

# CORROSION OF E-GLASS FIBERS IN DISTILLED WATER

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Submitted March 13, 2007; accepted June 6, 2007

**Keywords:** Chemical durability, Glass fibers, Leaching behavior

*In submitted paper the kinetic of E-glass fibers leaching in distilled water was studied. Time dependences of the total amount of elements (Si, B, Al, Ca and Mg) leached from glass fiber at temperatures 50°C, 70°C and 90°C into solution were determined under static conditions. The ratio of initial surface area of leached glass fibers and volume of corrosion solution  $S/V$  reached 3500  $m^{-1}$ . The time dependencies of concentration of leached elements were described in accordance with Helebrant's model corrected for an amount of elements carried into solution by the technical fiber in zero time. The kinetic of glass dissolution was described based on the amount of leached boron. Mean composition of oxides presented in precipitated layer and surface diffusion layer have been calculated provided that boron is not presented in that layer. Dependence of glass dissolution from solution composition and temperature was determined by statistical methods. The value of activation energy ( $46 \pm 4$ ) kJ/mol has been found.*

## INTRODUCTION

In the last decade the research related with nuclear power plants (NPP) is oriented not only on vitrification of radioactive waste but also on its safety during active operation. One of the factors, which can disturb operation of a nuclear power plant with a pressurized water reactor (PWR) is failure of the containment sump during creating hole of piping of primary cooling area of active zone of nuclear reactor named loss of coolant accident (LOCA). During accident the cooling water scours the thermal insulations, concrete and protective coatings of piping etc. Created debris can plug filtering devices of safety system pumps. This could lead to the failure of safety system of NPP [1-2].

In these connections the corrosion behavior of E-glass fibers that are used as a thermal insulation in Slovak NPP was conducted. In case of the accident fibers come into immediate contact with cooling solution which represents alkaline solution with  $pH \sim 9$ . Extent of the fibers degradation depends on chemical composition of insulating glass fibers. In this work the Eutal glass fibers known for their high chemical durability especially in alkaline environment are investigated. High temperature and aggressive composition of cooling solution can accelerate the degradation process of glass fibers. Contact of glass fibers with the cooling solution causes changes resulting in the structural transformation of the glass surface, dissolution of the glass itself, creation of a new glass surface layer [3] and also in mechanical degradation of glass fibers. Released fragments of fibers and the amorphous and crystal

layers created as a consequence of precipitation of the corrosive solution [4] accumulate on safety systems screens.

One of parameters influencing the glass water interaction is surface area to volume of corrosive solution ratio  $S/V$ . If the value of ratio  $S/V$  is high (more than 2000  $m^{-1}$ ), the corrosion process is greatly accelerated, because the  $pH$  of the leaching solution increases. On the other side, high corrosion rate causes relatively rapid saturation of solution with the elements originated from unleached glass resulting in slowing down of the high initial dissolution rate. When concentration of silica in solution reaches saturated condition, condensation reactions of the silanol groups take place forming a largely altered layer [5]. Created layers have strong protective effect [6]. Therefore tests with high value of  $S/V$  ratio are mainly used for qualitatively analysis of created corrosion products and simulation of long-term interaction of glass and the water solutions. For complete understanding and explanation of the chemical process, occurring in complicated matrix used as cooling solutions of NPP it is necessary to investigate interactions of glass fibers in reference system, distilled water in our case.

## EXPERIMENTAL

The static leaching tests of the Eutal glass fibers with the composition shown in the Table 1 were performed in the thermostats equipped with wagging devices.

Table 1. Composition (molar %) of the E-glass fibers (main components).

SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
56.6	4.8	8.7	25.8	2.3

To remove the surface sizing, the glass fibers had been exposed to the temperature of 350°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 fiber diameter was counted from the lognormal distribution of thousand fiber diameters and then the specific surface area of glass fibers was calculated. Static leaching tests had been carried out in a period of 30 days at temperatures of 50°C, 70°C and 90°C in distilled water at the beginning of the test meeting *pH* (20°C) ~ 5.9. For each temperature three parallel experiments were performed. The value of *S/V* ratio reached 3500 m<sup>-1</sup>.

In a given period the samples were filtered and stabilized by the nitric acid to meet *pH* < 2 at the laboratory temperature. The concentration of leached elements in solution (Si, B, Al, Ca and Mg) was determined by the optical emission spectroscopy with inductively coupled plasma (VARIAN - Vista MPX / ICP-OES).

## RESULTS AND DISCUSSION

### Regression analysis

According to the Equation (1) the total amount of elements (Ca, Mg, Al, B a Si) leached into solution, *Q<sub>i</sub>* [g/m<sup>2</sup>] and its normalized amount *NL<sub>i</sub>* [g/m<sup>2</sup>] (Equation 2) were determined for each parallel experiment [5, 6]:

$$Q_i^t = c_i \frac{V}{S} \quad (1)$$

and

$$NL_i^t = c_i \frac{V}{w_i S} \quad (2)$$

where *Q<sub>i</sub>* is the total amount of leached elements by unit glass surface area in time *t*, *S* is the glass surface area in contact with leaching solution, *c<sub>i</sub>* is the mass concentration of particular leached element in time *t* and *w<sub>i</sub>* represents the weight fracture of *i*-th element in the glass. Obtained experimental dependencies were fitted by the Helebrant equation describing the static test [7, 8]. Since some elements originated from the technical fibers remaining on the surface after thermal degradation of the fiber, were carried into reaction system in zero time. The Equation 3 includes the parameter *P<sub>a</sub>*, which represents constant shift of the leaching curve.

$$NL_i = P_a + NL_{eqv} (1 - e^{-P_b t}) \quad (3)$$

Parameters *P<sub>a</sub>*, *P<sub>b</sub>* and *NL<sub>eqv</sub>* were obtained by non-linear regression analysis by minimization of the sum of square differences between experimental and calculated values of *NL<sub>i</sub>*. Parameter *NL<sub>eqv</sub>* represents normalized amount of leached element *i* in the equilibrium state. Obtained time dependencies of normalized leached amounts of elements Si, B, Al, Ca and Mg are plotted in Figures 1, 2 and 3. The final parameters of regression analysis are summarized in the Tables 2, 3 and 4.

Generally from plotted graphs it is evident that regression curves are in good accordance with time dependencies of the amount of particular leached element, which is not the case of an element, where the maximum related to saturation and subsequent crystallization is observed. The slope of regression curves in the initial time abruptly grows with increasing temperatures due to rapid transfer of elements, documented as well by gradient of *pH* values shown in Figure 4. For Si, Al and Ca the stationary conditions were achieved, although more slowly without observing precipitation

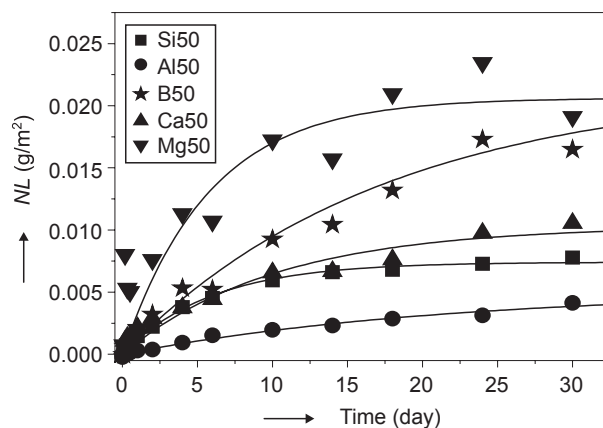


Figure 1. Time dependencies of normalized amounts of leached elements at temperature 50°C in distilled water, curves represent regression model (3).

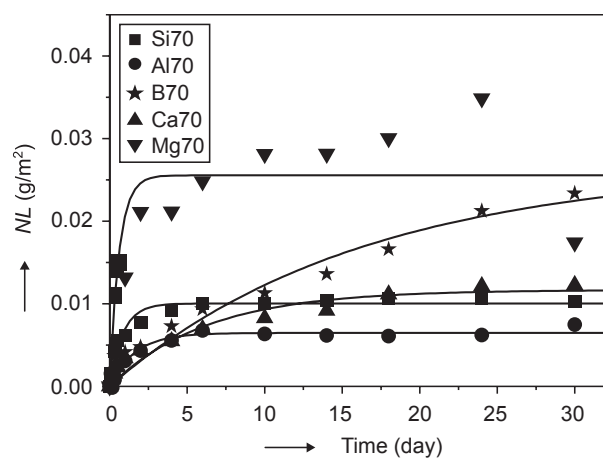


Figure 2. Time dependencies of normalized amounts of leached elements at temperature 70°C in distilled water, curves represent regression model (3).

of any element at 50°C. At the end of experiment for the temperature of 70°C slight decrease of leached amount of Mg in the solution is observed, more obvious precipitation occurs in case of 90°C. Therefore it was impossible to fit the experimental time dependencies by the Equation (3). Precipitation of Al observed after 6 days at the temperature of 90°C is probably caused by formation of the aluminate–silicate precipitated layers containing Mg<sup>2+</sup> and Ca<sup>2+</sup> cations on the fiber surface [9].

Theoretical composition of precipitated layers

Based on the normalized amount of leached boron the average composition of oxides creating new precipitated

layers was calculated from the material balance after 24 and 30 days. The stationary conditions were determined in accordance to regressions presumptions of the parameter  $NL_{eqv}$ . Obtained compositions are summarized in Tables 5, 6 and 7.

From the theoretical composition of precipitated phases it is apparent that oxides representing created precipitated layer of the glass are changing with temperature. Comparing to the initial glass the new layer has different chemical compositions, at 50°C. It is enriched with silicon and aluminum oxides, whereas lower amount of calcium and no magnesium was observed. On the other side for the temperature of 90°C presence of MgO in precipitated layer is higher as in the

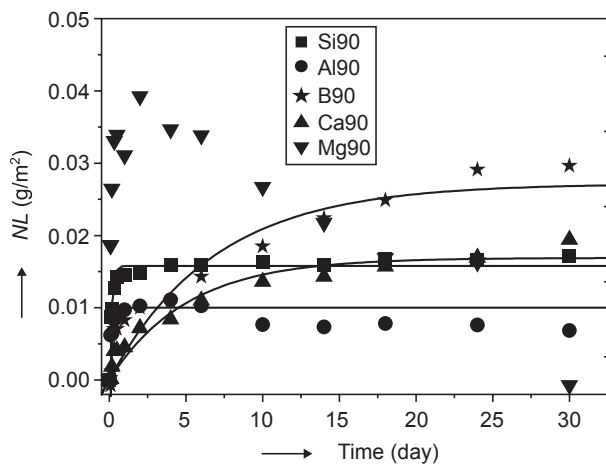


Figure 3. Time dependencies of normalized amounts of leached elements at temperature 90°C in distilled water, curves represent regression model (3).

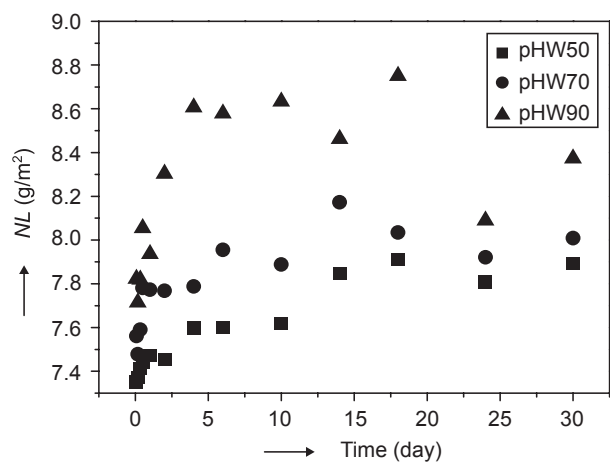


Figure 4. Time dependencies of pH for testing temperatures 50°C, 70°C and 90°C measured at laboratory temperature.

Table 2. The final parameters of regression analysis at 50°C and their standard deviations.

Element	$10^3 P_a$ (g/m <sup>2</sup> )	$10^3 NL_{eqv}$ (g/m <sup>2</sup> )	$10^3 P_b$ (day <sup>-1</sup> )	$R^2$
B	2.4 ± 0.4	20.9 ± 2.8	57.7 ± 15.7	0.97
Si	1.0 ± 0.2	7.4 ± 0.3	169.1 ± 20.1	0.98
Al	0.2 ± 0.0	5.1 ± 0.7	46.5 ± 10.7	0.98
Ca	5.0 ± 0.1	10.3 ± 1.9	98.8 ± 50.6	0.85
Mg	14.0 ± 2.5	20.6 ± 3.9	173.9 ± 104.6	0.74

Table 3. The final parameters of regression analysis at 70°C and their standard deviations.

Element	$10^3 P_a$ (g/m <sup>2</sup> )	$10^3 NL_{eqv}$ (g/m <sup>2</sup> )	$10^3 P_b$ (day <sup>-1</sup> )	$R^2$
B	6.6 ± 1.1	26.7 ± 5.9	61.6 ± 28.5	0.92
Si	1.3 ± 0.6	10.0 ± 0.6	1183.9 ± 220.7	0.96
Al	0.7 ± 0.4	6.5 ± 0.5	611.5 ± 143.8	0.95
Ca	5.3 ± 0.9	11.7 ± 1.4	160.1 ± 61.4	0.88
Mg	6.6 ± 4.3	25.5 ± 4.6	1654.6 ± 805.0	0.76

Table 4. The final parameters of regression analysis at 90°C and their standard deviations.

Element	$10^3 P_a$ (g/m <sup>2</sup> )	$10^3 NL_{eqv}$ (g/m <sup>2</sup> )	$10^3 P_b$ (day <sup>-1</sup> )	$R^2$
B	14.1 ± 2.6	27.2 ± 5.4	146.6 ± 85.5	0.80
Si	1.0 ± 1.1	15.8 ± 1.2	6474.3 ± 1112.5	0.94
Al	0.6 ± 1.0	10.0 ± 1.1	7596.8 ± 1900.7	0.94
Ca	7.7 ± 1.3	16.9 ± 2.0	198.3 ± 76.2	0.87

initial glass. In case of magnesium, solution had reached saturated conditions followed by back precipitation on the corroded glass fiber surface resulting in decline of the amount of silica phase. Percentage of aluminum containing precipitation phase after 24 and 30 days slightly increased which is in a good correspondence with Figure 3, where already after 10 days of leaching amount of aluminum dropped down. Within one temperature the theoretical composition of individual oxides in the layer significantly does not change from 24 days until equilibrium (Tables 5-7).

Table 5. The average composition (molar %) of solid phase created during corrosion process after 24 and 30 days and in stationary conditions at temperature 50°C.

	$x_{\text{eqv}}$ (%)	$x_{30}$ (%)	$x_{24}$ (%)
SiO <sub>2</sub>	64.9 ± 13.6	65.3 ± 3.7	64.0 ± 2.5
Al <sub>2</sub> O <sub>3</sub>	11.8 ± 2.2	14.4 ± 0.6	14.2 ± 0.4
CaO	23.2 ± 7.51	20.3 ± 1.6	21.9 ± 1.3
MgO	0.0 ± 0.9	0	0

Table 6. The average composition (molar %) of solid phase created during corrosion process after 24 and 30 days and in stationary conditions at temperature 70°C.

	$x_{\text{eqv}}$ (%)	$x_{30}$ (%)	$x_{24}$ (%)
SiO <sub>2</sub>	80.2 ± 22.3	62.9 ± 6.0	62.2 ± 4.1
Al <sub>2</sub> O <sub>3</sub>	15.2 ± 3.5	11.81 ± 0.8	13.6 ± 0.4
CaO	32.9 ± 10.4	24.17 ± 3.0	24.2 ± 2.5
MgO	0.5 ± 1.2	1.17 ± 0.9	0

Table 7. The average composition (molar %) of solid phase created during corrosion process after 24 and 30 days and in stationary conditions at temperature 90°C.

	$x_{\text{eqv}}$ (%)	$x_{30}$ (%)	$x_{24}$ (%)
SiO <sub>2</sub>	54.8 ± 28.1	56.7 ± 12.8	57.1 ± 5.5
Al <sub>2</sub> O <sub>3</sub>	12.8 ± 4.3	16.2 ± 1.9	15.2 ± 0.8
CaO	22.5 ± 13.2	21.3 ± 6.0	25.3 ± 2.9
MgO	5.4 ± 1.3	5.6 ± 0.7	2.4 ± 0.5

### Regression analysis

The general equation describing the time dependency of glass dissolution on temperature and saturation is deduced from the transition state theory. The equation was determined based on the analogy of glass leaching behavior and interaction of water solution on minerals by Aagard and Helgeson [10, 11]:

$$NR_{(B)} = k_0 \exp(-E_A / RT) (a_{H^+})^n (1 - A / K) \quad (4)$$

where  $k_0$  is the intrinsic rate constant,  $E_A$  the activation energy,  $R$  the gas constant,  $T$  the absolute temperature,  $a_{H^+}$  the hydronium activity,  $n$  the reaction order with respect to  $a_{H^+}$ . The final square bracket term describes the thermodynamic reaction affinity, where  $A$  is activity product of the rate limiting reaction and  $K$  the equilibrium constant.

The rate of glass dissolution  $NR_{(B)}$  was calculated based on the amount of leached boron, provided that boron is not in the precipitated layer but permanently dissolved in the solution during a test. The amount of leached boron is expressed in the equivalent weight of glass.

It was impossible to find appropriate statistical dependence of glass dissolution rate on  $pH$  value due to insignificant  $pH$  change of the solution. Therefore the parameter describing influence of  $pH$  was not considered and the following equation was used instead:

$$NR_{(B)} = k_0 \exp(-E_A / RT) (1 - A / K) \quad (5)$$

Individual parameters of the rate Equation 5 were found according to regression analysis. Comparison of the experimental and values obtained by calculation for the normalized leaching rates is shown in Figure 5. With respect to the results obtained by regression analysis it can be said that the glass dissolution rate depends on the amount of calcium and aluminum cations in the solution. The regression analysis resulted in the following equation:

$$A/K = [(c_{Ca}/\text{mmol} \cdot \text{dm}^{-3})^{0.017} \cdot (c_{Al}/\text{mmol} \cdot \text{dm}^{-3})^{0.009}] / 0.97 \quad (5a)$$

together with determination of the value of  $\log k_0 = 5.9 \text{ g m}^{-2} \text{ day}^{-1}$  and of activation energy,  $E_A = (46 \pm 4) \text{ kJ/mol}$ . Data available in literature for the activation energy of silica glass presents the value 60.9 kJ/mol and for sodium borate silica glass fibers NUKON, 55.8 kJ/mol [12, 13]. Values of the activation energy for borate silica glass in the literature are found to be in the range from 55 kJ/mol to 65 kJ/mol for temperature 90 and 300°C. [12, 14]. In our case the activation energies are lower comparing to the literature data due to lower temperatures used in our experiments. Similar temperature dependence of activation energy had been also observed by Helebrant and Jiricka [15].

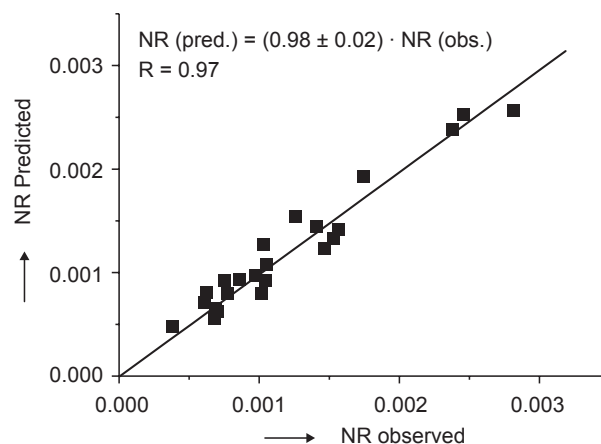


Figure 5. Comparison of the experimental and calculated values of normalized leaching rates.

## CONCLUSIONS

Time dissolution rate changes with time due to saturation effect and due to the protective function of precipitated layer. It was observed the back precipitation of magnesium and aluminum at the highest temperatures. Based on the normalized boron release, calculated composition of the created surface layer is different as the composition of the initial glass and changes with temperature. For dissolution of the E-glass fibers in distilled water the activation energy was 46.4 kJ/mol. With respect to the kinetic model and used corrosion medium can be concluded that dissolution of E-glass fibers depends on the concentration of calcium and aluminum ions presented in the solution.

## Acknowledgement

*This work was supported by The Agency for Promotion Research and Development under the contract APVV-20-P06405 and by the Slovak Grant Agency for Science under the grant VEGA 1/3578/06.*

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## KORÓZIA SKLENÝCH VLÁKIEN V DESTILOVANEJ VODE

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V práci sa sledovala kinetika lúhovania sklených vlákien typu Eutal v destilovanej vode pri troch rôznych teplotách. Za statických podmienok sa skúmala časová závislosť množstva jednotlivých zložiek vylúhovaných zo skla do roztoku v časovom intervale od 2 hodín do 30 dní, pri teplotách 50°C, 70°C a 90°C. Hodnota počítateľného pomeru plochy vzorky vlákien a objemu korózneho média  $S/V$  dosahovala 3500 m<sup>-1</sup>. Obsah jednotlivých prvkov (Si, B, Al, Ca, Mg) v lúžiacom roztoku bol stanovený pomocou optickej emisnej spektroskopie s využitím indukčne viazanej plazmy ICP/OES. Časové závislosti koncentrácií jednotlivých prvkov sa opísali Helebrantovou rovnicou s korekčným členom pre obsah prvkov vnesený do sústavy s technickým vláknom v čase nula. Kinetika rozpúšťania skla sa stanovovala na základe vylúhovaného množstva bóru. Za tohto predpokladu sa vypočítalo stredné oxidové zloženie precipitovanej fázy a povrchovej difúznej vrstvy zbavenej bóru. Závislosť rýchlosti rozpúšťania skla od zloženia roztoku a teploty sa určila štatistickými metódami. Pritom sa našla hodnota aktivačnej energie (46 ± 4) kJ/mol.