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CHEMICAL DEGRADATION OF BASALT FIBERS*

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INTRODUCTION. Basalt materials are attractive for creation of composites with polymeric and inorganic matrices. The main advantages are low price of raw materials, cheap production of filaments and possibilities of creation of textile structures (weaves, knitted forms etc.). Basalts are more stable in strong alkalis than glasses. Stability in strong acids is slightly lower. Basalt products can be used from very low temperatures (about -200°C)

up to the comparative by high temperatures, $700\text{...}800^{\circ}\text{C}$. At higher temperatures the structural changes occur. It is possible to use some dopes for increasing or enhancing of basalt properties as well. This contribution is devoted to investigation of degradation kinetics in hydrochloride acid HCl and sodium NaOH or calcium $\text{Ca}(\text{OH})_2$ hydroxides. The process of degradation is characterized qualitatively by scanning electron microscopy.

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BASALTS. Basalt is generic name for solidified lava, which poured out the volcanoes. The name is often applied to the solid rock, lava and magma, which on the eruption become lava. Basalt rocks are melted approximately in the range 1500...1700°C. Quickly quenched melt solidificated to glass like nearly amorphous solid. Slow cooling leads to more or less complete crystallization, to an assembly of minerals. Two essential minerals, plagiocene and pyroxene, make up perhaps 80% of many types of basalt. Classification on basaltic rocks based on the contents of main basic minerals is described in the book [1]. From the point of view of chemical com-

position the silicon oxide dominates, Al₂O₃ is next in abundance and CaO, MgO and FeO are closely similar, a little less then 10%. Other oxides are almost always below 5% level.

The color of basalt is from brown to the dully green in dependence on the ferrous oxides content. Basalts are more stable in strong alkalis that glasses. Stability in strong acids is lower [2]. Basalt products can be used from very low temperatures (about 200°C) up to the comparative high temperatures, 700...800°C [3]. At higher temperatures the structural changes occur. The basic physical properties of basalt fibers are presented in Table 1.

Table 1. Basic physical properties of glass and basalt fibers

Property	E-glass	Basalt
Diameter [μm]	9...13	8,63
Density [kgm ⁻³]	2540	2733
Softening temperature [°C]	840	960

EXPERIMENTAL PART. The roving from Ukraine was used for degradation experiments. Mean fineness of filaments was 2.44 dtex. Samples were firstly treated one day in acetone for removing of sizing agent. The degradation was realized at room temperature in 10 % solution of HCl, NaOH and Ca(OH)₂. After selected times samples were removed, rinsed three times in hot water, dried and weighted. The rest weight after degradation was computed from relation

$$R_Z = \frac{M_K}{M_P} \cdot 100 [\%], \quad (1)$$

where M_K [g] is weight after degradation and M_P [g] is sample weight after acetone cleaning. For comparison of degradation in various times it is better to use relative rate of degradation defined by relation

$$K_P = \frac{M_P - M_K}{t_P M_P} = \frac{100 - R_Z}{t_P} [\% \cdot \text{hour}^{-1}], \quad (2)$$

where t_P is degradation time [hours]. Higher relative degradation rate corresponds to more severe action of degradation agents. The values R_Z and K_P for HCl are in the Table 2 and for alkalis in the Table 3.

Table 2. Rest weights and relative degradation rates for acid

t [hour]	R _Z [%] 10% HCl	K _P [%·hour ⁻¹] 10% HCl
0	100,000	0,000
2	94,713	2,640
5	90,436	1,913
10	80,936	1,906
15	67,080	2,195
24	66,982	1,376

Table 3. Rest weights and relative degradation rates for alkalis

t [hour]	R _Z [%] 10% NaOH	K _P [%·hour ⁻¹] 10% NaOH	R _Z [%] 10% Ca(OH) ₂	K _P [%·hour ⁻¹] 10% Ca(OH) ₂
0	100,000	0,000	100,000	0,000
2	96,889	1,556	100,000	0,000
5	95,845	0,831	99,888	0,022
24	94,968	0,2097	99,278	0,030

DEGRADATION KINETICS. During the degradation process the chemical solution attacks the surface and subsurface layers. Direct investigation of fibers diameter after long-term degradation has shown that the predominant mechanism is opening of crazes and degradation in the volume of fibers. Step by step removal of surface layers was negligible. Therefore the reason of degradation is the reaction of chemical solution with some cations (in the case of acids) or anions (in the case of alkalis) from basalt fiber body. The kinetic model is therefore based on the assumption of first order reaction. The instantaneous rate of degradation is dependent on the difference between actual weight and weight in equilibrium

$$\frac{dM_t}{dt} = -K(M_t - M_\infty). \quad (3)$$

Solving of this differential equation in the intervals $[M_0, M_t]$ and $[0, t]$ results in the following equation

$$M_t = M_\infty + (M_0 - M_\infty)\exp(-Kt). \quad (4)$$

After introducing the rest weight the final relation is obtained

$$R_Z = R_\infty + (100 - R_\infty)\exp(-Kt), \quad (5)$$

where R_∞ [%] is equilibrium rest weight and K [hour^{-1}] is degradation rate constant.

DEGRADATION IN HCl. The parameters characterizing weight loss for degradation in 10% HCl are given in the Table 2. The parameters of degradation model $R_\infty = 54.883$ [%] and $K = 0.063$ [hour^{-1}] were obtained by using nonlinear least squares criterion. Experimental points and model curve are shown in the Fig. 1

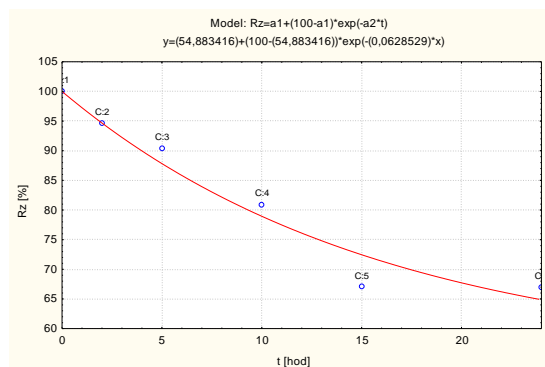
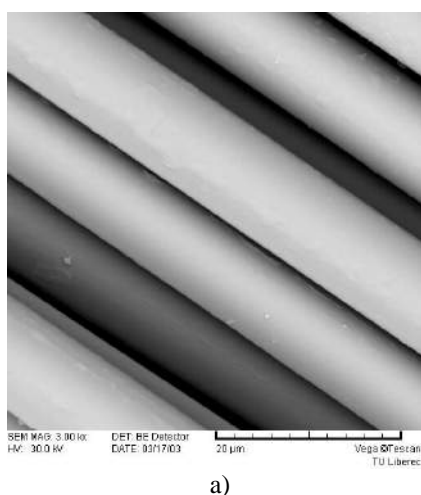
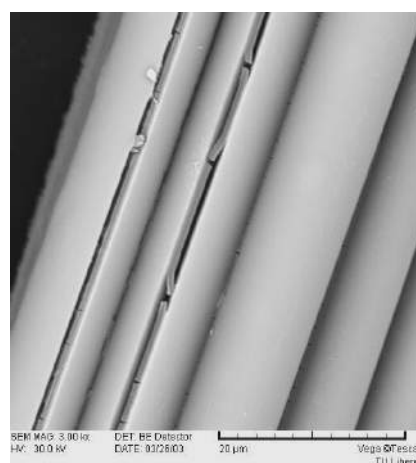


Fig. 1. Kinetics of weight loss in 10% HCl described by eqn. (5)

The surface of degraded fibers is shown in the Figs. 2, 3. It is very interesting that degradation is mainly due to opening and creation of long crazes in the fiber axis. After long-term exposure the crazes in direction perpendicular to fiber axis appeared.



a)



b)

Fig. 2 Basalt fiber after degradation in 10% HCl for 2 hours (a) and 5 hours (b)

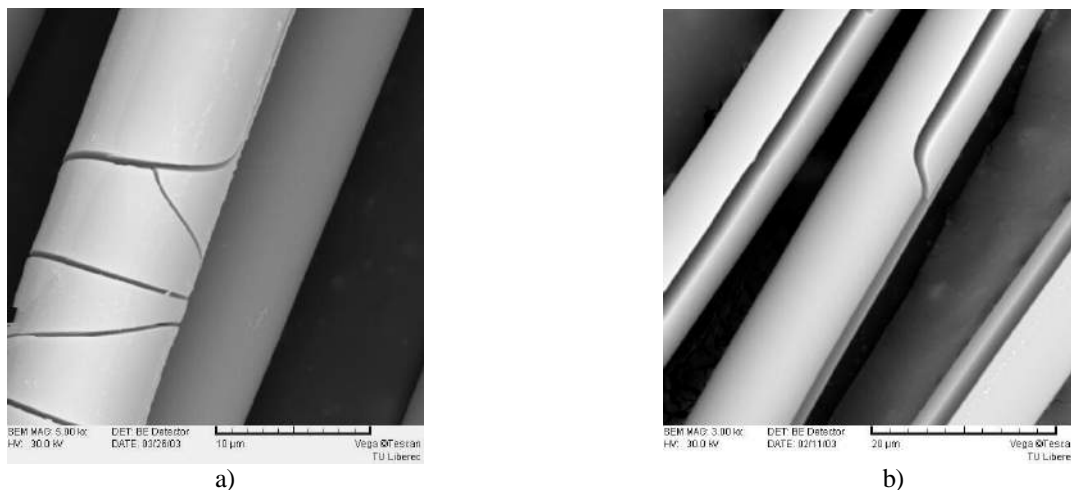


Fig. 3 Basalt fiber after degradation in 10% HCl for 15 hours (a) and 24 hours (b)

Result is great loss of durability and disintegration of fibers in long degradation times. The degradation is accompanied by the great loss of mechanical properties, especially tensile strength [6]. The volumetric density computed from diameter and weight of treated basalt is for 2 hours of acid action, 2511 kgm^{-3} . This value is slightly lower than volumetric density, 2572 kgm^{-3} , for untreated basalt fiber.

The increasing of pH acid solution after degradation is in accordance with assumption of reaction of HCl with cations and destroying the glass-like network. The chloride salts replace the intermediate oxides as MnO_2 , Fe_2O_3 and Al_2O_3 . These salts are typically well soluble in water and these phenomena supported the basalt degradation due to action of acid.

DEGRADATION IN AKALIS. It is known that alkali attacks the silica network directly. The hydroxyl ion of the alkali breaks the Si-O-Si linkage. The presence of intermediate oxides like MnO_2 , Fe_2O_3 and Al_2O_3 should always improve the alkaline durability [8]. Degradation in 10% alkaline solutions is relatively small. The durability in 10% $\text{Ca}(\text{OH})_2$ is excellent. Action of 10% NaOH is more severe but in comparison with acid the weight loss is very low.

The parameters characterizing weight loss for degradation in 10% alkalis are given in the Table 3. The degradation kinetics was modeled for the case of 10% NaOH only. The parameters of degradation model $R_\infty = 95.009 \text{ [%]}$ and $K = 0.440 \text{ [hour}^{-1}\text{]}$ were obtained by using nonlinear least squares criterion. Experimental points and model curve

are shown in the Fig. 4. The very high rest weight equilibrium and high rate constant in comparison to the same values for acid degradation indicate that the degradation processes are mainly on surface of fibers. The glass-like network breaking increases number of free hydroxyl group.

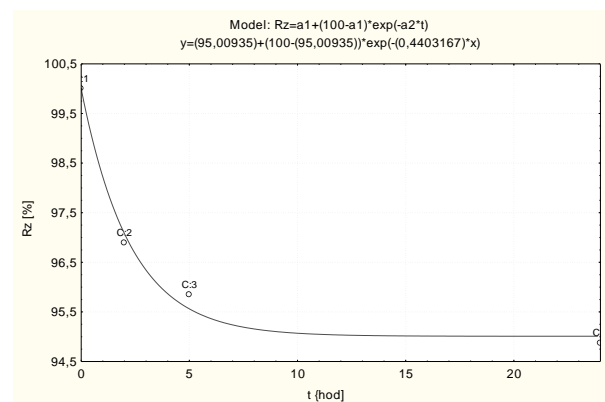
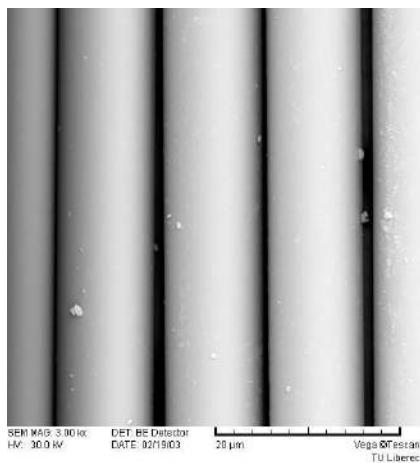


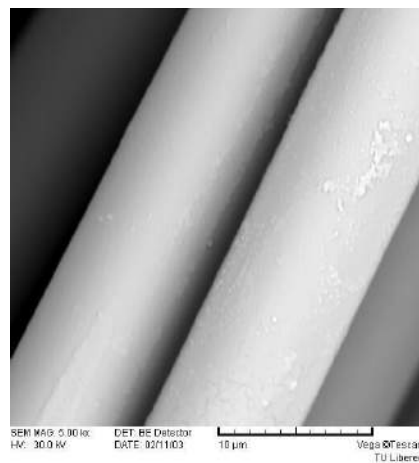
Fig. 4. Kinetics of weight loss in 10% NaOH described by eqn. (5)

The surface of degraded fibers is shown in the Figs. 5, 6. It is very interesting that the surface is now without crazes and the precipitation of insoluble materials on the fiber surface is visible.

The very small weight loss indicates good stability of basalt in strong alkalis. The small loss of mechanical properties, especially tensile strength was found [6]. The volumetric density computed from diameter and weight of treated basalt is for 2 hours of NaOH action equal to 2308 kgm^{-3} . This relatively low value supports assumption about surface ablation in alkaline conditions.



a)



b)

Fig. 5 Basalt fiber after degradation in 10% $\text{Ca}(\text{OH})_2$ for 24 hours (A) and in 10% NaOH for 24 hours (B)

CONCLUSION

According to the previous finding it was proved that the stability of basalt in alkalis is generally very good. The stability in acids is comparatively small. Prolonged acids action leads to the full disintegration of fibers.

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