

NOVEL “INORGANIC GEL CASTING” PROCESS FOR THE MANUFACTURING OF GLASS-CERAMIC FOAMS

Acacio RINCON, Enrico BERNARDO

Department of Industrial Engineering, University of Padova, Italy

acacio.rincon@unipd.it, enrico.bernardo@unipd.it

Introduction

The concept of ‘inorganic polymerisation’ through alkali activation has a large potential for the obtainment of porous components. In fact, highly porous geopolymers¹ have been successfully developed by entrapment of air at the first stages of gelification, by mechanical stirring with the support of a surfactant; the setting of the mixtures determines the ‘freezing’ of the cellular structure.

The process has been recently extended to the manufacturing of glass foams,² on the basis of the possibility of developing gels also from the alkali activation of glass powders (obtaining “glass-based mortars”³). Unlike geopolymeric gels, glass-derived gels are not chemically stable, but the cellular structure can be stabilised by a sintering step, at much lower temperatures than those required by conventional manufacturing of glass foams (in turn due to gas evolution, in a pyroplastic mass of softened glass, provided by substances undergoing thermal decomposition or oxidation).

The present paper exploits the new process for glass foams not only for pure glass powders, but also for glass powders mixed with a metallurgical waste, consisting of fayalite slag. A ‘weak alkali activation’ of the glass/slag mixtures is not intended for complete dissolution of components, but aimed at developing gels in turn allowing for low temperature hardening. A sintering treatment, at 800-1000°C, will be later applied to convert highly porous ‘glass-based mortars’ into glass-ceramic foams - owing to glass-slag interactions, limiting the leaching of alkaline ions. This technique allows the preparation of foams with a homogeneous microstructure and good mechanical properties, to be applied as lightweight thermally insulating building materials.

Materials and Methods

The starting materials consisted of soda-lime glass (later referred to ‘SL’; provided by the company SASIL SpA, Biella, Italy) in the form of fine powders with a mean particle size of 75 µm, and a slag deriving from copper metallurgy (CS) with a mean particle size of 60 µm. The chemical compositions are reported in Table 1.

The powders were suspended in aqueous solutions containing 2.5M KOH (reagent grade, Sigma–Aldrich, Gillingham, UK), for solid loading of 65 wt%, with a proportion between SL and FS of 70/30 wt%. The mixtures were subjected to alkaline attack for 3

h, under low speed mechanical stirring (500 rpm). The obtained suspensions of partially dissolved powders were cast in closed polystyrene cylindrical moulds (60 mm diameter), and cured at 75°C for 2 h. Partially gelified suspensions were later added (4 wt%) with a non-ionic surfactant Triton X-100 (Sigma-Aldrich, Gillingham, UK) and subjected to vigorous mechanical mixing (2000 rpm). Foamed gels were kept at 40°C for 24 h, before being demoulded. Finally, hardened foamed gels were fired at temperatures between 800-1000°C, for 1 h, with a heating rate of 10°C/min.

Table 1: Chemical compositions of starting materials

(wt%)	SiO ₂	Na ₂ O	CaO	Al ₂ O ₃	MgO	K ₂ O	Fe ₂ O ₃	BaO	ZnO	B ₂ O ₃
SL	70.8	13	9.4	2.4	2.1	1.1	0.3	0.2	0.12	0.12
CS	29	<1	2	4	1	<1	25	-	7	-

Results and Discussion

Figure 1 reports the FTIR spectra of SL glass and CS slag at the starting stage as well after alkali activation and thermal treatment at 900°C of the SL/CS mixture. A very broad absorption band between 3000 and 3700 cm⁻¹, assigned to stretching vibration of O-H groups, appears in all spectra due to the hydration; however, a much higher absorption appears for the green foam, due to the formation of hydrated compounds after the alkali activation, testified also by a weaker band around 1650 cm⁻¹ (assigned to deformation mode of O-H). For the green foam a band centred at 2900 cm⁻¹, assigned to C-H vibrations of the organic surfactant, is also detected. Bands from 1290 to 900 cm⁻¹ and at 800 and 450 cm⁻¹, are identified as effects of rocking and bending of the Si-O-Si group.⁴

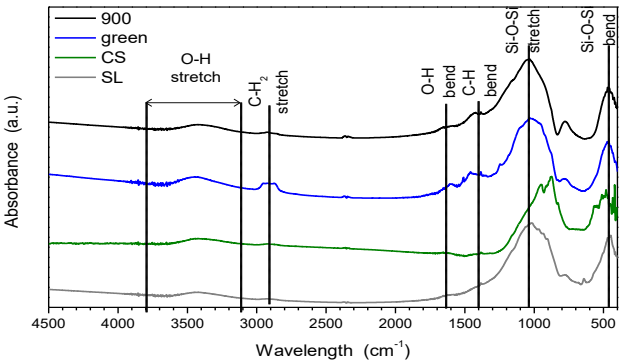


Figure 1: FTIR spectra of selected materials

Figure 2 illustrates the microstructure of ‘green’ foams, after 24 h of post-foaming curing (Figure 2a) We can appreciate the high uniformity, with most pores having a diameter around 250 μm After firing at 800°C (Figure 2b) foams exhibit slightly bigger pores indicating some reshaping of the pores during the heat treatment; several larger pores appear after the treatment at 900°C (Figure 2c), indicative of some cell coalescence, but an overall homogeneous cellular structure is maintained. A

significant coalescence is observed for foams obtained at 1000°C (Figure 2d), well above the softening point of soda-lime glass; oxygen coming from the reduction of Fe^{3+} to Fe^{2+} reasonably offered a secondary foaming effect.

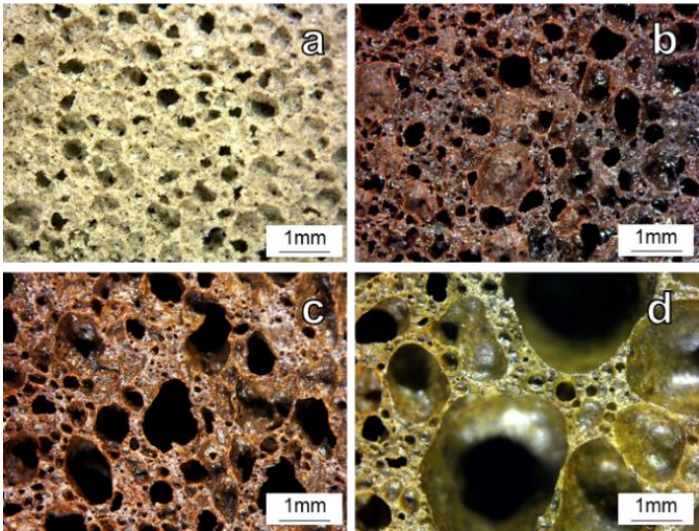


Figure 2: Microstructural details of hardened foamed gels and fired foams

Figure 3 (left) represents the diffraction patterns of as-received SL, CS and hardened foams after curing. Unlike soda-lime glass, the CS, in the as-received conditions, was partially crystalline, with fayalite (Fe_2SiO_4 or $2\text{FeO}\cdot\text{SiO}_2$, PDF#09-0484), as main crystal phase. This crystal phase was not dissolved upon alkaline activation; the pattern of hardened foams, however, reveals some shifting of the ‘amorphous halo’ at higher angles, from $2\theta=24^\circ$, for glass powders, to $2\theta=28^\circ$. This shift can be seen as a clear indication of the compositional modifications produced after the alkaline activation as the result of the incorporation of network modifiers in the glass.²

The heat treatments at 800, 900 and 1000°C determined significant changes, as shown by Figure 3 (right). Fayalite is no longer detected; in fact, heat treatments led to its ‘oxygenolysis’, with the formation of iron oxides, magnetite (Fe_3O_4 PDF#86-1351) and hematite (Fe_2O_3 , PDF#72-0469), are effectively visible at 800 and 900°C, while at 1000°C only magnetite can be noticed. This fact is consistent with the reduction of iron oxides in a viscous mass, at high temperature, associated with oxygen release, in turn leading to foaming,⁵ as effectively observed (Figure 2d). The main crystal phase actually come from the interaction of glass with (Ca- and Fe-rich) slag: wollastonite (CaSiO_3 , PDF#076-0186) and hedenbergite ($\text{CaFeSi}_2\text{O}_6$, PDF#071-1498) are present in all samples.

Table 2 presents the mechanical properties of the studied samples. Despite the high (and mostly open) porosity, the strength is significant, owing to the reinforcing effect of crystallisation. In particular, the specific strength (σ_c/ρ) well exceeds $10 \text{ MPa}\cdot\text{cm}^3/\text{g}$, a level exhibited only by the best variant of commercial Foamglas®.²

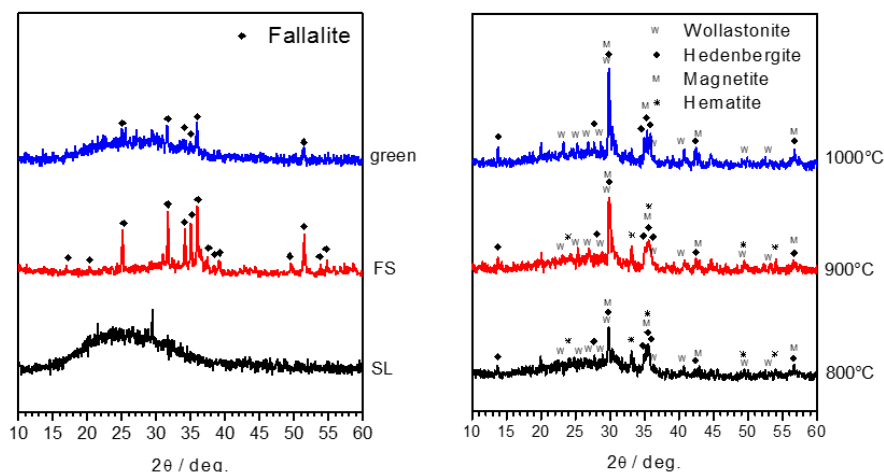


Figure 3: X-ray diffraction patterns of glass foams at ‘green state’ and after firing

Table 2: Summary of properties of the developed glass-ceramic foams

Firing T (°C)	% total P	% open P	ρ (g/cm ³)	σ_c (MPa)
800	76 ± 3	59 ± 9	0.23 ± 0.03	4.3 ± 0.9
900	78 ± 3	70 ± 4	0.22 ± 0.03	2.3 ± 0.4
1000	75 ± 7	45 ± 9	0.24 ± 0.07	3.3 ± 1.1

Conclusions

Glass-ceramic foams can be obtained by alkali activation of suspensions of glass particles and copper slag through a gel-casting technique, followed by sintering at 800-1000°C. Surfactants affect the morphology of ‘green’ foams, but do not determine ‘secondary foaming’; the secondary foaming depends on decomposition of hydrated compounds developed upon hardening and reduction of iron oxides during the heat treatment process.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie GA#642557.

References

1. M. S. Cilla, P. Colombo and M. R. Morelli, “Geopolymer foams by gelcasting”, *Ceram Int*, **40** (4) 5723-30 (2014).
2. A. Rincón, G. Giacomello, P. Pasetto and E. Bernardo, “Novel ‘inorganic gel casting’ process for the manufacturing of glass foams”. *J Eur Ceram Soc*, **37** (5) 2227-34 (2017).
3. M. Cyr, R. Idir and T. Poinot, “Properties of inorganic polymer (geopolymer) mortars made of glass cullet”, *J Mater Sci*, **47** (6) 2782-97 (2012).
4. I. M. Ponsot, Y. Pontikes, G. Baldi, R. K. Chinnam, R. Detsch, A. R. Boccaccini and E. Bernardo, “Magnetic glass ceramics by sintering of borosilicate glass and inorganic waste”. *Materials*, **7** (8) 5565-80 (2014).