STICLA POROASĂ CA O ALTERNATIVĂ DE RECICLARE A DEŞEURILOR DE STICLĂ▲
FOAM GLASS AS AN ALTERNATIVE FOR GLASS WASTES RECYCLING

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Foam glass as a building construction material is competing with insulating polymeric and fiber materials as it is a good insulator. The low flammability, thermal stability and high chemical durability are a distinct advantage over polymeric materials. The possibility to produce foam glass using industrial wastes was investigated in this paper: three types of recycled glass wastes (window panes, bottle glass and glassware) together with fly ash were the main raw materials while SiC was used as foaming agent. Two different weight ratios glass waste: fly ash: SiC (80:10:10 and 70:20:10) were used for the foam glass synthesis. The raw materials as powders were mixed together with and then pressed into cylinders using ethylene glycol as binder. The heat treatment was conducted at 900°C for 5 and 10 minutes respectively. Optical microscopy, apparent porosity and apparent density and chemical stability of the foam glasses were used in order to characterize the obtained products as insulator materials for the building industry. The foam glasses obtained from a 5 minutes heat treatment process had an apparent porosity of 37.8-41.3% and an apparent density of 1.03-1.22 g/cm^3 compared to those obtained from a 10 minutes heat treatment process, having an apparent porosity of 66.7-69.5% and apparent densities of 0.51-0.55 g/cm^3. The obtained results confirm the alternative producing foam glass from glass wastes.

Sticla poroasă ca material de construcţie cu rol de izolator termic şi fonic, concurează cu polimerii organici şi materialele fibroase. Sticla poroasă prezintă avantajele unui material ignifug, cu o foarte bună stabilitate termică şi chimică. Lucrarea de faţă abordează posibilitatea valorificării unor deşeuri industriale pentru obţinerea sticlelor poroase: s-au folosit trei deşeuri de sticlă (geam float, ambalaj şi menaj) şi cenuşă de electrofiltru iar ca agent de spongiere SiC. S-a pornit de la două rapoarte gravimetrice deşeu de sticlă:cenuşă:SiC (80:10:10 şi 70:20:10) ca reţete pentru obţinerea sticlelor. Materiile prime pulverulente au fost amestecate şi apoi presate sub formă de cilindri, folosind etilenglicol ca liant. Tratamentul termic al probelor s-a realizat la o temperatură de 900°C timp de 5 şi respectiv 10 minute. Caracterizarea probelor după spongiere s-a realizat prin microscopie optică, determinarea densităţii aparente şi a porozităţii. S-au obţinut sticle poroase având o porozitate aparentă cuprinsă între 37,8-41,3% şi o densitate aparentă între 1,03-1,22 g/cm^3 în cazul tratamentului termic timp de 5 minute respectiv porozitatea aparentă între 66,7-69,5% şi densitatea aparentă între 0,51-0,55 g/cm^3 în cazul tratamentului termic timp de 10 minute. Rezultatele obţinute susţin alternativa valorificării deşeurilor de sticlă pentru obţinerea unor sticle poroase.

Keywords: *thermal treatment, porosity, glass wastes, optical microscopy, insulator*

1. Introduction

The actual industrial development led to serious environmental problems. In the light of the concern for the environment, systematic treatment processes for solid, liquid and gaseous waste during industrial production was adopted. Glasses are among the materials which attract great interest in the recycling concept [1, 2], being one of the most effectively recycled materials in Europe (67% on average) with major benefits for the environment because when recycled glass is used, fewer raw materials are extracted, less waste is generated, less energy is used and less CO_2 is emitted [3]. The vitrification process starting from wastes, is economically advantageous only in the case of the manufacturing of new glass-based articles, like glass fibres [4], glass ceramics [5], glass or glass-ceramic matrix composites [6,7], glass foams [8,9] or glazes [10].

Foam glass is a porous heat-insulating and soundproof material, resistant to waterproof and fireproof. In its physical aspect, foam glass is a heterophase system consisting of the gaseous and the vitreous solid phases that forms thin walls of single cells several micrometers thick. Depending on destination, heat-insulating and soundproof foam glass can have predominantly closed or intercommunicating pores, respectively. Over the past few years there has been an increasing interest in the production and use of glass foams [11]. The main foam glass producers in Europe and North America now use a high percentage of processed post consumer glass in their products.

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Currently, there are three main product types of foam glass:

• Loose foam glass aggregate - continuous production of sheets of foam glass that are then broken into loose foam glass aggregate and sized.

• Blocks and shapes – generally continuous production of blocks and shapes in moulds that are then cut and shaped. Can also be manufactured by a batch process.

• Pelletisation – continuous production of spherical pellets of foam glass that are then used in the manufacture of blocks, panels and slabs.

Commercial glass foams exhibit porosity, apparent density and compressive strength values of about 45–85 vol.%, 0.1–1.2 g/cm^3 and 0.4–6 MPa, respectively [12].

The currently most common methods of fabricating glass, glass-ceramic, and composite porous materials are [13]:

- etching of the soluble constituent of liquating glass fibers;
- foaming of the viscous glass melt;
- sintering of: − narrow fraction glass powders;
  − glass powders in the presence of blowing agents;
- burn additive method;
- slip technology, polymer matrix duplication method;
- sol-gel technology: − gel foam method,
  − liquation gel separation.

The method used in this paper to obtain the foam glass is based on the sintering of glass powder in the presence of blowing agents.

2. Experimental

2.1. Sample preparation

The glass powder, containing the granulometric fraction under 0.1 mm, was obtained based on tree recycled glass: bottle glass, glassware and window panes. The compositions of the precursor glasses are summarized in Table 1.

The composition of the fly ash released by CET Timişoara thermal power plant is presented in Table 2.

Silicon carbide (ELSIC 98, SC Elsid S.A., granulometric fraction < 0.1 mm) was used as foaming agent because of the control and reproductibility of the foaming properties [14]. The composition of the studied foam glasses are shown in Table 3.

The oxidic composition of the investigated glasses are presented in Table 4

The raw materials were mixed together with 2% ethylenglycol (as binder) and then pressed into cylinders having the diameter and height around 35 mm. The samples were heated in an electrical furnace, the optimal treatment temperature, established from previous studies being 900°C. The heat treatment time together with the ceramic properties of the studied foam glasses are summarized in Table 5.

Table 1

Compoziția oxidică a deşeurilor de sticlă reciclate utilizate / *Oxidic composition of the recycled glasses used as precursors*

Deşeu de sticlă / *Recycled glass*	Compoziție / *Composition* (% gravimetrice / *weight %*)						
	SiO_2	Na_2O	K_2O	MgO	CaO	Al_2O_3	Fe_2O_3
Sticlă ambalaj / *Bottle glass*	72	13	-	1	12	2	–
Sticlă menaj / *Glassware*	75,9	14,46	1,21	–	7,43	1	–
Sticlă geam / *Window pane*	71,86	13,13	0,02	5,64	9,23	0,08	0,04

Table 2

Compoziția oxidică a cenuşii de termocentrală / *Oxidic composition of the fly ash*

Oxid / *Oxide*	Compoziție / *Composition* (% gravimetrice / *weight %*)						
	SiO_2	Na_2O	K_2O	MgO	CaO	Al_2O_3	Fe_2O_3
Cenuşă termocentrală / *Fly ash*	46.2	6.23	4.17	3.3	8.6	23.2	8.1

Table 3

Compoziția sticlelor spongioase sintetizate / *Composition of the studied foaming glasses*

Probă / *Sample*	Deşeu de sticlă / *Recycled glass* [g]			SiC [g]	Cenuşă *Fly ash* [g]
	Sticlă ambalaj *Bottle glass*	Sticlă menaj *Glassware*	Sticlă geam *Window pane*		
S1	80	-	-	10	10
S2	-	80	-	10	10
S3	-	-	80	10	10
S4	70	-	-	10	20
S5	-	70	-	10	20
S6	-	-	70	10	20

Table 4

Compoziția oxidică a sticlelor studiate / *Oxidic composition of the studied glasses*

Probă / *Sample*	Compoziție / *Composition* (% gravimetrice / *weight %*)						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
S1	76.53	2.97	0.77	6.48	0.31	11.61	1.32
S2	74.70	2.24	0.78	10.12	1.09	10.66	0.40
S3	73.45	2.27	0.80	7.85	4.61	10.60	0.41
S4	73.71	5.09	1.54	6.59	0.63	10.83	1.60
S5	72.07	4.48	1.56	9.77	1.31	9.99	0.81
S6	71.02	4.47	1.57	7.79	4.39	9.94	0.81

Table 5

Timpul de tratament termic şi proprietățile ceramice ale probelor studiate
Thermal treatment time and ceramic properties of the investigated glasses

Probă / *Sample*	Timp / *Time* [min]	Porozitate aparentă *Aparent porosity* [%]	Densitate aparentă *Aparent density* [g/cm^3]
S1.1	5	53.31	0.73
S2.1	5	52.33	0.74
S3.1	5	50.10	0.78
S1.2	10	69.15	0.52
S2.2	10	69.48	0.51
S3.2	10	66.96	0.55
S4.1	5	-	-
S5.1	5	-	-
S6.1	5	-	-
S4.2	10	37.77	1.22
S5.2	10	38.80	1.19
S6.2	10	41.23	1.03

2.2. Characterization methods

The shape, size and distribution of the pores in the glass matrix were analyzed by optical microscopy in reflected light, using a Guangzhou L 2020A microscope with digital camera.

The apparent density of the foam glasses was measured using the liquid saturation method under vacuum with water as working liquid.

The hydrolytic stability of the foam glasses was determined according to ISO 719-1985 using 2 grams of glass, having particles size under 500 µm, kept for 60 min in 50 mL de-ionized water at 98°C. 25 mL of the obtained solution was titrated against 0.01 mol/l HCl solution. The volume of HCl needed for neutralization is recorded in order to express the equivalent Na_2O extracted.

The chemical stability of the studied foam glasses was investigated by measuring the ions extraction using leaching tests performed according to the American Extraction Procedure Toxicity Test [15]. This procedure uses de-ionized water as an extractor fluid. The amount of water added was 16 times the amount of sample. The foam glasses were crushed to a particle size of less than 9.5 mm subsequently dried in an oven at 110°C for 24 h.

3. Results and discussions

3.1. Optical microscopy

The obtained foam glasses were sectioned in order to establish the pores dimension and distribution. The microscopic images are shown in Figure 1.

The microscopic images of the first group of samples (S1-S3) shows the influence of the thermal treatment time upon the pores dimensions. The glasses S1.1-S3.1, containing a waste glass:SiC:fly ash weight ratio 80:10:10, after five minutes are well sintered having a foam aspect with smaller (under 100 µm) and relatively uniformly sized pores, improving the homogeneity of porous structure. Doubling the treatment time for theses glasses (samples S1.2-S3.2), leads to rather inhomogeneous microstructures with irregular large pores (mostly over 100 µm) with a high scattering in their size. The second group of samples (S4-S6), containing more fly ash and less glass powder compared to the first ones (waste glass:SiC:fly ash weight ratio 70:10:20), present after five minutes of thermal treatment a lower degree of sinterization reflected in a fragile behaviour. The microscopic images of the samples

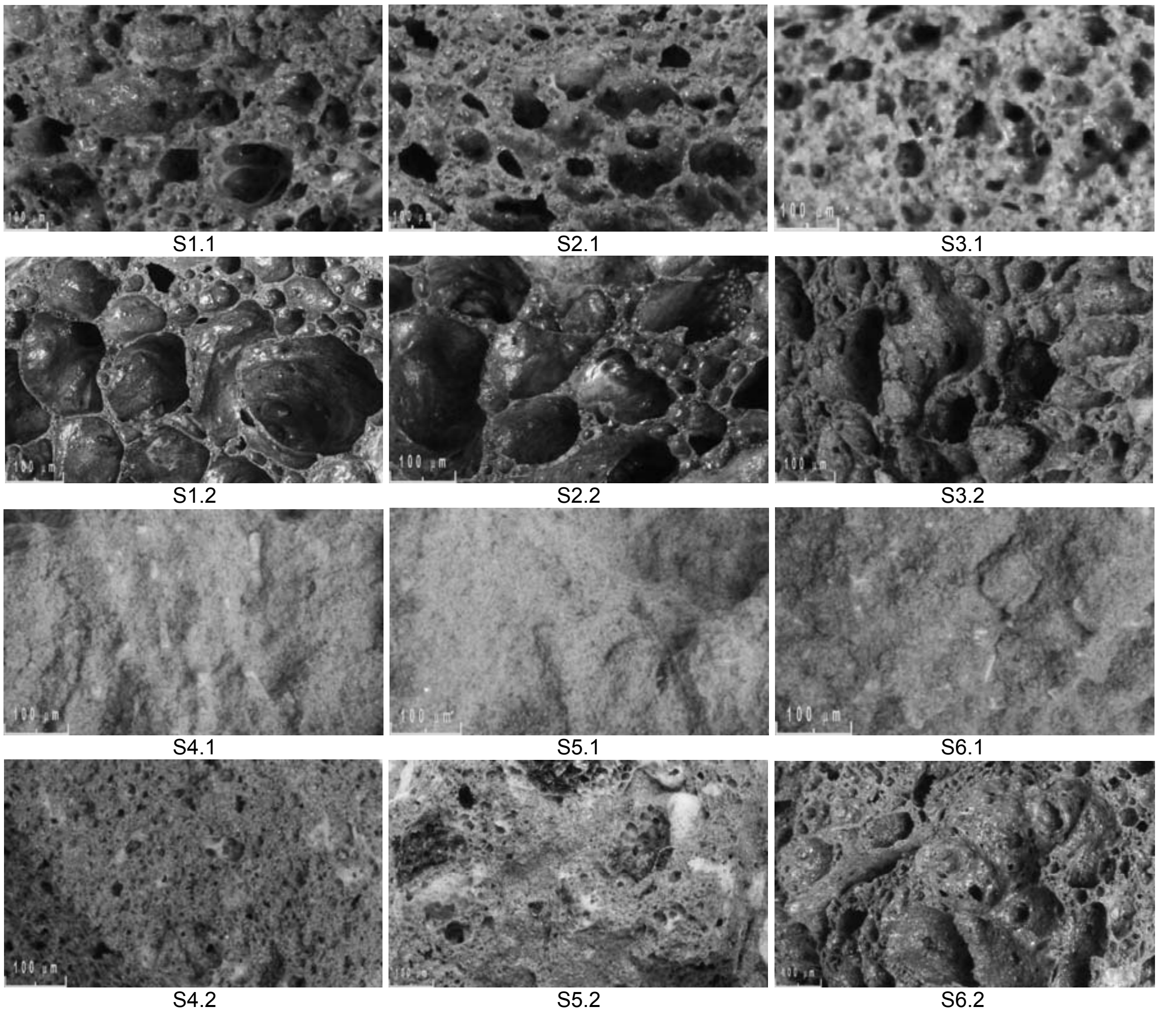

Fig. 1 - Imagini microscopice (lumină reflectată) ale secțiunilor transversale prin sticle .
Microscopic images (reflected light) of samples cross-sections.

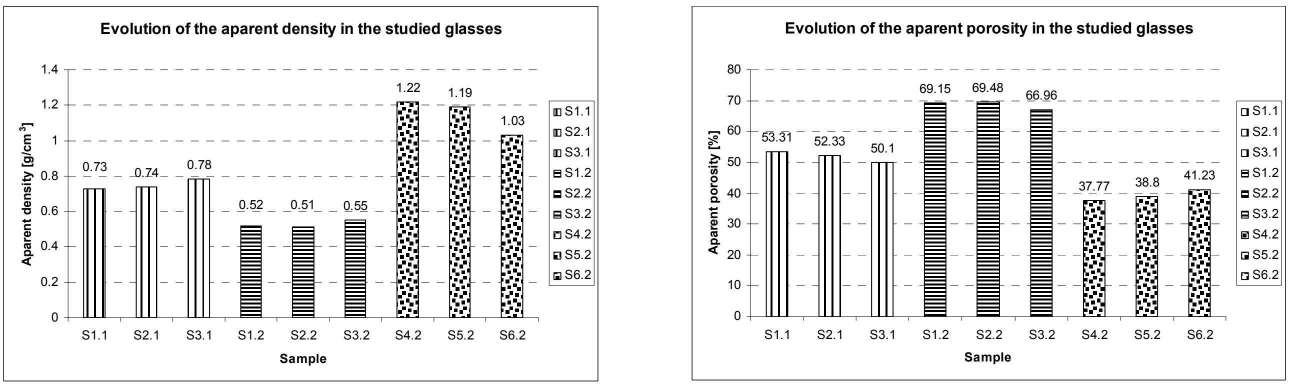

Fig. 2 - Densitatea aparentă şi porozitatea aparentă a sticlelor spongioase studiate / *The apparent density and apparent porosity for the studied foam glasses.*

S4.1-S6.1 shows inhomogenities and cracks, no pores beeing distinguished. After ten minutes, the samples (S4.2-S6.2) are sintered and presents a more homogeneousess porous structure with smaller pores (under 100 μm) for the samples containing bottle glass and more inhomogeneous when glassware wastes were used as precursor. The foam glasses obtained from window panes waste presents larger irregular pores with a scattered dimensional distribution.

3.2. The apparent density and the apparent porosity of glass foams

The results for the apparent density and apparent porosity of the glasses are ilustrated in Figure 2.

The foams sintered at 900°C for 5 minutes (S1.1-S3.1) showed higher values of apparent density (d_{ap} = 0.73–0.78 g/cm^3) and lower aparent porosity values (P_{ap} = 50.1-53.3%), due to denser microstructure. Doubling the heat treatement time (S1.2-S3.2) leads to a more open structure, larger pores and lesser apparent densities (d_{ap} = 0.51-0.55 g/cm^3, P_{ap} = 66.9-69.5%). Using less glass waste and more fly-ash in the second group of samples (S4.2-S6.2), leads to a lower porosity due to a lower retention of gases in the less sintered structures compared with the first group of glasses (d_{ap} = 1.03-1.22 g/cm^3, P_{ap} = 37.7-41.2%). The obtained values for the porosity and aparent density, comparable with those for similar industrial products, qualifiy the investigated glasses as medium-high density insulators.

The S4.1 – S6.1 samples, having a very fragile behavior due to their low sintering degree were excluded from the next investigations.

3.3. The hydrolitic stability of the glass foams

The resistance of the studied glasses toward water aggresivity was analyzed according with ISO 719-1985, the results being summarized in Table 6.

All the investigated glasses belong to the hydrolytic class HGB3. The glasses obtained at a glass waste:SiC:fly ash weight ratio 80:10:10, after five minutes of thermal treatment at 900°C, having a lower sinterization, possess lower resistance to the water attack compared to those heat treated for 10 minutes at the same temperature. The comparable values of the extracted Na_2O from the glasses S1.1-S3.1 and S4.2-S6.2 series having different porosities can be explained based on the fact that the less glass waste quantities from the last glass series did not assure a good encapsulation of the fly-ash particles, more sensible to chemical attack than the glass.

Table 6

Stabilitatea hidrolitică şi clasa de stabilitate corespunzătoare
The hydrolytic stability and the corresponding hydrolytic class of the porous glasses

Probă *Sample*	Echivalent Na_2O solubilizat *Extracted Na_2O equivalent* [µg/g]	Clasa de stabilitate *Hydrolytic class*
S1.1	121	HGB3
S2.1	118	HGB3
S3.1	114	HGB3
S1.2	108	HGB3
S2.2	105	HGB3
S3.2	102	HGB3
S4.2	128	HGB3
S5.2	125	HGB3
S6.2	123	HGB3

3.4. The ions immobilization in the glass foams

The leaching test had a duration of 14 days and 28 days respectively, after which the solid and the liquid were separated by filtration. The lixiviate was chemically analysed using a Varian SpectrAA 110 atomic absorption spectrophotometer. The results are presented in Figure 3.

The lixiviation values are under 0.1% for all investigated ions. The time has a very limited efect on the ion extraction for the S1.1-S3.1 and S1.2-S3.2 glass series. In the foam glasses obtained using a glass waste:SiC:fly ash weight ratio 70:10:20 a sensible increase in Ca^{2+} and Fe^{3+} was registered. This results confirm the assumption of the incomplete glass encapsulation of the fly-ash particles, who introduce the most of the Fe^{3+} ions in the foam glass. None of the ions specified in literature as hazardous and having their emission

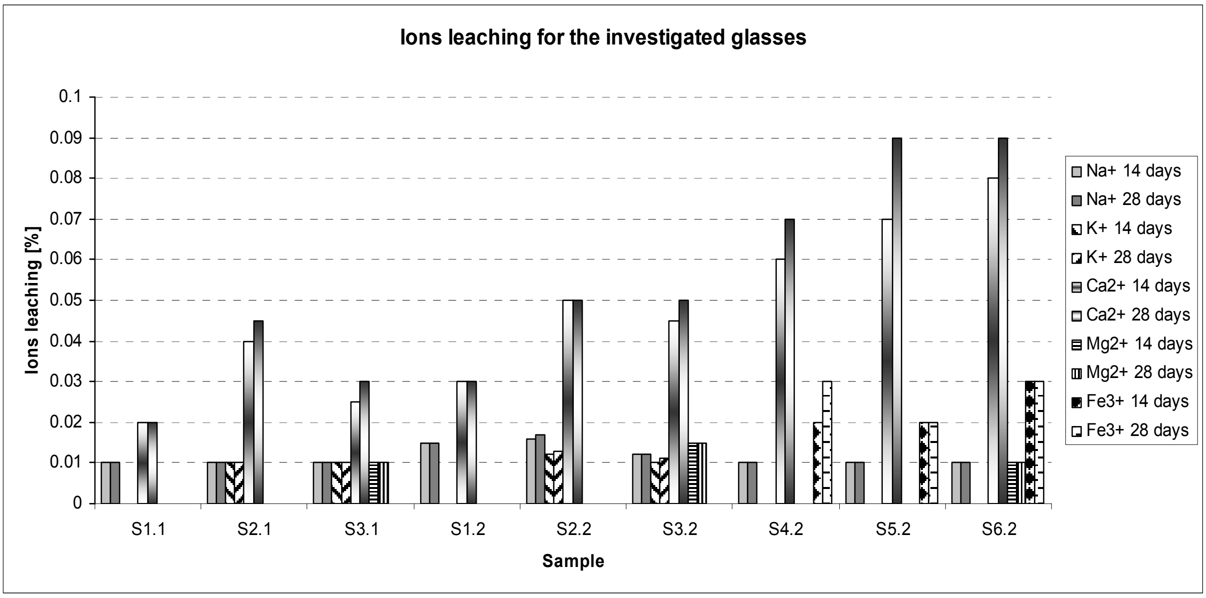

Fig. 3 - Solubilizarea ionilor din sticlele celulare studiate la 14 şi respectiv 28 zile / *Ions leachability for the investigated foam glasses at 14 and 28 days.*

levels limited [16] were identified so that all the studied foam glasses qualified as chemical stable insulator materials.

4. Conclusions

Porous glasses can be obtained using common glass wastes such as bottle glasses, glassware and window panes together with fly-ash and SiC as foaming agent.

The optimal glass waste:SiC:fly ash weight ratio was related with the heat treatment time for a fixed temperature of 900°C. For an 80:10:10 ratio, the increase of the heating time leads to an inhomogeneous microstructures having irregular large pores with a large dimensional distribution. Decreasing the glass waste ratio to 70:10:20 lead to a homogeneous porous structure with smaller pores for the samples containing bottle glass and more inhomogeneous for glassware wastes. The foam glasses obtained from window panes waste presents larger irregular pores having a large scattered dimensional distribution.

The apparent density and apparent porosity of the foam glasses ranged between 0.51-1.22 g/cm^3 and 37-69 % respectively, depending on the thermal treatement and glass composition. A longer heating time generates a more open structure having lower densification, and a higher porosity. Using less glass waste and more fly-ash leads to a lower porosity due to a lower retention of gases in the less sintered and more dense structures.

The hydrolytic stability of the porous glasses qualifies them as HGB3 glasses having a good resistance toward water aggresivity, according to ISO 719-1985. The heat treatment time affects the chemical stability of the glasses by modifying the sintering degree of the porous structure and therefore the glass encapsulation of the fly-ash particles, more sensitive to chemical attack than the glass.

The chemical stability of the studied foam glasses was characterised by measuring the ionic lixiviation according to the American Extraction Procedure Toxicity Test. The very low values of the leaching rate for the Na^+, K^+, Ca^{2+}, Mg^{2+} and Fe^{3+} ions and the complete absence of the other hazardous ions qualifies the all the studied foam glasses as chemical stable insulator materials.

The obtained results confirm the viability of the proposed solution for obtaining medium-high density foam glasses insulators having good chemical stability starting from glass wastes and fly-ash as raw materials.

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