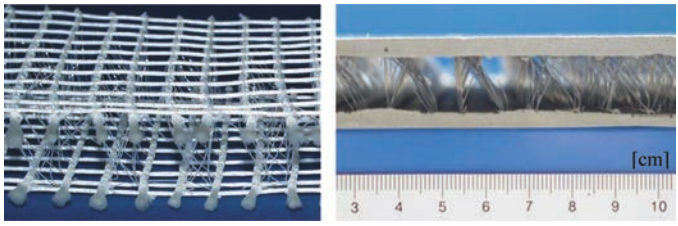

Fig. 3—Spacer fabric: a) Type A; and b) Type A with thin walled concrete layers on both sides.

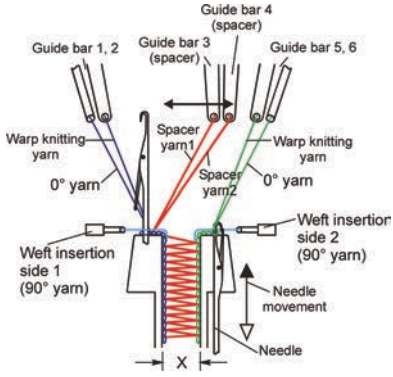

Fig. 4—Schematic cross section of warp knitting elements.

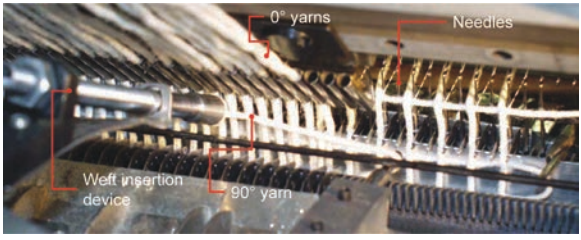

Fig. 5—Detail of warp knitting area with weft insertion yarns.

Durability of Textile Reinforced Concrete

by R. Hempel, M. Butler, S. Hempel, and H. Schorn

Synopsis: Concrete specimens with unidirectional embedded AR-glass rovings were stored in a climatic test chamber at 40 °C (104 °F) and 99 % r.h. After this storage, the bending strengths of the specimens were tested. The uncovered fibers were observed with an Environmental Scanning Electron Microscope (ESEM). The specimens made of the low alkaline matrix and AR-glass rovings showed no strength losses. Whereas, the specimens reinforced with E-glass showed dramatic losses of strength and corrosion of glass fibers. Also, the specimens made of the high alkaline matrix and AR-glass reinforcement showed losses of strength. A corrosion of the fibers could not be detected. Causes for the measured losses of load capacity when using AR-glass reinforcement and Portland cement matrix are the weak points inside the interface fiber-matrix, caused by portlandit crystals.
Storage tests in simulated pore solution of 80 °C (176 °F) and pH 13 showed clearly, that glass corrosion cannot start before the protective fiber size is at least partially dissolved. In this case, the VET-AR-glass fibers are of advantage. During the alkaline attack on the unprotected AR-glass surface, the content of zirconium dioxide determines the corrosion resistance for the respective glass. In this case, the NEG-AR fibers are of advantage. The investigations show, that durable fiber concretes and textile reinforced concretes with AR-glass respectively can be produced by optimizing the mixtures. In this respect, the climatic test chamber storage proved to be an accelerated aging test.

Keywords: accelerated aging test; AR-glass; corrosion resistance; durability; GRC; strength losses; textile reinforced concrete (TRC)

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INTRODUCTION

For more than 40 years experiences concerning the glass fiber concrete (GRC) are available. For 15 years now, one has worked on the development of textile reinforced concrete (TRC) on the basis of alkali-resistant AR-glass multi filament yarn. First applications were realized. Under certain conditions, strength losses at glass fiber concrete have been detected during the aging process. Therefore, the question had to be discussed, whether corrosives or other causes are responsible for these strength losses. This problem is of particular interest to the textile reinforced concrete because the fiber content is less than a quarter in comparison to the GRC.

The resistance of AR-glass against an alkaline attack is primarily secured by the chemical composition. By adding zircon-dioxide of more than 15 % to the molten glass, the glass network changes and the fast break open of the Si-O-bonds as well as the dissolving of the glass can be prevented as far as possible.

A further action to improve the mechanical properties of the glass fibers above all is the spreading of a size (common a polymer-dispersion combined with silane-bonding admixtures) with less than 100 nm thickness (Zinck, Mäder, and Gerard 2001). The fiber size is primarily intended to cover those imperfections on the fiber surface, which are due to conditions of manufacturing. Furthermore, this is done for generating a smooth surface overall. Consequently, the actual existing brittleness of the fibers is reduced and the fibers become processable. However, the fiber size represents also a barrier against a chemical (glass solving) attack (Mäder et al. 2004)

The ZrO_2-amount and the composition of the size are different depending on the origin of the fibers.

In the following, it will be reported about the results of accelerated aging tests for evaluating the durability of AR-glass fibers in concrete as well as the causes of possible strength losses during the aging. Additionally, results of storage tests with AR-glass rovings in simulated pore solution at increased temperature are presented. The influence of the corrosion resistance depending on the amount of zirconium dioxide in the glass and on the fiber size is clarified.

INVESTIGATIONS ON DURABILITY

Approach and testing program

--climatic test chamber storage

Inside the climatic test chamber a temperature of 40°C (104 °F) and a relative humidity of about 100 % were adjusted. Under these extreme conditions of storage an alkali-silica-reaction (ASR) will take place most rapidly. Consequently, if corrosion processes proceed at the glass body of the reinforcement fibers, they would be visible under these conditions. This exposure accelerates the process of a possible glass corrosion and is to categorize as accelerated aging test.

Under these conditions the specimens made of concrete with unidirectional inserted rovings of AR-glass were stored in a climatic test chamber for up to 3 years.

The matrix composition was varied concerning the alkalinity and the content of calcium hydroxide.

The bond behavior was tested in 4-point-bending tests with 5 specimens in each test series. The scattering was approx. +/- 10 %. The specimens with the dimensions 270 mm ($10\ ^{10}/_{16}$ in.) length, 60 mm ($2\ ^{6}/_{16}$ in.) width and 12 mm ($^{15}/_{32}$ in.) height were reinforced with 7 unidirectional embedded rovings with a roving space of 9 mm ($^{23}/_{64}$ in.). The rovings were inserted at 10 mm ($^{25}/_{64}$ in.) under the surface. The aim of the under reinforcement was to avoid a multiple cracking. The deformation behavior and the pull-out of the fibres should be detected only at one single crack.

The high alkaline matrix is characterized by a Portland cement (CEM I)-sand-matrix in the ratio cement : sand = 1 : 1 with a w/c = 0.3. The microstructure of the concrete is distinguished by a portlandit content increasing with the age of the concrete. Portlandit ($Ca(OH)_2$ = CH-phase) is formed as a byproduct of the hydration of the cement clinker. On the one hand, it maintains the alkaline milieu of the pore solution. On the other hand, it presents a weak point in the interface fiber-matrix. The portlandit is about 120 times bigger than the original hydrate-phases (CSH-phases). Compared with this, the portlandit is relatively soft and easily to split. With the high alkaline mixture, the effect of an aggressive high alkaline pore solution on the glass fibers embedded in the concrete is

studied. Furthermore, the influence of the bond behavior by the kind of the formed hydration products is observed.

In the low alkaline matrix the Portland cement was replaced by a mix of blast-furnace cement with a high amount of blast-furnace slag (CEM III-B) and pozzolan (silica fume and fly ash) in a ratio of blast-furnace cement : pozzolan = 2 : 1. Due to the blast-furnace cement, the potential for the formation of portlandit ($Ca(OH)_2$) is limited according to the reduced clinker content while simultaneously the alkali level is decreased. In addition, the admixed pozzolan effects a further buffering (degradation) of the alkalinity. At the same time, the formed portlandit will be consumed by the pozzolanic reaction. In this case, the microstructure of the concrete is affected by the CSH-phases.

As objective criterion the load-deflection behavior will be determined depending on the matrix composition and the duration of the climatic test chamber storage. The condition of the fibers after the respective storage will be evaluated with an environmental scanning microscope (ESEM). For comparison, specimens with embedded rovings from the non alkali-resistant E-glass are investigated. These investigations provide a basis for the validation of possible damage symptoms and for comparing the strength analysis.

-- Exposition in simulated pore solution

AR-glass rovings were stored in simulated pore solution by varying the temperature and the pH-value of the medium.

Under this extreme exposition the glass corrosion is definitely provoked. The investigations should provide a basis for clearing the interactions between the fiber size and the ZrO_2-content of the glass.

For the examinations the following fibers have been used:
--NEG-ARG 620 tex with a minimal ZrO_2-content of 18 % and
--VET-ARG 620 tex with a minimal ZrO_2-content of 15 %

--NEG-ARG 620 tex without fiber size (at the 28 day of storage)
--VET-ARG 620 tex without fiber size (at the 28 day of storage)

The fiber size was eliminated by pyrolysis in a muffle kiln at 600 °C (1112 °F) for a duration of 3 hours.

Within the scope of the represented results a simulated pore solution has been used for storing the AR-glass rovings in the alkaline solution.

The solution was produced as following:
--Mixing of 2.5 kg (88 $^3/_{16}$ oz) CEM I HR-HS with 13 l (3 $^7/_{16}$ gal.) tap water and homogenizing
--Leaving for 2 days and stir frequently, after this hermetically sealing
--After 2 days filtering

--The pH-value of this filtrate represented 12.9 to 13.0 (measured by a pH meter)

The filtrate had the following chemical composition (determined by photometry)

K^+	= 1.43 g/l	($^3/_{16}$ oz/gal.)
Ca^{2+}	= 1.08 g/l	($^9/_{64}$ oz/gal.)
SO_4^{2-}	= 1.32 g/l	($^{11}/_{64}$ oz/gal.)
Cl^-	= 30 mg/l	($^1/_{256}$ oz/gal.)
Mg^{2+}	= 30 mg/l	($^1/_{256}$ oz/gal.) } at the
Al^{3+}	= 1.5 mg/l	($^1/_{5000}$ oz/gal.) } detection limit
Na		(determined by EDX approx. 1.8 mass-%)

The focal point of the investigations was the storage of the rovings in a simulated pore solution of pH 13 and 80 °C (176 °F) for the duration of 1 year.

The observation of the fibers took place at the appointed days 1 d, 3 d, 7 d, 28 d, 56 d, 90 d, 180 d and 360 d respectively.

Furthermore, specimens have been stored at the ph-values 10, 11 and 12 and the temperatures 20 °C (68 °F), 40 °C (104 °F) and 60 °C (140 °F).

The rovings taken for the investigation, were purged in distilled water several times and than left to air-dry.

The investigation of the fibers was done with a scanning electron microscope in ESEM-mode that enables the observation of the specimens at a natural state without a conductivity layer.

For analysing the newly built phases or growth on the fibers an EDX-analyzer (energy dispersive X-ray analysis) was used. This way, using the measured atomic spectrum, the qualitative and quantitative composition of the found structures can be determined.

Particularly helpful for the investigations was the use of a micromanipulator, which is installed inside the microscope. The needle, installed at the manipulator, with a point diameter of 1 µm ($^4/_{1,000,000}$ in.) can be moved from the outside of the microscope in two rotations and one horizontal axis. For this reason, manipulations at the fibers are possible. Examples are the scraping off of growths for an EDX-analysis without external constituents, falsifications caused by the subsurface or the uncovering of interesting fiber areas.

RESULTS

Results after storage in the climatic test chamber

The concrete specimens with varied types of fibers and concrete compositions were stored in the climatic test chamber, tested and observed according to the testing plan.

The comparative specimens with E-glass rovings showed a clear corrosion in the low alkaline matrix after 360 days (Fig. 1). Due to the occurred damages at the filaments the load-bearing capacity drops towards zero after the first crack of the specimen (Fig. 2). An explicit connection exists between strength losses and glass corrosion.

After storing specimens reinforced with AR-glass rovings along with a matrix with blast–furnace cement (high blast-furnace slag amount) and pozzolan as binder, no strength losses are detected (Fig. 3). The hydration products consist mainly of CSH-phases. The microstructure of the built encasements on the fibers is smooth and thin-walled (Fig. 4). In the environmental scanning microscope (ESEM) some growths could be removed by using the micromanipulator. The uncovered surface was also undamaged. Any corrosion at the glass body could not be detected.

A complete different result is given after the tests with a matrix, which contains only Portland cement as binder. With proceeding duration of the storage in the climatic test chamber a permanent increase of the strength loss occurred at the concrete specimens reinforced with AR-glass (Fig. 5). The glass filaments situated in the “fill-in-zone” show thick-walled encasements. These encasements are dominated by CH-phases (portlandit-crystals), which the corresponding investigations show. They mark a weak point in the interface fiber-matrix. Of particular importance is the fact, that the uncovered fibers are without any visible appearance of corrosion (Fig. 6). The filaments still show her original shape and diameter. Therefore, it must be noted, that the cause for the dramatic strength losses is not to be found in corrosive changes of the AR-fibers. They are essentially conditioned by the inhomogeneous microstructure in the interface-zone “fiber-matrix”. Furthermore, it can be assumed, that the fiber size was partially solved due to the high alkaline pore solution of the Portland cement without pozzolan. As a result of this primary defects could be uncovered at the glass surface. These lead to additional high localized stresses, which may effect the strength losses.

The observation of the concrete specimens and the embedded AR-glass rovings, after being stored in a climatic test chamber, has occurred for more than 3 years now. Up to now, no corrosive damages at the glass bodies in both used matrix systems could be detected. Measurements concerning the erosion of the fiber size on AR-glass fibers, embedded in concrete, showed a longtime durability (Hempel 2003). Considering the fact, that glass corrosion is a stepwise process, a high durability of textile reinforced concrete based on AR-glass can be expected.

Results after the exposition in simulated pore solution

-- Fibers with size

The following specifications show the results of storing NEG-ARG and VET-ARG in a pore solution of pH 13 and 80 °C (176 °F) over the period of one year. Using this technique, the damages and developments which have occurred during the time of storage were best visible.

-- NEG-ARG

After a storage time of 1 to 3 days, no changes were detected on the surfaces of filaments (Fig. 7). The unevenness in surfaces, visible in picture 7, was caused by the fiber production, as well as an uneven and locally thickened application of size. When the size is evenly applied, it cannot be distinguished from the glass body. After a storage period of 7 to 14 days, a few filaments show unevenly formed structures on the surface, which indicates a commencing formation of damage (Fig. 8). The majority of filaments have not shown any changes yet.

With an increasing duration of an alkaline attack, a more obvious development and heaped appearance of defects on the filament's surface could be observed. In the beginning, they appeared as small holes, deepenings and roughness which unevenly cover big areas (Fig. 9).

After a storage period of 56 days, the state of damage was at a point, where on top of many fibers single holes as well as bigger and merging deepenings had developed (Fig. 10). The depth of deterioration had increased as well significantly. Yet, at this point in time, there were still filaments, which did not show any defects of surface.

The pictures of damage show a clear similarity to those of Kopecskó (Kopecskó 2004). However, the conclusion suggesting that this has to do with just a removal of size cannot be shared, simply because the depth of corrosion goes clearly beyond the depth of size. Therefore, after the removal of size, we are dealing with a commencing corrosion on the glass body.

After 180 days, the surface of the NEG-ARG fibers has changed entirely during the advancing decomposition of glass and turned into an alkali-silicate-gel-layer, which was interfused with calcite crystals (Fig. 11). Out of the unleashed silicon and the calcium resulting from the pore solution thick layers of CSH-phases being matted into each other were formed above, and mantled the fibers (Fig. 12). At this point, no more undamaged areas were to be found in the fibers.

The state after a storage period of 360 days is much different from earlier documented facts due to further decomposition of the fibers, which goes along with an increasing growth of CSH-phases. Due to these crusts, the single filaments have grown together into thick bundles (Fig. 13).

Using the micromanipulator, the CSH-shells could be broken open (Fig. 14, 15). As expected, those filaments laying underneath have almost entirely been destructed and could hardly be distinguished from those encasing shells.

-- VET-ARG

Until the 28th day of storage, no changes, which could have been defined as commencing damage, were observed on the VET-ARG fibers (Fig. 16). The filaments' surface

displayed itself as sleek and intact and was merely covered at varying frequency with $CaCO_3$-crystals from the pore solution.

Just after 56 days of storage, first damages became visible in form of circular holes of different sizes and frequency. Those appeared not just singly but also combined to larger deepenings. From this point on, the formation of CSH-phases was also to be noted (Fig. 17, 18).

All together, the extension of damage was rather little.

The condition after 90 days was not significantly different.

In the course of a further 90 days up to the 180th day, the damage has clearly increased. The roving piece was mantled with a thick crust of CSH-phases and the amount, size and depth of holes had noticeably risen. Their distribution on the filaments was irregular and towards their surrounding and undamaged surface, they were marked off sharply (Fig. 19). On the inside of the examined roving, fibers were found with less defects which hints towards a slower damage reaction on the inside of the roving due to a massive outer crust (Fig 20).

The holes were filled with alkali-silicate-gel, which mostly pours out spherically and was formed during the corrosion of glass.

With the help of the micromanipulator, the gel-like structure was scraped out of those holes (Fig. 21) and then examined concerning its composition in distance to the surrounding fibers using energy dispersive x-ray. The following elements were predominantly found in the results: Si (approx. 26%), Ca (approx. 28%), and Zr (approx. 39%) (Fig. 22). Therewith, the content of zircon within the formed calcium-silicate-gel is considerably higher than in the surrounding glass body (approx. 15%), which indicates varying dissolubility coming out of the glass network.

After 360 days, the formation of holes has further extended and the gels coming out have expanded partially into laminar-growing crusts. Partially, they chip off the underlying and highly corroded fibers, respectively, can be lifted by using the micromanipulator (Fig. 23, 24). In Fig. 25, it is clearly indicated that at the time of examination – in comparison to NEG-fibers stored under same conditions – along with damaged areas, bigger and undisturbed areas of filaments were still existent.

Fibers without size

For the both types of fibers, NEG-ARG as well as VET-ARG, the corrosion resistance was tested by comparative investigations, whereby, the influence of the fiber size was eliminated. The fibers without size were stored in a simulated pore solution of pH 13 and 80 °C (176 °F) for 28 days.

After one-day storage, the NEG- and VET-fibers showed no corrosions (Fig. 26, 27). At the third day of storage the NEG-fibers were still without visible damages (Fig. 28), whereas the VET-fibers show a commencing damage (Fig. 29).

After 7 days, the degradation started at the NEG-fibers (Fig. 30). Compared with this, the VET-fibers already show a dense formation of little holes at nearly all filaments (Fig. 31). Up to the 14th day of storage, a further increase of the damages was visible. It was a bit lesser at the NEG-fibers (Fig. 32). But at the VET-fibers, thick layers of reaction products were formed. Underneath blistered layers the totally destroyed glass body was visible (Fig. 33). Up to the 28th day, a further increase of the damage occurred at the NEG-fibers. However, undamaged areas could be found on the filaments (Fig. 34). At the VET-fibers the process of dissolving and conversion of the glass kept on increasing (Fig. 35).

CONCLUSION

Following conclusions could be drawn from the investigations.

A corrosion of AR-glass fibers, which are embedded in concrete, can first be released when the protecting layer has dissolved. The high alkalinity of the pore solution accelerates the dissolving of the fiber size. The alkaline attack can then hit the unprotected glass body. Furthermore, already existing primary defects can be uncovered. With the load application, high localized stresses develop which may as well cause a loss of stability. However, this is seen as a subordinate process. The size can still function as a sheet of drift inside the interface-fiber-matrix and thereby enable a gentle removal of load. Out of the two examined types of fibers at VET the firmness of size in alkaline medium is greatest.

If there are - due to a partial removal of size - unprotected working areas on the surface of the fibers' glass body, the content of zircon dioxide is the decisive parameter. As a result of the higher content of zircon dioxide, the NEG fiber has the higher resistance.

Up to now, no corrosive damages could be detected on the fibers, which have been embedded in concrete and stored in a climatic test chamber (T = 40 °C (104 °F), rel. humidity 99 %) for three years. The measured losses of load capacity of the AR-glass reinforced concrete samples are mainly caused by an unfavorable and inhomogeneous structural condition in the interface matrix-fiber. This is the case, when no or only insufficient pozzolanic reactions take place during the hydration. The part of CH-phases must be minimized by adding of suitable pozzolanes. The addition of the pozzolanes leads to a long-term decrease of the alkalinity connected with positive effects on the durability.

By using an aimed selection of suitable cements and pozzolanic additives, a high durability of textile reinforced concrete on the basis of AR-glass fibers can be ensured. Types of cement, which are especially suitable are blast-furnace cements with a high content of blast-furnace slag and portland composite cements. The essential portion of