Characterization of foam glass produced from waste CRT glass and aluminium dross

M Sassi1, J F M Ibrahim2, A Simon3
1,2,3Institute of Ceramics and Polymer Engineering, Miskolc University 3515, Hungary

1sassi90meriem@gmail.com, 2jamalfadoul@gmail.com, 3femandi@uni-miskolc.hu

Abstract. Increasing the energy efficiency of buildings has become very pertinent currently. This will be implemented by employing eco-friendly materials such as foam glass. Glass foaming is a process that depends strongly on the foaming mechanism and the initial composition of the mixture. This study deals with the investigation of foam glass properties consisting of recycled bottle glass material, CRT glass and aluminium dross. Experiments were carried out to investigate the thermal behaviour, optimal foaming temperature, density, water absorption, thermal conductivity and compressive strength of the foams. Microstructure and cell size distribution was analyzed as well. Effect of the CRT glass and the aluminium dross on the properties of the foams was evaluated in this paper. Adding aluminium dross decreased the foaming temperature, increased the foaming height and enhanced the compressive strength of the foam glass.

Keywords: Waste management, CRT, Aluminium dross, Glass foam, Cell size

1. Introduction
Foam glass is an ultra-light material with high thermal and acoustic insulating properties where density and texture can vary depending on the chemical composition. Foam glass produced by the world’s leading manufacturers has low density (120-160 kg/m³), low thermal conductivity (0.04-0.07 W/mK), low water absorption (≤ 5-6 kg/m² after 28 days) and good compressive strength (0.6-1.0 MPa), [1-4]. The application areas of foam glass are very wide. It can be used in wall insulation (sound absorption barrier and noise reduction), as a lightweight filler for the restoration of failed slopes, subgrade improvement material, and as a lightweight aggregate material in concrete [4-8].

Different material can be introduced to produce foam glass such as cathode-ray tubes (CRT) and aluminium dross. CRT comes from computer monitors and TV sets [12]. It contains many hazardous elements (lead, strontium, barium etc...) [13-14]. CRT glass can be added into raw materials to produce a variety of building materials like foam glass, glass ceramic, brick and concrete materials [14-15]. Aluminium dross is a by-product of melting aluminium scrap, usually by the application of NaCl-KCl-CaF₂ based salt flux [16-17]. Researches provide several possibilities to use aluminium dross in different fields depending on the treatment method. It can be used in ceramics, cement, glasses and glass ceramics [18-19].

The aim of the present work is to produce thermal insulation material with low density and thermal conductivity using bottle and CRT glass and aluminium dross. The effect of dross, size and amount of the CRT glass on the mechanical strength, thermal conductivity and microstructure of the glass foams were determined.
2. Experimental procedure

Bottle glass, CRT glass and aluminium dross was the starting materials to produce foam glass with the addition of slight amount of silicon carbide. At first the raw materials were pulverized, then grounded in ball mills under 70 microns in particle size. The powder was sieved and milled repeatedly so that particles would be under 63 microns (μm). Aluminium dross was water leached before using. The chemical composition of each material was determined using the ICP and XRF methods. The ICP instrument used was ICP spectrometer, 720 ES, made by varian Inc. X-ray fluorescence spectrometry (XRF) instrument was a Rigaku SuperMini 200. The particle shape and size of the raw materials was analyzed by Hitachi TM1000 and Zeiss EVO MA 10 scanning electron microscope (SEM). CRT glass with 63 and 32μm particles sizes were added in 5 and 10 wt%. Dross was added in 10 wt% in some of the mixtures. Composition and coding of the samples are listed in Table 1. The first number indicate the wt % of CRT, then the particle size of CRT glass of D₉₀=32μm or D₉₀=63 μm. Finally, letter D means the presence of 10 wt% dross in the mixtures. 80 g from each composition was prepared. Powders were analysed by a heating microscope. The change in the sample height in function of temperature was recorded. The temperature, where the maximum height detected, was identified as the foaming temperature. 3 g was measured from each mixture and poured in a cylindrical mold then pressed under 11 MPa. The samples were foamed at different temperatures for 10 min. The foamed samples were later cut into cubic shape. Geometrical parameters (length, width, depth, and diameter) were measured, and the densities were calculated as mass per volume (g/cm³). Microstructure, thermal conductivity and compressive strength was investigated for each sample. To evaluate the cell size distribution, the samples were cut across the longitudinal and characterized with optic microscope (C. Zeiss Discovery V.12) where the cells length was measured along with the wall thickness. The statistic was made in a total of 15 measurements per sample. Cell size was divided into six interval grades proposed by Zipeng et al [7]: d ≥3 mm, 2 mm ≤ d < 3 mm, 1 mm ≤ d < 2 mm, 0.5 mm ≤ d < 1 mm, 0.1 mm ≤ d < 0.5 mm, and 0.01 mm ≤ d < 0.1 mm. Thermal conductivity measurement was done by a C-Therm TCi Thermal Conductivity Analyser. Thermal conductivity and effusivity are measured directly. Compressive strength test was done on the samples using an Instron universal testing instrument. An X-Ray diffraction test was conducted using Rigaku Miniflex II to determine the different mineral phases.

| Sample Code | Composition (%) | Foaming temperature (°C) | Maximum Height (%) |
|-------------|-----------------|--------------------------|-------------------|
| BG          | Dross          | SiC | CRT63 | CRT32 | Bottle glass | 960 | 107 |
| 5CRT32      | 2              | 5   | 93    | 960   | 101 |
| 10CRT32     | 2              | 10  | 88    | 955   | 108 |
| 5CRT63      | 2              | 10  | 88    | 947   | 104 |
| 10CRT63     | 2              | 5   | 83    | 965   | 126 |
| 5CRT32D     | 10             | 2   | 5     | 83    | 965   | 124 |
| 10CRT32D    | 10             | 2   | 10    | 78    | 900   | 144 |
| 5CRT63D     | 10             | 2   | 5     | 83    | 965   | 124 |
| 10CRT63D    | 10             | 2   | 10    | 78    | 915   | 136 |

3. Results and discussion

Particle shape and size of the raw materials is presented in Figure 1. Most particles of bottle glass (BG), CRT and SiC are angular, and prismatically shaped with rigid surface. Aluminium dross particles have irregular shape and rough surface. The chemical composition of bottle glass, presented in Table 2, shows a typical composition where the major components are silica, sodium oxide with minor components like calcium and aluminium oxide. CRT and BG has almost the same constituents. The difference is the presence of hazardous elements as Pb, Sr, Ba in CRT (Table 3). Treated aluminium dross contains high content of spinel with the existence of corundum, aluminium nitride,
salts and a small percentage of aluminium hydroxides (Table 4). Aluminium nitride can enhance the foaming process as it acts as a foaming agent. It can be oxidized and then releases N\textsubscript{2}. The typical oxidation reaction can be written as follows [8]:

\[ 4\text{AlN(s)} + 3\text{O}_2(g) = 2\text{Al}_2\text{O}_3(s) + 2\text{N}_2(g) \]  

(2)

![Fig. 1. SEM analysis of bottle glass (A), silicon carbide (B), aluminium dross (C) and CRT (D)](image)

**Table 2.** Chemical composition of bottle glass powder and CRT (ICP analysis)

| Oxides     | SiO\textsubscript{2} | Na\textsubscript{2}O | K\textsubscript{2}O | CaO | MgO | Al\textsubscript{2}O\textsubscript{3} | Fe\textsubscript{2}O\textsubscript{3} | Cr\textsubscript{2}O\textsubscript{3} | TiO\textsubscript{2} | MnO | SO\textsubscript{3} | P\textsubscript{2}O\textsubscript{5} | BaO | ZrO\textsubscript{2} |
|------------|----------------------|----------------------|----------------------|-----|-----|-------------------------------|-----------------|-----------------|-----------------|-----|----------------|------------------|-----|------------------|
| Bottle glass| 71.5                | 12.5                 | 0.72                 | 8.75| 2.44| 1.75                          | 1.15            | 0.066           | 0.034           | 0.022| 0.21           | 0.009             | 0.068| 0.007            |
| CRT        | 55.9                | 5.96                 | 5.49                 | 0.52| 0.21| 1.7                          | 0.21           | -               | 0.005           | 0.005| 0.005         | .                 | .    | .                |

**Table 3.** Hazardous elements in CRT glass (XRF analysis)

| Elem | Cu | Zn | Pb | Rb | As | Cr | Co | Ni | Sr | Ba | Zr |
|------|----|----|----|----|----|----|----|----|----|----|----|
| ppm  | 45 | 1891 | 1071 | <10 | 53 | 93 | <10 | 143 | 3.6 | 7.2 | 5.7 |

**Table 4.** Composition of Aluminium dross (XRD analysis)

| Formula    | Phase   | Wt % |
|------------|---------|------|
| Al\textsubscript{2}O\textsubscript{3} | Corundum | 17.59 |
| MgAl\textsubscript{2}O\textsubscript{4} | Spinel  | 68.14 |
| AlN        | Wurtzit | 8.57 |
| CaF\textsubscript{2} | Fluorite | 1.51 |
| NaCl       | Halite  | 1.72 |
| KCl        | Sylvin  | 0.33 |
| Al(OH)\textsubscript{3} | Bayerite | 1.9 |
| Salt together |         | 3.57 |

Heating microscopy results are presented in Figure 2, where the temperature of the maximum height corresponds to the foaming temperature. We can distinguish 2 groups detailed in Figure 2. First group consisting of samples with high foaming height (almost 144 %) and lower foaming temperature (880 °C), contains aluminium dross. Dross free samples presented lower foaming height (108%) and higher foaming temperature (970 °C). Aluminium dross decreased the foaming temperature and made the foaming process more intense due to the presence of salts and AlN, respectively, residual salts (CaF\textsubscript{2}, KCl, NaCl) reduce the softening and melting temperature of the glasses, behave as fluxes in the glass melting process and act as melt accelerators. Based on Figure 2 (B), mixture with 5 wt% CRT 63D have the same height and foaming temperature with mixture containing 5 wt % CRT 32D. Adding 10 wt% of CRT decreases the foaming temperature and increases the height. Particle size of CRT glass has no effect on the foaming parameters. The viscosity curves of both TV panel and lead
glass are very similar to that of commercial soda lime glass [20]. Thus adding CRT glass does not affect the foaming behaviour of the bottle glass.

![Fig. 2. Heating microscopy curves of dross free powder (A) and dross containing powder (B)](image)

The average cell size and the frequency of the cell sizes was calculated and presented in Figure 3. Bottle glass shows that 66% cells are equal to 1.35 mm size. For samples composed by 5wt% CRT32, 70% of the cells sizes are between 0.5 and 1 mm. As we increase CRT content to 10 wt%, the cell sizes increase. Same results can be observed for samples composed by CRT63. Adding aluminium dross to the samples, the cells sizes for samples with CRT32 become wider where 64% of the pores are between 2 and 3 mm. For CRT63 the cell size is distributed between 1 and 3 mm and decreases as we increase CRT quantity.

![Fig. 3. Cell size distribution of dross free foam glasses (A) and foam glasses containing dross (B)](image)

Density results are shown in Figure 4. By adding 5 and 10 wt% CRT63 to the bottle glass the density increases to 0.44 g/cm$^3$ then decreases to 0.33 g/cm$^3$. Cells increased by adding 10 wt% of CRT 63 could affect the density of the foams. At the same time, the inverse behaviour can be observed when we add aluminium dross, the density reaches the minimum at 5 wt% of CRT63. For CRT32 (in both cases, with and without aluminium dross) the density continuously increases when adding 5 wt% and 10 wt% CRT to reach 0.61 g/cm$^3$. Sample with 5wt% CRT 63 and 10 wt% aluminium dross presents the optimal density, pore size distribution with density equal to 0.23 g/cm$^3$ and cell sizes ranges between 1 and 3 mm. PbO can enhance the tendency of crystallization in glasses. Glasses in crystal form have higher density then amorphous glasses, due to the ordered structure of crystal [21]. Thus samples having more CRT glass may be more crystallized. As a conclusion, the density of foam glasses is a result of two processes having opposite effect.

Usually, thermal conductivity decreases with increasing the cells size. Cells are able to block the heat flow transmission. Heat flow changes its direction when encountered with the cell, and propagate through the wall. The thickness of the wall will affect the thermal resistance; the thicker the wall the lower the thermal resistance. Thermal insulation can be enhanced in case of better distribution and
This can be applied in our case where the thermal conductivity of the foam glasses ranges between 0.038 and 0.055 W/mK (Figure 4). Cells size distribution and density affected the thermal conductivity. Sample 5CRT63D have the minimum thermal conductivity (0.038 W/mK). Thermal conductivity range obtained in this experiment is better than that of the commercial product where the thermal conductivity is equal to 0.085 W/mK.

Compressive strength test results show that glass foam strength varies from 1 to 6 MPa (Figure 5). Samples containing dross have higher compressive strength. By adding CRT, the strength slightly decreases except sample with CRT63 where the compressive strength have a local minimum. As a conclusion, smaller cells size obtained by adding aluminium dross allow the achievement of higher mechanical strength. To confirm this hypothesis, the mineral phase composition was analysed by X-ray. Spinel, albite and quartz are found in samples with dross while samples with CRT and bottle glass show mostly quartz and wollastonite. Spinel and albit can contribute to higher compressive strength and higher density.

### 4. Conclusions

In this research work, effect of CRT glass and aluminum dross on the foaming process and physical-mechanical parameters of foam glasses was studied. Conclusions are summarized as follows: Samples containing dross have foaming temperature lower than CRT/ BG samples. Aluminium dross decreases the foaming temperature and make the foaming process more intense due to the presence of salts and AlN. Residual salts (CaF$_2$, KCl, NaCl) reduce the softening and melting temperature of the glasses, behave as a flux in the glass melting process and act as melt accelerators. The presence of spinel, aluminium nitride and corundum in the initial composition favoured the strength of foam glass to let the formation of other mineral phases like albite (NaAlSi$_3$O$_8$) with high hardness which can contribute to higher compressive strength. The viscosity curves of both TV panel and lead glass are very similar.
to that of commercial soda lime glass. Thus adding CRT glass does not affect the foaming behaviour of the bottle glass. PbO containing in CRT, can enhance the tendency of crystallization in glasses. Glasses in crystal form have higher density then amorphous glasses, due to the ordered structure of crystal. Density of foam glasses is a result of two processes having opposite effect.

Acknowledgement

The research work was supported by the GINOP2.2.1-15-2016-00018 project in the framework of the New Széchenyi Plan of Hungary, co-financed by the European Social Fund. The described study was carried out as part of the EFOP-3.6.1-16-2016-00011 “Younger and Renewing University – Innovative Knowledge City – institutional development of the University of Miskolc aiming at intelligent specialization” project implemented in the framework of the Széchenyi 2020 program. The realization of this project is supported by the European Union, co-financed by the European Social Fund.

References

[1] N Karandashova, B Goltsman, E Yatsenko 2017 IOP Conf. Ser. Materials Science and Engineering 262 012020 https://doi.org/10.1088/1757-899X/262/1/012020
[2] H Wang, Z Chen, R Ji, L Liu, X Wang 2018 Ceramics International 44 https://doi.org/10.1016/j.ceramint.2018.04.207
[3] C Xi, F Zheng, X Jiahe, W Yang, Y Peng, Y Li, P Li et Q Zhen, 2018 Construction and Building Materials 190 https://doi.org/10.1016/j.conbuildmat.2018.09.170
[4] Foamit 2019 Applications for Civil Engineering http://www.foamit.fi/wp-content/uploads/2016/10/Foamedglass.pdf.
[5] Y Attila, M Guden, A Tasdemirci 2013 Elsevier Ceramics International 39 (5) 5869-5877 https://doi.org/10.1016/j.ceramint.2012.12.104
[6] Q Ma, Q Wang, L Luo, F Chaozhen 2018 IOP Conf. Ser. Materials Science and Engineering 397 (1) 012071 https://doi.org/10.1088/1757-899X/397/1/012071
[7] Q Zipeng, G Li, Y Tian, M Yuwei, P Shen 2018 Materials 12 (1) 54 https://doi.org/10.3390/ma12010054
[8] H Shi, K Feng, H Wang, C Chen, H Zhou 2016 International Journal of Minerals, Metallurgy and Materials 23 (5) https://doi.org/10.1007/s12613-016-1271-7
[9] J König, V Nemanic, M Zumer, R P Rasmus, B Ø Martin, Y Yue, D Suvorov 2019 Elsevier Construction and Building Materials 214 https://doi.org/10.1016/j.conbuildmat.2019.04.109
[10] R Ji, Y Zheng, Z Zou, Z Chen, S Wei, X Jin et M Zhang 2019 Construction and Building Materials 215 https://doi.org/10.1016/j.conbuildmat.2019.04.226
[11] D Khamidulina, S Nekrasova, K Voronin 2017 Materials Science and Engineering 262 https://doi.org/10.1088/1757-899X/262/1/012008
[12] G Mucsi, B CsYke, M Kertész, L Hoffmann 2013 Journal of Materials http://dx.doi.org/10.1155/2013/696428
[13] E Restrepo, R Widmer and M Schluep 2016 Step Green Paper Series https://www.researchgate.net/publication/309740263_Leaded_Glass_from_Cathode_Ray_Tubes_CRTs_A_Critical_Review_of_Reycling_and_Disposal_Options
[14] W Meng, X Wang, W Yuan, J Wang, G Songa 2016 Procedia Environmental Sciences 31 https://doi.org/10.1016/j.proenv.2016.02.120
[15] B Ø Martin, R P Rasmus, J König, M Bockowski and Y Yue 2019 Elsevier Journal of Non-Crystalline Solids 1 https://doi.org/10.1016/j.jnocs.2019.100014
[16] M Mostafa, A Ali 2018 Journal of Environmental Management 212 https://doi.org/10.1016/j.jenvman.2018.06.068
[17] P Tsakiridis 2012 Elsevier J. of Haz. Mat. 217 https://doi.org/10.1016/j.jhazmat.2012.03.052
[18] D Bajare, A Korjakins, J Kazjonovs 2011 *3rd International Scientific Conference*
https://www.researchgate.net/publication/260064925_Application_of_aluminium_dross_and_glass_waste_for_production_of_expanded_clay_aggregate

[19] M Arunabh et K Kamalesh 2018 *Resources, Conservation & Recycling* 130
https://doi.org/10.1016/j.resconrec.2017.11.026

[20] Glass Viscosity Calculation https://glassproperties.com/viscosity/

[21] O C Mocioiu, M Zaharescu, I Atkinson, A M Mocioiu, P Budrueac 2014 *Journal of Thermal Analysis and Calorimetry* 117 https://doi.org/10.1007/s10973-014-3652-3