BASALT FIBERS DEGRADATION IN LIQUID ALKALIS

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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 and cheap production of filaments and possibilities of creation of textile structures (weaved or knitted forms etc.) [1]. Basalt rocks [2] suitable for the preparation of fibers must meet the following requirements :

  (i) SiO_2 content around 46% and constant chemical composition;
  (ii)   (ii) the ability to melt without solid residues;
  (iii)   (iii) the optimal viscosity of the melted basalt;
  (iv)   (iv) the ability of the cooling without significant crystallization.

From the point of view of chemical composition the silicon oxide dominates, Al_2O_3 is next in abundance and CaO, MgO and FeO are closely similar. Other oxides are almost always below 5% level. Basalt fibers are produced by melt spinning in the range 1500-1700 ^{o}C. Fibers can be drawn at temperatures around 1300°C. The diameter of standard fibers is°.around 9-12 μm [5].

The main aim of this contribution is investigation of degradation kinetics of basalt filaments in aqueous solutions of sodium NaOH or calcium $Ca(OH)_2$ hydroxides. The simple rate model of weight loss due to degradation is proposed.

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 step by step removal of surface layers was negligible. Therefore the reason of degradation is the local reaction of chemical solution with some anions (in the case of alkalis) presented in basalt fiber and leaching of products. The proposed kinetic model for mass loss is based on the simple assumption of first order reaction. The instantaneous rate of degradation is dependent on the difference between actual weight and weight in equilibrium

$$\frac{dM_t}{dt} = -K \cdot (M_t - M_\infty) \qquad (1)$$

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

$$M_t = M_\infty + (M_0 - M_\infty) \cdot \exp(-K \cdot t) \quad (2)$$

After introducing the rest weight (see eqn. (4) the final relation is obtained

$$R_Z = R_\infty + (100 - R_\infty) \cdot \exp(-K \cdot t) \quad (3)$$

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

Experimental part

The basalt 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 were realized at room temperature in 10 % solution of NaOH and $Ca(OH)_2$. After selected times were samples removed rinsed three times in hot water, dried and weighted. The rest weight after degradation was computed from relation

$$R_Z = \frac{M_K}{M_P} \cdot 100 \ [\%] \qquad (4)$$

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 is better to use relative rate of degradation defined by relation

$$K_P = \frac{100 - R_Z}{t_P} \ [\%.\text{hour}^{-1}] \qquad (5)$$

where t_P is degradation time [hours]. Higher relative degradation rate corresponds to more

severe action oh degradation agents. The values of K_p for alkalis on the able I.

Table I. Relative degradation rates for alkalis

t [hour]	K_P [%.hour⁻¹] 10% NaOH	K_P [%.hour⁻¹] 10% Ca(OH)₂
0	0,000	0,000
2	1,556	0,000
5	0,831	0,022
24	0,2097	0,030

Degradation processes

It is known that alkalis attack 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 [3]. Degradation in 10% alkaline solutions is relatively small. The durability in 10% $Ca(OH)_2$ is excellent. Action of 10% NaOH is more severe but in comparison wit acid the weight loss is very low.

The parameters characterizing weight loss for degradation in 10% alkalis are given in the table I. The degradation kinetic was modeled for the case of 10% NaOH only. The parameters of degradation model $R_\infty = 95,009$ [%] and $K = 0,440$ [hour⁻¹] were obtained by using of nonlinear least squares criterion. Experimental points and model curve are shown on the fig. 1.
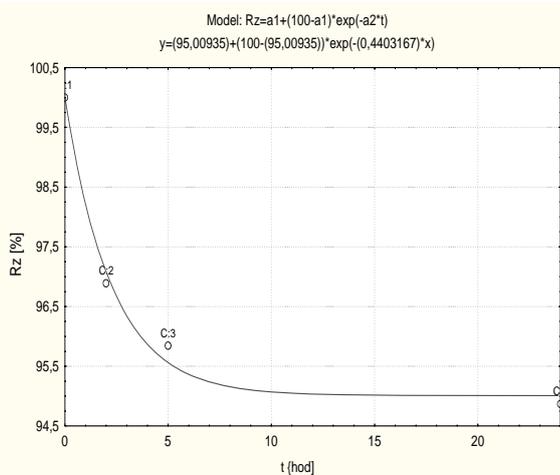

Fig. 1 Kinetics of weight loss in 10% NaOH described by eqn. (38)

The very high rest weight equilibrium and high rate constant indicate that the degradation

processes are mainly on surface of fibers. The glass like network breaking increases number of free hydroxyl group.

The surface of degraded fibers is shown on the fig. 2.
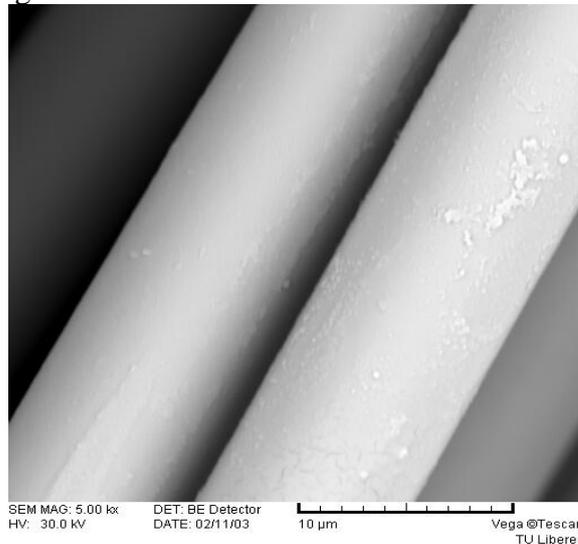

Fig. 2 Basalt fiber after degradation in 10% NaOH for 24 hours (b)

It is very interesting that the surface is 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 in [4]. The volumetric density computed from diameter and weight of treated basalt is for 2 hours of NaOH action was equal to 2308 kgm⁻³. This relatively low value supports assumption about local surface ablation in alkaline conditions.

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