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EVALUATION OF ALKALI RESISTANCE OF GFRP RODS

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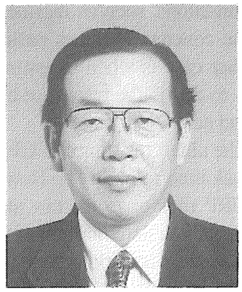

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In this study, accelerated tests of GFRP rods with aqueous NaOH are carried out in order to clarify the deterioration process of the rods in an alkali environment. Then, using an Electron Prove Microscope Analyzer (EPMA), the penetration of Na is observed within sections of the rods. From these investigations, it is clarified that the Na does in fact penetrate GFRP.
Tensile strength tests of GFRP rods which underwent accelerated-tests under high temperature and concentration in aqueous NaOH indicate that the tensile strength of the GFRP rods is reduced. The penetration process of Na in GFRP rods is simulated quantitatively using Fick's First law, and a method of predicting the deterioration in tensile strength of GFRP rods due to alkali is proposed.

Key Words : GFRP, alkali, penetration, diffusion, quantitatively, tensile, strength

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1. INTRODUCTION

Glass Fiber Reinforced Plastics (GFRP) are expected to be used as concrete reinforcing materials since they can significantly improve the durability of concrete structures but do not suffer salt corrosion like steel. However, GFRP rods are not guaranteed to always act as semi-permanent structural materials, deterioration of the mechanical properties of GFRP rods may be caused by chemical factors such as alkalis.

There are two chemical factors that may affect GFRP rods according to the conditions of use. One is where GFRP rods embedded in concrete are exposed to a high-alkali environment for a long period. In the case of concrete structures in wet conditions, such as marine structures, the water content of the concrete increases and the alkaline concentration in the concrete becomes particularly high by dissociation of hydroxide. This causes environment to deteriorate. The other case is when exposure conditions such as out-cable are affected by acid rain or car exhaust. Thus it is necessary to clarify the resistance of GFRP rods to chemical attack under the consideration that they may be affected by alkali and acid.

Various studies of the alkali resistance of GFRP rods have reported that their the mechanical properties deteriorate in the presence of an alkaline solution [1]. However, the amount of data was insufficient to report on the mechanism of deterioration of GFRP rods or to discuss methods of evaluating its progress quantitatively[1]. That is, there is an inability to predict the alkali deterioration of GFRP rods in the actual environment from the results of accelerated tests.

The authors have now their attention the glass fiber used in GFRP rods, and clarified the deterioration of these fibers due to alkali[2]. The authors initially assume that the poor alkali resistance of glass fibers result in the reduced mechanical properties of GFRP rods in the presence of alkalis, although it has generally been assumed that there is little possibility of fiber deterioration because they are protected by resin.

Thus, the objective of this research is to clarify the causes of tensile strength loss of GFRP rods due to alkali. The following investigations were carried out:

1) Sections of GFRP rods were observed using EPMA in order to clarify the penetration of alkali in the rods after accelerated exposure.
2) The condition of glass fibers in the rods after accelerated exposure was observed using a Scanning Electron Microscope (SEM).
3) The penetration of alkali in GFRP rods was simulated quantitatively by a model proposed on the basis of a diffusion controlled theory.

2. EXPERIMENTAL PROCEDURE

Fig.1 shows the experimental arrangement of GFRP rods immersed in alkaline solution[3]. The dimensions of the equipment are 10×10×20cm and it can accommodate twenty rods. The equipment is made of acrylic plate and is kept air-tight by closing with silicon the holes used to pour in the alkaline solution and insert the GFRP rods. The 20cm-long section of the GFRP rods immersed in the alkaline solution is the portion subjected to tensile tests ; the anchorages are not affected by the alkali.

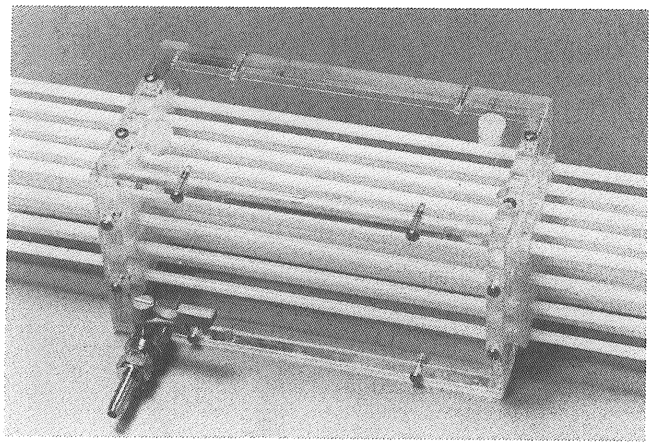


Fig.1 Accelerated tests on GFRP rods

Table 1 lists the material properties and the condition of the accelerated tests on GFRP rods. The tensile strength values indicated in the table are the results of averaging a hundred tests by NISHIMURA[3]. For the immersion test, it is realistic to use the alkali-ions existing in concrete and the same alkaline concentration as in concrete(=0.05N). But for this study, Aqueous NaOH (=1.0N) was used as the alkaline solution so as to accelerate the degradation of GFRP rods. The GFRP rods contained T-glass fibers. Vinyl resin was used for the matrix in consideration of elongation of the T-glass fibers. Table 2 lists the chemical compositions of the T-glass fibers and Table 3 lists the T-glass fibers and the matrix.

After the immersion tests, the rods are washed with distilled water and dried for 24 hours in a dessicator.

Tensile tests on the GFRP rods were carried out according to the method specified for continuous fiber reinforcement (JSCE). Split chucks developed by KOBAYASHI were used as the anchoring method in the tests[5]. A protective coating was added to the anchorage surface by first applying unsaturated polyester resin as a bedding treatment and then a uniform coating of a mixture of unsaturated polyester resin and iron powder (300 mesh) with a weight ratio of 1 : 1.8. Tensile tests were carried out at a temperature of 20±5℃. Twenty GFRP rods were tested for each case, with the cross-head speed maintained at 5.0 mm/min.

Table 1 Characteristics of GFRP rods and conditions of accelerated tests

Fiber Type	T-glass	Alkaline solution	NaOH
Matrix Type	vinyl resin	Concentration (mol/l)	1.0
Diameter (mm)	6.0	Temperature (℃)	40, 60
Strength (MPa)	1640	Curing time (day)	7, 30, 60, 90, 120

Table 2 Chemical compositions of T-glass fibers

ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O
0.8	65.1	23.9	0.108	0.296	9.74	0.084

Table 3 Material properties of T-glass fibers and matrix

	Tensile strength (MPa)	Yang's modulus (MPa)	Strain (%)
T-glass fiber	2510	85510	---
Vinyl resin	86	3300	5.1

3. INFLUENCE OF ALKALI ON GFRP RODS

3.1 EPMA Observations

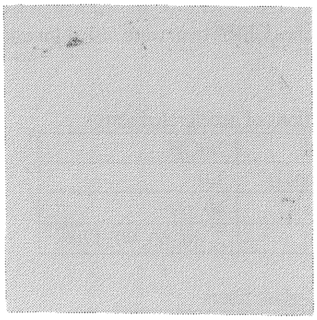
Fig.2 shows the penetration of Na into the sections of GFRP rods observed using EPMA after immersion times of 0, 7, 30, and 120 days. The black areas are those affected by Na due to penetration. These results show that hardly any Na existed in the rods before immersion ; that is, Na was not detected in the rod section at all. On the other hand, Na was detected in the rods immersed in aqueous NaOH. This demonstrates that the Na observed by EPMA had penetrated from the outside. It also clarifies that Na penetrates into the rods centripetally with time. Thus, it is demonstrated that resin cannot completely protect the glass fibers from alkali attack.

3.2 SEM observation

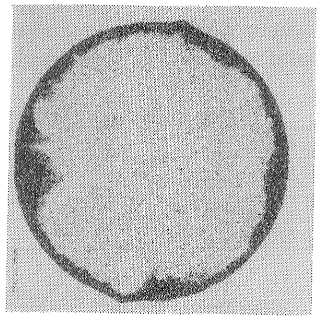
Fig.3 shows the condition of glass fibers in an area where EPMA showed Na to be present. Sections of glass fiber before immersion are smoothly circular, while in the Na penetrated area they were corroded by the alkali. It appeared that the bond between fiber and matrix had failed, and this was assumed to be the cause of reduced mechanical properties in GFRP rods immersed in alkali solution.

3.3 Alkali penetration

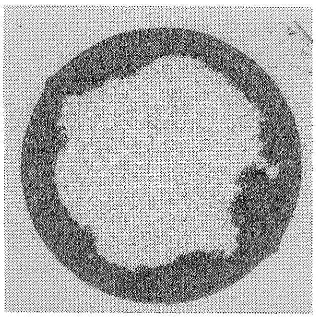
As noted, the alkali was seemed to penetrate into GFRP rods. The question of how the alkali penetrates into GFRP rods appeared interesting, so the authors measured Na levels in sections of AFRP and CFRP immersed into alkali solution to confirm whether alkali could penetrate into rods with other types of fiber. The same method was used. Fig.4 shows the results for AFRP and CFRP rods immersed for 60 days in 2.0N aqueous NaOH. The matrix was the same vinyl resin as used for GFRP rods. Results showed that, in spite of the alkaline concentration being twice as high as that in the case of GFRP rods, Na was hardly detected in the rod sections. However, there was same distribution of Na near the surface of AFRP rods. If alkali penetration is assumed to be caused by poor alkali resistance of the fibers, and given that the alkali resistance of aramid fibers is somewhat inferior to that of carbon fibers, Na might be expected near the surface of AFRP rods. Thus alkali penetration into FRP rods is dominated by the alkali resistance of the fibers in the rods. In order to grasp the progress of deterioration of glass fibers in GFRP rods, the distribution of Na in a rod was observed with a microscope. Fig.5 (a), (b) show the results of analyzing Na and Al ; these are enlargements of the area in which Na was detected in the section of the GFRP rod. Fig.5 (c) shows the condition of glass fibers in the same where Na and Al were observed. Results confirmed that glass fibers within this rod were corroded as shown earlier in Fig.3. This corrosion can be also be deduced from the Al count near the surface of the glass fiber, which is higher than in the center.



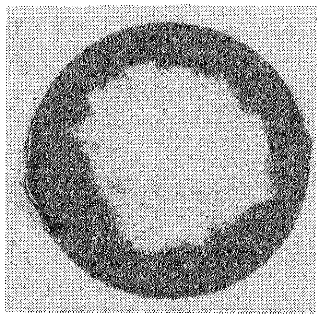
(before immersion)



(immersion times of 7days)



(immersion times of 30 days)



(immersion times of 120 days)

Fig.2 Na analysis of immersed GFRP rod section

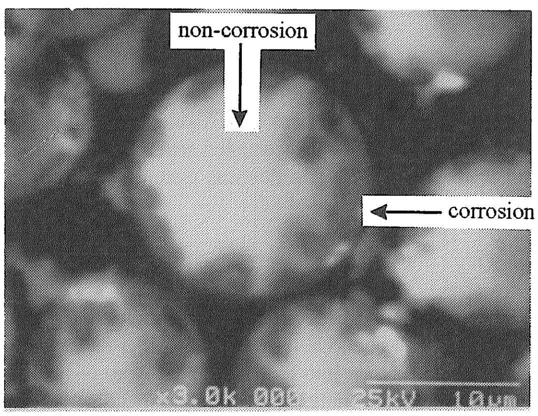
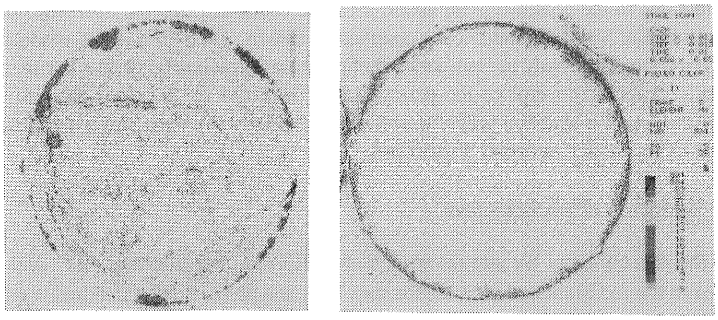
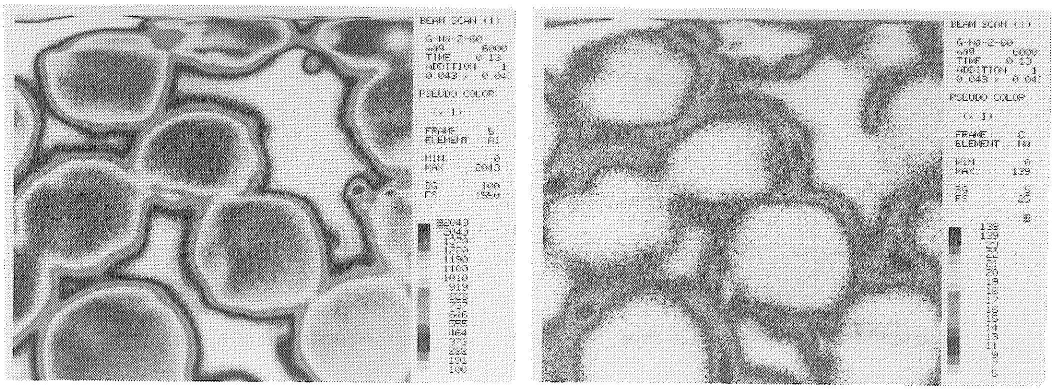


Fig.3 Condition of glass fibers in Na-penetrated area ($\times$3000)

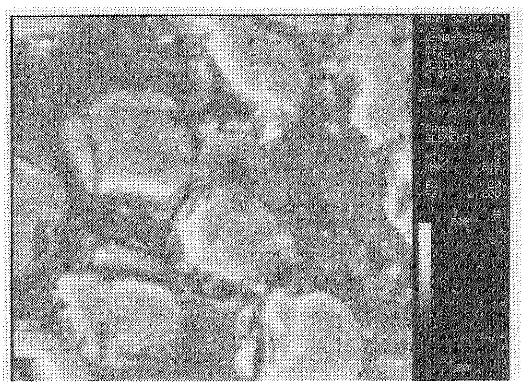


(a) AFRP (b) CFRP

Fig.4 Na analysis of immersed AFRP and CFRP rod section



(a) Al analysis (b) Na analysis



(c) SEM

Fig.5 EPMA analysis of deteriorated area of immersed GFRP rods

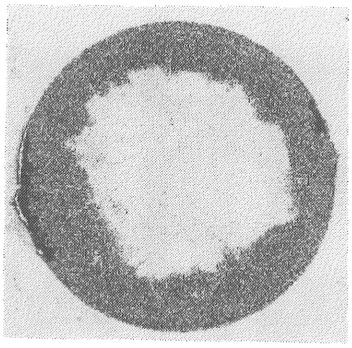
This indicates deterioration resulting from broken molecular chains in that Al detached from glass fibers. Fig.5 (b) shows that a lot of Na was detected in parts of the glass fibers deteriorated due to alkali, while hardly and Na was detected in the matrix. That is, glass fibers were corroded at the interface between fiber and matrix while deterioration of glass fibers did not progress inside the fibers. Therefore, it was seemed that 'Na' penetrated into GFRP rod through the layer that had high diffusive capacity ; namely, the part of deterioration took place on the interface between fiber and matrix.

It is known that silica-oxygen-silica bonds in glass fibers can be broken by hydroxyl attack. Given that glass fibers in

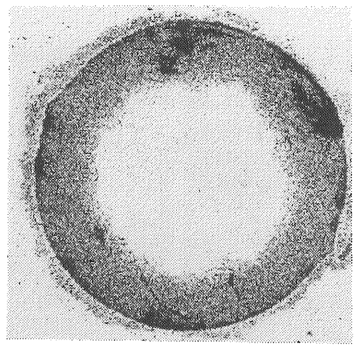
GFRP rods deteriorate due to the presence of an alkali, it can be concluded that the fibers are corroded by hydroxyl penetrating from outside. But hydroxyl could not be observed by EPMA. Then the authors assumed that hydroxyl and Na penetrated in the rod simultaneously in consideration of chemical attraction between a positive ion and a negative ion, so it was equally evaluated to replace the penetration of hydroxyl by the penetration of Na. In this paper, assuming that the area of Na and hydroxyl penetrated into GFRP rod was the same, this paper defined this area as the layer that glass fibers in the rod was corroded by hydroxyl.

3.4 Influence of temperature on alkali penetration1

Fig.6 (a), (b) show the penetration of Na into the section of GFRP rods accelerated at 40℃ and 60℃, respectively. The Na-affected area in the rod immersed at 60℃ for sixty days and at 40℃ for a hundred twenty days was almost the same. This indicates that the penetration rate of Na is directly proportional to temperature. That is to say, it is confirmed that temperature affects the penetration rate of Na.



(a) immersion at 40℃ for 120 days



(b) immersion at 60℃ for 60days

Fig.6 Influence of temperature on penetration speed

4. RESULTS OF TENSILE TEST

Results of tensile tests on GFRP rods including the standard deviation, are given in Table 4. Each tensile strength value is the result of averaging the twenty test data in the table. Results show that the tensile strength of GFRP rods falls when they are immersed in aqueous NaOH.

Table 4 Results of tensile tests

Temp.	immersion times (day)	7	30	60	90	120
40℃	tensile strength (MPa)	1260	910	-	560	480
	S.D. (MPa)	82	157	-	163	94
60℃	tensile strength (MPa)	-	664	577	-	-
	S.D. (MPa)	-	88	51	-	-

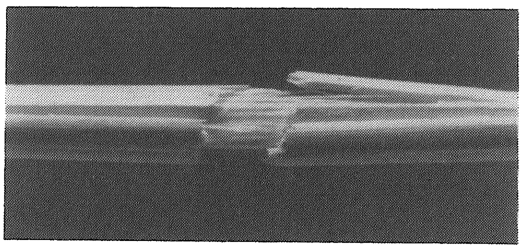


Fig.7 Fracture pattern of immersed GFRP rods

Fig.7 shows the nature of GFRP rod fractures offer immersion at 40℃ in 1.0N aqueous NaOH for 90 days. Fig.8 shows the load-displacement curve for the failure of a GFRP rod. Two kinds of time immersed penetration of Na, law (A) and high (B), are shown in this Fig.. In both load-displacement curves, the load falls once at a lower load level, then increases until the breaking point. The falling point of the load at a lower load level is decreased with increasing Na penetration, so it was seemed to be caused by the damage of the penetration area was large as long as time immersed. Therefore, by finding out that the falling point of the load at a lower load level certainly happened before the breaking of rod, it was assumed that deteriorated area was not undergone the tensile load at the failure strength.
It is observed that the fracture pattern near the surface differs from that around the inner part of the GFRP rod in Fig.7. That is to say, it seems that failure occurred near the surface at a lower load where glass fibers had suffered deterioration due to alkali penetration, whereas the fracture pattern of the inner part was broom-like, similar to the fracture pattern of GFRP rods before immersion.
From the results of EPMA analysis and the failure state of GFRP rods after accelerated deterioration in aqueous NaOH, it can be assumed that the fall of load at lower step occurs by breaking on the penetrated area in GFRP rod ; namely, glass fibers within the alkali-penetrated area have suffered deterioration due to alkali, and failure of these fibers is antecedent to the failure of glass fibers in non-alkali penetrated areas.
Consequently, failure strength can be evaluated by measuring the non-alkali penetrated area within a GFRP rod.

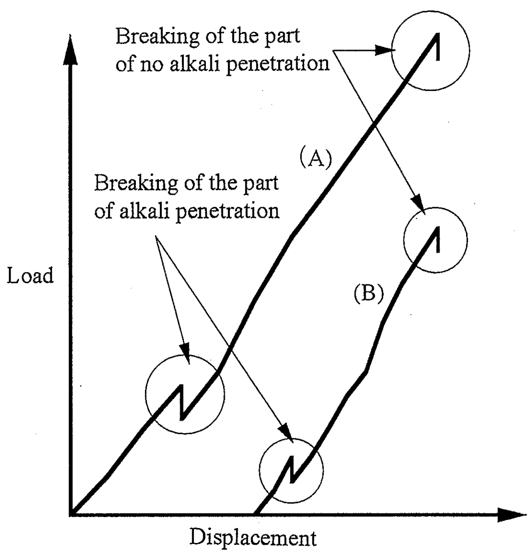


Fig.8 Load-displacement curve of GFRP rods after accelerated test

5. METHOD OF PREDICTION

In this chapter, a method of predicting the loss in tensile strength of GFRP rods immersed in alkali solution is proposed.
Degradation of GFRP rods was modeled on the basis of results obtained from EPMA analysis and tensile strength tests. The authors assume that failure strength can be obtained by measuring the non-alkali-penetrated area within GFRP rods ; namely, the tensile strength of alkali-penetrated areas can be assumed to be zero. If the extent of alkali penetration into GFRP rods can be predicted with time, it will then be possible to quantitatively predict the tensile strength of degraded GFRP rods. Thus, the authors tried to predict alkali penetration into GFRP rods using Fick's first law, as given in the form shown by Equation (1). Fig.9 shows a simple model for predicting alkali penetration. In order to apply Equation(1), the measured alkali-penetrated area is treated a circle in this model. The diffusion coefficient of alkali in GFRP rods was calculated from the depth of alkali penetration in Fig.7 and Equation(1). Hence, diffusion coefficients at 40℃ and 60℃ are as $2.8\times10^{-6}(cm^2/hr)$ and $7.5\times10^{-6}(cm^2/hr)$, respectively.

$$x=\sqrt{2\cdot k\cdot C\cdot t} \qquad (1)$$

where x, C, t indicate depth from surface of the rod (cm), alkaline concentration (mol/l), and curing time (hours), respectively. Also, k is the diffusion coefficient (cm^2/hr) of alkali in the rod.

Then, the formula to calculate immersed GFRP strength at a certain age is derived under the following assumptions:

1) Failure strength is decided by measuring the non-Na-penetrated area within the immersed GFRP rods; namely, the tensile strength of the penetrated area is zero.

2) The strength of the non-alkali-penetrated area is the same as that of GFRP rods before immersion.

From assumptions 1) and 2),

$$\sigma_0 = \frac{P_0}{S_0} = \frac{P_t}{S_t}$$

$$\therefore \quad P_t = S_t \cdot \sigma_0 \qquad (2)$$

where σ_0 and σ_t indicate tensile strength before immersion and at a certain age (MPa), respectively. P_0 and P_t indicate failure load before immersion and at certain age (kN), respectively. S_0 and S_t indicate the sectional area of the rod and the non-Na-penetrated area within the immersed rod, respectively.

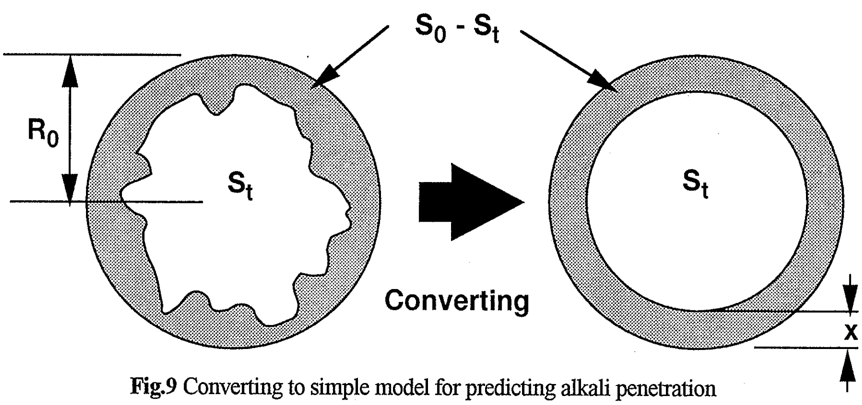


Fig.9 Converting to simple model for predicting alkali penetration

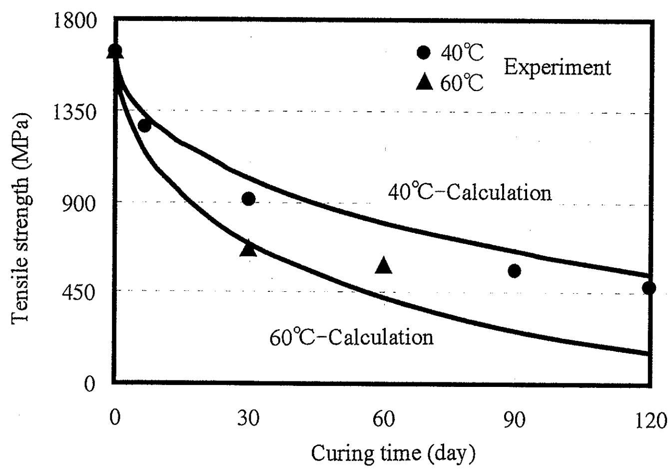


Fig.10 Results of tensile tests

Therefore, the tensile strength of an immersed GFRP rod is

$$\sigma_t = \frac{S_0}{P_t}$$

$$= \sigma_0 \cdot \frac{S_t}{S_0}$$

$$= \sigma_0 \cdot \frac{\pi \cdot (R_0 - x)^2}{\pi \cdot R_0^2} \qquad (3)$$

if we substitute Equation (1) into Equation (3), Equation (4) results as.

$$\sigma_t = \left(1 - \frac{\sqrt{2 \cdot k \cdot C \cdot t}}{R_0}\right)^2 \cdot \sigma_0 \qquad (4)$$

where R_0 indicates the radius of the GFRP rod (=3 mm)

The strength loss of GFRP rods in accelerated tests at 40℃ and 60℃ with 1.0N aqueous NaOH is illustrated in Fig. 10. Here, the calculated value is obtained by using the diffusion coefficients $k_{40}=2.8\times10^{-6}$(cm^2/hr) and $k_{60}=7.5\times10^{-6}$(cm^2/hrs) and alkaline concentration 1.0N. The results of the simulation match well with the experimental results. This confirms that the strength loss of degraded GFRP rods due to alkali can be predicted using this calculation method.

6. PREDICTION OF DETERIORATION FOR A LONG TERM

It was explained in Section 4 that temperature affects the speed of Na penetration. Experiments showed that the temperature effect is a variation in diffusion coefficient corresponding to temperature change, with a relation that can be expressed by the following Arrhenius equation:

$$\log_{10} k = -\frac{E}{R \cdot T} + \log_{10} F \qquad (5)$$

where, F, E, and T indicate frequency factor, activation energy, and absolute temperature, respectively.

Table 5 Prediction of deterioration of GFRP rods in concrete

immersion times (year)	3	6	9	15
strength loss (%)	30.0	40.8	48.6	59.7

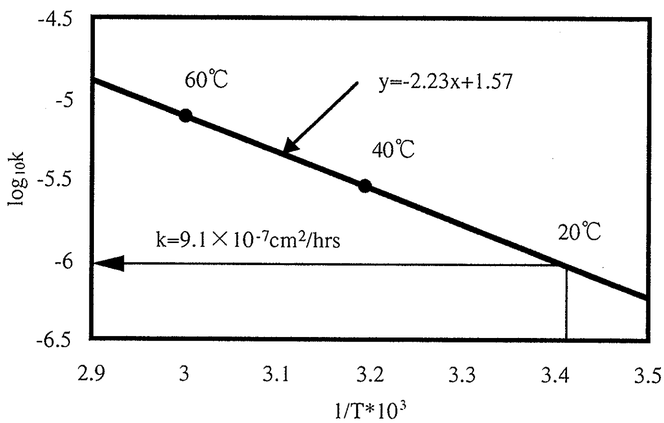


Fig.11 Arrhenius plots

Diffusion coefficients calculated in Section 5 at 40℃ and 60℃ using Equation (5) are illustrated in Fig.11. The diffusion coefficient calculated on the basis of two experimental data of them and Equation(5) is 9.1×10^{-7}(cm^2/hr) at 20℃.

Table 5 lists the results of predicted strength loss of GFRP rods using Equation (4) for a long term based on the following assumptions:

1) Diffusion coefficients do not vary with alkaline concentration.
2) Alkaline concentration in concrete is fixed at 0.05N (pH=12.7).

The results of this calculation could not be checked against measured data due to the non-availability of long-term data. However, it is possible to predict that the tensile strength of GFRP rods in concrete will decrease about 60% over 15 years.

7. CONCLUSION

The objective of this research was to clarify the cause of tensile strength loss in GFRP rod due to alkali, and to predict quantitatively the strength loss . The conclusions drawn from the research are as follows.

1) From the results of measured Na in the sections of GFRP rods immersed in aqueous NaOH using EPMA, it was confirmed that Na penetrated into the rods.
2) At the same time as alkali corroded the interface between glass fibers and matrix , it also penetrated the GFRP rods. This phenomenon happened due to the poor alkali resistance of glass fibers in the rod. Therefore, no Na penetration occurs in AFRP and CFRP rods, which include aramid and carbon fibers with high alkali resistance.
3) Alkali corroded glass fibers in GFRP rods, leading to tensile strength loss of the rod.
4) Temperature affected the speed of Na penetration in GFRP rods similar to that in glass fibers.
5) Failure of GFRP rods immersed in alkali solution occurs within the alkali-penetrated area before failure in the non-alkali-penetrated area.
6) A simple model is proposed in which the alkali penetration process in GFRP rods is simulated quantitatively by replacing alkali-penetration with a problem of diffusion. The decrease in tensile strength of GFRP rods due to alkali can be accurately estimated using the proposed model.

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