2.7
Glass Foams

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2.7.1
Introduction

Glass foam has a unique combination of properties: it is lightweight, rigid, compression-resistant, thermally insulating, freeze-tolerant, nonflammable, chemically inert and nontoxic, rodent- and insect-resistant, bacteria-resistant, and water- and steam-resistant. Moreover, glass foam facilitates quick construction and has low transport costs, it is easy to handle, cut, and drill, and is readily combined with concrete. This combination of properties makes glass foam practically irreplaceable both in construction (e.g., for the insulation of roofs, walls, floors, and ceilings under hot or cold conditions) and in many other fields [1].

Glass foam is generally obtained by the action of a gas-generating agent (termed gasifier or foaming agent, mostly carbon or carbonaceous substances), which is ground together with the starting glass to a finely divided powder. The mixture of glass powder, foaming agent, and occasionally other mineral agents is heated to a temperature at which the evolution of gas from the foaming agent occurs within a pyroplastic mass of the softened glass particles undergoing viscous flow sintering. The evolved gas leads to a multitude of initially spherical small bubbles which, under the increasing gas pressure, expand to a foam structure of polyhedral cells that, after cooling of the glass, constitute the pores in the glass foam.

The properties of finished foamed glass products depend strongly on the type and quantity of the added foaming agents, on the initial size of the glass particles, and on the firing schedule. The result is a glass foam with high compressive strength and dimensional stability, characterized by a density of only 0.13 to 0.3 g cm^{-3} [2].

2.7.2
Historical Background

The production of glass foam dates back to the 1930s, when major research activity was conducted throughout the industrialized countries. Owing to the many patents granted in the same period, it is uncertain who the first inventors of glass foam were. The patented processes can be divided into two fundamental types: manufacturing of glass foam by the above-described sintering of finely ground glass powders

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with a suitable foaming agent, and the direct introduction of fluids (air, CO_2, water vapor) into the molten glass.

The reports of Kern [3] and Kitaigorodski [4] can be considered to be the first examples of glass foam from a sintering process. Kern mixed finely ground amorphous silica with up to 20 wt% of combustible material, such as coal, lignite, or wood, and “plasticizing agents” (hydrochloric acid, chloride solution, or a NaOH solution). Heating the mixtures to 1500 °C resulted in highly porous silica glass articles. Kitaigorodski began industrial production of glass foam in 1932, on the basis of technologies developed at the Mendeleev Institute of Moscow. The starting mixture of finely powdered glass and $CaCO_3$ as foaming agent was heated in steel molds up to about 850 °C; after cooling to 600–700 °C, the foamed glass was demolded in the form of blocks and annealed in tunnel kilns. Later, anthracite and carbon black were also employed as foaming agents, as alternatives to $CaCO_3$. The final density was about 0.3 g cm^{-3}, and the pore size around 5 mm; the thermal conductivity ranged from 0.06 to 0.08 W m^{-1} K^{-1}.

The direct introduction of gases into molten glass was the subject of intense research activity, mainly in France (Saint Gobain) and the USA (Pittsburgh Plate Glass and Corning Glass Works) soon after the first experience with the sintering approach. In 1934 Long [5] demonstrated the feasibility of a “spongelike glass” based on the production of a glass with a notable amount of dissolved gases (mainly water) from a mixture of silica, borax, and zinc oxide. After fusion, the glass material was cooled slowly to the softening temperature, which ranged from 500 to 700 °C, and maintained at that temperature until the entrapped gases evolved, leaving a multitude of bubbles and resulting in a cellular body with a density of about 1.25 g cm^{-3}. To achieve a density comparable with that reported for the sintering process, the volume of bubbles in the glass was dramatically increased by injection of a gas or a vapor. In 1940 Lytle [6] described the production of glass foam by forcing carbon dioxide, steam, or air, continuously or intermittently, into molten glass: the glass was formed in a column furnace, and the gases were introduced at the bottom of the column. The foamed glass, still fluid, was poured into molds moving on a belt conveyor or laminated through two belts. A number of patents were granted concerning the same technology in the following years [7–10], with slight improvements, such as subjecting the glass with entrapped gas bubbles to a negative pressure (depressurization) to make the bubbles expand. Peyches [11] reported the foaming of glass by local overheating of glass on the electrodes of Joule-heated glass melters, which resulted in the evolution of dissolved gases; such action could be enhanced by the injection of gas into the glass directly through the surface responsible for overheating. Other modifications concerned the mechanism of gas injection into the molten glass: Powell [12] reported the formation of bubbles from the thermal decomposition of solid foaming agents such as sodium nitrate and sodium sulfate, introduced into the molten glass while casting into molds.

World War II boosted the research, development, and production of glass foam in the USA, since it was largely used as nonflammable thermal insulation in the internal walls, floors, and ceilings of ships and submarines [4]. The most important results were patented by Pittsburgh Plate Glass and Corning Glass Works, later merged as Pittsburgh Corning Corporation; the first large production plant for glass foam in the USA started up in Port Allegany, PA, in 1943. The patents referred mainly to the sintering of finely powdered glass with $CaCO_3$ and carbon as alternative foaming agents [13–16]. The use of sheet glass, that is, a glass with a conventional chemical composition instead of a specific composition, was mentioned for the first time in Ref. [15]. Reference [16] reported the use of negative pressure as a foaming aid. The currently employed methods for glass foam manufacturing are given in Ref. [17], in which carbon black is reported as foaming agent for conventional window glass or borosilicate glass; in the same patent particular attention was dedicated to the presence of oxygen-releasing agents, such as SO_3 in the glass composition or Fe_2O_3 and Sb_2O_3 as additives to the mixture of glass powders and foaming agents. Willis [18] developed a sort of compromise between the sintering and foaming approaches by using entrapped gases: glass powders were sintered under pressure to cause gases to permeate into the interstices, and subsequently heated to expand the bubbles.

2.7.3
Starting Glasses

The first glass foams, dating back to the 1930s, were developed from specially formulated pristine glasses [19], especially in the case of direct introduction of gases into the molten glass. This process is at present hardly used, since it requires more sophisticated industrial plants, and it is much more energy-intensive than the currently used sintering process, which is carried out at much lower temperatures and can employ large quantities of powdered recycled glass. In some cases the substitution of pristine glass with waste glass is almost complete, so that glass foam production can be considered an effective way of recycling a great number of glass products (container and flat glass, borosilicate glass for the chemical industry, and, more recently, even fluorescent lamp glass [20]). Tens of millions tons of waste glass are generated every year worldwide, a large percentage of which is in the form of crushed solids with a wide range of particle sizes in a mixture of various colors. Moreover, the glass is contaminated with metallic and nonmetallic fragments (plastics, ceramics, aluminum, iron, paper, organic substances, and so on). The costs of color sorting and impurity removal are high, especially if a significant portion of the glass is finely divided. The use of recycled glass in the production of new glass articles is consequently barely profitable; in addition, new articles produced with introduction of impure recycled glass may contain defects and thus may exhibit poor mechanical properties.

Besides waste glass, other vitrified solid wastes are being generated in increasing quantities, for instance, fly ashes from burning of coal or municipal solid waste (MSW), slags of various kinds, sewage sludge ashes, and so on. The use of fly ashes, calcined together with sand and other minor constituents (borax and sodium salts), as the basis material for glass foam manufacturing dates back to the late 1960s [21]; much literature was dedicated more recently to this raw material [22, 23]. The vitrification of a number of inorganic wastes is particularly advantageous [24], since the obtained waste glass generally has high chemical durability and can be safely disposed of in landfills, with no risk of pollution. However, the high costs of landfilling, together with those of vitrification, lead to the need for applications for the obtained glass, for example, manufacturing profitable products like glass foam [25]. Such a prospect could also be profitable for glasses from end-of-life cathode ray tubes (CRTs) [26, 27], direct recycling of which is particularly difficult, so that they are mainly disposed of in landfills.

Some research was performed on manufacturing glass foams from natural materials like clays [28–31]. Cowan et al. [28] described the foaming of montmorillonite clay with carbon or organic compounds as foaming agents and Na_2O as sintering "flux". Seki et al. [31] reported the foaming of mixtures of silicate glass, volcanic ashes (volcanic glass materials), and waterglass. Finally, some research focused on the use of slags directly as raw materials (without previous vitrification) [32].

2.7.4
Modern Foaming Process

The main industrial process currently employed for glass foam manufacture is sintering of powdered glass admixed with suitable agents. The main parameters of this process are described in what follows.

2.7.4.1
Initial Particle Size of the Glass and the Foaming Agent

The starting glass must be ground and sieved to a grain size size of less than 0.4 mm, otherwise the foaming process is almost completely halted [33]. There is a definite relation between the fineness of the initial particles and the pore diameter of the obtained glass foam. For example, Fig. 1a [34] shows the microstructures of foams obtained from soda-lime glass cullet with 5 wt% SiC as foaming agent with variation of the glass powder size as indicated. Figure 1b shows the pore diameter of these foams as a function of the glass powder size [34].

Likewise, the particle size of the foaming agent affects the cell size [35] and the foaming behavior. A sample containing coarse-grained SiC (74–78 μm) hardly foams at 950 °C, while a sample containing fine-grained SiC (4–7 μm) exhibits a very large increase in volume at lower temperatures [36]. Moreover, precompaction of the initial mixture is also very important for the resulting foam structure: precompacted samples always have a much more uniform structure than loose powder mixtures, probably due to earlier onset of closed porosity.

The microstructural homogeneity of the foams is limited if the glass and foaming agent powders have very different dimensions, as can be seen by comparing the morphology of glass foams obtained with the carbon content of fly ashes (not previously calcined; Fig. 2a) and carbon black (Fig. 2b) as foaming agent [37]. In the first case, the starting dimensions of the foaming agent and the glass powder are

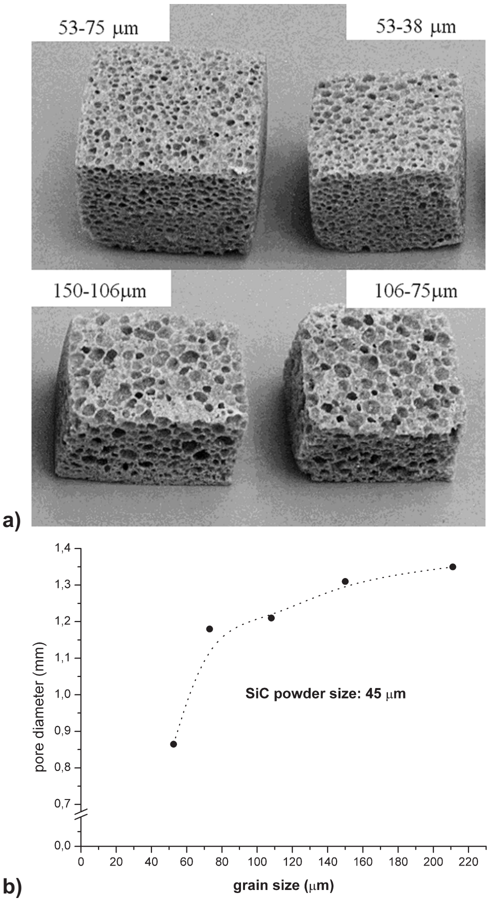

Fig. 1 a) Influence of glass powder grain size on the microstructure of the glass foam obtained with 5 wt% SiC (45 µm) as foaming agent. The range of glass powder sizes is indicated. b) Pore diameter of foam produced with SiC as a function of glass powder size.

notably different (1–20 µm and 75–150 µm, respectively), and the inhomogeneity of cell size distribution is probably due to agglomerating effects of fly ash, while in the second case they have about the same size. Another innovative strategy [37] to obtain homogeneous size distribution of pores is the use of a foaming agent homogeneously dispersed in the form of a solution, as in the treatment of finely ground soda-lime glass cullet by introduction of polymethylmethacrylate (PMMA) dissolved in CH_2Cl_2, which, after drying, produces a polymeric layer on the glass granules. The actual foaming agent is formed by pyrolysis of the polymer at 850 °C in an N_2 atmosphere for 5 min, followed by oxidation of the pyrolysis residues at the same temperature in air for 5 min. The layer of PMMA on the glass granules is transformed into a layer of carbonaceous products on pyrolysis of the polymer and thus leads to a very homogeneous distribution of pores, as illustrated in Fig. 2c.

A given foaming process leads to a precise density, corresponding to a certain global volume of pores. This volume, however, may be distributed in a limited number of large pores or in a great number of small pores. Such different distributions can

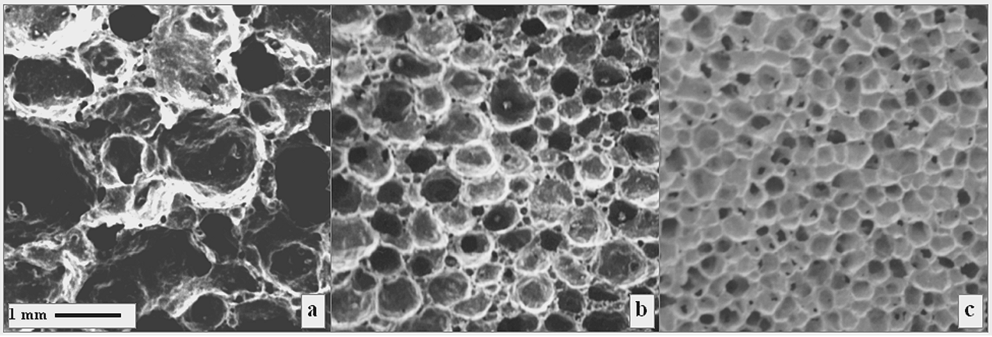

Fig. 2 SEM images of the microstructures of glass foams obtained by using the carbon content of a) fly ash (not previously calcined), b) carbon black, and c) PMMA pyrolysis residues as foaming agents and with comparable apparent densities of 0.28, 0.284, and 0.29 g cm^{-3}, respectively.

have a major influence on the performance and the properties of the glass foam. Generally, the lower the foam density, the lower the thermal conductivity (and the better the thermal insulation properties), without any evidence in the literature of dependence on cell size. On the other hand, the smaller the cell size, the higher the compressive strength of the product. The crushing strength is a function of the inverse square root of the cell size [38]. Ketov [39] observed a strong influence of the size of the initial glass particles on the density of the product. Decreasing the size of the particles to less than 25–30 μm leads to a final glass foam with a density of 160 kg m^{-3}, a thermal conductivity of 0.035 W m^{-1}/K^{-1}, and a compression strength of 1.3 MPa.

2.7.4.2
Heating Rate

The heating rate must be accurately controlled, because it is a very important factor for optimizing the glass foam product [23]. Owing to the fineness of the starting powders and the consequent high degree of dispersion, the foaming mixture contains a large amount of air entrained in the interstices between the particles of the glass and the gasifier. As a result, the foaming mixture has low thermal conductivity, so the rate of heating to the foaming temperature must not be too high. The larger the sample, the slower the heating rate should be to maintain a uniform temperature distribution in the poorly conductive material. When the temperature rise is rapid (i.e., 40 °C min^{-1}), large cracks develop throughout the glass mass. Heating rates of 5–10 °C min^{-1} are usually unproblematic. On the other hand, too a slow heating rate is also undesirable, since prolonged isothermal heating at high temperature could lead to premature generation of gases (i.e., before glass powder sintering). Also the temperature gradient in the furnace should be kept small (± 5 °C); otherwise, inhomogeneous foams are obtained.

2.7.4.3
Foaming Temperature

Proper selection of the maximum temperature for the foaming process is of basic importance. Glass viscosity (strongly dependent on temperature) and the foaming temperature are strictly related. The optimum foaming temperature must be selected by considering, on the one hand, the maximum foam stability, which is controlled by viscosity, and, on the other hand, the internal cell structure, characterized by homogeneous and regular shape and size of the pores and by the minimum thickness of their separating walls [23]. If the selected foaming temperature is too high, the melt viscosity is too low (i.e., $< 10^3$ Pa·s), and controlling the structure becomes difficult, because bubbles rise to the top of the mold (as in fining of glass) and consequently the bubble distribution is far from uniform. On the contrary, if the temperature is too low, the glass viscosity is too high, and gas expansion is difficult and little increase in volume oocurs. In this case, the formation of the separating walls does not go to completion, and residual open porosity results, so that water absorption of the glass foam in service increases.

At an optimum selected temperature, the increase in volume can be remarkable. Koese [40] reported the volume changes in a pressed soda-lime glass/8 wt% SiC pellet during heating and cooling in air. In the sintering range, from about 600 to 750 °C, he found a slight contraction, due to sinter shrinkage of the compacted glass powder. Above 750–800 °C the foaming agent became active and caused a strong increase in volume (about 700%) by a gas-generating reaction. Porosity increased at higher firing temperatures and the compressive strength was lowered.

2.7.4.4
Heat-Treatment Time

There is a definite dependence of glass foam density on the duration of heat treatment. During the period of gas release, the density continuously decreases down to a minimum value. When this stage finishes, a gradual process of destruction and collapse of the foam by coalescence of the pores begins. Thus the surface energy of the system is decreased by reduction of the specific surface area of the walls of the cells. This process leads to a new increase in density [37] (Fig. 3). Hence, it is necessary to calculate precisely the time of heat treatment and to remove the glass foam from the hot zone prior to the beginning of the coalescence process.

2.7.4.5
Chemical Dissolved Oxygen

A very important role on the foaming capability of glasses is played by chemical dissolved oxygen, which is related to the redox potential of the glass and can be released by reduction reactions. It is well known that a characteristic equilibrium always exists in an alkali silicate glass melt between tri- and divalent iron with oxygen evolution. This phenomenon is of great importance in the foaming process, because the

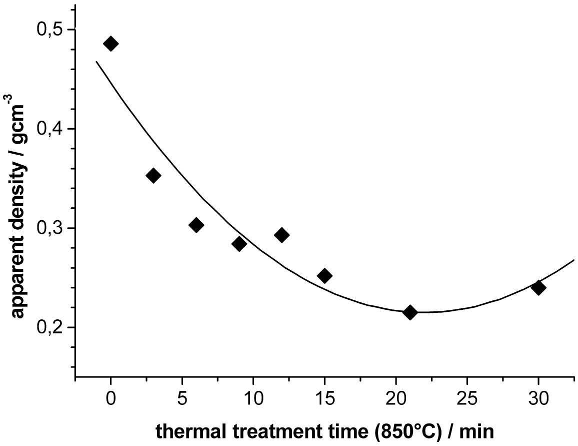

Fig. 3 Apparent density of foams obtained with carbon black as foaming agent as a function of thermal treatment at 850 °C.

reduction of Fe^{III} to Fe^{II} is presumably the gas-forming reaction, since oxygen is used to oxidize carbon (the most common foaming agent) in the pyroplastic glass. The equilibrium position depends on various parameters, such as temperature, heating rate, glass composition, and furnace atmosphere. The onset of dissociation is usually at a temperature above 1100 °C, but the presence of dispersed activated carbon catalyzes the oxidation/reduction process at much lower temperatures. The reduction of sodium sulfate, introduced during fabrication of most common glasses as fining agent, oxidizes carbon to CO:

$$Na_2SO_4 + 4\,C \rightarrow Na_2S + 4\,CO$$

The absence of sulfur-containing species in the off-gas indicates that sodium sulfate has been reduced to sulfide, and Na_2S dissolved in the glass [41].

2.7.4.6
Cooling Rate

Rapid cooling from the foaming temperature to a temperature slightly higher than the annealing range can be used to lock in – through the corresponding increase in viscosity – the obtained structure and the evolved gas. In any case, it is necessary to adopt a very low rate of cooling through the glass transformation range to eliminate any residual stress. During cooling the pressure in the cells drops, and this leads to some shrinkage and development of tensile stresses between the layers [23].

The annealing rate depends on several factors, among which are the chemical composition of the glass (and consequently its expansion coefficient) and the glass foam structure (in particular, number and size of the pores, thickness of the cell walls, type of foaming agent, shape and dimensions of the foamed products). Unlike the foaming process, which is governed mainly by the composition of the foaming mixture, annealing can be controlled only by the duration of the process. If the walls of the cells intercommunicate (i.e., open porosity) the thermal conductivity is higher, and thus the cooling rate can be up to 2 °C min^{-1} instead of 0.5–0.7 °C min^{-1}.

2.7.5
Foaming Agents

In general, any glass (preferably in powdered form) can be transformed into a foam by addition of suitable substances (foaming agents) which generate gaseous products by decomposition or reaction at temperatures above its softening (Littleton) temperature (corresponding to a viscosity of $10^{6.6}$ Pa·s). If gas generation occurs at temperatures below the softening point, the glass powder has not yet sintered to closed porosity, and the gaseous products cannot be retained by the mass, and if the gas generation takes place when the glass viscosity is too low, the gaseous products are released from the melt, as in the fining of glass melts.

It follows that the most convenient viscosity range for optimizing the foaming process for development of maximum of porosity and minimum apparent density is 10^5 to 10^3 Pa·s. This viscosity is similar to that used in hot drawing operations. For a standard sheet soda-lime glass composition, it corresponds to the temperature range of 800–1000 °C.

The interdependence of viscosity and foaming temperature is very sensitive to any change in chemical composition of the raw materials, especially the type and amount of foaming agent. The same type of foaming agent can differently influence the structure and properties of different glasses, and the same glass can be differently influenced by the addition of different foaming agents. Moreover, decomposition of many foaming agents leaves a finely distributed ash which can influence some properties of the glass, such as viscosity and crystallization tendency. Typically, fineness and quantity of foaming agent strongly influence the size of the final pores; therefore, the type, size, and optimum concentration of the foaming agent must be accurately chosen.

2.7.5.1
Foaming by Thermal Decomposition

Foaming agents that undergo thermal decomposition include carbonates such as $CaCO_3$ and Na_2CO_3. The foaming of glass with added $CaCO_3$ is possible, as stated by Koese [40], only with wet glass particles, because partial leaching of alkali metal oxides from the glass surface causes adhesion of the particles at lower temperatures at which $CaCO_3$ can act as a foaming agent. During the gradual softening of the sintered glass under continuous heating, the calcium or sodium carbonate particles decompose to the oxide with simultaneous release of gaseous carbon dioxide. The oxide is incorporated into the molten glass mass and acts as a glass modifier, thus altering the viscosity of the molten glass. The CO_2 gas which is released is trapped in the viscous glass mass and its pressure is gradually increased, forcing the molten glass mass to expand. On subsequent cooling the molten glass mass is solidified and a cellular structure is formed.

As foaming agents, $CaCO_3$ and Na_2CO_3 cause a different amounts of volume expansion [42]. A maximum expansion of over 450 % was obtained when 2 wt % of $CaCO_3$ was added to glass powder obtained from recycled colorless soda-lime glass, whereas a maximum volume expansion of only 90 % was achieved with 5 wt % of Na_2CO_3 as foaming agent. Such a large difference is probably attributable, to different characteristics of the glass melt due to incorporation of the residual oxide component from decomposition of the carbonate compounds. Both the viscosity and the surface tension of a silicate glass melt can be altered by the addition of CaO or Na_2O. In particular, the modification of the viscosity of the glass melt is dependent on the miscibility of the oxide system. Based on these considerations, it is conceivable that the addition of small amounts (1–3 wt %) of CaO to the silicate glass melt will give rise to a small degree of phase separation which consequently results in the formation of a glass melt with high surface tension, but low viscosity, thus permitting a greater volume expansion of the molten mass. On the other hand, the addition of 2–7 wt % of Na_2O to the glass melt will cause a larger degree of phase separation which leads to the formation of a glass melt with low surface tension, but higher viscosity, thus limiting the volume expansion of the molten mass.

As an alternative to carbonates, calcium sulfate (e.g., gypsum) can be employed, the foaming gas being SO_2, which has an advantageous thermal conductivity, lower than that of CO_2, but requires more control, since it is known to be noxious [43, 44].

2.7.5.2
Foaming by Reaction

Softened glass can be foamed by a chemical reaction between the interparticle atmosphere and a suitable agent. Carbon dioxide is commonly produced in the softened glass mass by oxidation of carbon-containing foaming agents, such as pure carbon, SiC, sugar, starch, or organic wastes (excreta [45]). The foam gas present in the closed pores is mostly a mixture of CO_2 and CO. Since the main glass foam manufacturer, Pittsburgh Corning, is known to employ carbon [17], foaming by oxidation can be considered the most important foaming process.

The foaming activity is strongly influenced by the type of carbon (coke, anthracite, graphite, carbon black) and the glass composition (sulfate content). Foaming occurs at temperatures in the range 800–900 °C, and the evolution of gaseous species is due, in addition to the oxidation of carbon by the atmosphere, to secondary reactions of carbon with some constituents of the glass, such as H_2O, alkali, and sulfates, so that foaming can even be performed in nonoxidizing atmospheres. The formation of CO/CO_2 by the reduction of oxides in the softened glass alters the chemical composition and viscosity of the system; like in the case of carbonates, which leave a certain amount of residual oxides to be dissolved in the glass, foaming cannot be attributed only to the formation of gas bubbles in an unmodified glass, but depends on the superposition of the physicochemical interactions in the glass on gas evolution. The foam products obtained by oxidation of carbon are usually fine-pored. The addition of carbon to the glass mass is in the range of 0.2–2 wt%.

The chemical reaction which leads to the development of gaseous products may be expressed as [46]:

$$\text{glass-}SO_4^{2-} + 2\,C \rightarrow \text{glass-}S^{2-} + CO + CO_2$$

The obtained glass foam contains a fair quantity of hydrogen sulfide trapped in its cells and, moreover, it can evolve this gaseous product if the sulfides contained in the glass come into contact with atmospheric moisture when the foam is ruptured. This drawback of several of the existing glass foam technologies limits the possible fields of its applications, because of the toxicity of hydrogen sulfide.

However, as emphasized by Demidovich [4], the evolving gas may be generated by oxidation of carbon by steam:

$$C + H_2O \rightarrow CO + H_2$$
$$C + 2\,H_2O \rightarrow CO_2 + 2\,H_2$$

Only chemically fixed water (as hydroxyl groups on the glass surface) can be a source of steam at the foaming temperature. Recently, Ketov [47] has had success with the introduction of hydroxyl groups at the stage of powder preparation. The main role in the hydration of the dispersed glass is played by the exchange of the surface sodium ions of the material for the H^+ ions of the water environment. A layer of polysilicic acids appears on the glass surface as a result of ion exchange and hydrolysis. Formation of polysilicic acids in the system results in evolution of steam at temperatures above 500–600 °C, at which glass is close to the pyroplastic state.

The employment of organic compounds (hydrocarbons or organic wastes) instead of carbon leads to the need to control the "carbon yield" of the compounds: Cowan et al. [28] found that sodium, calcium, and iron acetates, or other sodium salts like sodium lauryl sulfate, sodium oleate, sodium stearate, and so on, are much more effective as foaming agents than sugar, starch, and hydrocarbons that easily vaporize or sublime, since a certain amount of char, available for foaming, is formed on heating. For example, in the case of sodium acetate, the formation of free carbon is described by the following reaction:

$$2\,NaC_2H_3O_2 \rightarrow Na_2CO_3 + CO + 2C + 3\,H_2$$

Silicon carbide (SiC) is also considered a very effective foaming agent, capable of giving uniform, controlled and precise cell sizes in the glass foam [48]. Although carbon is preferred for manufacturing the most important type of glass foams (i.e., blocks and shapes), SiC is known as a foaming agent for other commercial applications. The foaming activity of SiC is generally reported for higher temperatures than for carbon (950–1150 °C), and the reactions of SiC with the atmosphere and with the constituents of the glass are much more complex than those of carbon. Bayer and

Koese [36] showed a number of thermodynamically possible reactions between SiC and the gas (Tab. 1).

Table 1 Possible reactions of SiC in various atmospheres

Reaction	**Δ*H*/kJ at 1000 K**	**Δ*H*/kJ at 1500 K**
SiC + [frac12] $O_2 \rightarrow$ SiO + C	–134.7	–179.08
SiC + [frac12] $O_2 \rightarrow$ CO + Si	–157.3	–204.60
SiC + $O_2 \rightarrow$ SiO + CO	–333.5	–412.3
SiC + $O_2 \rightarrow SiO_2$ + C	–656.1	–575.7
SiC + $O_2 \rightarrow CO_2$ + Si	–350.6	–357.3
SiC + 2 $O_2 \rightarrow SiO_2 + CO_2$	–1048.1	–970.7
SiC + 2 CO $\rightarrow SiO_2$ + 3 C	–258.6	–91.2
SiC + 3 $H_2O \rightarrow SiO_2$ + CO + 3 H_2	–279.9	–327.2
SiC + 4 $H_2O \rightarrow SiO_2 + CO_2$ + 4 H_2	–281.6	–316.3

Silicon carbide produces a certain amountvof carbonaceous products, which in turn are capable of foaming, and residual silicon oxide, to be incorporated in the glass. The release of silicon oxides from the foaming agent may result in partial crystallization of the glass, with precipitation of cristobalite, particularly pronounced in borosilicate glasses. The large volume changes due to the polymorphic transformation of such phases on cooling of foams may lead to microcracking and mechanically weak samples. Addition of kaolin to the glass powder (sometimes > 10 wt %) is effective in reducing cristobalite precipitation, since it increases the content of Al_2O_3, useful as devitrification inhibitor [36].

Secondary foaming effects due to reduction of oxides present in the foaming of glass with C and SiC can be regarded as a starting point for innovative foams, which although commercially unavailable are widely described in the literature. The key feature of such foaming is the lack of a reaction with the furnace, thus avoiding the risk of a differential access of comburent■Meaning?■ oxygen to C and SiC, and resulting in a rather homogeneous and fine-porous microstructure. Bayer [49] pointed out the efficiency of SiC or Si_3N_4 together with easily reducible compounds. In particular, Si_3N_4 reacts with transition metal oxides (MnO_2, Fe_2O_3, Co_2O_3, NiO, CuO) with the evolution of N_2 and N_2O, leading to a very large expansion (volume increase by a factor of about 10) and low bulk density (100 kg m^{-3}).

The foaming activity of nitrides was recently investigated for manufacturing of glass foams from CRT glasses. Mear et al. [27] used AlN together with Fe_2O_3, and thus obtained a pronounced expansion and a very fine microstructure.

The foaming agents normally employed are usable only below 850–900 °C and are hence not suitable for use with high-viscosity glasses. The patent by Camerlinck [50] pertains to the use of a foaming agent whose utilization temperature is on the order of 1050 °C and which can be consequently used when high-temperature foaming is desirable (e.g., if the starting glass is highly viscous or is to be converted to a glass ceramic, so it is important to operate above the devitrification temperature to avoid premature crystallization). This foaming agent is a mixture of finely powdered SnO_2

and SiC, with a slight excess of SiC. At about 1050 °C SnO_2 is reduced by SiC with evolution of CO_2, which acts as foaming agent.

2.7.6
Glass Foam Products

Although it has been known for a long time and has many potential applications and excellent properties, only relatively small quantities of glass foam are produced industrially, and the number of glass foam manufacturers is very limited. The main reasons for the lack of growth of the foamed glass industry in the past were probably cost and demand. However, while in the past glass foam was manufactured from a purposely produced glass (with corresponding raw materials, plant, and energy costs), now the growing availability of waste glass and a better knowledge of the process parameters make it possible to produce glass foam at reduced cost. Furthermore, the flammability of organic insulation and the toxicity of its combustion products have created the need for new inorganic materials. Foamed glass from waste is therefore expected to become more and more important in the near future.

Currently, there are three main types of glass foam (and, consequently, different types of glass foam processes) [44]:

Loose glass foam aggregate (for totally replacing natural aggregate in concrete and for applications as ground insulation, foundation piles, floor and roof insulation, backfill insulation), obtained by continuous production of sheets of glass foam. Due to commercial confidentiality there is little detailed information about the process [35, 51, 52].

A mixture of powdered waste glass (from container and/or flat glass) and foaming agent (reduced to a particle size ranging from 75 to 150 μm, first by a hammer mill and subsequently by a ball mill) is continuously fed onto a moving belt that passes through a furnace heated to the foaming temperature (between 700 and 900 °C). After cooling, the slabs of glass foam, of width up to 2 m and thickness up to 100 mm, can be broken up to form loose aggregate, graded into different ranges of particle size depending on the application. The feedstock can be dry or wet, but it is believed that the wet route will not produce completely closed cells and hence result in lower thermal insulation.

Glass foam blocks and shapes, up to sizes on the order of 1200 × 600 × 160 mm, are generally manufactured by a continuous process, though a batch process can also be employed. Possible applications of glass foam blocks are in precast concrete panels, concrete bricks, piping insulation, storage vessel wall insulation, block paving, but mainly floor and roof insulation. Pittsburgh Corning Corporation of Pittsburgh, PA, has developed and marketed a product known as Foamglas Insulation Systems. Although in this case, too, due to commercial confidentiality, the process used is not completely clear, it is possible, on the basis of some US patents [53–57], to suppose that the foam is manufactured in individual blocks contained in molds and passed through a furnace. After foaming, it is necessary to subject the blocks to prolonged annealing to reduce internal strains and obtain a stable product. With larger blocks, increasing difficulties arise with heat transfer, due to the high thermal insulation capability of both the feedstock and the product. Then it is likely that the core will not achieve sintering temperature before the outside cells start to collapse. The molded glass foam can be cut and, if necessary, machined to the required shape.

In addition, Pittsburgh Corning has patented [58] an innovative method of glass foam manufacturing by means of a fluidized bed. Gas is passed through the glass powder as it is sintered to produce the glass foam. However, it is not known if this process is currently being used.

The foams for block and shape manufacturing exhibit a very low density (100–170 kg m^{-3}), so that the porosity is well above 90 %; the thermal conductivity is consequently very low (0.04–0.05 W m^{-1} K^{-1}), and glass foams can thus be regarded as a valid alternative to polymer foams. Consequently, blocks and shapes can be considered the most important type of glass foam.

Spherical pellets are produced in a pelletization process. The finely ground glass and the foaming agent are formed into spheres and then fed into a rotary furnace where the granules soften and the foaming agent exerts its action. The spheres of glass foam are then annealed and cooled, and can be used in the manufacture of blocks, panels, or slabs, as they can be subsequently sintered.

Ducman et al. [33] found that with the addition of waterglass (up to 50 wt %, in the form of droplets) to a powdered waste glass (NaCa silicate waste glass, obtained by crushing bottles), after firing of the raw granules at 805 °C for 1 min, foamed granules of high porosity can be obtained.

Table 2 lists selected properties of commercial glass foam products [44].

Table 2 Typical properties of commercial glass foam products

Density	0.1–0.3 g cm^{-3}
Porosity	85–95 %
Crushing strength	0.4–6 MPa
Flexural strength	0.3–1 MPa
Flexural modulus of elasticity	0.6–1.5 GPa
Coefficient of thermal expansion	8.9×10^{-6} K^{-1}
Thermal conductivity	0.04–0.08 W m^{-1} K^{-1}
Specific heat	0.84 kJ kg^{-1} K^{-1}
Thermal diffusivity at 0 °C	$(3.5–4.9) \times 10^{-7}$ m^2 s^{-1}
Sound transmission loss at normal frequency	28 dB/100 mm

2.7.7
Alternative Processes and Products

A relatively rich literature is dedicated to special glass foam products from processes alternative to those industrially employed or from innovative raw materials. A summary of these “alternative” processes and products is listed below.

2.7.7.1
Foams from Evaporation of Metals

Munters [59] reported that zinc or cadmium powder could be introduced into a molten mass of glass with subsequent evaporation. After condensation of the vapors, fast cooling of the obtained glass foam created a vacuum inside the cells. The pores, being evacuated and covered with a heat-reflecting metallic layer, constituted a highly insulating object owing to the Dewar principle.

2.7.7.2
High-Silica Foams from Phase-Separating Glasses

Elmer et al. [60] patented a method for manufacturing high-silica refractory glass foam. The key point of the invention was the application of a phase-separating borosilicate glass. After the leaching of the silica-poor phase, the resulting microporous high-silica glass was finely ground and impregnated with an aqueous solution of boric acid; the powders were sintered with the formation of a number of bubbles due to the large amount of water entrapped during the impregnation stage. Johnson [61] later patented a much simpler process based on the direct foaming of a phase-separating glass by using alkali metal carbonates and sulfates; the leaching stage was performed on the foamed product. In both applications the composition of the borosilicate glass had to be designed to result in spinodal decomposition to two interconnected phases, which is essential for properly leaching out the silica-poor phase.

2.7.7.3
Microwave Heating

Microwave heating has been developed for industrial applications such as drying and sintering of ceramics. Although glass compositions are generally transparent to microwave radiation at room temperature, at higher temperatures, in excess of 500 °C, the glass structure relaxes [62] and absorption of microwave radiation increases rapidly with consequent rapid volumetric heating of the glass. Hence, it should be possible to realize a continuous furnace for production of glass foam by using dual heating: conventional electric heating in a preheat zone to take the feedstock up to 500 °C, and microwave radiation to reach the required foaming temperature of 800–900 °C. In this way the processing time would be shorter due to rapid uniform heating. The homogeneous absorption of microwave radiation throughout the glass mass is believed to cause homogeneous foaming.

In recent laboratory-scale experiments, glass foam samples containing short metallic fibers as reinforcing elements were produced by microwave heating [63]. The glass chosen for this investigation was a soda-borosilicate glass, which coupled with microwaves above 600 °C. Stainless steel fibers (10 vol%) were added to enhance the structural integrity of the foams and increase fracture toughness.

2.7.7.4
Glass Foam from Silica Gel

A new method of producing glass foam for refractory thermal insulation material has been patented by Lee [64]. A glass foam having a closed-pore structure is produced by using porous silica gel, so that heat resistance and corrosion resistance can be greatly enhanced. The method comprises the following steps of 1) preparing a silica gel according to a sol–gel method from an alkali metal silicate, which is obtained by fusing silica and alkali; 2) exposing the silica gel to wet air to absorb a certain amount of moisture (the amount of absorbed moisture can be adjusted to regulate the foaming rate); 3) adding a certain amount of silica gel to a heat-resistant mold to be shaped; 4) calcining the mold at a constant rate up to 980–1300 °C (at least to the softening temperature of glass) in a tunnel or shuttle kiln, whereby the silica gel is fused into a glass foam; 5) cooling the fused glass foam.

2.7.7.5
High-Density Glass Foam

A recent invention by Hojaji et al. [65] refers to large high-density glass foam tiles which can be used as a facade on both exterior and interior building walls. These heavy (0.45–1.15 g cm^{-3}) glass foam tiles are capable of absorbing a substantial portion of the shock wave caused by an explosion, and thus may be used on the critical surfaces of buildings at risk of terrorist attacks, in combination with concrete, steel, or other high-strength building materials. Moreover, these tiles also have the advantage of being more resistant to earthquakes. (Prior work by the inventors and others [22] developed methods for making glass foam tiles of a wide a variety of densities.)

2.7.7.6
Partially Crystallized Glass Foam

Ketov [39] achieved formation of crystalline structure in foamed silicate, with the consequence that the system forms a rigid skeleton at the softening temperature of the glass, thus preventing destruction of the foam structure. In this case, it was possible to observe the absence of any increase of density with time after reaching its minimum value at the foaming temperature.

This important result was obtained by the addition of various substances promoting glass crystallization. Partial crystallization of glass does not result, however, in changes of the specific volume of the substance and in material cracking. The crystalline phases should not exhibit any pronounced change in volume on cooling; crystal phases subject to such changes, due to polymorphic transformations, are undesirable.

2.7.7.7
Foaming of CRT Glasses

The foaming of CRT glasses with $CaCO_3$ is also interesting. Glass foams were prepared [26] from panel glass and mixtures of panel glass and funnel and neck glasses, by dry mixing of fine glass powders with $CaCO_3$. While the panel glass is a barium–strontium glass, the funnel and neck glasses, both employed in the rear parts of the CRTs (the neck being the envelop of the electron gun), are lead silicate glasses. It is known that lead-containing wastes are particularly difficult to recycle since lead is a noxious heavy metal.

The foaming of CRT glasses by $CaCO_3$ at 725 °C for 15–30 min led to lightweight articles with densities in the range 0.18–0.4 g cm^{-3} and fine-pored (pore diameter ca. 100 µm) and homogeneous microstructure (Fig. 4). Several openings between adjacent cells are clearly visible, that is, a fraction of the foam is open-celled. The XRD spectra revealed slight formation of wollastonite $CaO \cdot SiO_2$, a desirable crystal phase since it does not exhibit volume changes due to polymorphic transformations on cooling of glass foams.

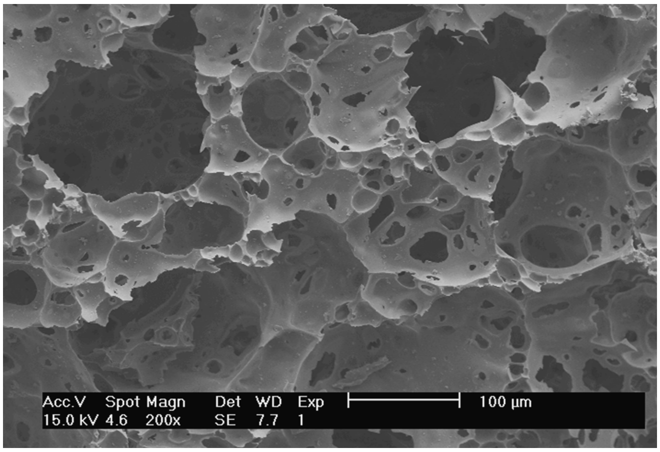

Fig. 4 SEM image of the microstructure of glass foam obtained from CRT glasses by using $CaCO_3$ as foaming agent.

The crushing strength of the foams (up to 5 MPa at a density of 0.4 g cm^{-3} and a porosity of 85 %) is remarkable when compared to the strength predicted [66] for such low density and partially open celled microstructure. Some preliminary chemical tests (acid attack) demonstrated that the heavy metal release of the foams was negligible and, above all, independent of the chemical formulation (ratio of panel/lead-rich glass) of the glass cullet employed. Therefore, the foaming of CRT glasses by $CaCO_3$ thermal decomposition appears to be a promising way of treating heavy metal containing glasses, since foaming does not depend on oxidation/reduction processes, which could cause the precipitation of metallic colloids by reduction of easily reducible oxides like PbO. Moreover, the relatively low temperature required (CRT glasses have a low softening point) prevents the volatilization of the PbO.

2.7.8
Summary

For more than seventy years glass foam production technology has been established as a valid method both for obtaining products having a unique combination of properties (with particular reference to high insulation capability, very low density, excellent resistance to fire, water impermeability, high compression strength, and dimensional stability) and for recycling growing quantities of glass waste. The continuously decreasing price owing to improvement of process technologies and the growing introduction of wastes as raw materials, as well as the advantages coming from energy saving through a better insulation capability, will certainly increase the application possibilities for this material in the near future.

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