Investigation of carbonized layer on surface of NaAlSi glass fibers

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Abstract. There are presented and discussed experimental results about carbonate shell on the sodium rich alumosilicate (NaAlSi) glass fibers and carbonization in wet air atmosphere and water uptake kinetic of such fiber fabrics. The analyzes of water uptake kinetic by regression technique, leaching and heating of carbonized glass fabrics helped to separate stages of fast and slow processes between fiber and carbonate shell and air atmosphere. The shell contains mixture of trona and hydrated sodium carbonate. Heating converts both substances to sodium carbonate. The weight uptake after heating encounters two fast exponential processes associated with water absorption on the surface of carbonated shell and its diffusion into volume. The slow process associates with CO_2 and H_2O absorption from air, hydration and sodium carbonate conversion to trona**.**

1. Introduction

Glass fiber fabrics are used in dry and wet atmosphere and in water at elevated and changeable temperatures. The changes in environment can initiate processes in the glass fabric that lead to a new its equilibrium state and changed physical properties. Some of them may be irreversible. It is accepted [1,2] that interaction of alkali silicate glasses with water or mineral acids proceeds by ionic exchange by diffusion of Na^+ ions to glass surface and H^+ or H_3O^+ from water into the bulk of glass to fill the vacancies of Na^+ ions. It looks that Na^+ ions and H_2O and CO_2 from surrounding atmosphere form the shell of $Na_2CO_3 \cdot H_2O$ (hydrated sodium carbonate) and $Na_3H(CO_3)_2 \cdot 2H_2O$ (trona) mixture on the surface of elementary glass fibers. Such shell can be dissolved in water and acids (leached) [3]. The heating can leads to weight loss by dehydration of $Na_2CO_3 \cdot H_2O$ over 100 ^{0}C, by decomposition reaction of

$$2(Na_3H (CO_3)_2 \cdot 2H_2O) = 2(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O) \quad 3Na_2CO_3 + CO_2 + 5H_2O \qquad (1)$$
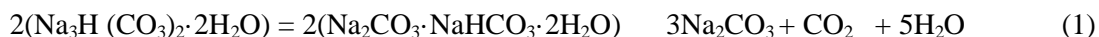
at temperature over 55-57 ^{0}C [4], and free water evaporation. There are studied the weight loss of stored at about 20 ^{0}C and 20% - 35% RH (room conditions in autumn and winter), stored and leached by acid Na-Al-Si glass fabrics, and leached powder (LP) of carbonates after its heating at different temperatures and followed long term uptake of weight in room atmosphere. The values of experimental weight uptake-time points were analyzed by regression technique.

2. Samples

The unleached and leached by acid samples of K-glass fabric with initial composition of [(18-22)Na_2O(3-5)Al_2O_3(73-79)SiO_2] from JSC õValmiera Glass Fiberö were studied. The threads of fabric

consist of 600 elementary glass fibers with diameter of 6 µm. The samples leached by acid have thickness about 0.34 mm. The unleached samples had been stored during the years at room conditions. In a result of interaction with surrounding air, the Na^+ ions leached from glass fibers to its surface and formed here the sodium carbonate shell. The long term limit of thickness of shell can exceed 2 µm. The thickness of carbonized fabric was in range 0.53 ó 0.58 mm. The leached powder (LP) was prepared by dissolving the shells in water and water evaporation.

3. Results and Discussion

XRD measurements showed that LP after receiving consists of trona and hydrated sodium carbonate. Heating over 110 ^{0}C (2 h) leads to its converting to sodium carbonate. Storing in air at room conditions causes inversed reaction (1). After 2000 h long storing, LP was converted back to trona (60%) and hydrated carbonate. This slow process needs to absorb water and CO_2 from air before mentioned reaction. An artificial increase of moisture content of unheated fabric samples over its equilibrium values with surrounding air showed that time, necessary for returning to equilibrium weight are some hours only. There is no weight loss and stabilization of weight has to be associated with free water evaporation to equilibrium with environment. It indicates that beginning (about 0, 25 h) of weight increase has to be associated mainly with water absorption. There are observed the fast uptake of weight　M(t) during the first tens of minutes after heating (Fig.1) and much slower (hundreds of hours) uptake up to equilibrium weight later (Fig.2) for not leached (a1n-a3n), leached samples S1 and S2 of fabric and LP.
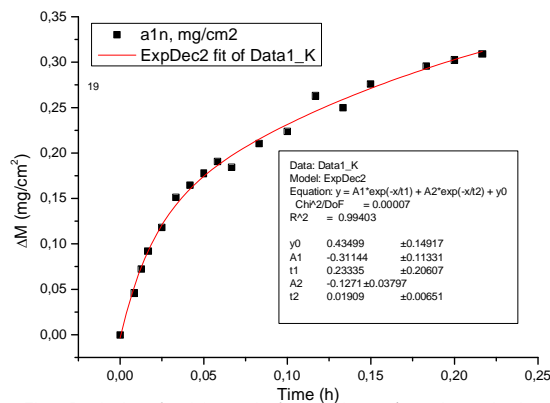

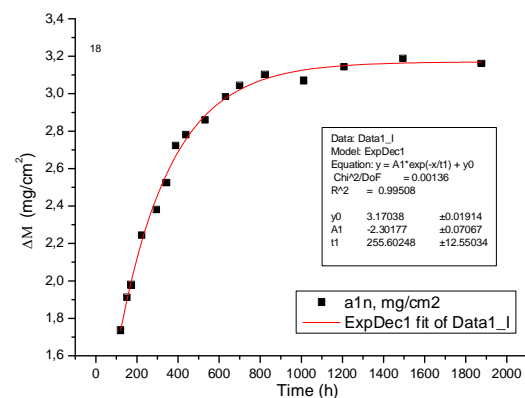Fig.1. Beginning of weight uptake for sample a1n (experimental points and regression line)

Fig.2. Late weight uptake for sample a1n (experimental points and regression line)

The experimental weight uptakeótime　M (t) points for the beginning period are well-fitted (R^2 > 0.99) to regression of

$$M (t) = A_0 - A_1 \exp (-t/t_1) - A_2 \exp (-t/t_2), \qquad (2)$$

where A_0, A_1, A_2 are weight constants and t_1, t_2 are time constants (t_1 Ö t_2), lim　M(t)=A_0 when t　Ô and lim　M_1(t)=A_1exp(-t/t_1)=A_1, and lim　M_2(t)=A_2, when t　0. In (2) A_0=A_1+A_2. Velocity of weight uptake can be owned from (2):

$$v(t) = \frac{A_1 \exp(-t/t_1)}{t_1} + \frac{A_2 \exp(-t/t_2)}{t_2} . \qquad (3)$$

The main fitting parameters for beginning of weight uptake are presented in Table 1 and for the late uptake in Table 2. The fitting results indicate to simultaneous water absorption on surface of shell with rate of 3.9 ó 6.6 mg/h·cm² (t_1 é 0.017 ó 0.04 h) and absorption associated with water that leaves the surface to volume (possible by diffusion) with rate of 1.0 ó 2.2 mg/h·cm² (t_2 × 0.17 h) - for unleached samples (Table 1). Heating temperature increase leads to increase of irreversible weight loss (Table2 and Fig.4) or equilibrium weight decrease.

Table 1. Parameters of weight uptake beginning.

Sample	$^0C/h$	A_0 (mg/cm^2)	A_1(mg/cm^2)	t_1(h)	A_2(mg/cm^2)	t_2(h)	$v_1(0)$, (mg/h cm^2)	$v_2(0)$, (mg/h cm^2)
a1n	90/2	0.435	0.1271	0.0191	0.311	0.233	6.65	1.34
a2n	130/0.167	0.539	0.1581	0.0173	0.383	0.173	9.14	2.2
a3n	130/2	1.09	0.155	0.039	0.932	8.1	3.94	1.15
S1	110/2	1.3	0.26	0.0074	0.769	0.064	35	11.8
S2	170/2	1.37	1.36	0.096	-	-	14.2	-
LP	110/2	0.07	0.07	0.012	-	-	5.9	-

Table 2. Parameters of late weight uptake.

Sample	$^0C/h$	A_0 (mg/cm^2)	A_1 (mg/cm^2)	t_1(h)	A_2 (mg/cm^2)	t_2 (h)	Weight loss (mg/cm^2)
a1n	90/2	3.17	-	-	2.3	256	0.21
a2n	130/0.167	3.54	-	-	3.13	171	0.548
a3n	130/2	3.0	-	-	1.91	125	2.03
S1	110/2	1.15	-	-	0.04	143	0.051
S2	170/2	1.59	0.123	22.6	0.102	195	0.232
LP	110/2	2.18	-	-	2.65	255	5%

The looks of fabrics after leaching are changed from matted to shine. The leached sample S1 heated at 110 ^0C (Table 1) has notably less values of t_1 and t_2 (about 0.007 h and 0.06 h) and higher values of surface absorption and desorption rates (about 35 and 12 mg/h·cm^2). The reason has to be associated with smoother surface of glass fibers and absence of notable carbonized shell compared to surface of not leached fibers ones. In this case there is only one time constant in beginning phase (Table 1). Increase of heating temperature to 170 ^0C causes significant increase of time constant t_1 and irreversible weight loss (sample S2, Table 2) in spite of absence of carbonated shell. It should be associated with pore volume (deepness) increase by loss of matter.
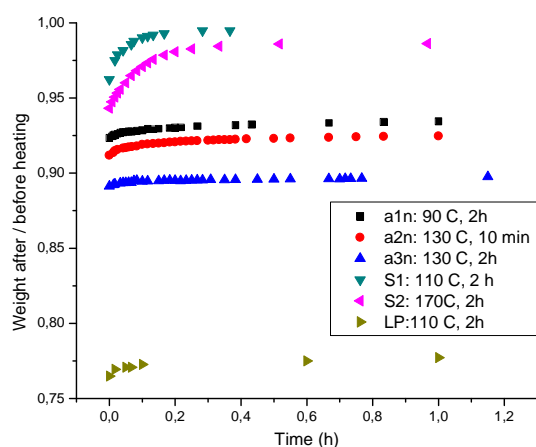

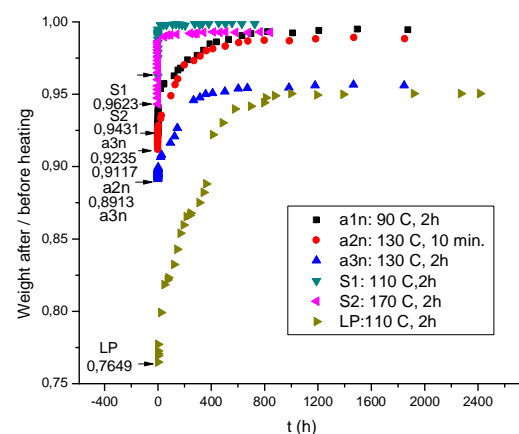Fig.3. Ratio of weight after and before heating for beginning of weight uptake

Fig.4. Ratio of weight after and before heating for late weight uptake

Following (1) the proportion of weights of heated and unheated sample (Fig.3, 4) has to be equal or more than 0.7035. In a case of LP (60% trona) the coincidence is good (0.7649 by weighing and 0.764 by XRD). In the other cases the proportions are significantly higher than mentioned value (0.7035) because in the weight are included the glass of fibers.

The late uptake of weight can be described with only one exponential function in equation (2). The values of late t_2=120÷250 h have to characterize the saturation with water (free and crystallized) and conversion sodium carbonate to trona in the all volume of shells of unleached fabric. There exists some slow water insertion in surface of glass of leached fabric also. One of reasons of slow rate of conversion to trona should be associated with low concentration of CO_2 in air. Late weight uptake dominates in unleached samples and beginning uptake in leached ones (Fig.4).

4. Conclusions

Leached in water powder from unleached and carbonized NaAlSi glass fiber fabrics consist of mixture of trona and hydrated sodium carbonate. Heating of powder above 110 ^{0}C (2 h) leads to dehydration and trona conversion to sodium carbonate. Storing the heated powder at about 20 ^{0}C and 20% - 35% RH during the months causes sodium carbonate conversion back to hydrated sodium carbonate and trona.

Heating of carbonized NaAlSi glass fabric causes weight loss that partly restores during the months in air at room conditions. The beginning stage of weight uptake consists of two exponential processes that should be associated with water absorption on the surface of carbonated shell and its diffusion to volume. The first process has time constant of 0.017 - 0.04 h and second of 0.2 - 8 h and velocity of 4 - 9 mg/h·cm^2 and 1.2 - 2.2 mg/h·cm^2 accordingly. The late phase of weight uptake appears after some hundreds hours and has time constant about 200 h. This slow process should be associated with CO_2 and H_2O absorption from air and converting sodium carbonate to hydrated sodium carbonate and trona.

The leached by acid NaAlSi glass fabric has initial weight uptake process more fast (about 47mg/h·cm^2) and more expressed compared to unleached ones (5 - 11 mg/h·cm^2).

References

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