

## KINETICS OF PROCESSES MODELING CORROSION OF GLASS FIBERS MIXED INTO CONCRETE

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*The presented work involved model corrosion tests of silica–zirconia glass fibers with two different types of lubrication (Anti-Crack HD with dispersible lubrication and Anti-Crack HP with non-dispersible lubrication). Also the corrosion tests of fibers with lubrication removed by firing was studied. All types of fibers were leached in alkaline solutions ( $\text{Ca}(\text{OH})_2$  with pH 12.7, KOH with pH 12.7 and 14) at temperature of 80°C for 7 - 42 days. Changes in corrosion solutions composition and in glass surface were measured and characterized (AAS, ICP-OES and SEM-EDS, XRF, XRD resp.). The leaching results were similar for both types of fibers with or without lubrication. After leaching in the  $\text{Ca}(\text{OH})_2$  (pH 12.7), the fibers were covered with calcium precipitates. On fibers with lubrication the precipitate contained mainly crystalline calcium carbonate and calcium hydroxide, while on fibers with removed lubrication the precipitate also contained silicate. After the calcium-containing precipitates were removed with an acid solution, pitting corrosion was visible on fibers with lubrication while fibers without lubrication were covered with a corrosion layer without a significant change in the surface composition. The fibers practically did not dissolve in that environment. In KOH (pH 12.7) the fibers slightly dissolved but without visible precipitates, the composition of all types of fibers did not substantially changed. In KOH (pH 14) the fibers dissolved more significantly. On the surface of the fibers a  $\text{ZrO}_2$  and silica containing corrosion layer was formed. The time dependences of dissolved glass components indicates the incongruent dissolution of the fibers with selective leaching of sodium ions or congruent dissolution followed by precipitation of  $\text{SiO}_2$ , or  $\text{SiO}_2$  with calcium ions from the solution. It is likely that both the created precipitates (calcium or calcium-silica) and the developed corrosion layers (silica – zirconia) may operate as a barrier which slows down further corrosion of glass fibers.*

### INTRODUCTION

A new generation of concrete developed in the past 30 years is the so-called Ultra High Performance Concrete (UHPC). UHPC means a composite cement-based material with extremely high strength, long service life, high quality of surface and minimum volume changes during setting [1]. One of the UHPC components are evenly distributed fibers the purpose of which is to suppress formation and propagation of micro- and macro-fissures and thus to improve mechanical properties of the composite. Materials usually used for reinforcement include steel, organic, polymers (PP, PVA), carbon, mineral or glass microfibers with the diameter up to 0.3 mm and usually ca. 10 mm long. [2, 3, 4]. Although steel fibers are still the most common, glass fibers have been increasingly used in recent years. Glass fibers have sufficient modulus of elasticity but, in comparison with steel fibers, they are cheaper and they have lower specific weight. In comparison with similarly priced polymer fibers they have higher tensile strength. The advantage of UHPC reinforced with glass fibers consists in good aesthetic properties of the final product which is important e.g. for architectural elements [2, 5].

From the viewpoint of corrosion of steel fibers, UHPC is significantly more suitable material than other concretes used for the same purpose, such as high performance concrete HPC or NPC concrete. As with other types of concrete, steel passivation in fresh concrete occurs as a result of strongly alkaline porous solution. The pH value in the porous solution, as reported in literature, is from 12.5 (pH of saturated lime solution) to 13.5, however, it can be even higher, depending on chemical composition of the raw materials [6, 7]. Thanks to the nature of its structure, penetration of aggressive substances into UHPC is limited, particularly penetration of carbon dioxide (causing carbonation of concrete), chloride ions (causing steel activation) and oxygen (causing oxidation of steel). This results in substantially slower corrosion of the steel fibers and longer life of UHPC.

First attempts to replace steel fibers with glass fibers for reinforcement of concrete were made in 1970s. However, the first experiments with fibers made of soda-lime glass showed that such concrete quickly loses its strength as a result of corrosion of the fibers [8]. Later, experiments were conducted with E-glass (borosilicate glass with low content of alkaline

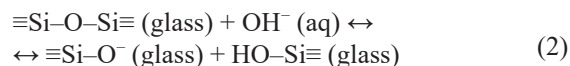
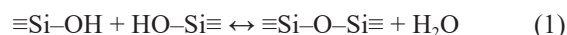
earth elements) but even those fibers were not durable enough [7]. Due to the strongly alkaline character of UHPC it was necessary to use fibers with increased durability to alkaline environment and, if possible, also to reduce alkalinity of the concrete matrix (addition of microsilica, cement with high aluminum content) [7]. It had been empirically proved in the past [9, 10, 11] that an addition of zirconium oxide significantly improves glass durability in alkaline environment and based on this observation Majumdar and Ryder prepared (and later patented [12]) a glass with high zirconia content (16 wt. % of  $\text{ZrO}_2$ ) that is referred to as Alkali-Resistant glass (AR-glass). First experiments showing higher resistance of AR-glass to alkaline environment compared to E-glass were published in 1968 [13]. The experiment evaluated loss of tensile strength of fiber samples after their exposure to cement leachate at 80°C in intervals from 24 to 96 hours [9].  $\text{ZrO}_2$  (equally as  $\text{SiO}_2$ ) creates a network but the bond  $\text{Zr-O}$  in comparison with  $\text{Si-O}$  is stronger which is demonstrated by the higher stability in presence of  $\text{OH}^-$  ions that cause the glass dissolution (see below). The mechanism of a positive effect of  $\text{ZrO}_2$  on corrosion was later described in a number of publications [9, 14, 15, 16]. For this reason AR-glass is currently used to produce UHPC reinforced with glass fibers. However, not even fibers made of AR-glass are completely inert in the strongly alkaline concrete environment and they corrode.

Corrosion of silica fibers in concrete occurs as a result of their interaction with the so-called porous liquid, i.e. water solution of concrete components. The interaction generally involves three basic processes [17]:

- Inter-diffusion of mobile ions (particularly alkaline cations, alkaline earth cations) from the glass and hydrogen cations from the solution. The ion exchange is characterized by selective leaching of alkalis, while the silica network is not attacked. The process is therefore incongruent.
- Reaction of the silica network with hydroxyl anions from the solution which leads to dissolution of the glass matrix as a whole. In this case the dissolution is congruent, i.e. all components pass from the glass into the environment in the same ratio.
- Potential precipitation of corrosion products from components of the environment or from products of reactions between components of the environment and dissolved glass components.

The processes described above may occur at the same time and they may mutually influence each other. The resulting course of the corrosion process depends on kinetics of the individual partial processes and it is closely connected with the pH value of the corrosion medium. The process b) dominates in alkaline environments, i.e. electrophilic attack of the silica network with hydroxyl ions which disrupt siloxane bonds  $\equiv\text{Si-O-Si}\equiv$  to form silanol groups  $\equiv\text{Si-OH}$ . The silanol groups may be

transformed again by condensation into  $\equiv\text{Si-O-Si}\equiv$  (1). However, without the condensation the glass matrix dissolves (2) [8, 18]:



Dissolution of glass, similarly as dissolution of any other solid material, consists of three subsequent steps – the dissolution as such (i.e. surface reaction), followed by transport of a dissolved component from the interface glass/solution and potential precipitation. The process controlling the reaction is the slowest one. More detailed analyses of interactions of glass with water solutions are available e.g. in [17-20]. In case of corrosion of glass fibers in concrete the process includes not only dissolution of silica network but also precipitation of corrosion products, usually represented by silicates, carbonates or aluminates. Due to the high content of alkali metal ions and alkaline earth ions in concrete the inter-diffusion process is usually negligible.

With regard to complexity of corrosion of glass fibers in concrete there is no general description of this process and it is impossible to find it. In fact, the speed and character of the course of the corrosion depends on a number of parameters, particularly on composition of the concrete matrix and of the fibers [7]. At the same time, it is impossible to define any uniform procedure for investigation of the interaction of fibers with the matrix. Many authors in their works deal with mechanical changes caused by corrosion of fibers (or resp. overall degradation of concrete) but the chemical aspects are rather ignored. Evaluation of chemical changes of fibers is most frequently performed by means of accelerated aging during which the fibers are placed into a sample of concrete grout, extracted porous solution or, last but not least, strongly alkaline solution which more or less simulates the porous concrete solution. The most frequently used solutions include saturated solution of  $\text{Ca(OH)}_2$ , cement leachate, NaOH solution or solution containing a mixture of NaOH, KOH and  $\text{Ca(OH)}_2$  [8]. To accelerate the processes the experiments are usually performed at elevated temperatures. The fibers are placed in the corrosion medium (with or without continual exchange of the corrosion medium) and after a certain time both the fibers and the corrosion medium are analyzed. The degree of corrosion can be most effectively evaluated from the change of fiber diameter (optic and electron microscopy) or based on changes in composition of the corrosion environment (atomic absorption/emission spectrometry, UV-VIS spectrometry etc.). It is also possible to evaluate weight changes, as described in many standards (e.g. ASTM C 1203-91, ISO 659:1991). To understand the mechanism of interaction between fibers and concrete matrix it is necessary to conduct more detailed investigation e.g. X-ray diffractometry,

X-ray fluorescence analysis, atomic absorption/emission spectrometry etc. and, particularly, to monitor the dependence on time or also on temperature. Based on an analysis of potential processes and empirical data it is possible to describe a specific case of corrosion with a mathematical model.

Results of numerous experiments have shown that during alkaline corrosion of AR-glass a layer rich in  $\text{ZrO}_2$  develops on its surface which subsequently operates as a partial diffusion barrier that decreases the rate of further corrosion [8, 9, 14, 15, 16, 23, 24]. The protective effect of the  $\text{ZrO}_2$  layer is obvious in comparison with the corrosion rate of glass without  $\text{ZrO}_2$  with a similar ratio of the other components [14]. Yilmaz in its article [9] described corrosion behavior of AR-fibers (initial diameter 12  $\mu\text{m}$ ) in Portland cement grout setting at 55°C in a period of one year. Changes of the fibers were evaluated with electron microscopy with an energy-dispersive spectrometer (SEM-EDS), including element mapping on the fibers cross section. It was found out that the interaction of fibers with cement grout produced a corrosion layer (1 - 3  $\mu\text{m}$  thick) with significant contents of Zr and Ca, the content of Si was lower than in non-corroded bulk material of the fibers and Na was practically not present in the corrosion layer. As a result of corrosion the ratio of Zr/Si increased ca. four times, the ratio of Ca/Si increased 14 times and the ratio of Na/Si decreased 2.5 times. Those results were used to conclude that during the corrosion the silica network on the surface of fibers dissolved (while the bonds Zr-O were disrupted much less and therefore the relative representation of Zr increased in comparison with Si) and the alkaline metal ions (particularly  $\text{Na}^+$ ) diffused into the porous solution. Calcium ions moved in the opposite direction due to the concentration gradient, i.e. from the porous solution to the surface of fibers. At the end of the experiment the pH value of the porous solution extracted from cement matrix was 13.8 (25°C), however, the author failed to indicate the original value. Corrosion products were found on the surface of the fibers, however their adhesion to the fibers was weak, as reported also by Makishima et al. [15]. Amorphous character of the corrosion products was determined by X-ray diffraction (the particles failed to provide any diffraction pattern) and microscopic investigation showed their porous character. This means that corrosion products did not prevent diffusion of  $\text{OH}^-$  ions to the surface of fibers. However, the results of this experiment are not in complete agreement with conclusions resulting from tests performed in solutions that simulated porous liquid, as described e.g. in the article [14]. Larner et al. [14] performed static tests of glass fibers (AR-glass and for comparison also E-glass and the so-called A-glass, i.e. Na-Ca glass) exposed to water leachates from concrete mixture based on Portland cement. The fibers were leached for a period of 1 year (with the interval of 20 days) at temperatures 50, 65 and 80°C. Several

methods were used to analyze the test, e.g. optic and electron microscopy, SEM-EDS, atomic spectrometry etc. Also in this case the tests resulted in formation of a surface layer on AR-fibers that was rich in  $\text{ZrO}_2$ , due to dissolution of the silica network (in this case the ratio Zr/Si increased only two times) and leaching of sodium ions (the leaching rate decrease with time, particularly at low temperatures). The surface layer demonstrated “pitted” surface. Also other corrosion products were found and their main component was hydrated gel of calcium silicate in which a part of calcium was replaced with sodium and potassium ions. Within the first 10 days a substantial portion of calcium passed from the solution into corrosion products on the surface of fibers, in the form of  $\text{Ca}(\text{OH})_2$  or the product mentioned above. Presence of Zr in the corrosion products was not demonstrated. Decrease of pH was observed in both solutions and at all the temperatures and it was the lowest in case of AR glass (by ca. 0.5 units, in comparison with 2.5 for E-glass and 1.5 for A-glass). The experiment confirmed significantly higher chemical durability of AR-glass against alkaline environment in comparison with the other types of tested fibers. It is obvious that the main characteristic of AR-fibers corrosion in alkaline environment (i.e. the low corrosion rate and formation of a zirconium rich surface layer) corresponds with the tests in concrete matrix [9], nevertheless more detailed results (such as e.g. the character of corrosion products on the surface of fibers) were different, depending on specific experimental conditions. The same conclusion can be made from the other tests performed with the intention to understand corrosion of AR-fibers in UHPC [8, 15, 16, 23].

## EXPERIMENTAL

In the presented work model tests were used to monitor corrosion of 2 types of commercially produced glass fibers in alkaline solutions. The first type of fibers with dispersible lubrication was labeled by the producer as Anti-Crack HD, the second type with non-dispersible lubrication was labeled as Anti-Crack HP. Both types of fibers were made of alkali-resistant silica-zirconia glass (Tab. I). To evaluate effects of lubrication during the corrosion tests a part of both types of fibers was fired in a furnace for 3 hours at 560°C, which removed the surface lubrication layer. Glass fibers with and without lubrication were exposed to a model leaching test in water solution  $\text{Ca}(\text{OH})_2$  at pH = 12.7 (i.e. pH of saturated solution) and also to two water solutions of KOH – one with the comparable pH = 12.7 and one with more aggressive pH = 14. The alkaline solution of KOH was selected for the tests in order to determine components that passed from fibers into leachates because the glass does not contain any potassium components. All tests were performed under increased corrosion conditions,



i.e. at the temperature of 80°C for 7 - 42 days. The components that passed from the fibers into the leachate were measured with AAS (Na, Si, or Ca) and ICP-OES (Zr); the composition and appearance of the fibers before and after the leaching in model solutions were evaluated with XRF, XRD and SEM-EDS techniques.

## RESULTS AND DISCUSSION

Table 1 presents compositions of the two glasses as analyzed with XRF. The results indicate that the compositions of both types of the fibers were the same.

Table 1. Composition of glass fibers (main components) as analyzed by XRF.

wt. % (XRF)	SiO <sub>2</sub>	ZrO <sub>2</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>
Anti-Crack HD	56.8	20.0	16.2	6.2	0.3
Anti-Crack HP	56.8	20.0	16.2	6.2	0.3

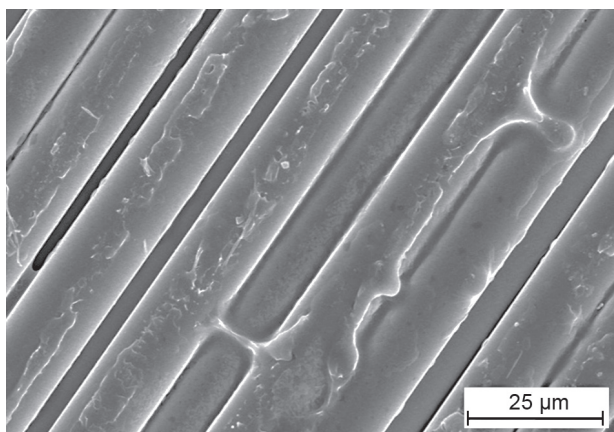


Figure 1. Fiber Anti-Crack HP with a lubrication layer before firing in a furnace (SEM).

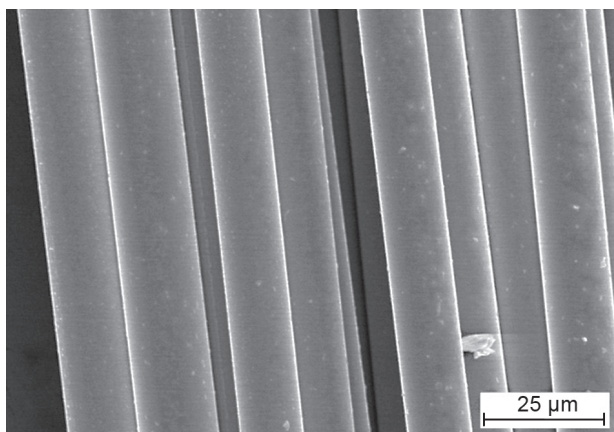


Figure 2. Fiber Anti-Crack HP after firing of the lubrication layer in a furnace (SEM).

Further, it was found out that after complete firing of lubrication layers in the furnace the compositions of both types of the fibers, as found by XRF, did not change. In the case of Anti-Crack HD, i.e. fibers covered with dispersible lubrication, the surface lubrication was removed by leaching in the solution while in the case of Anti-Crack HP covered with non-dispersible lubrication the layer had to be removed by firing in a furnace. The comparison of appearance and composition of the surface of Anti-Crack HP fibers with SEM-EDS before firing (Figure 1) and after firing (Figure 2) in a furnace clearly shows that the firing removed the lubrication but the composition of the fibers surface nearly did not change (Table 2).

Table 2. Composition of the fibers surface before and after firing of the lubrication layer (SEM-EDS).

wt. %	SiO <sub>2</sub>	ZrO <sub>2</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>
fibers with lubrication	56.8	20.0	16.2	6.2	0.3
fibers without lubrication	56.8	20.0	16.2	6.2	0.3

Figures 3 through 8 present results of leaching of Anti-Crack HD and Anti-Crack HP fibers in alkaline solutions at 80°C. Results of Na, Si, or Ca concentrations found in the leachates analyzed with AAS were used to calculate normalized dissolved quantities of the individual glass components based on the equation:

$$NL_i = c_i \cdot x_i^{-1} \cdot S^{-1} \cdot V \quad (1)$$

where  $c_i$  is concentration of the component  $i$  in the solution [mg/l],  $x_i$  is a mass fraction of the component  $i$  in the original material,  $S$  is the sample surface in contact with the corrosion solution in [m<sup>2</sup>] and  $V$  is a volume of the corrosion solution [m<sup>3</sup>]. The resulting  $NL_i$  in [g/m<sup>2</sup>] was recalculated to the initial weight of the fibers before leaching, i.e.  $NL_i$  in [mg/g]. Figures 3 and 4 present leaching of fibers in Ca(OH)<sub>2</sub> solution (pH 12.7), Figures 5 and 6 present leaching of fibers in KOH solution

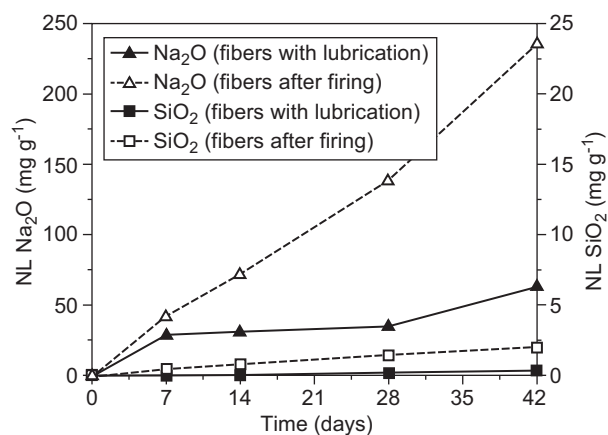


Figure 3. Normalized quantities of fiber components that passed into Ca(OH)<sub>2</sub>, pH 12.7 – AntiCrack™ HD–Ca(OH)<sub>2</sub>.

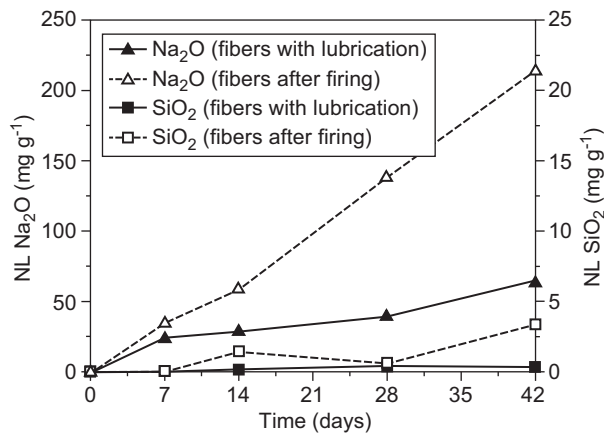


Figure 4. Normalized quantities of fiber components that passed into Ca(OH)<sub>2</sub> solution, pH 12.7 – AntiCrack™ HP–Ca(OH)<sub>2</sub>.

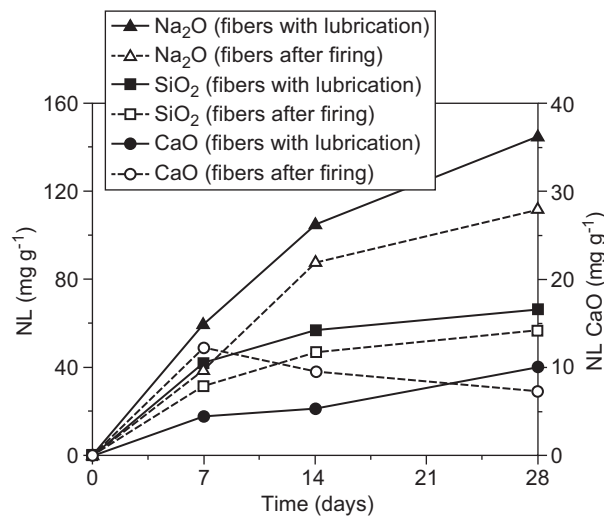


Figure 5. Normalized quantities of fiber components that passed into KOH solution, pH 12.7 – AntiCrack™ HD–KOH.

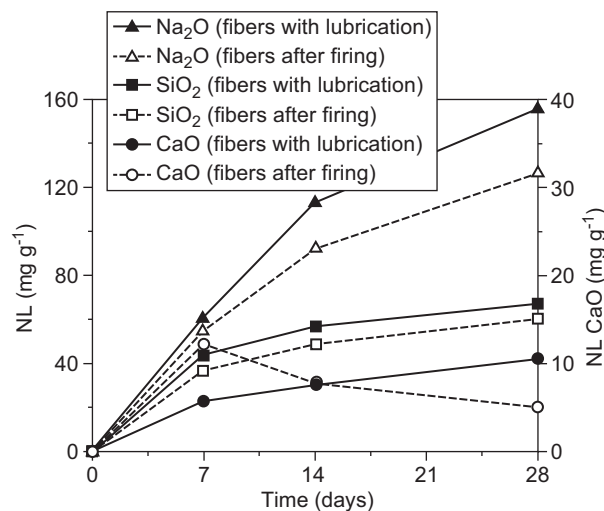


Figure 6. Normalized quantities of fiber components that passed into KOH solution, pH 12.7 – AntiCrack™ HP–KOH.

(pH 12.7) and Figures 7 and 8 present leaching of fibers in KOH solution (pH 14).

The results of model tests indicate that leaching of fibers with dispersible lubrication (Anti-Crack HD) and fibers with non-dispersible lubrication (Anti-Crack HP) was in all the environments very similar. Also similar was leaching of Anti-Crack HD fibers and Anti-Crack HP with the surface lubrication removed after firing in a furnace.

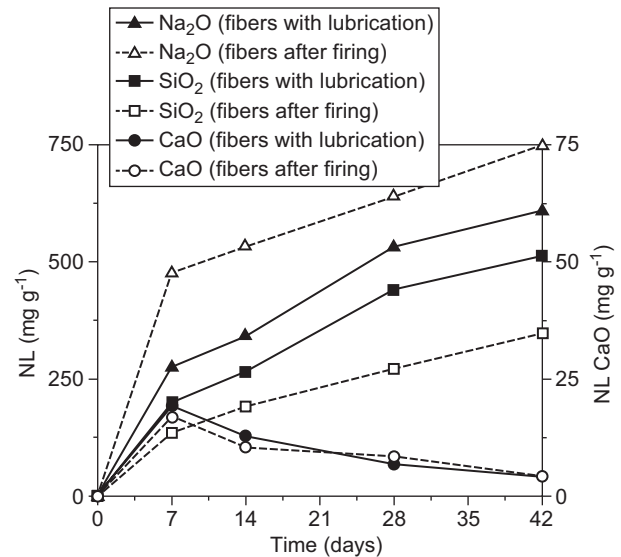


Figure 7. Normalized quantities of fiber components that passed into KOH solution, pH 14 – AntiCrack™ HD–KOH.

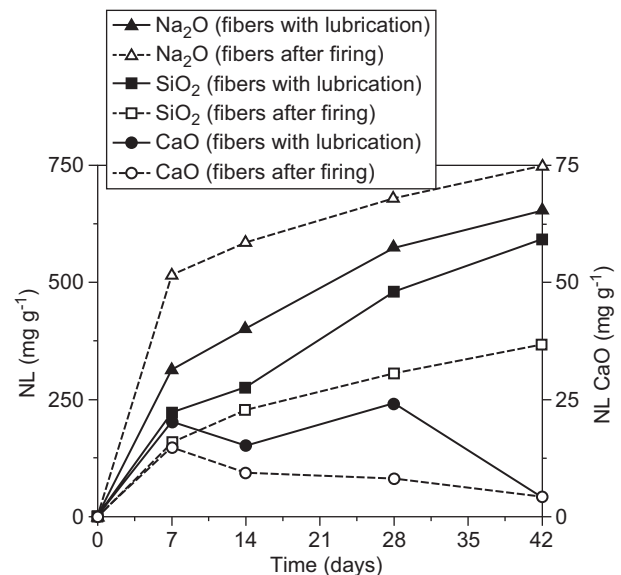


Figure 8. Normalized quantities of fiber components that passed into KOH solution, pH 14 – AntiCrack™ HP–KOH.

In the alkaline environment of Ca(OH)<sub>2</sub> it is mainly sodium ions that leach from the fibers into the solution and the fibers nearly do not dissolve, as documented by

the low concentration of  $\text{SiO}_2$  in the leachates (Figures 3, 4). A significantly lower concentration of Na was found in leachates from fibers with lubrication compared to fibers from which the lubrication was removed by firing in a furnace (Figures 3, 4). White precipitates were developing in the leaching solutions already in the course of the tests and their analysis by XRD has shown that they mostly consisted of calcium carbonate and calcium hydroxide (Figure 9) in the ratio ca. 8:5. Moreover, significant quantities of crystalline precipitates were found with SEM on the surface of the fibers (Figure 10). Lower quantities of such precipitates were found on fibers with lubrication (Figure 11), while on the fiber surface without lubrication (fired in a furnace) the quantities of precipitates were significantly bigger (Figure 12).

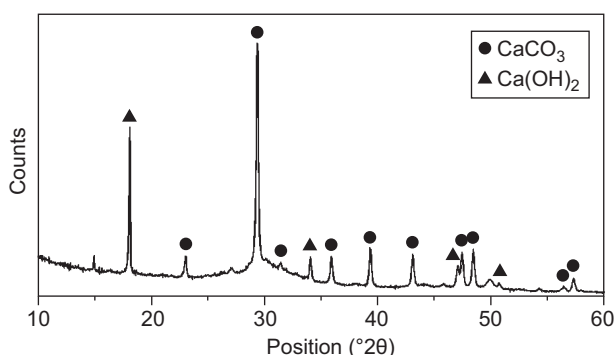


Figure 9. Analysis of precipitates developed in the  $\text{Ca}(\text{OH})_2$  solution during the model tests (XRD).

Based on the SEM-EDS results the precipitate formed on the surface of fibers with lubrication consisted of 98.9 wt. %  $\text{CaO}$  and 1 wt. %  $\text{SiO}_2$ , the precipitate formed on fibers with removed lubrication, i.e. on the bare glass surface, consisted of 61.4 wt. %  $\text{CaO}$  and 36.6 wt. %  $\text{SiO}_2$ . In order to determine the condition of the surface of fibers with lubrication and without lubrication under the precipitates, the calcium-containing products were removed by washing with diluted nitric acid. Figures 13 and 14 show disruption of the surface under the calcium-containing products, while the disruption was more significant on fibers from which the lubrication was removed before leaching by firing in a furnace (Figure 14). With regard to those images and also with regard to results of analysis of the solutions and EDS analysis of fiber surfaces (Table 3) we can assume that a crystalline layer of calcium carbonate and calcium hydroxide is formed on the surface of fibers with lubrication and that degradation of the lubrication occurs primarily under that layer (nearly zero concentration of  $\text{SiO}_2$  in the solutions, only small difference in composition of the surface before and after the exposure). Results of analyses of leachates from fibers with removed lubrication also indicate nearly zero concentration of  $\text{SiO}_2$  (Figures 3 and 4) but results of EDS analyses (Table 3) suggest that precipitates on

the surface of fired fibers consist not only of calcium carbonate and calcium hydroxide but also of silicate.

Unlike in  $\text{Ca}(\text{OH})_2$ , slight dissolution of fibers occurred in  $\text{KOH}$  environment with comparable pH 12.7. No precipitates were found in the leaching solutions or on fiber surfaces, neither on fibers with lubrication

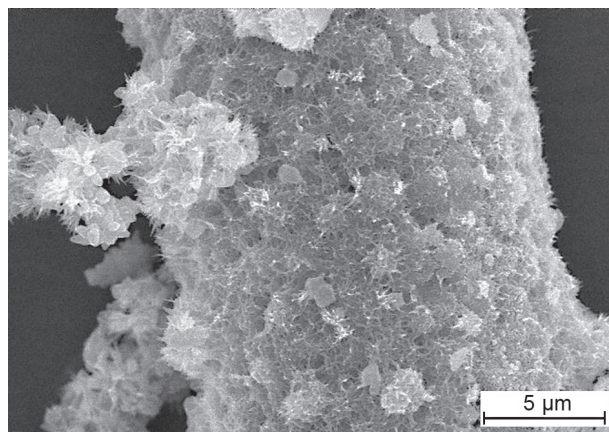


Figure 10. Crystalline precipitates on Anti-Crack HD fibers with lubrication leached for 42 days in  $\text{Ca}(\text{OH})_2$  (SEM).

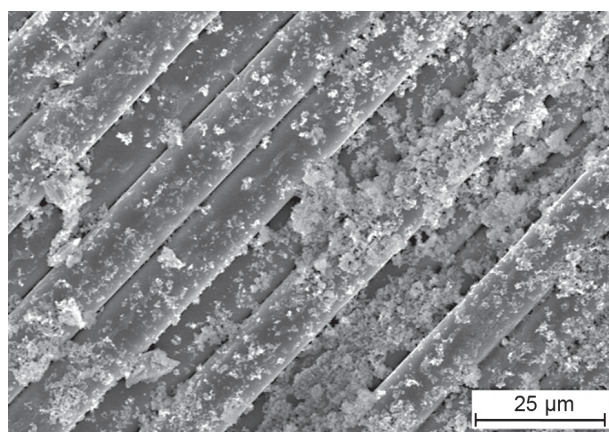


Figure 11. Precipitates on Anti-Crack HP fibers with lubrication after leaching for 28 days in  $\text{Ca}(\text{OH})_2$  (SEM).

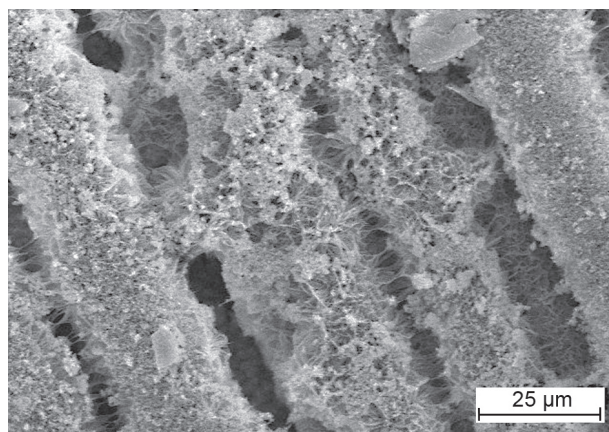


Figure 12. Precipitates on the surface of Anti-Crack HP fibers with removed lubrication (fired in a furnace) after leaching for 28 days in  $\text{Ca}(\text{OH})_2$  (SEM).



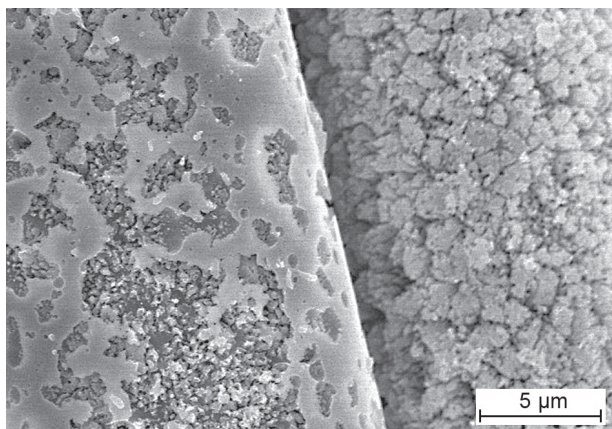


Figure 13. Surface of fibers with lubrication after leaching in  $\text{Ca(OH)}_2$  and after washing of calcium-containing precipitates with an acid solution (SEM).

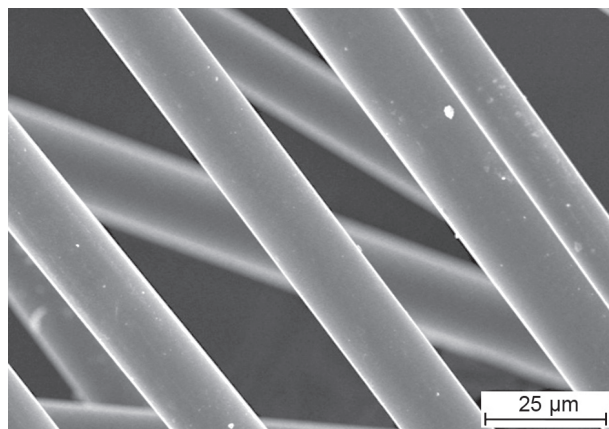


Figure 15. Surface of fibers with lubrication after leaching for 42 days in KOH, pH 12.7 (SEM).

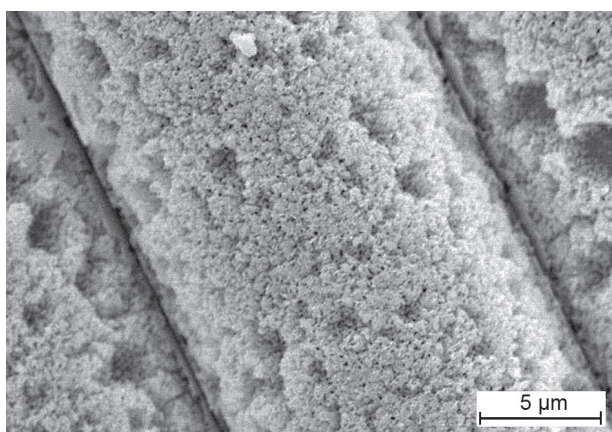


Figure 14. Surface of fibers without lubrication (fired in a furnace) after leaching in  $\text{Ca(OH)}_2$  and after washing of calcium-containing precipitates with an acid solution (SEM).

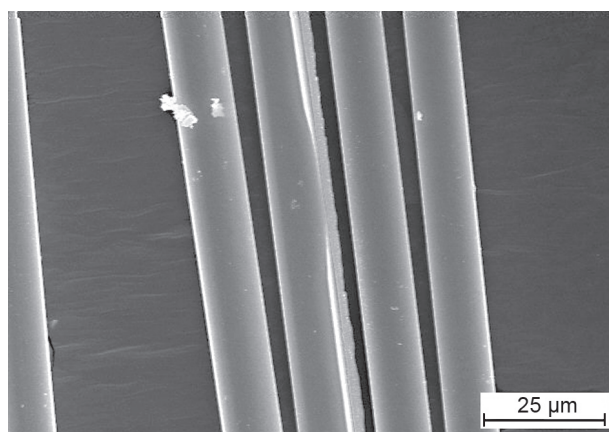


Figure 16. Surface of fibers without lubrication (fired in a furnace) after leaching for 42 days in KOH, pH 12.7 (SEM).

Table 3. EDS microanalysis of fiber surface after leaching for 42 days in  $\text{Ca(OH)}_2$ .

wt. %	fibers with lubrication			fibers without lubrication			
	before leaching	after leaching	precipitate	before leaching	after leaching	precipitate	after acid-washing
$\text{SiO}_2$	59.1	55.1	1.1	59.9	32.4	36.6	63.6
$\text{ZrO}_2$	22.1	23.4	–	22.5	27.7	–	22.4
$\text{Na}_2\text{O}$	11.1	8.2	–	11.5	2.1	–	6.8
$\text{CaO}$	6.3	12.5	98.9	5.6	37.4	61.4	5.8
$\text{Al}_2\text{O}_3$	1.3	0.8	–	0.5	0.4	–	1.4

Table 4. EDS microanalysis of fibers surface after leaching for 42 days in KOH, pH 14.

wt. %	fibers with lubrication			fibers without lubrication	
	before leaching	after leaching	under delaminated corrosion layer	before leaching	after leaching
$\text{SiO}_2$	59.1	33.0	58.1	59.9	41.0
$\text{ZrO}_2$	22.1	50.1	25.1	22.5	43.4
$\text{Na}_2\text{O}$	11.1	0.9	10.8	11.5	2.9
$\text{CaO}$	6.3	15.1	5.5	5.6	12.1
$\text{Al}_2\text{O}_3$	1.3	0.9	0.5	0.5	0.6

(Figure 15), nor on fibers without lubrication (Figure 16). SEM-EDS investigation has shown that the composition of surfaces of all types of fibers nearly did not change after the leaching.

In the strongly alkaline KOH environment with pH 14 the fibers dissolved more significantly which was documented by the high content of  $\text{SiO}_2$  in the leachates (Figure 7 and 8). The leachates were also analyzed for Zr by ICP-OES but the results confirmed nearly zero quantity of Zr throughout the entire period of leaching. SEM was used to investigate the surface of fibers with lubrication which was dissected and locally disrupted with fissures in the surface layer (Figure 17) and, exceptionally, the top corrosion layer peeled off from the fiber core (Figure 18). On the contrary, the surface of fibers with removed lubrication seemed relatively compact and there were practically no disrupted places. EDS analyses have shown that corrosion layers formed on all types of fibers and they consisted mostly of zirconium oxide and silicon oxide (Table 4).  $\text{ZrO}_2$  in corrosion layers prevailed (Table 4) which is in agreement with its absence in the leachates.

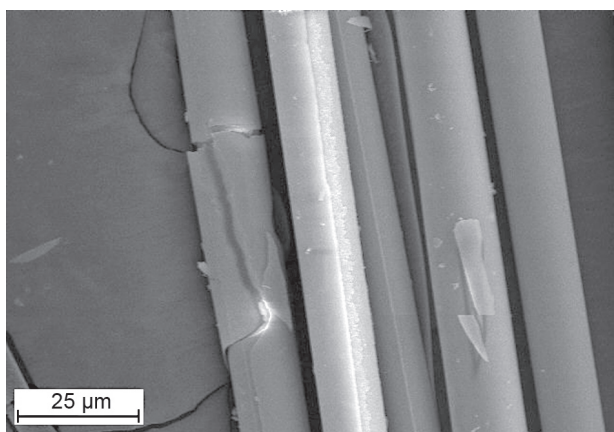


Figure 17. Surface of fibers with lubrication leached for 42 days in KOH, pH 14 (SEM).

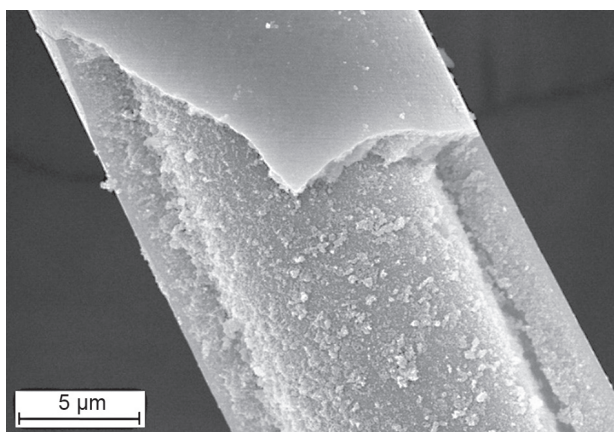


Figure 18. Top corrosion layer partly peeled off from the fiber core after leaching for 42 days in KOH, pH 14 (SEM).

## CONCLUSIONS

The presented work involved model corrosion tests of 2 types of glass fibers made of silica-zirconia glass (Anti-Crack HD with dispersible lubrication and Anti-Crack HP with non-dispersible lubrication). The tests investigated corrosion of fibers with surface lubrication and also corrosion of glass fibers after the lubrication layer was removed by firing in a furnace at  $560^\circ\text{C}$ . All types of fibers were leached in alkaline water solutions ( $\text{Ca}(\text{OH})_2$  with pH 12.7, KOH with pH 12.7 and 14) at the increased temperature of  $80^\circ\text{C}$  for 7 - 42 days. The tests were evaluated based on concentration of glass components that passed into the leaching solutions (AAS, ICP-OES) and also based on appearance and composition of the fibers surface before and after leaching in the alkaline solutions (SEM-EDS, XRF, XRD).

It was found out that leaching of Anti-Crack HD and Anti-Crack HP fibers was similar, both for the fibers with lubrication and after the lubrication was removed by firing in a furnace. The firing in a furnace had no impact on composition of both types of the fibers.

After leaching in the alkaline  $\text{Ca}(\text{OH})_2$  environment with pH 12.7 the fibers were covered with calcium precipitates. On fibers with lubrication the precipitate contained mainly crystalline calcium carbonate and calcium hydroxide, while on fibers with removed lubrication the precipitate also contained silicate. After the calcium-containing precipitates were removed with an acid solution, pitting corrosion was visible on fibers with lubrication while fibers without lubrication were covered with a corrosion layer without a significant change in the surface composition. The fibers practically did not dissolve in that environment.

In KOH solution with pH 12.7 the fibers slightly dissolved but there were no visible changes in the appearance; the composition of all types of fibers did not substantially change after the leaching and there were no precipitates on them. In KOH solution with pH 14 the fibers dissolved more significantly. On the surface of the fibers with lubrication and without lubrication a corrosion layer was formed made of zirconia and silica with an increased content of  $\text{ZrO}_2$  (50 wt. % and 43 wt. % respectively).

The analyses mentioned above suggest incongruent dissolution of the fibers with selective leaching of sodium ions or congruent dissolution followed by precipitation of  $\text{SiO}_2$ , or  $\text{SiO}_2$  with calcium ions from the solution. It is likely that both the created precipitates (calcium or calcium-silicate) and the developed corrosion layers (silica-zirconium dioxide) may operate as a barrier which slows down further corrosion of glass fibers.

Under real conditions of concrete preparation and hardening the glass fibers are often exposed to a mixture of alkaline solutions and the conditions are less extreme (lower temperature and shorter time of exposure) than in the tests performed here under. Therefore it is possible



to expect that the tested types of glass fibers are suitable for alkaline concrete mixtures. The authors will continue their efforts to confirm such expectations by preparing specific concrete mixtures of UHPC and NPC with glass fibers and they will monitor their corrosion for 1 year.

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