# CORROSION OF E-GLASS FIBERS - SECURITY FACTOR OF NUCLEAR POWER PLANTS

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*The flow-through leaching experiments have been conducted at two buffered pH values (8.5 and 10.0) of borate leaching solutions and at two temperatures (70°C and 90°C) on the EUTAL glass fibers, used as an insulation in nuclear power plants. Time dependencies of the total amount of leached elements Si, Al and Ca in corrosive solution have been determined. From the leaching rates in stationary conditions the values of activation energies, Ea, have been calculated. Lower Ea values were found for leaching at higher pH value. Higher Ea values were found for atoms so called network-forming oxides (Si, Al). Surface of corroded fibers was analyzed by scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDX). Formation of relatively smooth continuous surface layer of corrosion products was detected at higher pH value.*

## INTRODUCTION

In case of an accident the emergency system of a nuclear power plant is used in order to preserve pressure of a coolant in the primary cooling circuit and to dispose heat from the active zone of nuclear reactor. The system consists of the tanks filled with the boric acid solution and the pumps transporting solution to the primary cooling area. Moreover the low-pressure pumps are activated when the tanks are not able to bring the cooling water into the system. After pumping out, water is pumped in again from the heat exchanger placed at the bottom of the hermetic boxes. Loss of coolant accident - LOCA (damage of the primary cooling area) causes rapid increase of pressure in the hermetic boxes. Therefore the spraying system is activated. Required decrease of pressure is achieved by spraying the area of the hermetic boxes and by condensation of steam and air mixture [1].

The glass fibers play a significant role regarding the security system of the nuclear plants. Glass fibers are mainly used as thermal and electrical insulation and in case of accident fibers get in immediate contact with cooling solution. It is well known that water solution in contact with a glass causes changes resulting in the structure transformation of glass surface, dissolution of a glass itself and formation of new glass surface layer [2]. Intensity of this phenomenon depends on well known factors. To the most important belong composition of the corrosive solution, its *pH* and temperature, and exposure time. In the case of LOCA, the glass fibers used as insulation are exposed to very aggressive environment for a relatively long time. Corrosion products can plug filtering devices of the cooling system and consequently prevent pumping of a coolant from the hermetic boxes. This causes insufficient even functionless circulation of the cooling solution during accident. To assure safety of the cooling system is important to describe behavior of the glass fibers in the environment meeting aggressive conditions, and to predict composition and behavior of created corrosion products due to the long-term contact of insulation with the corrosive medium.

## EXPERIMENTAL

The flow-through leaching tests have been conducted on the EUTAL glass fibers with the composition shown in table 1.

Table 1. Composition (wt.%) of the EUTAL glass fibers (main components).

| $SiO_2$ | $B_2O_3$ | $Al_2O_3$ | CaO | MgO |
|---|---|---|---|---|
| 54 | 5.3 | 14.3 | 22.9 | 1.5 |

To remove the lubrication, the glass fibers had been exposed to the temperature of 300°C in the furnace for one hour. Diameters of burned glass fibers were determined by the optical microscopy using the image analysis (LUCIA). The mean value of the fiber diameter was counted from the lognormal distribution of a thousand

fiber diameters. The specific surface of fibers was then calculated:

$$\frac{S}{m} = \frac{2}{\rho\, r} \tag{1}$$

The flow-through leaching tests had been carried out in a period of 10 days with the flow rate of 15 $cm^3/h$ at temperatures of 70°C and 90°C. As a leaching medium two borate solutions of different composition with buffering effect were used. The composition of buffering solutions is given in the table 2. First leaching solution marked as B meets composition of the cooling solution used in the nuclear power plant. The *pH* value of 8.5 at the temperature of 22°C was achieved by addition of KOH. The *pH* of second leaching solution marked as CP meeting value of 10.0 was assured by addition of KOH together with 6-(cyklohexylamino)-1-propanesulfone acid (CAPS). This highly alkaline solution was chosen in order to simulate more aggressive conditions for dissolution of the EUTAL glass fibers known for their high chemical durability in alkaline environment.

Table 2. Composition of the leaching media (g/l).

| Abbreviation | B | CP |
|---|---|---|
| $H_3BO_3$ | 9.36 | 9.36 |
| KOH | 2.99 | 7.00 |
| $NH_3$ | 0.89 | 7.58 |
| $N_2H_6SO_4$ | 0.93 | 0.93 |
| CAPS | - | 2.00 |
| *pH* at 22°C | 8.5 | 10.0 |

Table 3. Experimental conditions of flow-through tests.

| | |
|---|---|
| Weight of fibers in reactor | 1.00 g |
| Volume of reactor | 5.00 $cm^3$ |
| Density of fibers | 2.644 $g/cm^3$ |
| Mean value of fiber diameter | $11.2\times10^{-6}$ m |
| Specific surface | 0.133 $m^2/g$ |
| Flow rate of leaching solution | 15 $cm^3/h$ |

For each temperature and leaching medium four parallel experiments were performed. The concentrations of leached Si, Al, and Ca were determined by the atomic absorption spectrometry (it was impossible to determine the amount of leached boron in the solution due to significantly lower concentration comparing with boron presented in the initial solution). The corrosion layer created on the surface of elementary fiber and its composition were analyzed by the scanning electron microscopy with energy dispersive X-ray analysis.

## RESULTS AND DISCUSSION

The weight loss of glass fibers leached in the corrosive medium B at the temperature of 70°C for 10 days meets the value (5.2 ± 0.2) % and (6.8 ± 0.2) % in case of using the medium CP, whereas the weight loss of glass fibers exposed to medium B at the temperature of 90°C meets the value (15.0 ± 0.1)% and for medium CP the value (16.7 ± 0.1)%.

The total amount of leached elements and its normalized amounts determine the following equations [3,4]:

$$Q_i^t = c_\mathrm{i}\frac{F}{S}\Delta t + Q_i^{t-\Delta t} \tag{2}$$

$$NL_i^t = \frac{c_i F \Delta t}{x_i S} + NL_i^{t-\Delta t} \tag{3}$$

where $Q_i$ is the total amount of leached elements by unit glass surface area in time $t$, $S$ is the glass surface area in contact with the leaching solution, $c_i$ is concentration of particular leached element in time $t$, $F$ is the flow rate, and $x_i$ represents the weight fraction of $i$-th element in the glass. Comparison of $NL_\mathrm{i}$ values tells us about mechanism involved in dissolution of a given glass. In case of congruent dissolution the $NL_\mathrm{i}$ values are in mutual compliance unlike for incongruent dissolution. The time dependence of total amount, $Q_i$, and normalized amount, $NL_\mathrm{i}$, of Si, Al, and Ca are plotted in figures 1 and 2.

Normalized amount of Ca at both temperatures and for both leaching solutions was higher as normalized amount of Si and Al. This fact is related to the position of Ca in the silicate network. Calcium modifies the silicate network and leaching of its ions is higher in confrontation with Al, which participate on formation of the silicate network.

Values of the initial and stationary leaching rates may be evaluated from experimental time dependencies of $Q_i$ by graphical or numerical methods. The graphical method is not reliable for determination of the initial leaching rates, therefore the following empirical equation is commonly used [2, 5]:

$$Q_i = P_\mathrm{a}\left(1 - e^{-P_\mathrm{b}t}\right) + P_\mathrm{c}t \tag{4}$$

Due to low thickness and quick formation of the calcium depleted surface diffusion layer in alkaline conditions, the obtained $Q_i(t)$ dependences are almost perfectly linear (figures 1, 2) in the time scale studied. The simple linear regression model with non-zero intercept has to be used instead of the equation (5) in this case. The stationary leaching rate is then simply given by the slope of the regression line.

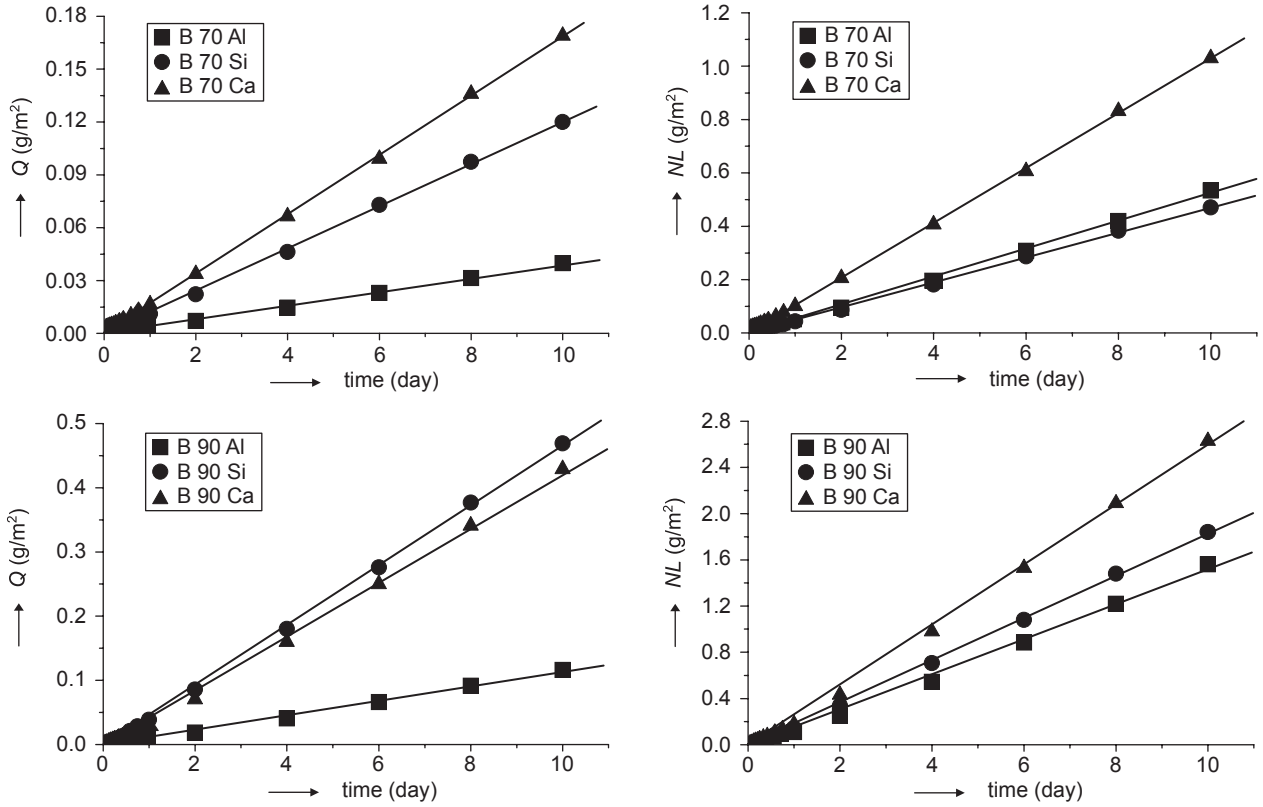



Figure 1. Time dependence of the amounts and normalized amounts of leached elements at temperatures 70°C a 90°C for leaching solution B. Lines represent the linear regression model.

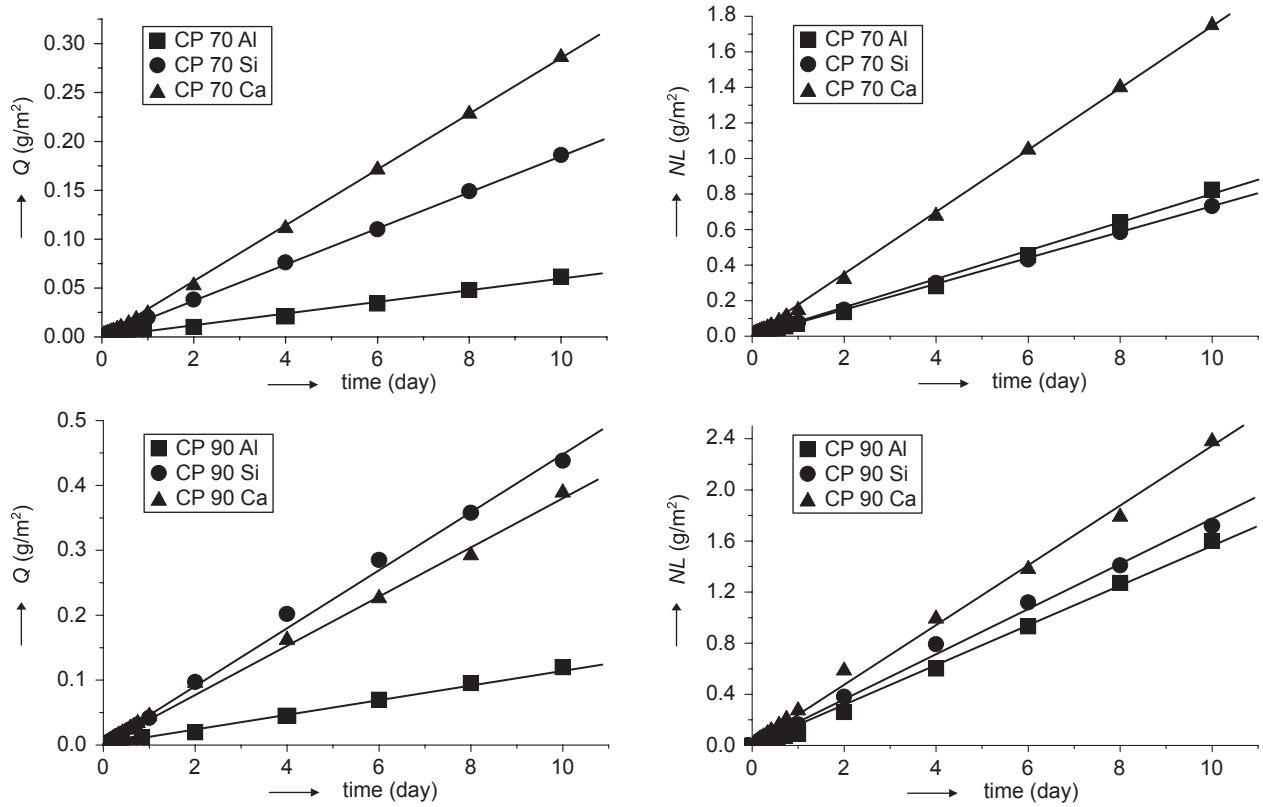
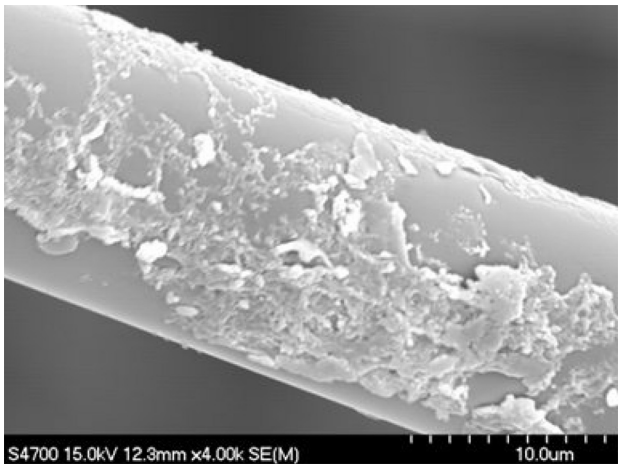



Figure 2. Time dependence of the amounts and normalized amounts of leached elements at temperatures 70°C a 90°C for leaching solution CP. Lines represent the linear regression model.

In alkaline environment when almost non-alkaline E-glass fiber had been leached, very thin diffusion layer is developed very fast. Alkaline solution in a contact with glass fiber surface causes fast breaking of Si–O–Si bonds followed by dissolution of silicate network as the rate controlling step of the corrosive process. The alkali metals, participating on the corrosive process as a diffusion component, are mostly not presented in the structure of the EUTAL glass. The obtained time dependences are practically linear after one hour of leaching. Therefore only the leaching rates in stationary conditions were evaluated. The values of the leaching rates in stationary conditions are summarized in table 4.

Table 4. Values of dissolution rates in stationary conditions and their standard deviations.

| medium/ temperature | $v_\infty$ (Si) (mg/m$^2$ day) | $v_\infty$ (Al) (mg/m$^2$ day) | $v_\infty$ (Ca) (mg/m$^2$ day) |
|---|---|---|---|
| B 70 | 47.5 ± 0.7 | 52.8 ± 1.6 | 102.1 ± 2.7 |
| B 90 | 185.2 ± 4.4 | 154.9 ± 1.0 | 262.9 ± 6.1 |
| CP 70 | 73.5 ± 2.1 | 80.9 ± 1.9 | 175.4± 6.3 |
| CP 90 | 176.9 ± 3.7 | 162.0 ± 3.6 | 231.4 ± 10.5 |



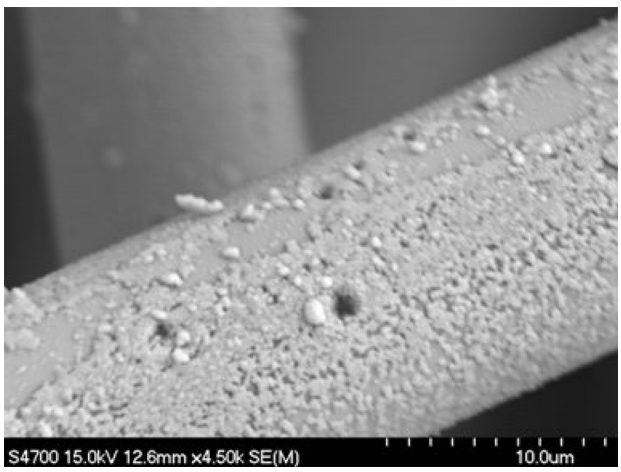




Figure 3. SEM micrographs of corroded fibers.

From the stationary leaching rates obtained for two distinct temperatures, the formal mean activation energy, $E_a$, was calculated from the Arrhenius equation:

$$v_\infty = A.\exp\left(-E_a/RT\right) \tag{5}$$

Mean values of activation energies, $E_a$, and their standard deviations are shown in table 5. Standard deviations of $E_a$ were calculated from four parallel experiments for each temperature. It can be concluded, that lower $E_a$ values were found for leaching at higher *pH* value. On the other hand, higher $E_a$ values were found for atoms of network-forming oxides (Si, Al).

Table 5. Values of mean activation energies and their standard deviations.

| medium | $E_a$ (Si) (kJ/mol) | $E_a$ (Al) (kJ/mol) | $E_a$ (Ca) (kJ/mol) |
|---|---|---|---|
| B | 72.3 ± 1.8 | 55.8 ± 0.8 | 49.0 ± 1.8 |
| CP | 45.5 ± 2.4 | 36.0 ± 1.4 | 14.4 ± 1.8 |

The presented figures (figure 3) obtained from SEM analysis indicate formation of the corrosive products on the surface of glass fibers. SEM/EDX analysis confirmed formation of alumino-silicate precipitated layer on the surface of corroded fiber. Observed layer on a glass fiber leached in the solution B is not as compact as in case of CP leaching solution.

## CONCLUSION

Performed flow-through leaching tests on the EUTAL glass fibers used as insulation in the nuclear plants confirmed the fact that the E-glass fibers show high chemical durability in alkaline solutions. Dissolution of the glass fibers used in our experiments is incongruent. The dissolution rate of Al and Si is almost the same. In the corrosive environment was observed back-precipitation of Si, Al and Ca elements participating on formation of a new layer on the fiber surface.

## Acknowledgement

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KORÓZIA SKLENÝCH VLÁKIEN - BEZPEČNOSTNÝ FAKTOR JADROVÝCH ELEKTRÁRNÍ

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Na sklených vláknach Eutal, používaných ako izolácie v jadrových elektrárňach, boli vykonané prietokové lúžiace experimenty. Testy prebiehali v dvoch pufrovaných roztokoch kyseliny boritej s *pH* 8,5 a 10 a pri dvoch teplotách (70°C a 90°C). Boli zistené časové závislosti vylúhovania celkového množstva jednotlivých zložiek Si, Al a Ca do roztoku. Z rýchlostí lúhovania v ustálenom stave sa vypočítali hodnoty aktivačných energií, $E_a$. Nižšie hodnoty $E_a$ sa stanovili pre lúhovanie sklených vlákien v roztokoch s vyšším *pH*. Vyššie hodnoty $E_a$ boli nájdené pre atómy sieťotvorných oxidov (Si, Al). Povrch korodovaných vlákien sa sledoval pomocou skenovacej elektrónovej mikroskopie v kombinácii s mikroanalýzou (SEM/EDS). Pri vyšších hodnotách *pH* bol detekovaný vznik relatívne hladkej, kontinuálnej vrstvičky na povrchu korodovaných vlákien.