Environment Humidity Effect on the Weight of Carbonized Na-Al-Si Glass Fabrics Recovery after Heating

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Abstract. Na-Al-Si glass fabrics fibres contain Na\(^+\) ions that diffuse to its surface and along with CO\(_2\) and H\(_2\)O from atmosphere create here the shell of carbonate hydrates. The heating of fabric leads to weight loss by evolving these substances. In this work the results of weight recovery study at room relative humidity (20% - 50%) and elevated humidity (near 70%) of fabrics after its heating at different temperatures (70\(^\circ\)C - 150\(^\circ\)C) are compared. The experiments showed the different weight recovery kinetics. The initial exponential stages up to 0.3 h - 0.5 h of the both recoveries are associated with water absorption and differ by its levels. In a case of lower environment humidity the later weight increase are restricted by its value, but at an elevated humidity has a maximum and followed weight increase. The reasons of observed differences are discussed.

1. Introduction

The object of research was industrially produced fabrics of Na-Al-Si glass fibres. It is known that Na\(^+\) ions diffuse to surface of fibres [1] and due to reaction with H\(_2\)O and CO\(_2\) from atmosphere form here the carbonated shell. It leads to increase the weight and thickness of fabrics and change its look from bright to mat. Heating of carbonated fabric up to 90-130\(^\circ\)C and higher temperatures leads to its weight loss [2], associated with evolving of H\(_2\)O and CO\(_2\) from samples. Sodium carbonate (Na\(_2\)CO\(_3\)) is stable up to melting temperature (851 \(^\circ\)C). The known sodium carbonate hydrated forms decompose by heating to sodium carbonate and water. Heptahydrate (Na\(_2\)CO\(_3\)∙7H\(_2\)O, not known in mineral form) begins to decompose over 32 \(^\circ\)C, decahydrate (Na\(_2\)CO\(_3\)∙10H\(_2\)O) over 33.5 \(^\circ\)C, and monohydrate (Na\(_2\)CO\(_3\)∙H\(_2\)O) over 100 \(^\circ\)C. Trona (Na\(_3\)H\((CO_3)_{2}\)∙2H\(_2\)O) begins to decompose to Na\(_2\)CO\(_3\), water and CO\(_2\) over 56 \(^\circ\)C [2]. Besides, the weight loss by heating moves the shell and fabric out of its equilibrium with environment atmosphere and water and CO\(_2\) absorption tends to restore it. The weight recovery after heating of carbonated fabric during to reaching the equilibrium weight at room conditions was analysed in [3]. The experimental weight recovery – time W (t) points for the beginning period up to 0.2 h-0.4 h are well-fitted (R\(^2\) > 0.98, see Table 1 and 2) to regression of

\[
W (t) = A_0 - A_1 \exp (-t/t_1) - A_2 \exp (-t/t_2),
\]

(1)
where $A_0$, $A_1$, $A_2$ are weight constants and $t_1$, $t_2$ are time constants ($t_1 \leq t_2$), \( \lim W(t) = A_0 \) when $t \to \infty$ and \( \lim W(t) = A_1 \exp(-t/t_1) = A_1 \), and \( \lim W(t) = A_2 \), when $t \to 0$. In (1) $A_0 = A_1 + A_2$. Velocity of weight recovery is

$$v(t) = (A_1 \exp(-t/t_1)) t_1 + (A_2 \exp(-t/t_2)) t_2.$$  \hspace{1cm} (2)

In the present study there are compared and analyzed the weight recovery - time characteristic parameters of relations (1, 2) and possible process that leads to equilibrium at room and environment relative humidity (RH) near 70%.

2. Experimental
For every heating temperature there were used one carbonized fabric sample, cut from one lump of fabric. The heating duration of every sample was 1 h. Relative humidity about 70% was limited by saturated salt solution in a glove box. There are used DTG and RTD measurements to analyze the content of carbonated shells in fabrics and dissolved from fabric and evaporated matter in this research.

3. Results and discussion
The shell can be dissolved in water up to 96% of its weight, dissolved by acid industrially. RTD showed that evaporated powder consists of mixture of trona (60%) and sodium carbonate monohydrate. Content of trona in a powder increased during the storing time. The shell of long time (years) stored fabric consists of trona (DTG measurements). The main weight loss after heating of fabrics is under 100 °C (Figure 1), related with decomposition of trona to sodium carbonate or carbonate monohydrate, water and CO$_2$. Some weight loss (seen in Figure 1) above 100 °C could be caused with evolving of residues of lubricator and/or components from glass. In a case of evaporated powder such loss absents. As in the case [3], when after heating the samples are placed in room conditions (humidity and temperature), up to 0.2 h-0.4 h the weight recovery closely follows regression (1), where the first, more fast component ($\Delta W_1(t)$) is associated in [3] with water absorption on surface of shell and the second one ($\Delta W_2(t)$) with an additional absorption to released sites of water, diffused into the shell. Some results (lower) tend to associate the first component of the relation (1) rather with absorption of CO$_2$.

The mean time constants for the first component ($t_1$) of weight recovery in relation (1) for nine samples (heated to different temperatures) is 0.7 min, and for the second component ($t_2$) - 20.4 min. At the beginning ($t=0$) of weight recovery, the mean velocity of recovery is 11.31 mg/h·cm$^2$ ($v_1$) and 0.676 mg/h·cm$^2$ ($v_2$) accordingly (Table 1). The values of parameters $t_1$, $t_2$ are significantly dissipated, that could be associated not only with different treatment temperatures, but with different samples for every of heating temperature also. Amplitude of the second component $A_2$ in Table 1 dominates at low heating temperatures, but first one $A_1$ is relative stable. The mean values of amplitudes are comparable ($A_1=0.113$ mg/cm$^2$ and $A_2=0.17$ mg/cm$^2$). No pronounced correlation was observed between parameters ($t_1$, $A_1$, $v_1$) and heating temperature of samples and humidity of environment, that looks prospective for the stable concentration of CO$_2$ in atmosphere.

It may be supposed that during mentioned above beginning time interval there are going mainly accumulation of water and CO$_2$ on the surface and inside the shell. We cannot be able to indicate an increase of thickness of fabric during this period (Figure 3).

The next pronounced increase of weight in Figures 2 and 3 are caused by a notable RH increase of environment along with increase of thickness of samples (Figure 3). As it seen from the weight kinetics in figures, the main part of absorbed weight are installed in sodium carbonate molecules (may be of different kind) and only a small part of weight follows to the fast decrease of RH of environment after 2500 h storing (Figure 2) and 6000 h storing (Figure 3). This part of weight (somewhat more than 12% of absorbed weight in a case of Figure 2) has to be associated with free water in shell and may be in pores of glass and characterizes the new state of water equilibrium of fabric with
environment. Later there are observed the weight stabilization (Figures 2 and 3) and some decrease of thickness that indicates to packaging of shell along time (Figure 3).

**Table 1.** Parameters of regression (1) for time interval up to 0.4 h after heating at different temperatures and velocity components $v_1$ and $v_2$ of weight recovery in relation (2) at the recovery beginning ($t=0$)

| $T_{\circ C}$/sample | $t_1$, h | $t_2$, h | $A_0$, mg/cm$^2$ | $A_1$, mg/cm$^2$ | $A_2$, mg/cm$^2$ | $R^2$ | $v_1(0)$, mg/h cm$^2$ | $v_2(0)$, mg/h cm$^2$ |
|---------------------|---------|---------|-----------------|-----------------|-----------------|-------|----------------------|----------------------|
| 74/1a-3             | 0.01538 | 0.143   | 0.3571          | 0.1148          | 0.2412          | 0.9964 | 7.46                 | 1.69                 |
| 74/1a-5             | 0.01844 | 0.1883  | 0.4041          | 0.165           | 0.2349          | 0.998  | 8.95                 | 1.25                 |
| 78/2n1              | 0.00693 | 0.2929  | 0.3375          | 0.0835          | 0.2541          | 0.9833 | 12.05                | 0.87                 |
| 84/2n2              | 0.01216 | 0.8076  | 0.5457          | 0.1064          | 0.4385          | 0.9976 | 8.75                 | 0.543                |
| 94/2n3              | 0.00791 | 0.1418  | 0.1822          | 0.0975          | 0.0843          | 0.996  | 12.33                | 0.59                 |
| 103/2n4             | 0.00535 | 0.165   | 0.1845          | 0.0777          | 0.1068          | 0.9921 | 14.52                | 0.647                |
| 114/3a1             | 0.0195  | 0.874   | 0.212           | 0.111           | 0.0999          | 0.9821 | 5.69                 | 0.113                |
| 130/3a2             | 0.0131  | 0.278   | 0.1547          | 0.1119          | 0.041           | 0.989  | 8.54                 | 0.147                |
| 150/3a3             | 0.0063  | 0.1682  | 0.1874          | 0.148           | 0.0394          | 0.9967 | 23.49                | 0.231                |

**Figure 1.** Relative weight decrease of fabric samples, heated at different temperature

**Figure 2.** Weight recovery of heated fabric samples 1h at 70°C and room RH vs time

**Figure 3.** Weight recovery of heated fabric samples 1h at 78°C at room conditions and fabric thickness vs time

The change of room environment to more stable and elevated humidity level near RH 70 % and room temperature highly elevates the mean values of amplitude $A_2$ (1.41 mg/cm$^2$) and velocity $v_2$ (3.64 mg/h·cm$^2$) in the beginning time period of weight recovery (Table 2).

**Table 2.** Parameters of regression (1) for time interval up to 0.3 h after sample heating at different temperatures (during 1 h) and velocity components of weight recovery in relation (2) at the beginning of recovery ($t=0$)

| $T_{\circ C}$/ (sample) | $R^2$   | $t_1$, h | $t_2$, h | $A_{b}$, mg/cm$^2$ | $A_1$, mg/cm$^2$ | $A_2$, mg/cm$^2$ | $v_1(0)$, mg/h cm$^2$ | $v_2(0)$, mg/h cm$^2$ |
|------------------------|---------|---------|---------|-----------------|-----------------|-----------------|----------------------|----------------------|
| 70/(1-1)               | 0.99937 | 0.0124  | 0.2358  | 1.022           | 0.10994        | 0.90867        | 8.89                 | 3.854                |
| 72/(1-2)               | 0.99976 | 0.0052  | 0.2635  | 1.169           | 0.14231        | 1.0266         | 27.26                | 3.896                |
| 76/(1-3)               | 0.99958 | 0.0086  | 0.732   | 2.4445          | 0.1379         | 2.3056         | 16.07                | 3.154                |
The other parameters of second components and all parameters of the first components of relations (1 and 2) were without notable changes, compared to lower humidity case, discussed above. It directly indicates that second components of relations (1 and 2) characterize the absorption of water. Then symmetrically, the first components of the both relations have to characterize the absorption of CO₂ (it is not a proof). The later weight recovery kinetics (Figures 4, 5, 6) compared to lower humidity environment (Figures 2, 3), have the weight maximum at about 40 h - 50 h by high absorption and desorption of water. The recovered weights overcome its values before heating up to 10 % in its maximum, compared to low humidity cases. As it proceeds from data in literature [2], it could be associated with formation of sodium carbonate heptahydrate, that most commonly occurs and which readily effloresces to form monohydrate by water releasing and evaporation.

The anhydrous sodium carbonate can arose from partly decomposed by heating trona. The heating temperature increases in temperature region above 70 °C leads to the fast volume increases of anhydrous sodium carbonate and its conversion to sodium carbonate heptahydrate by water absorption from humid atmosphere (Figure 4). It explains the high sensitivity of maximum values in Figures 4, 5, 6 to heating temperatures of samples. When weight minimum is reached, the weight begins the slow and almost linear increase in linear scale along time (Figures 5 and 6 in log scales). The short and fast humidity decrease to its room levels leads to the decrease of weights near its values before heating. It indicates that increase of weights in Figures 5 and 6 could be caused by increase of free water content and hygroscopicity of samples up to at least 6000 h long storing in humid atmosphere. It is seen that equilibrium of fabric with humid environment during this time is not reached.

4. Conclusions
At room conditions the main part of recovered weight of carbonated glass fabric samples after heating (70 °C- 150 °C / 1 h) is associated with water installation in sodium carbonate molecules of carbonated shell and only a small part of recovered weight (above 12%) is associated with recovered free water in shell and may be in pores of glass.

The change of room environment to more stable and elevated humidity level near 70% RH principally changes the kinetics of weight recovery after heating (70 °C - 76 °C / 1h) and increases the beginning weight recovery velocities and level, and creates a maximum could be caused with formation of sodium carbonate heptahydrate and its transformation to monohydrate later with water evolvoling.

References
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