POROUS GLASS-CERAMICS FROM ALKALI ACTIVATION AND SINTER-CRYSTALLISATION OF VITRIFIED BOTTOM ASH

Patricia RABELO MONICH[1], Hugo LUCAS[2], Bernd FRIEDRICH[2], Enrico BERNARDO[1]

[1] Dipartimento di Ingegneria Industriale, Università degli Studi di Padova, 35131 Padova, Italy
[2] IME Process Metallurgy and Metal Recycling, RWTH Aachen University, 52056 Aachen, Germany

patricia.rabelomonich@studenti.unipd.it, hlucas@metallurgie.rwth-aachen.de, bfriedrich@metallurgie.rwth-aachen.de, enrico.bernardo@unipd.it

Introduction

The incineration of municipal solid waste can reduce up to 90 vol% of waste, making it an alternative to landfill.[1] This process mainly generates flue gas, slags and ashes, such as bottom ash (BA),[2] which can be treated and further employed in the production of building materials.[3] However, as this residue can contain a high quantity of heavy metals, BA continues to be mainly landfilled.[4] Vitrification of BA is an alternative to produce a safe and chemically stable glass, with metal recovery.[5] In addition, the high costs of vitrification can be decreased by valorising the vitrified residue into high added value products,[5] such as glass foams.[6] This type of material is known to be light, strong, thermally and acoustically insulating and flame resistant. As a consequence, it provides a much safer option, in buildings, than polymer foams.[6]

An economic process to develop glass foams is the combined technique of alkali activation, gelification and sintering of glasses.[7] After the partial dissolution of fine glass powders in an alkaline solution of low molarity, the suspension undergoes hardening due to the formation of calcium silicate hydrate (C–S–H) compounds[7] and/or carbonates.[8] This gel can then be easily foamed by intensive mechanical stirring, with the support of a surfactant. Once the stirring is ceased, the increase of viscosity prevents the collapse of the bubbles trapped inside the gel.[7] The porous material is finally dried and sintered by viscous flow.[7] In this study, after the extraction of ferrous particles from BA, the residue was smelted, obtaining a glass. The obtained vitrified bottom ash (VBA) was further valorised into porous glass-ceramics by alkali activation, gelification and sintering.

Materials and Methods

MSWI BA was kindly provided by the company AVR (Netherlands) and dried at 200°C for 24 h. Thereafter, a magnet was used to extract ferrous particles from BA. After the extraction, BA was added to a graphite crucible and smelted in a lab-scale electric arc furnace at around 1450°C. The melt residue was subsequently quenched in water, dried and milled until the particle size was below 75 µm. The obtained VBA presented the following main composition (in wt%): SiO_2: 49.2%; Al_2O_3: 19.9%; CaO: 18.8%; Na_2O: 4.1%; MgO: 2.6%; Fe_2O_3: 1.4%. Porous glass-ceramics were produced by firstly mixing at 400 rpm fine powders of VBA to an alkaline solution of 1 M NaOH (S/L = 2.33). After the partial dissolution of the fine powders, 4 wt% of surfactant (Triton X-100, Sigma-Aldrich, UK) was added to the suspension, which was then submitted to an intensive mechanical stirring at 2000 rpm. The foamed suspension was subsequently dried at 40°C for 48 h, demoulded and fired at 1000°C, with heating rate of 10°C/min and a holding time of 1 h. The foams were cut into cubes of approximately 10 mm of length and used for further characterisation. The bulk density of the porous materials was calculated by the weight-to-volume ratio. The apparent and true densities were measured by using a He gas pycnometer (Micromeritics AccuPyc 1330, Norcross) with the foams and fine powder, respectively. The compressive strength of 9 porous materials was assessed by using an Instron 1121 UTM (Instron Danvers, MA), with cross-head speed of 1 mm/min. The morphological structure of the foams was assessed by optical stereomicroscopy (AxioCam ERc 5 s Microscope Camera, Carl Zeiss Microscopy, USA). The mineralogical composition was determined by X-Ray diffraction (XRD, Bruker D8 Advance, Germany). Leaching tests were performed on the foams based on norm EN 12457-4 with a liquid (water) to solid equal to 10. Inductively coupled plasma mass spectrometry (ICP-OES, Spectro Genesis, Germany) was used to measure the heavy metals content of the leachate. The leachate values allowed for waste acceptable at landfills for inert waste (Directive 2003/33/EC, 2003) was used as a reference.

Results and Discussion

The density, porosity and results of leaching test of the porous glass-ceramics are shown in Table 1. The foams present very low relative density with a total porosity of 80.2 vol%, mainly open. Regarding the leaching test, the content of metals leached was below the limit for inert materials (reference values are listed inside brackets).

The compressive strength of the developed porous glass-ceramics was 3.0 ± 0.5 MPa. In addition, the bending strength of the solid phase was estimated to be 179.2 MPa by applying the Gibson-Ashby model[9]. These results indicate that the developed foams could be potentially applied as thermal and acoustic insulators given its high strength and porosity, as well as low leaching of heavy metals

Table 1: Physical and mechanical properties of VBA foams

Density (ρ) and Porosity (ϕ)		Leaching test	
ρ_{bulk} (g/cm^3)	0.54 ± 0.01	As: 0.0070 [0.5]	Mo: < 0.0033 [0.5]
$\rho_{apparent}$ (g/cm^3)	2.70 ± 0.01	Ba: 0.0346 [20]	Ni: < 0.0014 [0.4]
ρ_{true} (g/cm^3)	2.81 ± 0.00	Cd: < 0.0002 [0.04]	Pb: < 0.0047 [0.5]
ϕ_{total} (%)	80.7	Cr: 0.0255 [0.5]	Sb: < 0.0099 [0.06]
ϕ_{open} (%)	79.9	Cu: 0.0493 [2]	Se: < 0.0122 [0.1]
ϕ_{closed} (%)	0.8	Hg: < 0.0004 [0.01]	Zn: < 0.0203 [4]

Figure 2 presents the morphological structure of the developed foams before and after firing. The porosity distribution is quite heterogeneous and it is possible to observe the open-celled morphology of the foams, as indicated by Table 1. After the firing treatment, the solid phase presents a shinier aspect, typical from glassy materials, indicating densification.

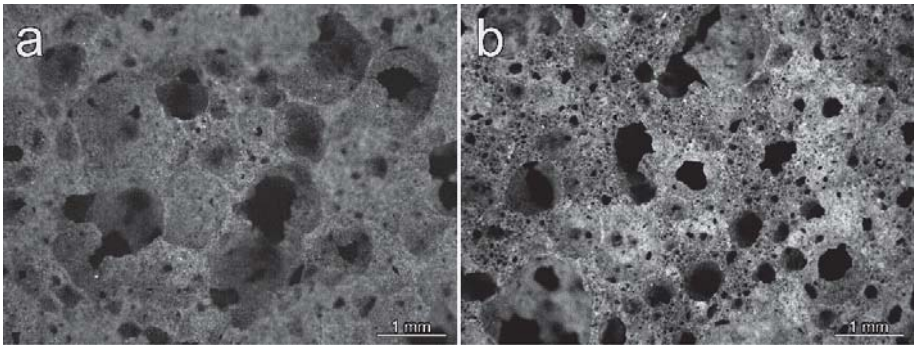

Figure 1: Micrographs of VBA foams: a) before and b) after firing

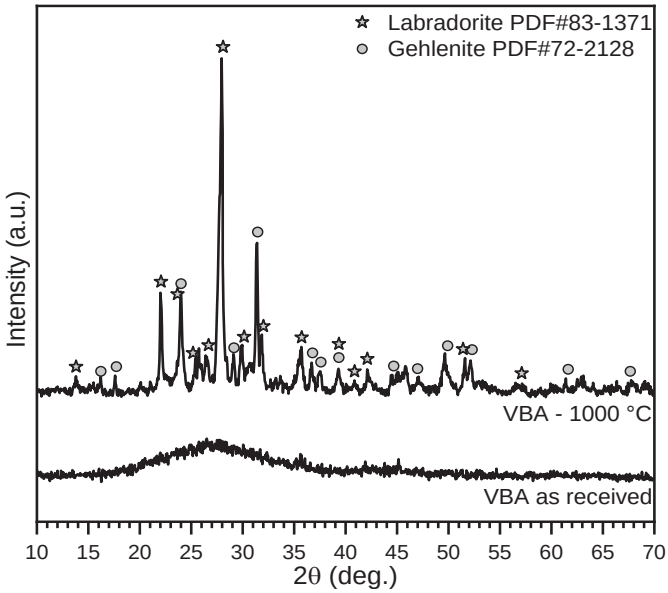

Figure 2: XRD patters of VBA as received and of the fired foam

As confirmed by the XRD pattern (Figure 2), VBA is amorphous and presents the typical "halo" of glasses. The firing treatment led to the crystallisation of labradorite ($Ca_{0.64}Na_{0.35}(Al_{1.63}Si_{2.37}O_8)$) and gehlenite ($(Ca_{1.96}Na_{.05})(Mg_{.24}Al_{.64}Fe_{.12})(Si_{1.39}Al_{.61}O_7)$). These two crystal phases have already been previously detected in glass-ceramics made with plasma vitrified MSWI fly ashes.[10]

Conclusion

Highly porous, safe and strong glass-ceramics were successfully produced by alkali activation, gelification and sintering of vitrified bottom ash. Due to the high porosity, the foams could be potentially applied as thermal and acoustic insulators.

Acknowledgement

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreements No. 721185 "NEW-MINE" (EU Training Network for Resource Recovery through Enhanced Landfill Mining; http://new-mine.eu/).

References

1. D.A. Tillman, K.M. Vick, A.J. Rossi, *Incineration of Municipal and Hazardous Solid Wastes*, Academic P, Elsevier, 1989.
2. P.H. Brunner, H. Rechberger, "Waste to energy - key element for sustainable waste management", *Waste Manag*, **37** 3-12 (2015).
3. R. V. Silva, J. de Brito, C.J. Lynn, R.K. Dhir, "Use of municipal solid waste incineration bottom ashes in alkali-activated materials, ceramics and granular applications: A review", *Waste Manag*, **68** 207-220 (2017).
4. P.J. He, H.X. Pu, L.M. Shao, H. Zhang, "Impact of co-landfill proportion of bottom ash and municipal solid waste composition on the leachate characteristics during the acidogenesis phase", *Waste Manag,* **69** 232-241 (2017).
5. P. Colombo, G. Brusatin, E. Bernardo, G. Scarinci, "Inertization and reuse of waste materials by vitrification and fabrication of glass-based products", *Curr Opin Solid State Mater Sci,* **7** (3) 225-239 (2003).
6. A. Rincón, M. Marangoni, S. Cetin, E. Bernardo, "Recycling of inorganic waste in monolithic and cellular glass-based materials for structural and functional applications", *J Chem Technol Biotechnol,* **91** (7) 1946-1961 (2016).
7. A. Rincón, G. Giacomello, M. Pasetto, E. Bernardo, "Novel 'inorganic gel casting' process for the manufacturing of glass foams", *J Eur Ceram Soc,* **37** (5) 2227-2234 (2017).
8. A. Rincon Romero, M. Salvo, E. Bernardo, "Up-cycling of vitrified bottom ash from MSWI into glass-ceramic foams by means of 'inorganic gel casting' and sinter-crystallization", *Constr Build Mater,* **192** 133-140 (2018).
9. L.J. Gibson, M.F. Ashby, *Cellular solids: structure and properties*, Cambridge University Press, Cambridge, 1999.
10. E. Bernardo, A. Dattoli, E. Bonomo, L. Esposito, E. Rambaldi, A. Tucci, "Application of an industrial waste glass in "glass-ceramic stoneware", *Int J Appl Ceram Technol,* **8** (5) 1153-1162 (2011).