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The mechanism of glass foaming with water glass

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ABSTRACT

Water glass is a common additive in the process of direct foaming of glass, however, the currently accepted foaming mechanism lacks experimental validation. A foaming mixture of waste cathode ray tube panel glass and water glass was investigated for its expansion and gas evolution behavior via hot stage microscopy and thermogravimetry coupled with mass spectroscopy, respectively. The evolution of a significant amount of CO₂ during the heating of the foaming mixture was detected and an overwhelming presence of CO₂ within the pores of the foamed glass was confirmed with gas chromatography. With this investigation, we reveal an underlying foaming mechanism, where a carbonate phase forms after mixing water glass with the glass powder and later acts as the foaming agent. The unveiled mechanism could help further research in the field of foamed glass, with the potential to produce more sustainable materials with better performance via less energy-demanding processes.

1. Introduction

Development of materials along with the general sustainability trends should be beneficial from an ecological as well as from an economic point of view. This especially applies to the materials developed for the building sector as one of the biggest energy consumers, globally accounting for 36 % of final energy use and 39 % of CO₂ emissions [1]. New, efficient and sustainable materials are therefore required to help improve the current state.

Foamed glass is thermally-insulating material with applications in industry and construction. Low thermal conductivity, excellent chemical and mechanical stability, non-combustibility, and water-impermeability are the main characteristics that define foamed glass [2]. Amongst the processes of foamed glass production, direct foaming is the most relevant and well-researched [3–9]. Several investigations have shown that foamed glass can be prepared by direct foaming process from the mixture of waste glass and foaming additives, without high-temperature melting of the cullet [3–12]. The main principle of the direct foaming is to heat the glass powder to the point where it becomes viscous [13], allowing its expansion, driven by the increased internal pressure, generated by the trapped gas phase. The gas evolves from the gas-generating additives, i.e., foaming agents, admixed to the glass powder. Foaming agents can be distinguished according to the manner they release gas, i.e. decomposition, reaction, or combination of both

(foaming couples). The use of foaming couples can be especially suitable when foaming with waste glass due to the lesser effect of the matrix phase composition on the evolution of gases [6,14].

Water glass (WG) is a common additive that can be used either as an aid or as a sole foaming agent in the direct foaming process [15–19]. WG is a technical name used for alkali silicates, most commonly designating sodium silicate ((Na₂O)_x(SiO₂)_y). Structurally, WG is described as a colloidal suspension of aqueous sodium silicate solution (or a sodium silicate sol) [20]. Colloids and silicate anions/molecules are the main components of WG, and water is present between them in various configurations, i.e. as OH groups interacting with the Si network or as molecular water molecules which can be either hydrogen bonded to the nonbridging oxygens, interacting with the SiOH groups or interacting with the siloxane bridges [21,22]. The ratio between SiO₂ and Na₂O affects the size of silicate molecules and the solubility of WG. The physical properties of WG change drastically with the content of water, it can be either hard solid glass or a liquid where the mixture remains homogeneous in almost all mixing proportions (sodium silicate to water). Drying of WG solution leads to the formation of a xerogel with a glass-like structure, which with further heating transitions to a soft phase and starts to foam due to the evaporation of leftover water. Both phenomena are accompanied by a structural evolution, characterized by increased network connectivity [22].

Mixing the glass powder with WG affects its characteristic

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temperatures, consequently promoting the sintering and decrease of the foaming temperature (T_{foam}) [23,24]. The use of WG also enables the implementation of carbon-based foaming processes in the air atmosphere [17,25] which contributes to the identification of WG as a “green” foaming agent.

Although water glass is a well-known foaming additive in research and industry, the mechanism behind the foaming remains yet to be explained and experimentally proven [15,16,25]. Currently, the literature predicts that the expansion of the glass body occurs due to the release of the structurally-bonded water from WG [19]. Although plausible, this explanation remains to be backed by experimental evidence. Furthermore, an interesting question of, what happens to such pore-trapped water upon cooling, remains unanswered. There are three possible outcomes regarding the state of the trapped water vapours during the cooling of such foam. During cooling, water vapours can either react with glass, condense, or remain as part of the atmosphere in the form of vapours. The equilibrium between condensed water and water vapours is greatly in favour of condensate since water vapour pressure at room temperature (~ 0.03 bar) is one order smaller than the lowest evaluated internal pressures [14]. Detection of water vapours at high temperatures (~ 600 °C) during the heating of WG [25] suggests that water could indeed be one of the main expansion gases. This can be experimentally proven by the pore gas analysis.

Soluble silicates, such as WG, react with CO_2 [20] forming carbonates [26,27]. It is well known that carbonates can be used as foaming agents for the direct foaming of glass [28–30]. Therefore, it is also likely that the effect of the (air) atmosphere on the WG-containing foaming mixture is not negligible. Studies on the consolidation process of foundry cores [31] have dealt with the effect of CO_2 on the sintering behaviour of the sand-water glass mixtures and have shown that CO_2 decisively affects the sintering behaviour of the material. Consequently, the reaction between CO_2 and WG could significantly affect the foaming process and should be examined.

It is essential to study the foaming mechanisms of WG since it is already used in several industrial production processes and could become an even more important additive for glass foaming. This paper aims to unveil the mechanisms of foaming with WG by revealing the composition of pore gas, the structural and microstructural evolution of the material during heating and the effect of the processing atmosphere on the foaming process. The results of this paper offer insight into the mechanism of foaming with WG, helping the development of the foamed glass production processes in the future.

2. Methodology

2.1. Sample preparation

Waste cathode ray tube (CRT) panel glass and K_3PO_4 (2 wt%) were mixed and milled in a planetary ball mill (PM 200, Retsch, Haan, Germany) for 35 min at 250 rpm, reducing 50 % of particles below 9 μm (see Supplementary Information, Fig. S1 and Table S1). The obtained powder was manually mixed with 24 wt% of water glass (WG). Technical grade WG with SiO_2 to Na_2O weight ratio of 1.85:1 and with a total water content of ~ 50 wt% was used. The obtained mixture was then either i) immediately heat-treated (within 1 hour) to minimize the effect of air atmosphere on its properties or ii) processed further. Further processing performed on the mixture was either drying, storing in a CO_2

Table 1
Description of the foaming mixtures and their corresponding labels.

Further processing of the foaming mixture	Label
None	<i>Fresh</i>
Drying	<i>Dried</i>
Storing in CO_2 atmosphere for 24 h	<i>Fresh-CO₂-stored</i>
Drying and subsequently storing in CO_2 atmosphere for 24 h	<i>Dried-CO₂-stored</i>

atmosphere or a combination of both (Table 1).

Foaming mixtures were compacted in a steel mould (3 g in ϕ 15 mm) and heat-treated in an electric chamber furnace with a heating rate of 5°C min^{-1} . The final temperature of the heat treatment varied between 500 and 900 °C and the holding time was 5 min. Weight and volume of the powder compacts were determined before (m_i , V_i) and after (m_f , V_f) the heat treatment to determine the initial (ρ_i) and the final apparent density (ρ_f), and the expansion (E), according to Eq. (1).

$$E = \frac{V_f - V_i}{V_i} = \frac{\frac{m_f}{\rho_f} - \frac{m_i}{\rho_i}}{\frac{m_i}{\rho_i}} = \left(\frac{\rho_i(1-x)}{\rho_f} - 1 \right) \times 100\% \quad (1)$$

Where x is the relative weight loss of the sample: $1 - \frac{m_f}{m_i}$. The volume of the powder compacts before and after the heat treatment was measured with the laboratory calliper and the Archimedes principle (in distilled water), respectively. Uncertainties of density measurement via calliper and Archimedes principle are below 1 % and 0.2 %, respectively.

2.2. Sample analysis

2.2.1. Foaming mixture behaviour during heating

Hot stage microscopy (HSM; EM201x, Hesse instruments) and thermogravimetry coupled with mass spectroscopy (TG/MS; NETZSCH STA 449 C/6/G Jupiter, 403 C Aeoloss QMS 403) were performed on the *Fresh*, *Dried*, *Fresh-CO₂-stored* and *Dried-CO₂-stored* foaming mixtures to observe their behaviour during heating. A smaller amount (~ 30 mg) of foaming mixture was compacted in a steel mould ($\theta = 3$ mm) and heated at a rate of 5 and 10 $^\circ\text{C min}^{-1}$ for HSM and TG/MS, respectively. Air and synthetic air atmospheres were used for HSM and TG/MS, respectively. Intense contrast is achieved by shining a strong light source on the sample during the HSM measurement and continuously measuring the area of its shadow, i.e. its silhouette area, given in the form of a normalized value. The characteristic starting points of sintering and foaming (T_s and T_{foam} , respectively) from HSM are defined as in ref. [32].

Deviation between the sample duplicates from the HSM measurement was evaluated and is near 1.7 % below the collapse temperature and near 8 % above the collapse temperature.

2.2.2. Composition of pore gas

Gas present in the pores (pore gas) was determined by crushing the samples in a He-filled cell and inspecting the cell atmosphere with a gas chromatograph (7890A GC System, Agilent Technologies) on a 30 m long Rt-MSieveTM 5A and Rt-QPLOTTM (Restek) columns with an inner diameter of 0.320 and 0.530 mm, respectively. Measurement of the cell atmosphere was always performed in triplicates. For a thorough description refer to ref. [33]. Standard curves were used to evaluate the quantity of detected CO and CO_2 gas. The background signals of N_2 and O_2 gases were determined in the He-filled cell before crushing the foam sample. The increase of the N_2 and O_2 during the measurement was insignificant and was likely related to the contamination with the air atmosphere during cell handling and gas injection into the instrument. Average deviation between the triplicates was near 50 % and further suggests an error due to the air contamination (see Supplementary Information, Table S2). Additionally, an Ultraportable Greenhouse Gas Analyser (Los Gatos Research) was used to detect possible H_2O presence in the pore gases. For the analysis, 5 ml of gas from the cell was injected into the analyzer.

2.2.3. Sample structure

Powder compacts prepared from the foaming mixtures were treated at various temperatures (500, 600, 700, 800 and 900 °C), quenched to room temperature, crushed, mixed with KBr (sample:KBr ratio of 1:12) and analysed by FTIR (Perkin Elmer Spectrum 400 MIR, DRIFT mode) to correlate the change in the sample structure with the behaviour during

the heating.

Foaming mixtures were examined for the presence of crystalline phases before the heat treatment and after heating to 500 and 800 °C by X-ray powder diffraction (Malvern PANalytical Empyrean diffractometer, Netherlands, Cu-K α radiation source, $\lambda = 1.54187 \text{ \AA}$, 45 kV and 40 mA). Results were analysed using HighScore Plus software, and the PDF-4 database [34].

3. Results and discussion

3.1. Foaming mixture behaviour during heating

Expansion behaviour of water glass (WG)-containing foaming mixtures can be significantly altered by the presence of carbon dioxide during their processing. Fig. 1 shows the expansion behaviour of the foaming mixtures compacts during heating. Additional figure, showing the recalculated volume change can be seen in Supplementary Information (Fig. S2). Heating of the samples up to $\sim 500 \text{ }^\circ\text{C}$ does not result in any significant deviation from their initial dimensions. Above $\sim 550 \text{ }^\circ\text{C}$, the expansion/sintering behaviour of the samples starts to differ (Fig. 1). Only the *Fresh-CO₂-stored* sample exhibits a significant shrinkage with T_s at 560 °C. At the same temperature, the other three samples already start to expand, whereas they exhibit a two-stage expansion with a smaller initial step, followed by a more intensive expansion. The two-stage expansion is most probably observed due to the overlap of the sintering and gas evolution. *Fresh*, *Dried* and *Dried-CO₂-stored* samples exhibit a similar expansion slope. These samples undergo minimal shrinkage above 500 °C, start expanding at $\sim 575 \text{ }^\circ\text{C}$ and begin to collapse at $\sim 790 \text{ }^\circ\text{C}$. *Fresh-CO₂-stored* sample, on the other hand, shrinks significantly more and starts expanding at $\sim 640 \text{ }^\circ\text{C}$ (i.e. at 130 °C higher than other samples), followed by collapse above 850 °C. The expansion curves, therefore, show a significant effect of the CO₂ atmosphere on the non-dried foaming mixtures. The difference in the maximum expansion between the samples is apparent. The *Fresh* expands the most (near 375 % of silhouette area which can be evaluated to approximately 500%

volume increase) and *Fresh-CO₂-stored* the least (above 150 % of silhouette area which can be evaluated to approximately 100% volume increase). The shape of the *Fresh-CO₂-stored* sample expansion curve suggests that treatment of the powder with CO₂ affects the evolution of the expansion gas or/and the sintering process, i.e., preventing the closing of the pores and thus enabling the evolved gas to escape which strongly limits the expansion. Interestingly, the sintering behaviour of the dried samples does not change after exposure to CO₂. In these samples water is removed during the drying step, indicating the importance of water for the process. It is reported that the reaction between WG and CO₂ requires the presence of water vapour [27], suggesting that carbonate-forming reactions could be the reason for the changed expansion behaviour.

Heating of the foaming mixtures results in several mass loss regions accompanied by signals for H₂O and/or CO₂ (Fig. 2). The total mass loss of the dried mixtures (Fig. 2b) is significantly smaller in comparison to fresh ones (Fig. 2a). Both dried mixtures behave similarly in terms of mass loss and gas evolution (Fig. 2b, d, f) which matches with their similar expansion behaviour observed by HSM analysis (Fig. 1). Gas evolution suggests two mass loss regions, with CO₂/H₂O being evolved at low-temperature ($< 500 \text{ }^\circ\text{C}$) and CO₂ at high-temperature ($> 500 \text{ }^\circ\text{C}$). The difference in mass loss between the dried mixtures can be observed at low temperatures where the *Dried-CO₂-stored* mixture exhibits an additional mass loss $< 200 \text{ }^\circ\text{C}$ accompanied by a signal for CO₂. On the other hand, both fresh mixtures exhibit a more pronounced low-temperature mass loss due to the evaporation of less strongly bonded molecular H₂O [21]. *Fresh* mixture initially exhibits an intense mass loss due to the evolution of H₂O which, at $\sim 200 \text{ }^\circ\text{C}$, starts overlapping with the CO₂ desorption. With higher temperatures ($\sim 600 \text{ }^\circ\text{C}$) an additional mass loss and CO₂ signal can be detected, similar to the dried samples. The total mass loss of the *Fresh* powder is slightly lower than theoretically expected ($\sim 5.8 \text{ wt.}\%$ instead of $\sim 9.6 \text{ wt.}\%$), which can be related to the non-intentional drying of the mixture during the homogenization of the mixture in an agate mortar. The first mass loss of the *Fresh-CO₂-stored* mixture is accompanied by a less intense H₂O and more intense CO₂ signal in comparison to the *Fresh* mixture (Fig. 2a and e). The second mass loss (above 500 °C, 2.1 wt%) of the *Fresh-CO₂-stored* mixture significantly differs from all other mixtures, which in this range exhibit a similar response regarding the shape of the CO₂ signal and mass loss amount (0.22, 0.34 and 0.38 wt% for the *Fresh*, *Dried* and *Dried-CO₂-stored* mixture, respectively). CO₂ signal for the *Fresh-CO₂-stored* starts decreasing at $\sim 720 \text{ }^\circ\text{C}$ and becomes negligible $> 760 \text{ }^\circ\text{C}$. The presence of the gas signal at this stage above 760 °C indicates that some of the pores are still open, despite the sample already being in the expansion stage ($> \sim 650 \text{ }^\circ\text{C}$, Fig. 1b). This could explain a lesser expansion of the *Fresh-CO₂-stored* in comparison to other foaming mixtures. Above 800 °C there is no apparent mass loss for any of the foaming mixtures, however, sharp CO₂ signals can be detected in all cases except for the *Fresh-CO₂-stored* mixture (Fig. 2e and f). These signals appear in the foam-collapse temperature region where the pores start to burst, releasing the gas instantly, resulting in a distinct shape of the signal. Note, that no sharp signals are detected in the high-temperature range for H₂O.

Detection of CO₂ at relatively high temperatures (above 600 °C, Fig. 2e and f) suggests that carbon is incorporated in all of the foaming mixtures with stronger interactions than only physical adsorption of CO₂. It is known that WG reacts with CO₂ [27] and the reaction products, i.e. carbonates, could be the source of CO₂, which evolves in the softened glass and considerably contributes to the expansion of the foam.

To further inspect when the carbonate forming reaction occurs additional TG/MS analysis of the raw initial components was done (Fig. 3). Milled CRT panel glass releases a small amount of CO₂ between 400 and 550 °C (as in [35]), while WG does not. Note, that the ion current signal scale in Fig. 3 is ten times smaller than in Fig. 2. Milled CRT panel glass powder compact expands negligibly during heating [3,

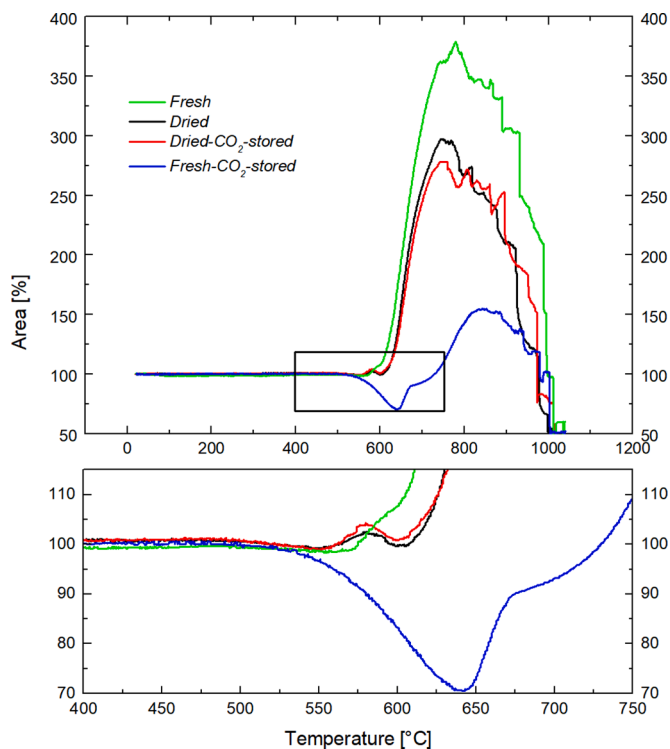


Fig. 1. Silhouette area of the *Fresh*, *Dried* and *CO₂-stored* samples during heating (above), with a closer view of the sintering stage (below).

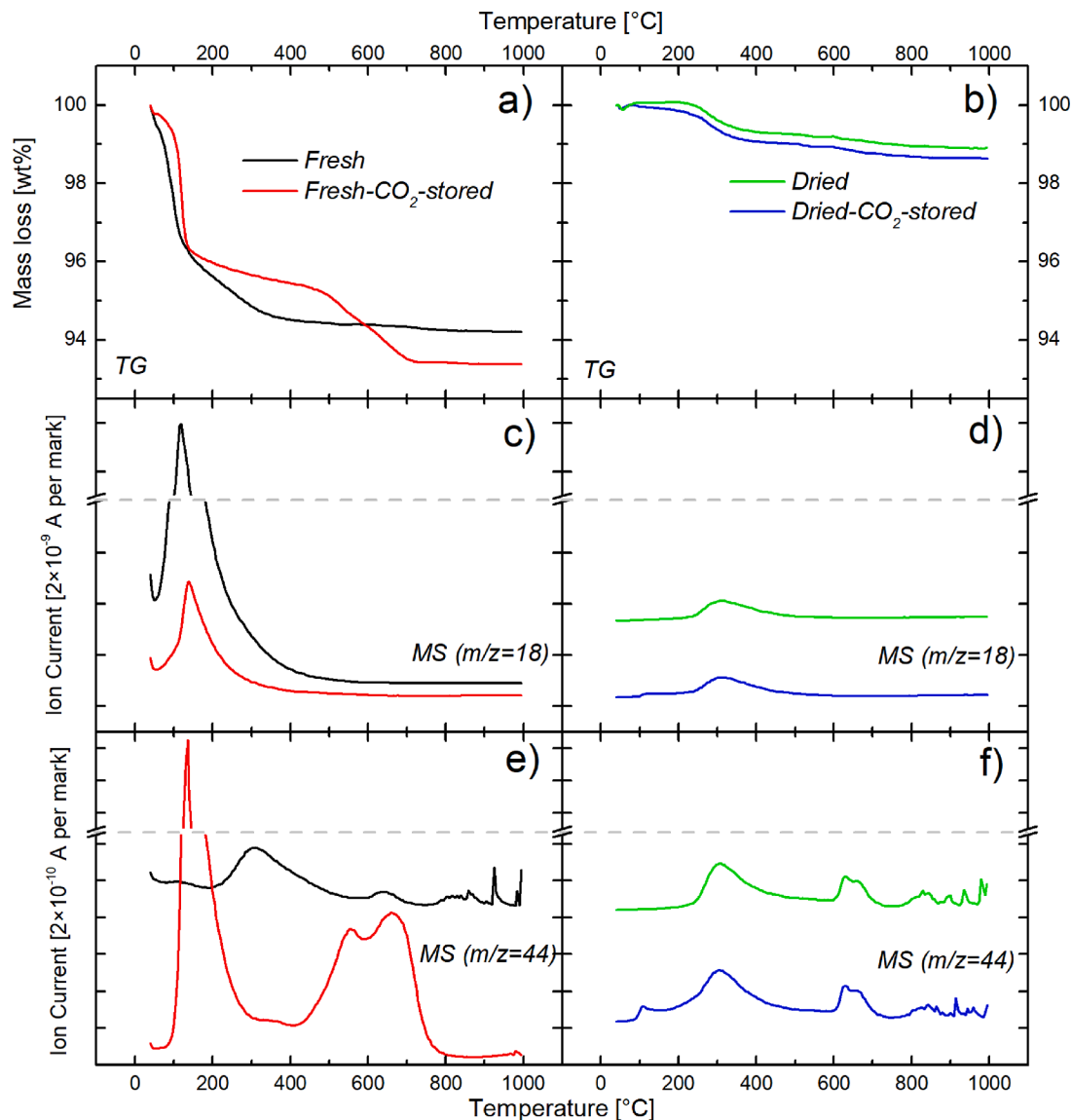


Fig. 2. Mass loss (a, b) and simultaneously detected ionic current signals corresponding to H₂O (c, d) and CO₂ (e, f) for the *Fresh* and *Fresh-CO₂-stored* (a, c, e) and *Dried* and *Dried-CO₂-stored* samples (b, d, f). Ion Current signals are shifted for better clarity.

36]. Sole components of the foaming mixtures, therefore, do not release sufficiently enough CO₂ at high temperatures (CRT and WG in Fig. 3b), which means that a CO₂-producing component is formed during the processing of the foaming mixture, i.e. mixing of the glass powder and WG. This is experimentally demonstrated with the following case. If WG is dried (200 °C, 3 h) before the TG/MS analysis, it starts to exhibit a distinct mass loss and CO₂ signal in the 600–700 °C temperature range (dried WG in Fig. 3). Temperature range and the shape of the signal are similar to the result from the foaming mixtures (Fig. 2a, > 600 °C). Both actions, drying of WG or admixing it to CRT panel glass, result in a similar evolution of CO₂. An important parameter is the surface area of the WG which is increased during mixture homogenization and thus promotes the carbonate-forming reaction. TG/MS results thus suggest that the reaction between WG and CO₂ from the air is decisive for achieving the expansion during the foaming process.

Exposing a fresh foaming mixture to a pure CO₂ atmosphere decreases its expansion as seen in Fig. 1. Pronounced evolution of CO₂ at 500–700 °C from the *Fresh-CO₂-stored* mixture suggests that its carbonate content is higher in comparison to other compositions, while it was shown before that exaggerated carbonate content leads to smaller expansion [29,37]. Several mechanisms occurring in such a case lead to

a smaller foaming effect, the reaction between WG and CO₂ produces precipitated SiO₂ [27] suppressing the materials' ability to sinter, while the increased gas evolution rate breaks the pore walls making the material open porous. Such behaviour follows the results from the investigations on the sand–WG mixtures for foundry cores [26,31]. It was shown that exposing the sand–WG mixture to pure CO₂ for a short period inhibits the sintering [31]. Inhibited sintering behaviour in the case of the direct foaming process leads to higher content of open pores, allowing more gas to escape, which decreases the foam expansion.

The exposure of the foaming mixtures to CO₂ gas affects only the fresh powders. The dried powders behave very similarly during the foaming process, regardless of the storage atmosphere. Such behaviour is related to the peculiarities of the CO₂ reaction with soluble silicates, where water acts as a catalyst [27,38]. Some investigations on the efflorescence of soluble silicates suggest that the reaction can proceed only in the presence of water [27,39]. Drying could therefore be perceived as a practical way of stabilizing the foaming mixtures, i.e. making them less susceptible to the atmospheric effects.

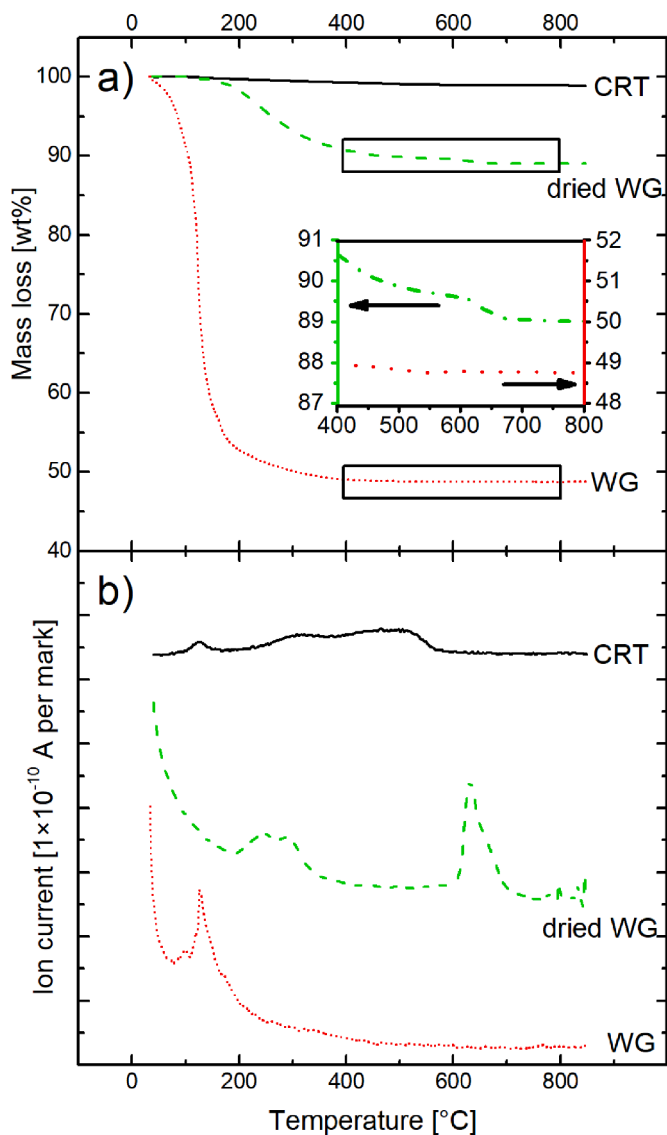


Fig. 3. (a) Mass loss and simultaneously detected (b) ion current for (m/z 44, CO_2) from the TG/MS analysis of the raw components.

3.2. Structural changes during heating

XRD analysis of foaming mixtures and foamed glass samples reveals that a small amount of hydrous silicate and carbonate crystal phases (best coinciding with PDF 00-003-0433 and 00-008-0448, respectively) is present within the starting foaming mixtures (Fig. 4a). Heating of the mixtures results in a transformation of carbonate species, their eventual decomposition and final formation of crystalline phase of calcium silicate (PDF 01-077-0420). The content of the crystal phase becomes more pronounced when the foaming mixture is stored in a CO_2 atmosphere (Fig. 4b). Higher content of crystal phases, in this case, suggests that higher partial pressure of CO_2 allows for the reaction of carbonate formation to proceed further. However, a comparison between the diffraction spectra at 500 °C (Fig. 4a and b, curves labelled 500 °C) reveals that at this stage the samples still contain different amounts of crystalline phase, which can significantly affect the foam stability and the expansion dynamics. Higher content of crystalline phase in the *Fresh- CO_2 -stored* sample can be related to significantly different gas evolution and expansion behaviour in comparison to other samples. Even at 900 °C, the intensity of the peaks in *Fresh- CO_2 -stored* sample is visibly higher in comparison to *Fresh* sample.

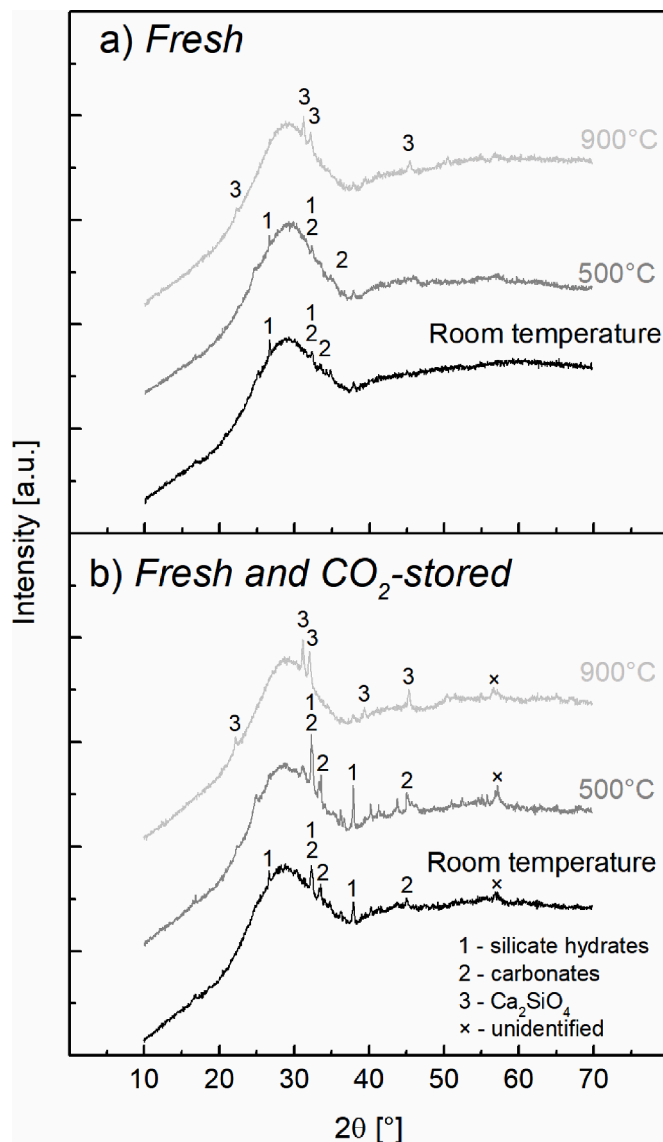


Fig. 4. XRD patterns of the *Fresh* (a) and *Fresh- CO_2 -stored* (b) foaming mixtures treated at 500 or 900 °C.

Further analysis was performed on the foam samples from different stages of heating using FTIR (Fig. 5). The peaks with maxima at $\sim 1000 \text{ cm}^{-1}$ and 750 cm^{-1} correspond to the vibrations of the silicate network. These peaks do not vary significantly with the temperature and can serve as a reference point for the changes in each curve. The signals at $2250\text{--}3800 \text{ cm}^{-1}$ and $\sim 1650 \text{ cm}^{-1}$ indicate the presence of OH^- groups and water, respectively [21]. A significant decrease of intensity in this range happens as the powders reach 500 °C. The intensity of the $\sim 3600 \text{ cm}^{-1}$ peak stops decreasing at 700 °C, indicating that H_2O is still evaporating even $> 600 \text{ °C}$. The peaks at $\sim 1450 \text{ cm}^{-1}$ can be attributed to the presence of carbonates [40] and are accompanied by a less intense shoulder at $\sim 1400 \text{ cm}^{-1}$. Such a narrow split ($1400\text{--}1450 \text{ cm}^{-1}$) indicates that CO_3^{2-} group is nearly undistorted from ideal trigonal symmetry which is characteristic for crystalline carbonates [40]. In contrast, splitting of the 1450 cm^{-1} peak can be observed for the *Fresh- CO_2 -stored* mixture, suggesting more varied interactions of CO_3^{2-} with the matrix material or less crystalline nature. Additional peaks around 1650 cm^{-1} for the *Fresh- CO_2 -stored* sample at room temperature (Fig. 5b) can be attributed to the presence of water. The shape of the $\sim 1450 \text{ cm}^{-1}$ peak changes for both samples when the mixture is heated to 500 °C indicating the transformation of carbonate species, agreeing with the XRD

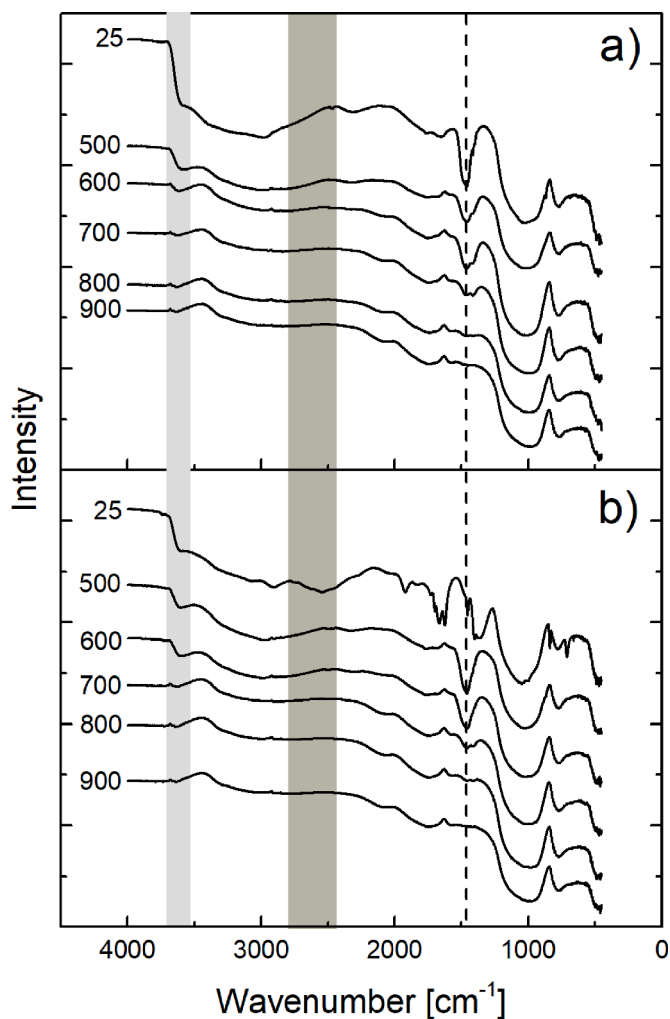


Fig. 5. FTIR spectra of a) *Fresh* and b) *Fresh-CO₂-stored* samples from different stages of heat treatment (labels in °C). Wider bands at ~3600 and 2600 cm⁻¹ denote Si(OH) stretching and bending, respectively. The dashed line at ~1450 cm⁻¹ designates the presence of carbonates.

results (Fig. 4). Additionally, the intensity of the peaks at ~1450 cm⁻¹ starts to decrease above 600 °C, suggesting that carbonate decomposition is taking place which correlates with the results from the TG/MS analysis (Fig. 2).

Structural changes offer an additional explanation for the sample behaviour during the heating. It is apparent that *Fresh* sample, contains detectable amounts of carbonate crystalline phase, which explains the evolution of CO₂ during the heating. The same is true for the *Fresh-CO₂-stored* sample whereas its much different gas evolution profile and hindered expansion behaviour can be attributed to the formation of additional carbonate phases.

3.3. Pore gas composition

Results of the analysis of the pore gas using gas chromatography (GC) on the foamed glass samples prepared from the *Fresh* and *Dried* foaming mixtures, treated at 800 °C, indicate a predominant presence of CO₂. The results also show that the samples do not contain any traceable amounts of CO. Small amounts of O₂ and N₂ were detected in the case of several samples. Since the foaming process is implemented in an air atmosphere and the sample expansion is relatively low, air (N₂/O₂ mixture) may remain trapped within the sintered body which could theoretically result in the pore gas containing a maximum of 10–15 % N₂ and O₂ gases. However, it is expected that the majority of the air atmosphere

within the sample is displaced during heating due to the evolution of CO₂/H₂O (Fig. 2), and it is assumed that the N₂/O₂ signal appears due to the measurement issues (contamination during crushing of the sample in the cylinder). Since H₂O is not possible to detect with a gas-chromatograph, an additional analysis was performed using the Ultra-portable Greenhouse Gas Analyser instrument allowing also the detection of potentially present H₂O (Fig. 6). Here, an apparent signal for CO₂ can be seen at the time of the injection while the H₂O content remains unchanged, providing additional evidence for the CO₂-dominated expansion.

3.4. Foamed glass sample properties

The characteristics of the foamed glass samples confirm the conclusions made from the TG/MS and HSM analyses: atmosphere and/or drying step critically affect the process of foaming. After the processing of the mixtures, the samples were foamed at 800 °C, their appearance and expansion values are presented in Fig. 7 and Table 2, respectively. Prolonged exposure of the foaming mixture to the air or CO₂ atmosphere before the heat treatment results in decreased expansion and less-homogeneous pore size, with a more pronounced effect in the case of CO₂. The reaction proceeds relatively quickly in both atmospheres since there is no significant difference between the samples stored for 1 day or 1 week, which could be related to the elimination of the water from the sample. Especially, since the dried foaming mixtures, unexposed or exposed to the CO₂ atmosphere, produce visually similar foams (Fig. 7, bottom row) with relatively constant expansion values (Table 2).

Storing of the foaming mixture in a CO₂-containing atmosphere in combination with moisture therefore detrimentally affects the foam characteristics. It was shown that higher partial pressure of water aids the sintering process of glass powders [24] by decreasing the materials' characteristic temperatures. A comparison between the *Fresh* and *Dried* samples (Fig. 7a and b, respectively) suggests that this effect could also promote the coalescence of pores. A higher degree of coalescence typically results in a decreased number of pores and larger pores with irregular shapes [41]. The difference in the pore size distribution between the samples is apparent (see Supplementary Information, Fig. S4).

For achieving optimal thermal and mechanical properties of foamed glass it is desirable to obtain high expansion values while maintaining a stable porous structure. The use of *Fresh* composition allows the highest expansion values with the downside of larger pores with less regular

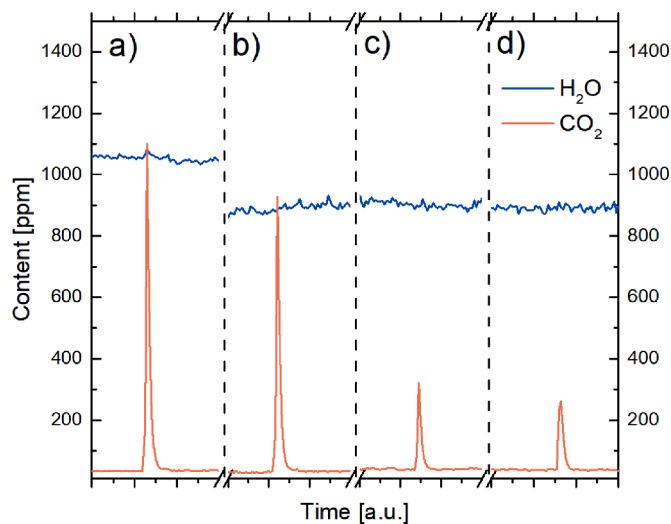


Fig. 6. CO₂ and H₂O content within the He-filled closed cell after breaking the foamed glass sample prepared from *Fresh* (a and b) and *Dried* (c and d) foaming mixtures. No H₂O is detected and note, that *Fresh* and *Dried* samples were not stored in CO₂.

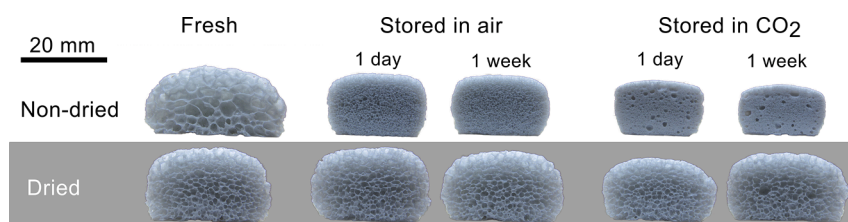


Fig. 7. Foamed glass samples prepared at 800 °C from non-dried and dried foaming mixtures which were fresh, stored in air or stored in CO₂ atmosphere for 1 day or 1 week. Labels a, b, c and d denote *Fresh*, *Dried*, *Fresh-CO₂-stored* and *Dried-CO₂-stored* compositions, respectively.

Table 2

Expansion values (E , defined in Eq. (1) and relative density (ρ_{rel}) of the foamed glass samples from Fig. 7. Labels a, b, c and d denote *Fresh*, *Dried*, *Fresh-CO₂-stored* and *Dried-CO₂-stored* compositions, respectively.

	Non-dried		Dried		
	E (%)	ρ_{rel} (%)	E (%)	ρ_{rel} (%)	
Fresh	620±37 ^a	9.0±0.3 ^a	320±11 ^b	11.4±0.1 ^b	
Stored in air	1 day	162±8	18.5±0.5	325±9	11.6±0.1
	1 week	154±8	19.6±0.5	322±9	11.7±0.1
Stored in CO ₂	1 day	120±7 ^c	24.0±1.0 ^c	320±17 ^d	11.6±0.4 ^d
	1 week	104±6	25.0±1.0	340±18	11.6±0.4

shape and sensitivity to the atmosphere. Here, the expansion and pore structure can be adjusted by optimizing the foaming temperature. However, the *Fresh* mixture is unstable and, if not processed immediately, the reaction with the atmosphere considerably decreases the maximum achievable expansion as seen in Table 2. Drying of the mixture decreases the maximum achievable expansion while improving its stability in the air atmosphere. Drying of the mixtures is therefore the optimal processing path concerning the obtained densities and pore structures, whereas the high expansion value of the *Fresh* mixture suggests the possibility of further improvements. As other studies have shown [16,17,25], additional expansion can be achieved by using additional foaming agents in combination with water glass.

4. Conclusions

When foaming with the addition of water glass, the control of the atmosphere and its time of contact with the foaming mixture is even more important for the foamed glass characteristics as the foaming temperature and time.

Heat treatment of CRT panel glass powder and water glass mixture leads to expansion and formation of a porous material. The foaming mixture is sensitive to the air atmosphere, as crystalline carbonate phases are formed during the preparation due to the reaction with the carbon dioxide. The observed evolution of carbon dioxide during the heating of the mixture and its predominant presence in the pore gas suggests that the decomposition of the carbonates during heating has a decisive effect on the expansion and formation of the porous material. Prolonged exposure to air atmosphere or, more pronounced, to pure carbon dioxide results in the formation of additional crystalline carbonates, significantly altering the expansion behaviour and characteristics of the pore structure. Drying of the mixture prevents the reaction with the atmospheric carbon dioxide, which results in foams with more consistent properties.

Most of the literature considers that the foaming of glass with the addition of water glass occurs due to the water evaporation. However, we showed that the foaming occurs due to the decomposition of the carbonates, the formation of which is primarily influenced by the exposure of the foaming mixture to carbon dioxide in the surrounding atmosphere. With this, we have revealed a hitherto unmentioned mechanism that significantly affects the course of glass foaming with the addition of water glass. In general, the influence of the atmosphere on

the properties and composition of the foaming mixture is an unexplored parameter that allows additional control over the properties of the foamed product in future research and/or optimization of the foaming process with water glass.

CRedit authorship contribution statement

Uroš Hribar: Writing – original draft, Investigation, Methodology. **Martin Bonderup Østergaard:** Investigation, Writing – review & editing. **Niels Iversen:** Investigation. **Matjaž Spreitzer:** Writing – review & editing, Funding acquisition. **Jakob König:** Supervision, Writing – review & editing, Conceptualization, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jnoncrysol.2022.122025.

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