Glass foam experiment with eggshell as foaming agent and red mud as additive material

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Érkezett: 2023. 08. 10. ▪ Received: 10. 08. 2023. ▪ https://doi.org/10.14382/epitoanyag-jsbcm.2023.18

Abstract
Glass foam tablets were produced from green, brown, and white glass bottles, eggshell was used as foaming agent, Na-bentonite as binder and red mad as additive material.
Each tablet was 10 g and contained 2.5% Na-bentonite and 0.1% eggshell and different content of red mud (0-40 wt%), the rest of the mixture was glass powder. The ground raw materials were homogenized and pressed into glass foam tablets at 30 MPa using a hydraulic piston press.
The obtained glass tablets were heat treated at different temperatures. The study shows the chemical compositions of the raw materials, the specimen density of tablets before and after heat treatment, abrasion resistance and falling test of the tablets. From the results it can be concluded that the addition of red mud can reduce the foaming temperature to 800 °C from 900 °C, even at 1 wt% of red mud content. In this case a significant reduction in specimen density was observed from 1.33 g/cm^3 to 0.33 g/cm^3. Since the aim is to have a porous, lightweight product suitable for insulation, the specimen density value is important.
Keywords: recycling, glass foam, glass waste, eggshell waste, red mud, pressure agglomeration
Kulcsszavak: újrahasznosítás, üveghab, üveg hulladék, tojáshéj hulladék, vörösiszap, nyomással történő agglomeráció

1. Introduction

According to the Circular Economy Directive set by the European Union, 75% of glass waste should be recycled by 2035. This rate is much lower in Hungary, based on the latest known data which is 36%. The main cause of the problem in Hungary is that there is no domestic glass factory that would accept the generated amount of glass waste [1]. One way of recycling glass is glass foam. Glass foam production can be incorporated into the circular economy method, since 100% of the glass can be recycled, besides that other type of wastes can be used also during the process, such as eggshell waste and red mud creating high added-value products with less energy and raw material consumption [2].

Environmentally friendly insulation materials such as glass foams are gaining ground due to the wide spread of green technologies. Glass foams are used in the field of thermal and acoustic insulation in the construction industry [3, 4]. Glass foams are porous, lightweight materials (>80 V/V%) of gas and solid phase, they have inorganic chemical structure, relatively low transport costs, and they are easy to handle and combined with concrete [4, 5]. They are made from glass powder and foaming agent. After homogenization of the mixture the next step is heat treatment at high temperature in the range of 700-900 °C [6]. During the heat treatment the furnace reaches higher temperatures where gas formation occurs, and the glass viscosity is less than 106.6 Pa.s. The particles of the foaming agent are wrapped by the softened glass until the decomposition or reaction temperature of the foaming agent is reached, and releases gases that form bubbles in the softened glass. The glass viscosity and the surface tension decrease with the increasing temperature. The glass decreases the pressure over the gas bubbles and increases the expansion, which leads to the coalescence of the pores because of surface tension reduction [7, 8].

The combination of these properties makes glass foam suitable for a large-scale of applications in the construction industry.

Most of the glass waste is derived from mixed container glass bottles, window glass, or other types of glasses such as cathode ray tubes (CRT) in industrial glass foam production [9-11].

The goal of this paper is to produce high-added-value products with low-cost raw materials such as recycled glass bottles, eggshell waste, and red mud.

2. Materials and methods

Different colors of container glass bottles were used as the basis for glass foam tablets, eggshell waste as foaming agent, Na-bentonite as binder material and red mud as additional material. The main constituent of eggshell is calcium carbonate (94-96 wt%), and due to the high carbonate content, it is suitable for foaming because CO_2 is generated during the thermal decomposition of calcium carbonate at high temperature, which cause the forming porous structure of glass foam tablets. Several studies showed [12-15], that if red mud which is an alkaline leaching waste was added to the glass foam ceramics lower temperature was required during the foaming process, so in the end of the production less energy consumption required. Short terms used for sample materials in results and discussion part: ES – eggshell and RM – red mud.

The glass was prepared by crushing with a roll crusher with a screen size of 1 mm, then milling with a ball mill using stainless steel balls (Ø 20 mm) for 180 min under dry conditions to achieve the optimal particle size of the glass, which is < 100 µm because in other cases the foaming process will not be sufficient [16-19].

The foaming agent was milled for 120 minutes in a ball mill under dry condition with ceramic grinding balls (Ø 30 mm), and in the case of binder material and red mud which was additional material; no grinding was required because their particle size was in the fine size range. It was necessary to remove the organic content of the eggshell before milling, so it was heat treated in boiling water for 30 minutes.

Chemical compositions of glass powder, eggshell and red mud were measured by X-ray fluorescence (XRF) analysis.

The raw materials were sieved through a 32 µm opening sized sieve under wet conditions. This was necessary for each material to fall in the same size range, so the pore structure of the glass foam tablets was homogeneous.

The ES as foaming agent was added to the glass powder in 0.1 wt% and 2.5 wt% Na-bentonite as a binder material. The RM as additive was added to the tablets in different ratios: 0% (this contained only ES), 1 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%. The rest of the mixture were glass powder depended on the foaming agent, additive material, and binder material ratios. The tablets were prepared with a hydraulic piston press at 30 MPa pressure. Each tablet was 10 g.

The obtained raw tablets were heat treated in Nabertherm L (T) 3 laboratory static furnace at different temperature (700 °C, 800 °C and 900 °C) with 120 minutes residence time (furnace heating time 90 min +30 min residence time) using different heating rate (7,66 min, 8,77 min, 10 min).

The specimen density (ρ_s) of the tablets before and after heat treatment was determined by their geometrical measurements, using a calliper and their masses with an analytical balance.

The abrasion resistance of the products was measured in a laboratory ceramic-lined mill. 30 g from each RM ratio were tested. The 30 grams of material remained in the machine at 30 rpm for 10 minutes, and after removing the material, the fine fraction was sieved using a sieve with 1 mm opening size. From the mass of the fine fraction and the feeding material, the degree of abrasion was calculated using *Eq. 1*, where Δm_{abr} is the amount of abrasion (%), m_{fine} is the amount of material passed through the 1 mm sieve (g), and m_{feed} is the feeding material (30 g).

$$\Delta m_{abr} = \frac{m_{fine}}{m_{feed}} \cdot 100[\%] \qquad (1)$$

For each of the RM contents, falling test was carried out to test the strength of the tablets. Each tablet was dropped from a height of 2 m with its edge until it broke, the number of drops was recorded.

3. Results and discussion

3.1 XRF results

Table 1 shows the chemical composition of the raw materials.

Eggshells have a high content of CaO which leads CO_2 formation during the foaming process. Glass contained high amounts of SiO_2, CaO and Na_2O. These results showed that these are typical soda-lime glasses. Red mud was Al- and Si-rich material because according to the results had a relatively high SiO_2 and Al_2O_3 content.

3.2 Density measurements

At 700 °C, it is clearly visible that the specimen density was reduced minimally compared to the pre-foaming condition, no significant foaming was observed (*Fig. 1*). At 800 °C and 900 °C, a significant decrease in specimen density occurred for tablets containing 0-5 wt% RM (*Fig. 2-3*). The addition of RM was done to reduce the temperature demand and thus make the process more energy efficient. From the results it can be concluded that RM is an effective additive material to decrease the temperature.

At both temperatures, the tablets containing 5 wt% RM had the lowest specimen density, 0.38 g/cm^3 (at 800 °C) and 0.35 g/cm^3 (at 900 °C).

The only significant change was seen in tablets containing 0 wt% RM, which contained only foaming agent. These tablets foamed at 800 °C but their specimen density was only 0.98 g/cm^3, but after RM addition the value decreased to 0.47 g/cm^3, even with 1 wt% addition. However, when 5 wt% RM was added to the tablets, the specimen density further decreased to 0.38 g/cm^3. For tablets with RM content above 10 wt%, it was observed that their specimen density also increased linearly with the increasing RM content. This was observed in all temperature ranges, which clearly shows that the sintering intensity decreases with RM content above 10 wt%.

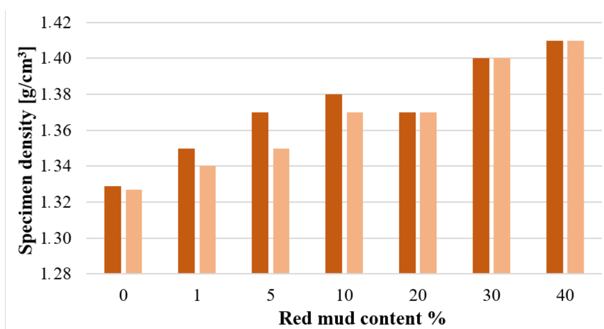

Fig. 1 Specimen density of tablets prepared at 700 °C before (dark orange) and after heat treatment (light orange) according to RM content

1. ábra A 700 °C-on készített tabletták testsűrűsége hőkezelés előtt (sötét narancssárga) és hőkezelés után (világos narancssárga) vörösiszap arány szerint

	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	Fe_2O_3	MnO	TiO_2	P_2O_5	S	F	LOI
Unit	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%	$^m/_m$%
ES	0.3	0.0	0.62	54.4	0.13	0.13	0.03	0.001	0.002	0.499	0.21	<0.3	45.71
Glass powder	73.6	1.2	2.25	9.89	11.9	0.62	0.47	0.008	0.049	0.014	0.20	<0.3	-
RM	16.10	17.90	1.66	8.50	9.98	0.08	35.10	0,31	4.08	1.39	1.59	<0.3	12.8

Table 1 Chemical composition of raw materials

1. táblázat A nyersanyagok kémiai összetétele

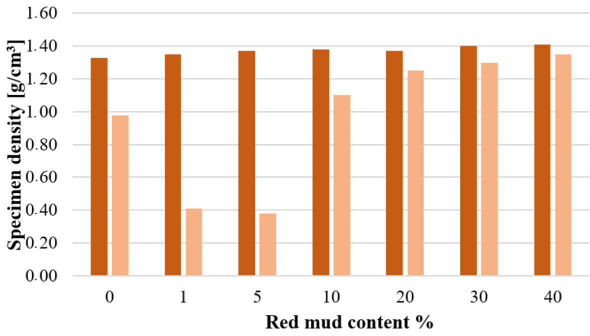

Fig. 2 Specimen density of tablets prepared at 800 °C before (dark orange) and after heat treatment (light orange) according to RM content
2. ábra A 800 °C-on készített tabletták testsűrűsége hőkezelés előtt (sötét narancssárga) és hőkezelés után (világos narancssárga) vörösiszap arány szerint

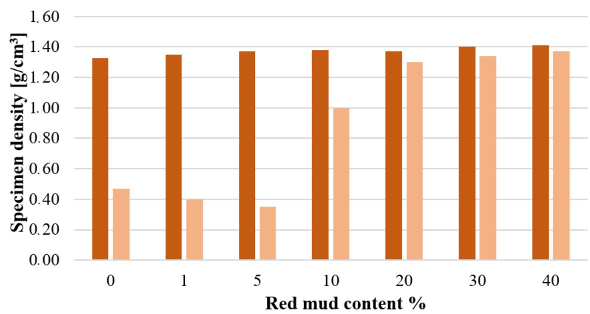

Fig. 3 Specimen density of tablets prepared at 900 °C before (dark orange) and after heat treatment (light orange) according to RM content
3. ábra A 900 °C-on készített tabletták testsűrűsége hőkezelés előtt (sötét narancssárga) és hőkezelés után (világos narancssárga) vörösiszap arány szerint

3.3 Abrasion test

The tablets with higher RM content showed higher abrasion, even though the abrasion rate was basically negligible for tablets. For the tablets containing only foaming agent, the highest abrasion was at 900 °C because the foaming mechanism was the highest level in this case in the three temperature ranges, where the specimen density was the lowest. This trend was also observed for the 1 and 5 wt% RM tablets. The smallest abrasion value was observed for the 10 and 20 wt% RM tablets at 700 °C, but there the foaming was not significant. This was followed in turn by tablets containing 1 wt% RM at 800 °C, where a significant decrease in specimen density was already observed compared to the density before heat treatment (*Fig. 1*). Overall, it can be concluded from the abrasion resistance test that the abrasion rate was below 2% at all temperatures.

Tablet type	Abrasion resistance value (%)		
	700 °C	800 °C	900 °C
0.1% ES	0.85	0.82	0.90
1% RM	0.78	0.72	0.74
5% RM	0.80	0.90	0.95
10% RM	0.70	0.78	0.75
20% RM	0.70	0.73	0.76
30% RM	0.80	0.81	0.79
40% RM	1.00	0.88	0.90

Table 2 Abrasion resistance values at different temperatures for each RM content
2. táblázat Kopásállóság értékei különböző hőmérsékleten az egyes vörösiszap tartalmak esetében

3.4 Falling test

From the falling test, the 700 °C tablets broke the fastest compared to the 800 °C and 900 °C tablets. It can be clearly seen from the results that tablets at 800 °C broke later at 1-10 wt% RM content than tablets at 900 °C, this may be since the decrease in specimen density was greater at 900 °C and thus greater foaming occurred, resulting in less compacted tablets and thus less breakage. The best value was obtained at 800 °C with 5 wt% RM, where the tablets withstood 20 falls, and at 900 °C, also with 5 wt% RM, with a value of 16 falls without breakage. It was observed that above 10 wt% RM the tablets broke sooner overall for all three temperature ranges. They were less mechanical resistant than tablets with less RM content, despite the higher foaming rate, resulting in a more porous structure, which could be a reason for the tablets breaking sooner.

Dropped tablet	Number of drops		
	700 °C	800 °C	900 °C
0.1% ES	8	12	12
1% RM	9	16	13
5% RM	10	20	16
10% RM	9	11	10
20% RM	7	10	7
30% RM	8	9	8
40% RM	7	10	8

Table 3 Falling test results for tablets prepared at different temperatures for each RM content
3. táblázat Ejtési vizsgálat eredményei különböző hőmérsékleten az egyes vörösiszap tartalmak esetében

4. Conclusion

From the preliminary experiments it can be concluded:

1. At 700 °C with 7.66 °C/min heating rate the specimen density of the tablets decreased minimally.
2. In the case of 800 °C and 900 °C with 8.77 °C/min and 10 °C/min heating rate the specimen density of the tablets containing 0-5 wt% RM significantly decreased because of the higher level of foaming.
3. Above 10% RM content, the tablets broke earlier during the falling test, so adding higher content of RM reduces mechanical strength of the tablets.
4. In addition, it was observed that tablets made at 900 °C with 0-5 wt% RM content broke earlier than those made at 800 °C, due to the higher foaming, even though there was no significant difference in specimen density reduction between the two temperatures. It can be concluded from the abrasion resistance test that the abrasion rate was below 2% at all temperatures.
5. The only significant difference between the tablets prepared at 800 °C and 900 °C was that although the tablets contained 0 wt% RM (contained only foaming agent). The resulting specimen density was significantly lower at 900 °C and foaming was more intense at 800 °C, which leads to the conclusion that the addition of RM can reduce the temperature demand and thus make the process more energy efficient.

5. Acknowledgement

„Supported by the ÚNKP-22-3 New National Excellence Program of the Ministry for Culture and Innovation from the Source of the National Research, Development and Innovation Fund."

Új Nemzeti Kiválóság Program

Kulturális és Innovációs Minisztérium

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Ref.:
Fóris, Ildikó – **Mucsi**, Gábor: *Glass foam experiment with eggshell as foaming agent and red mud as additive material*
Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 75, No. 4 (2023), 132–135. p.
https://doi.org/10.14382/epitoanyag-jsbcm.2023.18