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Reutilization and stabilization of wastes by the production of glass foams

E. Bernardo [a,*], R. Cedro [a], M. Florean [a], S. Hreglich [b]

[a] *Dipartimento di Ingegneria Meccanica, Settore Materiali, Università di Padova, Via Marzolo 9, 35131 Padova, Italy*
[b] *Stazione Sperimentale del Vetro, Via Briati 10, 30121 Murano, Venezia, Italy*

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Abstract

Glass foams are known to represent highly valuable products for thermal and acoustic insulation, often produced by employing wastes. Although the usage of recycled glass is widely reported for developing the glass matrix, little research has been due to the usage of wastes for the foaming reaction. In this work the cellular structure is achieved after oxidation of SiC-based wastes coming from the polishing of glass articles. The foamed recycled soda-lime glass incorporated the residues from oxidation and provided a reasonably good chemical stability. The addition of MnO_2 to the starting mixtures of wastes led to a certain improvement of the oxidation of SiC, and a complex effect on the correlation between density and mechanical strength. For selected additions, a more homogeneous foaming was found to provide a stronger cellular structure.

Keywords: A. Sintering; C. Mechanical properties; D. Glass; E. Insulators

1. Introduction

Glass foams represent a highly valuable solution for thermal and acoustic insulation, since they possess a generally higher mechanical, chemical and thermal stability than the polymeric foams currently employed [1]. For instance, in the case of a fire, polymeric foams are known to be largely damaged with the evolution of potentially toxic gases; glass foams, on the contrary, due to their inorganic nature, are un-inflammable [2].

The costs of glass foams have constituted a key disadvantage for their diffusion in the building industry. In order to reduce the production costs, several modifications have been applied to both the processing techniques and the starting materials. Firstly, the direct introduction of gases (“blowing”) into molten glass (employed for the first industrial processing, dating back to the 1930s [3]) was substituted by a sintering approach, starting from fine glass powders, in which a pyroplastic mass (determined by the sintering of the same glass powders) is foamed by the development of gases, available from the decomposition or oxidation of specific powder additives (the so-called “foaming agents”) [4–6]. Secondly, the usage of fine glass powders allowed the exploiting of recycled glass as a potential substitution for pristine glass [7]. A double remarkable energy saving is consequently achieved, since sintering may be applied at much lower temperatures than those for blowing, and expensive glass-making may be avoided (by considering fully recycled glasses as raw materials).

The costs of glass foams are affected also by the foaming agents [1]. As previously mentioned, the foaming depends on decomposition or oxidation reactions. The decomposition reactions are due to carbonates and sulphates, while oxidation reactions are determined by the interaction of carbon-containing species mainly with the atmosphere of the sintering furnace. Silicon carbide represents an excellent foaming agent, owing to a complex oxidation process (capable of a high flexibility), but its high cost generally causes the producers of glass foams to prefer inexpensive carbon (carbon black, graphite, pyrolytic residues of organic compounds). A certain economic (and environmental) benefit could be found if SiC could be available from wastes. In this paper we report the feasibility of glass foams from recycled soda-lime glass and SiC-based wastes constituted by the residues of the polishing of artistic glass articles. The relevant hardness of SiC, in fact, causes it to be largely employed as an abrasive material. The current production of polishing waste from glass abrasion, in the artistic glass factories in Venice, is about 200 tonne/year, and represents a pressing environmental problem, since no

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* Corresponding author. Tel.: +39 049 8275510; fax: +39 049 8275505.
E-mail address: enrico.bernardo@unipd.it (E. Bernardo).

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application is available; moreover, the disposal of this kind of waste is complex and expensive, due to the presence of significant traces of heavy metal oxides, due to the formulation of the abraded artistic glasses.

The production of glass foams was found to be advantageous both for the reutilization of SiC and the dissolution of the un-combustible fraction of the polishing waste, mainly represented by glass powders (the abraded material). After a proper selection of thermal treatment and additives, the produced glass foams exhibited a complex of physical properties similar to those of commercial products.

2. Experimental

Common soda-lime glass form municipal recycling activity was employed as the base material. The chemical analysis of this glass is illustrated in Table 1.

The glass was dry ball-milled and sized in order to achieve powders with a maximum dimension of 37 μm. Dried SiC-based polishing waste, whose composition is also illustrated in Table 1, was added to the glass powders in different concentrations, varying from 2.5% to 17.5 wt.%. The polishing waste contains SiC (about 50%) and some abraded glass; a certain presence of heavy metal oxides is visible, since they are normally contained, as previously reported, in the formulation for the abraded (artistic) glass. The relatively high content of Fe_2O_3 is due to the fact that SiC powders (with a maximum dimension of about 50 μm) are generally employed deposited on cast iron discs, which are subjected to a certain abrasion during the polishing of glass. Selected samples featured a further addition of MnO_2 powders (reagent grade, 10 μm, Sigma–Aldrich Co. Ltd., Gillingham, UK), in two different concentrations (for a ratio between MnO_2 and SiC-based waste equal to 1/5 or 1/3). The SiC waste–glass mixtures were homogenized in a ball mill for 30 min and subsequently gently pressed in a rectangular die. Glass sintering and foaming were achieved by subjecting the mixtures to a thermal treatment at 950 °C, with a heating rate of 10 °C/min and a holding time of 1 h. This schedule was chosen after previous investigations about the foaming of soda-lime glass by usage of pure SiC as the foaming agent [8]. Like for the materials described in [9], the foams were drastically cooled (more than 10 °C/min) from the foaming temperature to 600 °C, in order to "freeze" the microstructural evolution for the selected holding time, then slowly cooled (~1 °C/min) to 500 °C, in order to perform a sort of "annealing" treatment, in a temperature range close to the transformation temperature ($T_g \sim 570$ °C [10]) and again quickly cooled (~5 °C/min) to room temperature. The obtained foams were subjected to compression tests (Instron 1121 UTS machine, Danvers, MA) with a crosshead speed of 2 mm/min, employing samples of about 15 mm × 15 mm × 10 mm, cut from larger specimens. Each data point represents the average of at least 10 measurements. The density of foams was measured both geometrically, for the estimation of the apparent density, and by means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA) for the measuring of the true density from powdered samples.

Table 1
Composition (expressed in wt.%) of the starting materials

Oxide (wt.%)	Soda-lime glass	Polishing waste
SiO_2	70.8	25.0
Al_2O_3	2.4	
Na_2O	13.0	5.0
K_2O	1.1	2.0
CaO	9.4	2.0
MgO	2.1	
BaO	0.2	
Fe_2O_3	0.3	15.0
MnO		0.2
CuO		0.2
TiO_2	0.1	0.2
ZrO_2	0.1	
B_2O_3	0.12	
PbO	0.07	0.3
ZnO	0.12	0.6
As_2O_3	0.02	
Sb_2O_3	0.01	1.0
Cr_2O_3		0.3
F	0.08	0.1
SO_3	0.09	
SiC		48.0

A chemical analysis, constituted by a leaching test in acetic acid 0.5 M (for 24 h), analogous to that reported for other glass foams [11], was conducted on a representative glass foam, with the aim of verifying the chemical stability of the product, mainly in relation to the heavy metals dissolved in the polished artistic glass and consequently embedded in the foams as residues from the oxidation of the polishing waste. The test was performed on small bricks, identical to those used for the mechanical characterization. The leachate was analysed by means of inductively coupled plasma (ICP) mass spectrometer (TJA, IRIS-DUO-HR, Thermo Electron Corporation, Waltham, MA).

The morphology of the glass foams was studied by means of optical and scanning electron microscopy (Philips XL 30 ESEM, Eindhoven, The Netherlands). Powdered samples were investigated by X-ray diffraction (Philips PW 3710, Eindhoven, The Netherlands), employing Cu Kα radiation (0.15418 nm).

3. Results and discussion

The progressive addition of SiC-based residue to soda-lime glass resulted in a dramatic decrease of the relative density (i.e. the ratio between apparent and true density) upon the heat treatment, as shown in Fig. 1. It must be noted that the similarity of the maximum dimension of glass and foaming agent powders (37 μm for the glass and 50 μm for SiC) represents the best condition for the achievement of a homogeneous cellular structure [1].

The minimum density is reached for 12.5 wt.% of SiC-based waste, corresponding to a relative density of 0.08, and consequently to a porosity content of 92%. This result is comparable to the porosity degree of commercial samples [12]. As reported in previous investigations [9], the density did not

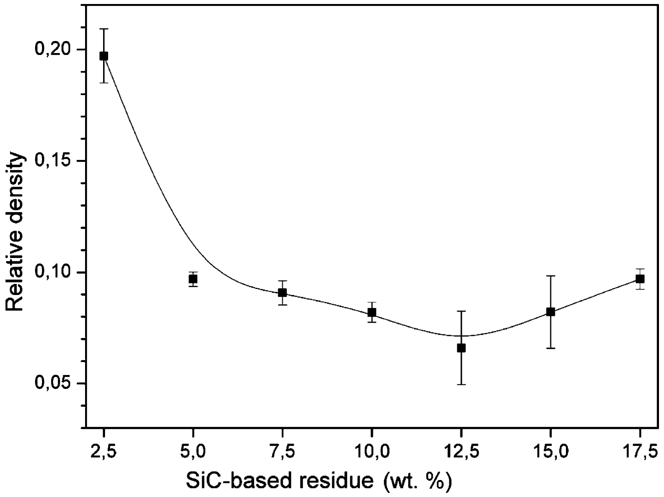

Fig. 1. Dependence of the density of glass foams on the percentage of SiC-based waste addition.

decrease continuously with increasing foaming agent content, likely due to the occurring, over a certain ''threshold value'', of coalescence phenomena, i.e. of the coarsening of the cellular structure; smaller pores likely dissolved in larger ones, favoured by the decrease of the surface energy of the system. This phenomenon, widely reported in the literature [1], has a secondary effect in the increase of the thickness of the cell walls, with a certain increase of density; the crushing strength does not increase, since the enhanced thickness of the cell walls provides an enhanced probability of finding critical flaws. This situation is confirmed by the evaluation of the optical microscope images of Fig. 2, in which the foams from a SiC-based waste content lower than 12.5% exhibit a very high homogeneity.

The compressive strength is typically a function of the relative density, as illustrated in Fig. 3 and predicted by the following equation [13]:

$$\sigma_{\mathrm{f}} = \sigma_{\mathrm{bend}} f(\Phi, \rho_{\mathrm{rel}}) = \sigma_{\mathrm{bend}}[C(\Phi\rho_{\mathrm{rel}})^{3/2} + (1-\Phi)\rho_{\mathrm{rel}}] \qquad (1)$$

where is the bending strength of the employed glass and f is a ''structural function'', depending on the relative density (ρ_{rel}, the ratio between the measured density of the foams and the ''true density'', i.e. the density of the solid phase) and its distribution (open or closed porosity), acting on the Φ parameter. In fact, the quantity $(1-\Phi)$ expresses the fraction of solid laying in the cell faces; if the foam is open-celled, the pores are fully interconnected, with material only on the cell edges, so that $\Phi = 1$ $(1-\Phi = 0)$; on the contrary, for a closed-cell foam, Φ is lower, with some material constituting the separation walls between the pores. In practice, $(1-\Phi)$ represents the contribution to the mechanical strength given by the cell faces in the cellular structure. C is a dimensionless calibration constant, being ~0.2. For a typical example of foamed solid (rigid poly-urethane closed cell foam) Φ is reported to be about 0.7 [13]. The reference bending strength for the plots of Fig. 3 (see dashed lines) was 70 MPa, a typical value for the soda-lime glass employed as basic material [10].

Fig. 3 illustrates the correlation between the compressive strength and the relative density for the prepared foams. It must be noted that the compressive strength is close to that for commercial products [12]. Most of data points lay in a zone for Φ values being between 0.8 and 0.9. This means that the mechanical behaviour is substantially similar to that of open-celled foams, the cell faces having a poor influence on the strength. This finding is consistent with previous results [9] about glass foams; the strength of cell faces is conditioned by

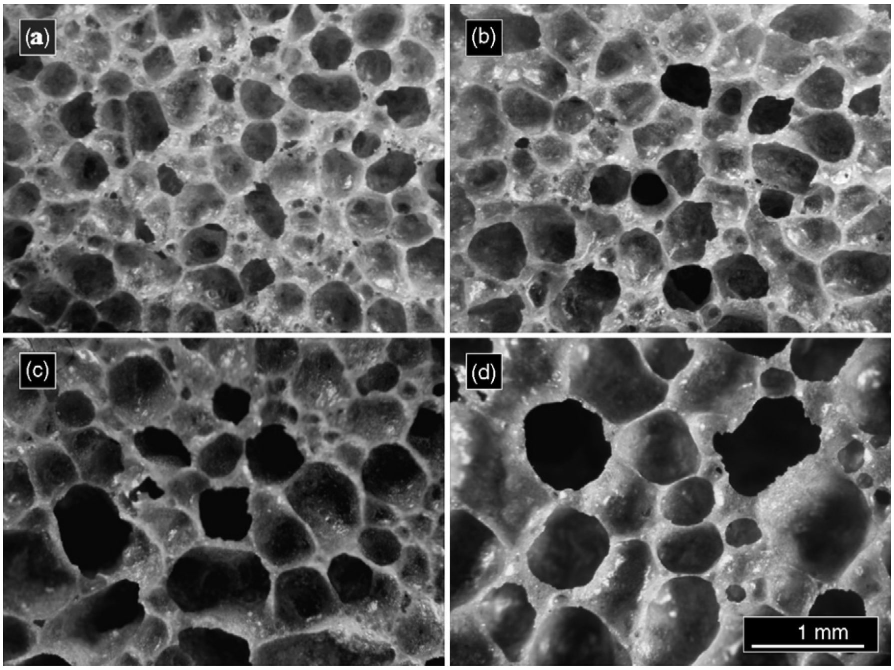

Fig. 2. Appearance of glass foams due to different foaming agent content: (a) 5 wt.% SiC-based waste; (b) 7.5 wt.%; (c) 12.5 wt.%; (d) 17.5 wt.%.

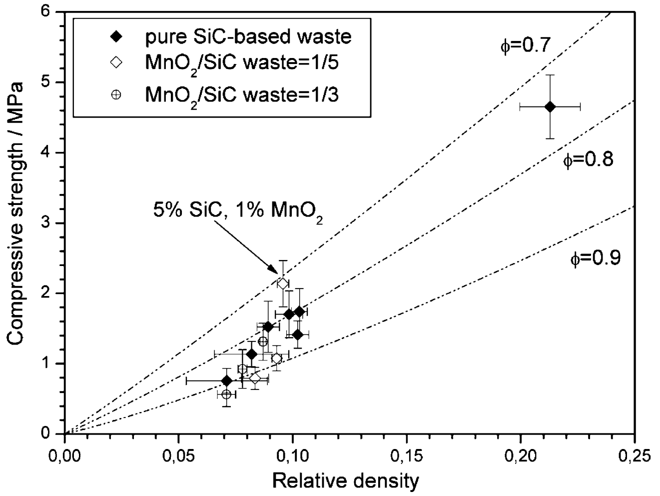

Fig. 3. Correlation between the compressive strength and the relative density of the investigated glass foams.

the presence of secondary pores just at the separation of main pores, which is confirmed by the SEM images of Fig. 4. In addition, coarse microstructures, with larger pores, may correspond to high Φ values, due to the low ratio between the thickness of the cell faces, t_f, and the length of the cell edges, l, owing to the relation [13] $t_f/l = 1.4(1 - \Phi)\rho_{rel}$.

The X-ray diffraction analysis (illustrated in Fig. 5) showed the presence, in the produced glass foams, of devitrite $Ca_3Na_2Si_6O_{16}$ (JCPDS-ICSD, PDF #770410) and wollastonite $CaSiO_3$ (PDF #760186) as the only practical crystal phases. Some traces of SiC (PDF #731708) are also present reasonably due to incomplete reaction. Devitrite is a well known crystal phase developing upon heat treatment of soda-lime glass [14]. The tendency of this glass towards devitrification was likely enhanced by the high specific surface of highly porous bodies, like the obtained foams (it is well known that objects with high specific surface, like fine powders, are easier to crystallize than bulk glass [15]). Also wollastonite is quite common as devitrification product of soda-lime glass [16], and it may be favoured by the sintering of glass foams at the temperature (950 °C) of its maximum crystallization ability by a surface mechanism [17]. This phase is generally desirable, since it is not subjected to any polymorphic transformation (and consequent drastic volume variation) upon cooling of the foams from the sintering temperature to room temperature [1].

The most porous glass foam, from the usage of only SiC-based waste as the foaming agent (see Fig. 5), was subjected to chemical attack in a solution of acetic acid. Italian standards suggest the testing of ceramic materials in the form of coarse powders with specific surface of at least 3.1 cm^2/g. The attacked glass foam sample, because of its low density and high porosity, featured an hugely larger specific surface, higher than 25 cm^2/g, so that the leaching test can be considered to be extremely severe. The analysis of the leachate did not reveal heavy metals (As, Cd, Cr, Cu, Pb, Se, etc.) in significant concentration, as shown in Table 2. As a consequence, the glass foam may be considered to be chemically resistant.

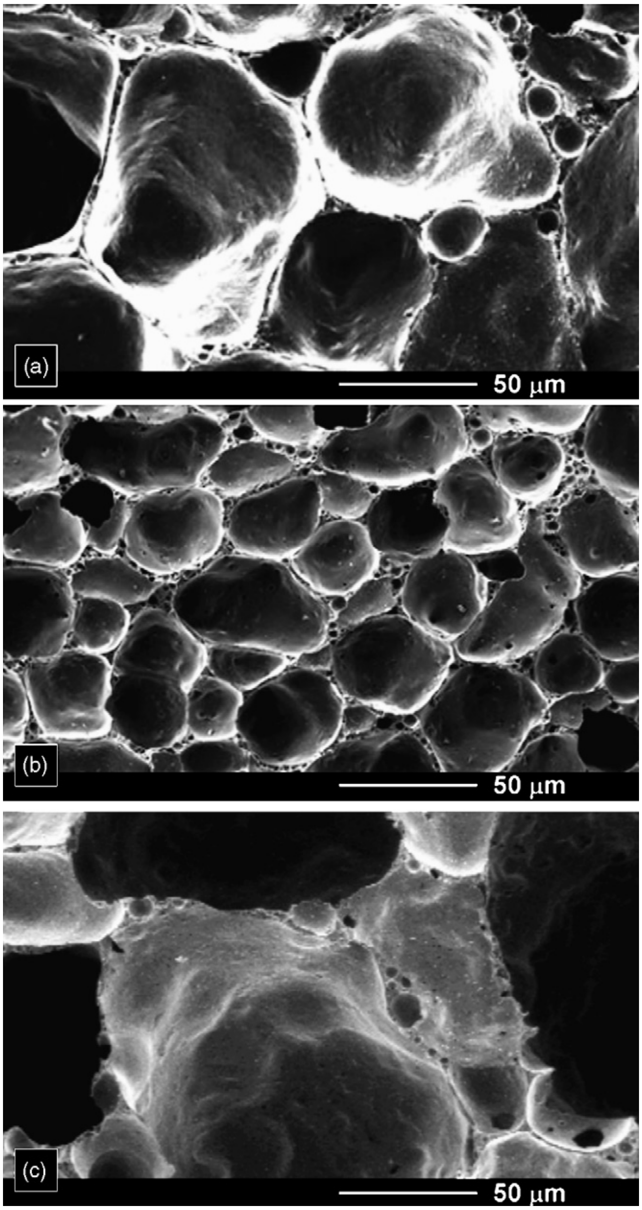

Fig. 4. SEM images of glass foams: (a) 5 wt.% SiC-based waste, no addition of MnO_2; (b) 5 wt.% SiC-based waste, 1 wt.% MnO_2 (1/5); (c) 5 wt.% SiC-based waste, 1.6 wt.% MnO_2 (1/3).

The effect of the addition of MnO_2 is rather complex. This oxide was intended to influence the oxidation of SiC, due to the fact that Mn may change its oxidation state with the release of oxygen, as follows:

$$2MnO_2 \rightarrow 2MnO + O_2$$

Due to the reported reaction, MnO_2 may be used as the exclusive foaming agent for the production of glass foams, as reported by Ducman and Kovačević [18], MnO being incorporated by the foamed glass. As illustrated in Fig. 3, the addition of the “oxidizer” substantially causes the production of foams fitted by a high Φ value.

In order to illustrate the effect of the foaming conditions (addition of SiC-based waste and MnO_2) the strength of foams was plotted again in Fig. 6. The strength is here expressed by a

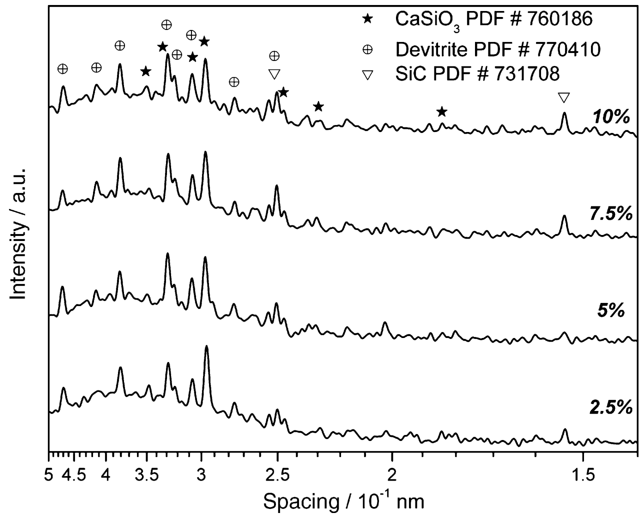

Fig. 5. XRD patterns of selected glass foams.

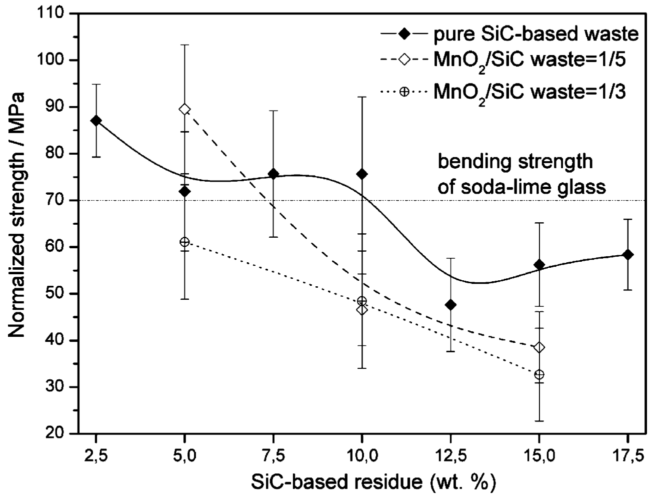

Fig. 6. Normalized strength as a function of the content of SiC-based waste, for different additions of MnO_2.

"normalized strength" parameter, which in turn is represented by the ratio between the compressive strength and the above reported "structural" function (f), calculated for every data point from its relative density and for a fixed Φ value ($\Phi = 0.8$, which almost represents the average value for all the tested samples). For foams whose mechanical behaviour is fitted by the selected Φ value, the normalized strength is obviously coincident to the reference bending strength of soda-lime glass (70 MPa). Fig. 6 demonstrates that this behaviour is effective only below 10 wt.% SiC waste addition (a sort of "threshold value"). Further additions are effective in reducing the density (see Fig. 1) but cause a dramatic decrease of mechanical strength (about 30%), attributable to the coarsening of the cellular structure. In practice, large additions of foaming agent are not particularly advantageous, since the loss of mechanical strength is quantitatively much more relevant than the reduction of relative density. The same effect is substantially found for MnO_2 additions (see coarse structure of Fig. 4c); a remarkable exception to this trend is represented by the foams prepared from 5 wt.% SiC-based waste and 1 wt.% MnO_2, with a normalized strength of about 90 MPa (with an increase of about 20% compared to the foams prepared without oxidizer). As illustrated also in Fig. 4, this combination brought foams with a very regular and homogeneous microstructure, with a great number of relatively small pores having relatively thin separation walls. The different distribution of solid phase in the cell edges and faces positively influenced the mechanical strength, likely due to a more uniform stress distribution upon loading (the cell faces were thinner compared to the cells of foams from the other formulations but, above all, the cell dimensions and edges were much shorter, so that the t_f/l ratio is relatively high and corresponds to a lower Φ value).

Table 2
Leachate of a glass foam (12.5 wt.% SiC-based waste) after chemical attack

	Concentration in the leachate (ppm)	Limits (ppm)
As	0.17	0.5
Ba	0.03	20.0
Cd	<0.02[a]	0.02
Cr VI	<0.02[a]	0.2
Fe	0.03	2.0
Ni	0.11	2.0
Pb	0.19	0.2
Cu	0.07	0.1
Se	<0.05[a]	0.03
Sn	<0.1[a]	10.0
Zn	0.07	0.5

[a] Concentration below the resolution of the spectrometer.

If in the foams with no oxidizer there is a sort of "homogeneity threshold" for about 10 wt.% SiC waste, the enhancement of gas evolution due to MnO_2 probably shifts this limit to lower concentrations. The preparation of foams from limited introduction of foaming agents will be the object of future work. Foams prepared from a limited introduction of SiC waste may be advantageous also for the chemical durability: the leachability of foams, already low from 12.5 wt.% SiC and no MnO_2, will be reasonably lowered by using a limited content of foaming agent; in fact, the lowering of SiC (a reducing agent) and the addition of an oxidizer likely impede any risk of reduction of heavy metal oxides, present in the polishing waste.

4. Conclusions

Recycled conventional soda-lime glass was successfully converted into glass foams by employing residues from the polishing of glass, rich in SiC. The main features of the obtained glass foams may be summarized as follows:

- The addition of SiC-based waste, for a sintering treatment at 950 °C, causes an extensive foaming of soda-lime glass, with the achievement of a minimum relative density of 8% (92% porosity).
- The porosity and the mechanical strength of the achieved foams are close to that of commercial samples; the proposed approach, as a consequence, may have the potential for producing useful materials from a mixture of wastes.

- The leachability of the produced foams is reasonably low, so that the process may be employed for the absorption of the presented wastes in a chemically stable material; it must be noted that this stabilization is reached by a sintering approach (that corresponding to the foaming of glass) and not by a much more expensive melting approach.
- The addition of an ‘‘oxidizer’’ (MnO_2) is useful for obtaining very resistant and homogeneous foams for a limited addition of SiC-based waste.
- The mechanical strength is strongly influenced by the homogeneity of the foaming, which in turn depends on the additions of SiC and oxidizer.

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