meteorological growth carbon fiber.

In the air of 200~290 °C, the carbon fiber will begin to produce oxidation reaction. When the temperature is higher than 400 °C, there is significant oxidation. The form of oxide loss is CO, CO2. Therefore, the heat resistance of carbon fibers in air is worse than that of glass fibers. The oxidation resistance of high modulus carbon fibers is significantly higher than the high strength type. If treated with 30% acid, the antioxidant capacity will be improved. The strong oxidant can remove the oxygen radicals that oxidize the surface carbon, so that the bonding properties of the carbon fiber surface are improved (Napoli et al., 2015; Wang and Cheng, 2015; Ciampi et al., 2016; Sibillio et al., 2016).
Carbon fiber can only be oxidized by strong oxidants, the general effect of acid and alkali on it is very small. So it has better corrosion resistance than glass fiber. Carbon fiber composite materials have good water resistance, and it has characteristics of oil resistance, anti-radiation and slowdown neutron motion.

(2) Glass fiber material
Glass Fiber Reinforced Polymer is also called GFRP tendon, and it consists of glass fiber and matrix. Glass is composed of Si O2 and various metal oxides, which belong to the amorphous ionic structure material. SiO2 is the main component of glass, it can form the basic skeleton of glass, and it has high melting point (Esposito et al., 2016; Li et al., 2017; Liu et al., 2016; Sarno et al., 2017; Yu and Liang, 2016).

The strength of the glass fiber after soaking in water will be reduced. After drying, some of its strength will be restored, but the strength of the other part of the loss is irreversible. The former is the strength loss, which is caused by the physical effect of water on the glass fiber, so it is reversible. The latter is also the strength loss, which is caused by the chemical reaction of water and glass fiber, so it is irreversible. The chemical reaction equation is as follows:

\[
-\text{Si} - \text{O} - \text{Na} + \text{H}_2\text{O} \rightarrow -\text{Si} - \text{OH} + \text{Na}^+ + \text{OH}^- \quad (1)
\]

\[
-\text{Si} - \text{O} - \text{Si} + \text{OH}^- \rightarrow -\text{Si} - \text{O} - - - \text{Si} - \text{OH} \quad (2)
\]

\[
-\text{Si} - \text{O} + \text{H}_2\text{O} \rightarrow -\text{Si} - \text{OH} + \text{OH}^- \quad (3)
\]

From the above equation can be learned that the greater the amount of alkali, the faster the rate of glass fiber erosion. In addition, if there are micro-cracks in the fiber, the durability of glass fiber will be greatly reduced. Under the synergistic effect of stress and water, the crack tip will be enlarged. In general, glass is a good corrosion-resistant material. Glass can be corrosive by hydrofluoric acid, but it has good corrosion resistance to acids, bases, salts and organic solvents.

(3) Aramid fiber material
Aramid includes meta-aramid polyamide fiber and p-aramid polyamide fiber. The p-aromatic fiber has high strength and high modulus, which is used as advanced composites. Kevlar fiber belongs to this category. Kevlar fiber has many types, including Kevlar-29, Kevlar-49, Kevlar-68, Kevlar-100, Kevlar-129, Kevlar-149 and Kevlar M/B. These products have different applications. Kevlar is mainly used in reinforced rubber and reinforced plastic products. Kevlar-29 is mainly used in ropes, cables, belts and bullet-proof facilities. Kevlar-49, Kevlar-119 and Kevlar-149 are used in composites.

2.2 Analysis of FRP tendon basic properties

(1) The basic components and effects of matrix materials
The polymer is the main component of the matrix, which has a direct effect on the technical performance of the composite, the molding process and the price of the product. Resins are often used as synthetic composites, which have high mechanical properties, dielectric properties, aging resistance and corrosion resistance. In the meantime, it has good process characteristics.

The phenolic resin can be cured under heating without the addition of a curing agent, and the acid and alkali can promote the curing reaction. Resin curing process has a small molecule precipitation, so resin curing needs to be carried out under high pressure, and curing volume shrinkage will be increased. The cured resin has good compressibility, water resistance, high temperature resistance and chemical resistance. But it has a low elongation at break, large brittleness, so phenolic resin is often used in powder compressed plastic, short
fiber reinforced plastic. It can also be used in glass fiber composites and ablative materials. But it is rarely used in carbon fiber and organic fiber composites (Driscoll et al., 2016).

The matrix material is a continuous phase which joins a single fiber as a whole, so that the individual fibers are co-supported in order to exhibit the properties of the reinforcing material. When the composite material is stressed, the force is transmitted through the matrix to the fiber. Therefore, the substrate can carry an equilibrium load and transfer load. The fibers can withstand the pressure under the support of the matrix. Moreover, the substrate can withstand fiber bending. In the production and application of composite materials, the matrix can protect the fiber and prevent fiber wear.

(2) Corrosion resistance analysis of matrix materials

The chemical medium can penetrate into the polymer, and react with the polymer, so as to cause the polymer to swell. It can produce salts, hydrolysis, saponification, sulfonation, oxidation and nitrification, which causes the main valence bond breakage and cracking. These reactions cause the polymer to be etched, resulting in a decrease in performance. In general, the resin has a large degree of cross-linking and good resistance to medium corrosion. Therefore, when the thermosetting resin is cured, it is necessary to control the degree of curing. Low curing will seriously affect its corrosion resistance. The ability of curing resin to resist water, acid, alkali and other media is mainly related to the hydrolytic activation energy of its hydrolyzed groups in the corresponding acid-base medium. The hydrolysis reaction can be shown in Table 1. The higher the activation energy is, the higher the hydrolysis resistance energy is (Zhao et al., 2016).

<table>
<thead>
<tr>
<th>Group type</th>
<th>Medium</th>
<th>Amide bond</th>
<th>Imide bond</th>
<th>Ester bond</th>
<th>Ether bond</th>
<th>Siloxane bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>activation energy</td>
<td>Acid</td>
<td>~83.6</td>
<td>~83.5</td>
<td>~75.2</td>
<td>~100.2</td>
<td>~50.1</td>
</tr>
<tr>
<td>i/(Kj/mol)</td>
<td>Alkaline</td>
<td>66.9</td>
<td>66.9</td>
<td>58.4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The corrosion resistance of the epoxy resin varies depending on the curing agent. An ester bond formed by curing with an acid anhydride is not resistant to alkali, —O— and C—N located in amine cured epoxy resin, which can be hydrolyzed by strong acid, weak acid and organic acid. Different amine curing agents have different cross-linking type and resin corrosion resistance. Resin cured by aromatic diamine has volume shielding effect. So its acid and alkali resistance are better than aliphatic amine curing agent. Phthalic anhydride curing epoxy resin has good acid resistance.

In polymer composites, the properties of the composite matrix play a decisive role in corrosivity. The degree of corrosion depends on: the nature of the material itself, the environmental conditions (temperature, pressure, the nature and state of the contact medium), and the time in a given environment.

According to the above conditions, the main form of corrosivity can be summed up.

①Under the action of active medium, media molecules may react with macromolecules, such as oxidation, hydrolysis. It can cause the macromolecules to be destroyed and cracked.

②Solvent molecules can destroy the secondary bonds of macromolecule, and result in solvent reaction.

③Under the action of stress and medium, the material will crack and generate brittle fracture.

④Infiltration damage. Some of the material in the material will diffuse from the inside of the solid, migrate, and dissolve into the environment medium to deteriorate the material. The details are shown in Figure 1.

![Figure 1: Corrosion mode of polymer](image-url)
3. Experiments on the durability of FRP tendons

3.1 Experimental program

In the condition of the feasible and scientific settings, the equipment and reagents used in the test are shown in Table 2.

Table 2: Instruments and reagents

<table>
<thead>
<tr>
<th>Instruments</th>
<th>Number</th>
<th>reagent</th>
<th>Concentration(mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
<td>1</td>
<td>NaOH</td>
<td>0.05/0.1/0.2</td>
</tr>
<tr>
<td>drying baker</td>
<td>1</td>
<td>NaOH</td>
<td>0.05/0.1/0.2</td>
</tr>
<tr>
<td>volumetric flask</td>
<td>6</td>
<td>HCL</td>
<td>0.05/0.1/0.2</td>
</tr>
<tr>
<td>etch tank</td>
<td>6</td>
<td>HCL</td>
<td>0.05/0.1/0.2</td>
</tr>
<tr>
<td>tester</td>
<td>1</td>
<td>Assembly glue</td>
<td>---</td>
</tr>
</tbody>
</table>

18 CFRP tendon sample were made and the original mass was weighed with a balance, and place it in a volumetric flask of NaOH solution and HCl solution. Under the room temperature, measure the weight after 30d, 60d, 90d, 120d, 150d and 180d. The material was dried by DHG-9240A electric heating oven. The number of drying is twice, each time sustains two hours. Constant weight is recorded, the water absorption and mass are measured, and the rate of corrosion of the CFRP tendon is obtained. In this experiment, CFRP helical surface gluten was used. The composition materials were shown in Table 3.

Table 3: Components of CFRP tendon

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Resin</th>
<th>Plasticizer</th>
<th>Fiber content</th>
<th>Resin content</th>
</tr>
</thead>
<tbody>
<tr>
<td>12K carbon fiber</td>
<td>epoxy resin</td>
<td>anhydride</td>
<td>65%</td>
<td>35%</td>
</tr>
</tbody>
</table>

3.2 Corrosion mechanism and data analysis of CFRP tendon

(1) Alkaline environment

Due to the structural properties of the carbon fiber, the CFRP tendon hardly reacts with the NaOH solution. Corrosion is caused by the interaction between the resin and the medium, which includes physical and chemical effects. Physical action refers to the resin adsorption medium caused by swelling, resulting in resin structure is destroyed. Chemical action refers to the chemical bonds of resin molecules are destroyed, resulting in decreased performance. So the chemical structure is the main reason for the ability of resin to resist solvent medium. Polarity, electronegativity and solvation capacity all affect chemical resistance. NaOH solution can be chemically reacted with acid anhydride curing agent - ester bond saponification, which has an irreversible effect on the composition of CFRP tendon. Therefore, the water absorption and quality of the CFRP tendon are changed. The corrosion principle is as follows:

Figure 2: The trend of water absorption of CFRP tendon

Figure 2 is drawn from the data on the water absorption of CFRP tendon. In the 0~60d, the water absorption rate of CFRP tendon increased continuously. Different concentrations of NaOH solution have different increasing trend. When the concentration is 0.1mol / L, the water absorption is the largest. When the concentration is 0.2mol / L, the water absorption is the smallest. In the 68th days, the water absorption of CFRP tendon reached the maximum in NaOH solution. With the increase of corrosion time, the water absorption began to decrease. In the 130th day, the water absorption of CFRP tendon was reduced to the minimum. According to the concentration of NaOH solution, the influence of water absorption on CFRP tendon within 120 days is shown in Figure 4.
When the concentration of NaOH solution is 0.11 mol/L, the influence rate of CFRP bars is the highest. Under room temperature, the corrosion rate of CFRP tendon is the fastest. Corrosion reaction is most active, molecular motion is intense and unstable.

(2) Acid environment
The CFRP tendon is immersed in the acid solution. Carbon fiber has good stability, so it does not react chemically with HCl. In addition, it can absorb a certain amount of water, and result in a reversible physical effect and irreversible chemical effect. After the ether bond is hydrolyzed, the product will remain in the interior of the specimen and the surface of the specimen, resulting in an increase in mass. At the later stage of corrosion, the HCl solution itself undergoes a weak chlorination reaction. The reaction can produce chloride ions, resulting in ether bond hydrolysis. After the hydrolysis of the ether bond and the chlorination reaction, the ether bond has a complex irreversible effect on the CFRP tendon specimen.

Figure 3 is obtained by integrating the recorded data. It shows the trend of water absorption of CFRP tendon. The water absorption of CFRP tendon in HCl solution is similar to the NaOH solution. In 0~60 days, the water absorption of CFRP tendon tends to grow steadily. In the 64th days, the water absorption rate reached the highest. In 60th to 120th days, the water absorption gradually decreased. After 130 days, the water absorption rate almost no longer changes. The effect of the solution on the CFRP tendon is slow and it gradually becomes balanced.

4. Conclusions
Through this test, the following conclusions can be obtained. In the corrosion of NaOH solution, the water absorption rate of CFRP tendon reached the maximum at the 68th day. After 68 days, the water absorption began to drop. In the 130 days, the water absorption was the lowest. In addition, the epoxy resin is formed by curing the anhydride. Therefore, NaOH can react with the acid anhydride esterification of the ester bond, causing chemical bond damage. In this case, the new substance will be generated and attached to the surface of the CFRP tendon specimen. The new product has a certain hindrance to OH- ions. It can affect the reaction of OH- ions with anhydrides and slow the reaction rate. In the early stage of corrosion, 0.1 mol/L NaOH solution has the most obvious effect on the specimen. Strong chemical reactions can lead to negative changes in the quality of the specimen. With the increase of corrosion, the reaction rate began to slow down, and finally gradually stabilized. In the corrosion of HCl solution, the water absorption rate of CFRP tendon
reached the maximum in the 64th days. After 64 days, the water absorption began to drop. In the 130th day, the water absorption rate reached the lowest.

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