Effect of the Properties of Basalt Fibers Aging in Salt Solution

Qichang Zhang 1,2, Tan Yan 1,2, Lida Luo 1,2, Qingwei Wang 1,2 and Jin Liu 1,2
1. State Key Laboratory of Modification of Fiber Materials, Shanghai, 201620, China; 2. Engineering Center of Advanced Glass Manufacturing Technology, Ministry Of Education, Donghua University, Shanghai 201620 Email: 2180271@mail.dhu.edu.cn

Abstract. Basalt fiber is widely used in various fields such as military industry and civil use due to the characteristics of high strength, high temperature resistance and good chemical stability. In this paper, the aging of basalt fiber immersed in different concentrations of NaCl solution at different times was studied. The surface morphology and structure changes of basalt fiber brine after immersion were studied by scanning electron microscopy and Fourier transform infrared spectroscopy. The Fracture strength and weight loss rate of basalt fiber were used to characterize the salt water corrosion resistance of basalt fiber. The results showed that the surface of fiber was slightly corroded and ion exchange occurs in the solution when basalt fiber was soaked in NaCl solutions. The tensile strength of basalt fiber increased first and then decreased with time. It was inferred the ion exchange resulted in surface compressive stress increase the strength of the basalt fiber just like as tempering principle of glass.

1. Introduction
Basalt fiber is a kind of continuous fiber made by basalt ore melting at 1450°C - 1550°C and drawn at high speed through a platinum-iridium alloy drawing and draining plate [1, 2]. It has a series of excellent properties on high temperature resistance, high tensile strength, good chemical stability, as well as the advantage of non-toxic, natural, eco-friendly and inexpensive. At present basalt fiber has been gradually popularized and applied in acoustic thermal insulation materials, chemical filters, electrical insulation materials, composite materials and products with high chemical stability, reinforcing materials, structural materials and other composite products [3-8].

The development of the economic belt in the coastal areas is essential for the development of the whole country, especially the construction of bridges, tunnels and roads, which was called as “The era of marine economy”. Now there are nearly 80% basalt fiber used to strengthen the civil engineering due to the excellent stability, good mechanical properties, eco-friendly and low price [9-12], and it would be vital to explorer the aging properties on the environment of the salt for the application of basalt fiber.

Wei et al. studied the aging properties of basalt and glass fiber reinforced epoxy resin in seawater aqueous solution. The results show that the strength decreases with time [13]. Hu Haitao et al. studied the aging properties of basalt fiber sheets under neutral salt spray conditions, and the aging phenomenon was not obvious [14]. Zhu Ying et al. studied the durability of basalt fiber cloth in alkaline environment, acid environment, salt environment and water environment. The results show that the tensile strength of basalt fiber sheet is obviously reduced after corrosion by alkali solution and acid solution [15]. The salt and water environments have little effect on their tensile strength. Yang Yongxin et al. found that the basalt fiber cloth has a slight decrease in tensile strength and elongation under the environment of 3.5 times concentration and 5 times concentration of artificial seawater. The...
elastic modulus is improved and the basalt fiber cloth has good resistance. Seawater corrosion performance [16]. Yang Miaomiao et al. found that the tensile strength of basalt fiber and glass fiber monofilament decreased with the increase of soaking temperature and soaking time in seawater immersion conditions, and the tensile strength decreased rapidly in the early stage of immersion, and then the rate slowed down [17]. El Refai et al. studied the aging of basalt fiber reinforced polymer ribs (BFRP) in salt solution. After aging for 70 days in salt solution at room temperature, the fatigue strength of BFRP ribs was reduced by 25% [18]. Shi et al. studied the aging properties of BFRP in salt solution at different temperatures and times. The results show that the strength of BFRP decreases with increasing temperature and time [19]. Wang et al. studied the aging properties of BFRP in brine. The results show that the static strength of BFRP shows negligible degradation after aging in salt solution, while the aging of salt solution in fatigue load, the adverse effect of brine becomes obvious [20]. At present, most of the researches focus on the durability study of basalt fiber composites, and lack of research on the properties of basalt fiber monofilaments. The aging performance studies on the basalt fiber salinity environment are much less than the acid and alkali resistance studies.

These studies have focused on the materials that the fibers are covered by the matrix. The resistance of the filaments to corrosion is primarily determined by the corrosion resistance of the resin or cement, which is also related to the toughness of the resin or cement. The lack of a complete understanding of the basic mechanisms of fiber damage and degradation is evident.

The purpose of this work was to study the salt solution soak a direct impact on the performance of basalt fiber filaments, excluding the effect of the matrix, and reveal a clear and accurate response to salt corrosion fiber, provide a richer theory for the development of the use of basalt fibers later reference.

2. Experiment

2.1. Preparation of Basalt Fiber Used in the Experiment
The basalt fiber used in this experiment is prepared by laboratory basalt ore. The raw material is selected from the basalt ore in a certain area of Shandong. First, the basalt ore is broken into small pieces and heated to 1280~1350°C by using platinum-plated monofilament furnace. Drawing is started by a fiber monofilament drawing machine. The fiber monofilament is quickly wound onto a lower roller to collect the desired fibers. The diameter of the fiber is controlled by the rotational speed of the wire drawing drum. The composition is shown in the table below. The prepared basalt fibers have an average diameter of 18 μm and an average density of 2.5167g/cm³.

After the fiber is finished, the sample number is set. About 200 monofilaments are selected for each group of samples, the length is 5 cm, and 20 monofilaments are selected from each group of samples to prepare a fiber tensile strength test sample, which is to be dried after the glue is completely dried. Silk tensile strength test.

Five samples were taken in 3.5 wt% and 15 wt% NaCl solutions, placed in 5 beakers, sealed with plastic wrap, placed in a constant temperature and humidity chamber, and tested at a temperature of 90°C. The reaction time was taken as 1d, 3d, 5d, 7d, and 14d, and a total of 10 samples were collected. After taking out the drying, carry out the diameter test, the strength test, and send the sample to the testing center for further testing by infrared spectroscopy and scanning electron microscopy.

The NaCl is analytically pure, and the experimental water is deionized water. First, a certain amount of basalt fiber is weighed by an analytical balance, placed in a 3.5 wt% and 15 wt% NaCl solutions, and placed in a constant temperature and humidity chamber to set the temperature. It is 90°C. Take 1 day, 3 days, 5 days, 7 days, and 14 days as reaction time, and take them out in order. It is washed several times with deionized water and then dried to obtain basalt fiber after salt treatment.

2.2. Sample Performance and Characterization
The breaking strength of basalt fiber was tested by an electronic single fiber dynamometer. The test standard was in accordance with GB/T7690.3-2001 (method of breaking strength and elongation at break of glass fiber), and the test result was the average value of 20 experiments. The weight loss rate of basalt fiber was tested by testing the weight of the fiber before and after aging of the salt solution.
The apparent morphology changes of basalt fiber before and after treatment were observed by scanning electron microscopy. Characterization of ionic precipitation after immersion of basalt fiber in NaCl solution by ICP. The structure change of basalt fiber surface was characterized by Fourier transform infrared spectroscopy.

3. Results and Discussion

3.1. Effect of Salt Solution on Surface Morphology of Basalt

The SEM image of basalt fibers treated with sodium chloride was shown as Figure 1. It can be seen from Figure 1 that the untreated basalt fiber has a cylindrical shape with a smooth surface and few defects. After the basalt fiber is immersed in a 3.5 wt% NaCl solution at 90°C for 3 days, the surface of the basalt fiber has obvious aging phenomenon. Dense and uniform fiber surface defects appeared. Compared with the NaCl solution with a concentration of 15wt%, the surface of the fiber immersed in a NaCl solution with a concentration of 3.5wt% was more severely corroded. Compared with the fiber immersed for 3 days, the basalt fiber immersed for 14 days has more surface defects and more serious corrosion.

![Figure 1. SEM Image of Basalt Fibers Treated with Sodium Chloride (a-3.5wt% 3d; b-15wt% 3d; c-3.5wt% 14d; d-15wt% 14d; e-untreated)](image)

3.2. Analysis of Ion Concentration Precipitation

Figure 2 shows that the basalt fiber has a relatively obvious ion precipitation after immersion aging in 3.5 wt% NaCl solution. In particular, Si$^{4+}$, Ca$^{2+}$ and K$^{+}$ precipitated 3.87%, 4.04% and 16.94%
respectively after two weeks, and the precipitation content gradually increased with time. It can be seen from Figure 3 that only K⁺ is evident after immersion aging of basalt fiber in 15wt% NaCl solution. The precipitation was gradually increased with time, and 39.12% was precipitated after two weeks. It can be seen that during the immersion aging experiment of NaCl solution, the basalt fiber produced a corrosion reaction of ion displacement.

3.3. Weight Loss Test Results
The weight loss rates were shown in Figure 4 and Figure 5. It can be seen from the figures that after two weeks of aging experiments, the weight loss of basalt fiber clearly increased, and had a gradually increasing trend with time. However, compared with the 3.5wt% NaCl solution, the basalt fiber has less weight loss in the 15wt% solution, and it was inferred the salt concentration is too large to inhibit ion exchange, which makes the basalt fiber weight loss smaller, which is also consistent with the results of the ICP in the previous section.

3.4. Infrared Spectroscopy Test Results
Infrared Spectra of basalt fibers soaked in different concentrations of NaCl solution at 90°C were shown in Figure 6 and Figure 7. Results showed that a broad medium-strong absorption peak appeared
at 3290 cm\(^{-1}\). It shows that under the soaking of 3.5wt% NaCl solution, -OH is produced on the surface of basalt fiber. As the reaction progresses, the -OH formed by the reaction further causes a breakdown with the Si-O bond in the fiber skeleton structure, which is also the cause of Si\(^{4+}\) precipitation. It can be seen from Figure 8 that the basalt fiber has little change in composition after immersion in a 15 wt% NaCl solution, or the composition change has little effect on the fiber. The absorption peak at 3290 cm\(^{-1}\) is small. It is speculated that it may be that a high concentration of NaCl solution inhibits the production of -OH, and the Si-O bond is less destroyed.

3.5. Tensile Strength Test Results
The Weibull profile of the tensile strength for the basalt fiber in different concentration of NaCl solutions is shown as Figure 8 and Figure 9. The chart evaluates the strength of basalt fiber monofilaments using the Weibull distribution law. There are 20 filaments of samples for each. Results showed that the fracture strength of the basalt fiber in the 3.5wt%, 15wt% NaCl solution was increased first and then decreased. In the first 7 days, the basalt fiber immersed in the 3.5wt% NaCl solution gradually increases the fracture strength, and then the fracture strength decreases. The basalt fiber immersed in the 15 wt% NaCl solution increases in strength on the first day, and then the strength gradually decreases. The strength of the basalt fiber soaked in the 15 wt% NaCl solution is higher than that of the basalt fiber soaked in the 3.5 wt% solution.
3.6. Discussion

3.6.1. Relation of Weight Loss Rate and Ion Precipitation Mechanism. It can be seen from the above experiments that the greater the concentration of sodium chloride solution, the smaller the weight loss of basalt fiber in the salt solution, and the higher the concentration, the inhibition of the production of -OH on the surface of basalt fiber, the decrease of silicon ion precipitation, Si-O bond destruction is reduced. As the Si-O bond is destroyed, the Ca$^{2+}$ and Mg$^{2+}$ precipitates decrease, and only K$^+$ precipitates most, but at the same time, more Na$^+$ enters the gap, and in the low concentration sodium chloride solution, not only K$^+$ Precipitation, silicon ions, calcium ions are also precipitated, especially the precipitation of silicon as a network forming body, the structure will be destroyed, so the smaller the concentration of sodium chloride solution, the greater the weight loss rate.

![Figure 10. Sketch Map of Ion Exchange of Basalt Fiber in NaCl Solution](image)

3.6.2. Effect of Ion Precipitation on the Strength of Basalt Fiber. As shown in the figure 11, the strength of the basalt fiber after immersion in NaCl solution will increase first and then decrease, because the smaller radius Na$^+$ enters the vitreous body instead of the larger radius K$^+$, and the vitreous void is filled with Na$^+$, which will generate a compressive stress. The strength of basalt fiber is increased, and the mechanism is similar to the principle of glass tempering [21]. However, with the increase of time, the destruction of silicon tetrahedron in the glass body is gradually increased, and the K$^+$ migration in the glass body is also saturated, and its strength is no longer increased. On the contrary, the strength of the fiber is lowered due to the precipitation of other ions. The higher the concentration of NaCl solution, the faster Na$^+$ will reach saturation in the vitreous. Therefore, the strength begins to decrease after soaking for 1 day in 15wt% NaCl solution, and the strength begins to decrease after soaking for 3.5 days in 3.5wt% NaCl solution. When immersed in a higher concentration of NaCl solution, more Na$^+$ will enter the vitreous body, resulting in a larger pressing force, and the strength of the basalt fiber will be higher.
4. Conclusion

At 90°C, different concentrations of NaCl solution have different effects on the aging properties of basalt fiber. After immersed in 3.5wt% NaCl solution, the surface morphology of basalt fiber is slightly corroded, and a white film is attached to the surface. The strength increases first and then decreases with time. On the 7th day, the strength reaches the maximum value, and then the strength gradually decreases. In the 15wt% NaCl solution, the surface morphology and weight loss are less than 3.5wt% NaCl solution. The intensity of the first day increases gradually with time, then gradually decreases, because the Na⁺ in the solution exchanges with K⁺ in the glass. The composition of the surface layer of the glass fiber is changed, and a surface compressive stress layer is generated to increase the strength of the basalt fiber [22].

5. Acknowledgment

This work was supported by the National Science Foundation of China (NSFC, No. 51873032), and the Fundamental Research Funds for the Central Universities (223201900003).

6. Reference

[1] Jamshaid H, Mishra R. A green material from rock: basalt fiber—a review [J]. The Journal of the Textile Institute, 2016, 107(7):923-937.
[2] Fiore V, Scalici T, Di Bella G, et al. A review on basalt fibre and its composites [J]. Composites Part B: Engineering, 2015, 74:74-94.
[3] Dong L Q, Chen J F, Guo C M, et al. Application Status and Prospect of Basalt Fiber in Environmental Protection, Contemporary Chemical Industry, 2018, 47(2):387-391.
[4] Lopresto V, Leone C, De Iorio I. Mechanical characterization of basalt fibre reinforced plastic [J]. Composites Part B: Engineering, 2011, 42(4):717-723.
[5] Sun G Y, Tong S W, Chen D D, et al. Mechanical properties of hybrid composites reinforced by carbon and basalt fibers [J]. International Journal of Mechanical Sciences, 2018, 148:636-651.
[6] Wei B, Cao H L, Song S H. Tensile behavior contrast of basalt and glass fibers after chemical treatment [J]. Materials & Design, 2010, 31(9):4244-4250.
[7] Deák T, Czigány T. Chemical Composition and Mechanical Properties of Basalt and Glass Fibers: A Comparison [J]. Textile Research Journal, 2009, 79(7):645-651.
[8] Kizilkanat A B, Kabay N, Akyüncü V, et al. Mechanical properties and fracture behavior of basalt and glass fiber reinforced concrete: An experimental study [J]. Construction and Building Materials, 2015, 100:218-224.
[9] Ying X N, Zhou X D. Chemical and thermal resistance of basalt fiber in inclement environments [J]. Journal of Wuhan University of Technology, 2013, 28(3):560-565.
[10] Hu X Q, Shen T N. The Applications of the CBF in War Industry & Civil Fields [J]. Hi-Tech Fiber & Application, 2005, 30(6):7-13.

[11] Dhand V, Mittal G, Rhee K Y, et al. A short review on basalt fiber reinforced polymer composites [J]. Composites Part B: Engineering, 2015, 73:166-180.

[12] Wang Y, Yu X, Zhang J J, et al. Development and Application of Basalt Fibers [J]. Fiber Glass, 2017(4):28-31.

[13] Deák T, Czigány T. Chemical Composition and Mechanical Properties of Basalt and Glass Fibers: A Comparison [J]. Textile Research Journal, 2009, 79(7):645-651.

[14] Wei B, Cao H L, Song S H. Degradation of basalt fibre and glass fibre/epoxy resin composites in seawater [J]. Corrosion Science, 2011, 53(1):426-431.

[15] Hu H T, Wang X B, Yang Y X. Experimental study on durability of BFRP sheets under salt fog corrosion environment [J]. Industrial Construction, 2010, 40(04):9-12.

[16] Zhu Y, Zhang G C, Wu G. Experimental study on the corrosion resistant performance of BFRP laminates in corrosive solutions, 2013, 38(1):43-47.

[17] Yang Y X, Chen W, Ma M S. Durability of basalt fiber sheets under wet-dry cycling in seawater [J]. Industrial Construction, 2010, 40(4).

[18] Yang M M. Effects of artificial seawater immersion on the long term properties of basalt and glass fibers reinforced bars [D]. Harbin Institute of Technology, 2014.

[19] El Refai A. Durability and fatigue of basalt fiber-reinforced polymer bars gripped with steel wedge anchors [J]. Journal of Composite for Construction, 2013, 17(6): 04013006.

[20] Wang X, Zhao X, Wu Z. Fatigue degradation and life prediction of basalt fiber-reinforced polymer composites after saltwater corrosion [J]. Materials & Design, 2018, 163:107529.

[21] Cheng J S, Zhu L R, Lou X C, et al. Method discussion of glass tempering [J]. Materials Review, 2012, 26(s1):135-137.