

ENVIRONMENTAL IMPACT OF FOAMED GLASS PREPARED FROM SEWAGE SLUDGE ASH

*Marin Ganjto*¹, *Jasna Hrenović*², *Vladimir Bermanec*²

¹University of Zagreb, Faculty of Chemical Engineering and Technology and Zagreb Wastewater - Management and Operation Ltd., Zagreb, Croatia

²University of Zagreb, Faculty of Science, Zagreb, Croatia
E-mail: ganjto.marin@gmail.com

ABSTRACT

Management of waste materials for sustainable development imply their recycling and reuse. In this work the foam glass (FG) was prepared from powder mixture of waste materials: sewage sludge ash (SSA), recycled bottle glass cullet, and carbonate foaming agent through one-step thermal process at temperatures up to 850°C. Prepared FG, with wollastonite as a major mineral phase, had open and connected pores from several mm to closed small pores <1mm and can be classified as macro- or meso-porous materials. FG fulfil requirements for masonry mortars. Low leaching of heavy metals confirmed its safely incorporation inside glass matrix. FG exhibited the antibacterial activity against emerging pathogenic bacterium *Acinetobacter baumannii* due to the alkaline reaction of FG in water medium. SSA and bottle glass could be successfully transformed by simple production method to FG as environmental friendly material.

Keywords: bacteria, foam glass, sewage sludge ash, carbonates, macro-porous, meso-porous, material

INTRODUCTION

Ongoing construction of wastewater treatment plants worldwide result in continuous increase of surplus sewage sludge production. Nowadays the management of surplus sewage sludge prefers the incineration which reduces volume, destroys organics and pathogens in SS^[1]. Waste material from incineration is sewage sludge ash (SSA), which could be used in different areas of building industry^[2]. Another type of widely produced waste is bottle glass, which also could be used in production of lightweight materials such as foam glass (FG)^[3]. FG is heterogenous system consisted of solid (glass cell walls) and gaseous phase (trapped inside cells) with porosity up to 90%, made from virgin or cullet glass with addition of foaming agent (SiC or TiN) that produce uniform cells inside controlled thermal regime and atmosphere. FG is applied in building industry for isolation (sound, heat, water) and in chemical industry (reactors, separators, filters)^[3]. High production costs of FG is tended to be reduced by the addition of softener and flux agents which can lower temperatures and shorten thermal regime, and by usage of more waste glass materials, but are still far from commercial usage. Finding a suitable thermal regime, mixture composition, influence of different additive oxides for improved foaming, to obtain high porosity of uniform cells which gives good properties of final product, with reduction of heavy metals mobility are still in the focus of researchers^[4-7].

The aim of this work was to produce FG from powder mixture of SSA, recycled bottle glass cullet, and carbonate foaming agent through one-step thermal process at temperatures up to 850°C. The leaching of heavy metals and antibacterial activity of product was examined.

EXPERIMENTAL

Preparation of FG

The SSA was obtained by ignition of anaerobically digested and dewatered sewage sludge at 550°C for 2h. Waste glass was recycled bottle glass, prewashed, dried, and crashed to form

cullet. Calcium carbonate was a by-product originating from dedusting limestone mills. Raw materials of particle size $\leq 0.71\text{mm}$ were homogenized separately before preparation of FG. In the base mixture of waste glass and 2wt% of CaCO_3 13, 17 and 23wt% of SSA was added. Preparation of FG was done by wet homogenization of powdered samples with 96% ethanol, drying for 6h at 80°C , followed by dry molded uniaxial pressure of 12 tons. Molded samples were kiln in a furnace at ambient air pressure through one-step heating process of $5^\circ\text{C}/\text{min}$ to 850°C , and then holding for 15 min at 850°C . Three FG samples showed visually homogenous pores, appropriate hardness, stability and lightweight were labelled as FG1 to FG3.

Characterization of FG

Decomposition behaviour of raw materials was examined by simultaneous differential scanning calorimetry-thermogravimetric (DSC-TGA) analysis. The morphology of FG and microanalysis of phases were examined by scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS). Mineral phases were determined by X-ray diffraction (XRD) analysis. Compression tests and water absorption were determined according to norms^[8,9]. Density and porosity of FG were analysed by direct methods for determination of the bulk volume. The leaching of major heavy metals from SSA and FG were determined in deionized water^[10] and leachates were analysed by inductively coupled plasma optical emission spectrometry. The ability of the waste glass as a binder of heavy metals was evaluated through leaching in aqua regia^[11].

Antibacterial activity of FG

The antibacterial activity of FG and SSA was tested on the multidrug-resistant environmental isolate of *Acinetobacter baumannii*^[12]. Bacterial biomass was suspended in autoclaved commercially available natural spring water into which 3-100 g/L of dry-sterilized FG samples of particle size 0.125-0.250mm or original SSA were added. Experiments were performed at 37°C for 24h with shaking at 170rpm. The number of *A. baumannii* was determined as colony forming units (CFU) per 1mL of slurry after 0 and 24h of incubation in triplicate after decimal dilution of sample in sterile physiological solution, inoculation of dilutions on nutrient agar, and subsequent incubation at 42°C for 24h. Minimum inhibitory concentration (MIC) of FG was determined as the lowest concentration of FG which caused the visible inhibition of bacterial growth as compared to positive control (without FG addition) and were confirmed by CFU counting and SEM analysis. The influence of elevated pH on *A. baumannii* was confirmed in artificially adjusted pH of the natural spring water as described for FG.

RESULTS AND DISCUSSION

According to DSC-TGA analysis chosen thermal regime at 850°C was above glass transition temperature of all raw materials and inside range of decomposition of CaCO_3 , allowing developed bubbles of foaming agent to spread out through viscous melted glass matrix. Reaction time of 15 min was sufficient for foaming without disrupting molded sample forms by retained stable volume expansion.

SEM micrographs (Fig 1) showed that thermal regime was sufficient to avoid total crystallization of FG respectively to surface crystallization on the place of rupture, assuming that crystallization takes place inside cell walls of FG, as confirmed by EDS analysis. Prepared FG had open and connected pores from several mm for FG1 to closed small pores $<1\text{mm}$ for FG3 (Fig 1), and can be classified as macro- or meso-porous materials. Pore sizes in FG and water absorption decreased with increase of SSA added, while the compressive strength and bulk density increased with increase of SSA added (Table 1). Water absorption indicates that samples contained certain share of open cells with interconnection enabling capillarity related to pore size. Samples FG2 and 3 fulfil demand according to mortar testing for masonry.

Consequently, materials are breathable in both cases. XRD analysis of FG showed wollastonite as a major mineral phase. Amorphous phase is mixed with wollastonite, CaSiO₃ and SiO₂ (quartz and HT quartz) with traces of meixnerite, pyroxene, lissetite, mica (muscovite) and microcline. The wollastonite phase correlated with high compressive strength of FG1, while FG2 and FG3 can be classified according to mortar testing for masonry as the best category.

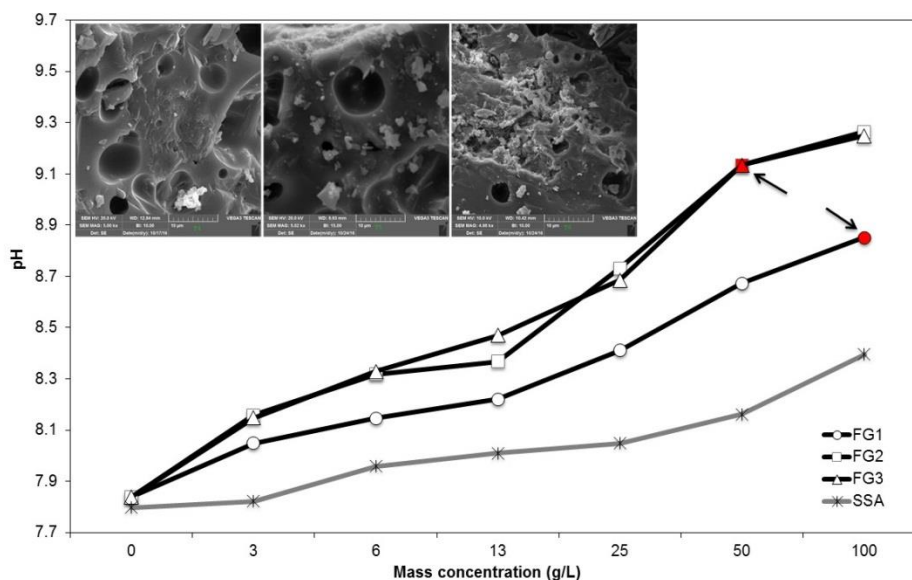


Figure 1. SEM micrographs of samples FG1 (left), FG2 (middle) and FG3 (right), increase of the pH value of spring water by addition of different amounts of FG samples, and the MIC values of FG against *A. baumannii*. MIC values are marked in arrows; MIC were observed above pH 8.85; c_0 (log CFU/mL) = 7.05±0.01.

Table 1. Physical characteristics of FG and leachate composition of SSA and FG samples in deionized water and aqua regia.

Parameter	SSA	FG1	FG2	FG3	SSA	FG1	FG2	FG3	
Compressive strength (Mpa)		5.437	9.883	19.924					
Bulk density (g/cm ³)		0.422	0.719	1.049					
Water absorption (kg/m ² min ^{0.5})		0.53	0.39	0.25					
		Deionized water				Aqua regia			
pH	9.40	12.13	11.75	11.43					
Cr (mg/kg)	24.90	4.81	4.42	7.69	84.3	13.9	16.3	19.2	
Pb (mg/kg)	<2	<0.01	<0.01	<0.01	408	9.63	12.5	8.6	
Mo (mg/kg)	5.23	1.04	1.08	1.24	8.71	5.3	3.7	14.7	
As (mg/kg)	<0.05	0.039	0.008	<0.01	5.88	<0.1	<0.1	<0.1	
Cu (mg/kg)	<1	<0.01	<0.01	<0.01	736	44	50.8	70.3	
Ni (mg/kg)	<2	<0.01	<0.01	<0.01	29.6	7.04	10.2	7.93	
Zn (mg/kg)	1.77	<0.01	<0.01	<0.01	1460	52	71	108	

Leaching of heavy metals from SSA and FG (Table 1) showed that major heavy metals are incorporated inside stable glass matrix. Increased leaching of some metals from FG for both medium indicates that decrease of waste glass and increase of SSA content inside mixture results in higher crystallization regardless to glass forming. Heavy metals were safely incorporated inside glass matrix making FG product environmentally friendly.

After 24h of contact FG samples increased the pH values of spring water (Fig 1). The MIC values, confirmed by 56% of reduction of *A. baumannii* appeared above the final pH of 8.85 at

mass concentration of 50 g/L for FG2 and 3 and 100 g/L for FG1. The SSA did not rise the pH above 8.40 and no MIC was observed after 24h of contact. In order to confirm the elevated pH as a reason of antibacterial activity of FG, a dependence of the growth of *A. baumannii* at the elevated pH was tested. *A. baumannii* showed undisturbed survival in spring water up to pH 8.82, above which 59% of reduction of bacterial numbers was observed, which was in excellent agreement with the MIC values of FG observed above pH 8.85. Therefore, the antibacterial activity of FG is attributable to the elevated pH caused by the alkaline reaction of FG in water medium and not to the leaching of potentially toxic ions or species. The antibacterial activity of FG in contact with water is a valuable property for control of pathogenic multidrug-resistant bacteria in environment.

CONCLUSION

FG obtained by simple production method from waste materials without additives showed comparable characteristics to commercial FG material and fulfil requirements for masonry mortars. Low leaching of heavy metals and antibacterial activity classify prepared FG as environmental friendly material.

ACKNOWLEDGEMENTS

This work has been supported in a part by the Croatian Science Foundation (project no. IP-2014-09-5656). We thank to V. Soukup, Cemtra d.o.o. for analyses of leachates.

REFERENCES

- [1] L. Batistella, V. Silva, R. C. Suzin, E. Virmond, C. A. Althoff, R. F. P. M. Moreira, H. J. José, *Waste Manag.* **2015**, *46*, 430–439.
- [2] P. H. Brunner, H. Rechberger, *Waste Manag.* **2015**, *37*, 3–12.
- [3] A. A. Francis, M. K. Abdel Rahman, A. Daoud, *Ceram. Int.* **2013**, *39*, 7089–7095.
- [4] M. Zhu, R. Ji, Z. Li, H. Wang, L. Liu, Z. Zhang, *Constr. Build. Mater.* **2016**, *112*, 398–405.
- [5] J. König, R. R. Petersen, Y. Yue, D. Suvorov, *Ceram. Int.* **2017**, *43*, 4638–4646.
- [6] Y. Guo, Y. Zhang, H. Huang, X. Meng, Y. Liu, S. Tu, B. Li, *Constr. Build. Mater.* **2016**, *125*, 1093–1100.
- [7] M. Tarrago, M. Garcia-Valles, M. H. Aly, S. Martínez, *Ceram. Int.* **2017**, *43*, 930–937.
- [8] U. E. 1015-11, *Methods of Test for Mortar for Masonry. Determination of Flexural and Compressive Strength of Hardened Mortar*, **2007**.
- [9] U. E. 1015-18, *Methods of Test for Mortar for Masonry. Determination of Water Absorption Coefficient due to Capillary Action of Hardened Mortar*, **2002**.
- [10] U. E. 12457-4, *Characterisation of Waste - Leaching - Compliance Test for Leaching of Granular Waste Materials and Sludges*, **2004**.
- [11] U. E. 13657, *Characterization of Waste - Digestion for Subsequent Determination of Aqua Regia Soluble Portion of Elements*, **2002**.
- [12] J. Hrenović, I. Goić-Barišić, S. Kazazić, A. Kovačić, M. Ganjto, M. Tonkić, *Eurosurveillance* **2016**, *21*, 30195.