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# Fabrication of Foamed Glass by Valorization of Ferrochromium Slags and Flint Container Glass Waste

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## Abstract

Ferrochromium processes generate a vast quantity of ferrochromium slags which are accumulated in landfills. Not only economical uselessness but also detrimental environmental effects occur due to the accumulation of these wastes in nature. In the present study, based upon great opportunity of utilization of different waste materials in foam glass systems, the ferrochromium slags, supplied from Antalya ETİ Elektrometalurji Inc., with varying amounts of 10, 20 and 30 in wt.% were added in flint container glass (soda-lime-silica) waste obtained from municipal waste storage. A mixture of water glass and glycerol was also used as foaming agent while sufficient content of water was included as moisturizer in batch mixture. The samples were heated to the temperature of 850 °C with the heating rate of 10 °C/min, and then were kept for 30 min at the peak temperature. The valorisation of ferrochromium slags in foam glass systems were successfully fabricated by evaluating the properties of bulk density, porosity, water absorption and compressive strength. The results have a promising aspects and serve as a basis for advances in waste derived products to foster circular economy model in the perspective of zero waste. Further, a lightweight foam glass having 0.365 g/cm$^3$ of bulk density with satisfactory mechanical properties having 1.48 MPa of compressive strength can be used in building applications.

**Keywords:** Ferrochromium slags; Flint container glass waste; Foamed glass; Lightweight materials; Waste valorisation.

## 1. Introduction

Recently, waste management strategies from the perspective of the circular economy model and environmental sustainability have been identified as significant paradigms. In general, hazardous solid waste materials have been accumulated in landfills which causes to face with contamination into soil and groundwater [1]. These solid waste materials are originated from industrial processes such as metallurgy, mining or energy production plants [2]. In particular, metallurgical processes generate a great number of slags that are uselessly deposited in landfills, and ferrochromium slags which are emerged as a result of ferrochromium production are one of the most crucial waste material.

Ferrochromium has extensively been used in stainless steel production. As the stainless steel industry is enlarged to meet the demand, the ferrochromium industries are concurrently forced for higher production rates. Ferrochromium is produced by carbothermic reduction processes and the resultant slag amount is about 1.1 to 1.5 times that of ferrochromium metal produced. Under these circumstances, approximately 12 to 16 million tonnes per year ferrochromium slags are emerged in worldwide [3]. In Turkey, Elazığ and Antalya that are the important ferrochromium production plants actively operates to meet the demand [4], [5]. Annually, 1 to 2 million tonnes of ferrochromium are produced. From the point of emerging slag view, for instance, Antalya production plant causes to originate 100K tonnes of slags per year [4]. Although several tentative attempts have been made to utilize these slags in asphalts, construction applications or refractory industries almost no sustainable actions for the circular economy model have managed, yet [6], [7], [8].

In recent years, glass materials have excessively been taken attention due to being environmentally friendly material. Because glass materials can easily be reused or recycled without causing any harmful effects to nature or community health. More effectively and strangely, glass waste materials can be able to be produced as foamed glasses under favorable conditions. As an emerging kind of construction and building material, foamed glasses, provide great advances including utilization of various hazarous solid waste materials inside while ensuring unique technical properties like being lightweight, thermally insulating, mechanically strength, chemically inert and resistance to vermin, etc. [1]. Perhaps, the most striking feature of foamed glasses is the low cost of production routes, namely composed of a great deal of solid waste materials.

Many researchers have studied foamed glasses by adding different solid waste materials such as iron tailings, fly ashes, blast furnace slags, bricks and clays, etc. At this point, Kahina et al. [9] studied bricks and clay solid wastes in float glass waste to produce foamed glass while H. Yin et al. [10] produced a foamed glass composed of iron tailings and soda-lime glass. Likewise, M. Zhu et al. [11] focused on valorization of fly ashes in foamed glass by utilizing container glass waste whereas L. Ding et al. [12] added value on blast furnace slag utilization in E-glass to fabricate foamed glasses. Not only fabrication of foamed glasses is intended but also the effect of chemical composition variations due to unstable constituent amounts of solid waste materials and the influence of various foaming agents were examined by J. König et al. [13], J. Li et al.[14], R.R. Petersen et al.[15], Kavas et al. [16], etc. All in all, scientists and researchers have put great efforts to utilize hazardous solid waste materials by transforming them into a value-added products.

The present study aims to fabricate a foamed glass by the valorization of ferrochromium slags and flint container glass waste to be used as building material. Preliminary results on addition of varying amounts of ferrochromium slags in foamed glasses were given by revealing bulk density, porosity, water absorption and compressive strength.

## 2. Material and Method

### 2.1. Material

The ferrochromium slags supplied from Antalya Eti Elektrometalurji, Inc. have a roughly chemical composition of $33.5SiO_2$-$0.5Cr_2O_3$-$45CaO$-$12MgO$-$8Al_2O_3$-$1Fe_2O_3$. The waste flint container glass collected from Afyonkarahisar/Turkey municipal solid waste storage area has a typical chemical composition of $71.5SiO_2$-$14.2Na_2O$-$7.9CaO$-$4.1MgO$-$1.7Al_2O_3$-$0.05Fe_2O_3$ *and the others* in wt%. The glycerol was supplied from Talya Glicerina Company (Lot No.: 8682) while water glass (sodium silicate) was purchased from Merck Company (No: 105621.2500). Water was used as demineralized.

### 2.2. Method

The supplied ferrochromium slags were initially separated by coning methodology, and then four pieces were separated. The representative sample were obtained as 100 grams. Sieving operation was then performed to get particle size of lowering than 63 microns. The flint container glass waste was firstly washed in a water tank followed by drying operation in an oven at 105 °C for 4h. Then, the glass sample was wrapped with a paper towel and crushed with a 4-kg hammer by hand. The fractured pieces were carefully collected and put in a porcelain jar including alumina balls for being ground at 125 rpm for 1h. After that, the sieving operation was performed to obtain a particle size of lowering than 125 microns. The glycerol and sodium silicate was used as received.

As soon as the constituents of the present study were made ready, the sample preparation stage was followed. Table 1 shows the batch design of foamed glass fabrication. A mixture of water glass and glycerol was used as particle enveloping and foaming agent, respectively while sufficient content of water was included as moisturizer in the batch mixture. The amounts of water glass, glycerol and water were chosen with respect to the studies experienced by [17], [18]. As can be appreciated from Table 1 that sample S1 has 10% of ferrochromium slag content (in total solid amount) whereas samples S2 and S3 have 20% and 30%, respectively. The amounts of glycerol, water glass and water were kept constant in order to observe the effects of ferrochromium addition.

Table 1. Batch design of samples produced.

| **Constituents (wt. %)** | **S1** | **S2** | **S3** |
|---|---|---|---|
| **Glass Waste** | 81 | 72 | 63 |
| **Ferrochromium Slag** | 9 | 18 | 27 |
| **Water Glass** | 6 | 6 | 6 |
| **Glycerol** | 3 | 3 | 3 |
| **Water** | 1 | 1 | 1 |
| **Total** | 100 | 100 | 100 |

For the preparation of foamed glass samples with respect to batch designs, firstly, the weighing stage was precisely completed to fulfill 10 grams of each sample. Later, the mixing step was carried out in a rotary mill at 125 rpm for 1h to obtain homogeneous mixture. Afterward, the mixture was poured into cylindrical mold to prepare samples having a diameter as 27-mm and height as 10 mm. Uniaxial pressing was performed at 0.6 MPa and the cylindrical samples were obtained. After drying at 105 °C for 4h, the pellets were heated to 850°C with a heating rate of 10 °C/min and kept at the peak temperature for 30 min in a conventional electrical resistance furnace. Finally, the samples were cooled down to ambient temperature without applying any cooling rate trend.

### 2.3. Characterisation

For cystallographic determination, X-ray diffraction (XRD) analysis with a Cu-Kα radiation source and a voltage of 40 kV with ampere of 30 mA was carried out via Bruker D8 Advance (Afyonkarahisar, Turkey). The measurements were performed in the range of 2 to 80° by applying step size of 0.02°. The powdered samples having a particle size of lowering than 63 microns were analyzed.

Thermogravimetric (TG) and dilatometric thermal analysis (DTA) were performed to determine wieght losses and thermal behaviour of flint container glass waste by using NETZSCH (STA 449F3, Eskisehir/ Turkey) device. In this test, the powdered samples were put in small platinum crucible and the test temperature range was defined as 20 to 1200 °C by applying a heating rate of 25 °C/min under nitrogen atmosphere. Further, for determination of mass change and thermal characteristics of ferrochromium slags at high temperature, the thermogravimetric (TG) and differential scannig calorimeter (DSC) analysis were conducted via NETZSCH (STA 449F3, Afyonkarahisar/ Turkey). In the test conditions, the powdered sample (6.85 g) were placed in a small alumina crucible and the temperature range was adjusted from 20 to 1450 °C with a heating rate of 20 °C/min under air atmosphere.

The bulk density measurement was determined by applying Archimede's principle in demineralized water. After three times repetition was performed on density measurements the readings were recorded so as to calculate bulk density of foamed glass samples by using mass to volume ratio. The water absorption of samples were specified by immersing samples into boiling water by providing free circulation of water all around the specimen at 105 °C for 4h. Subsequently, the cooling was performed through room temperature, naturally. The equations (I) and (II) were used to calculate the percentage of porosity (P%) and water absorption (WA%) where $W_d$ is the weight of water absorbed sample in air, $W_k$ is the weight of dry sample in air and $W_a$ is the weight of water absorbed sample in demineralized water.

$$P\% = [\ (W_d - W_k) / (W_d - W_a)\ ] \qquad \text{Eqn. (I)}$$

$$WA\% = [(W_d - W_a) / W_k\ ] \times 100 \qquad \text{Eqn.(II)}$$

Mechanical properties of samples produced under the compressive strength were investigated by conducting a compression test via a universal mechanical test device (Shimadzu AG IS 100 kN, Afyonkarahisar/Turkey). The loaded surfaces of samples were gently ground to obtain a flat and smooth surface for achieving uniform distribution over the surfaces. Additionally, a mobile phone camera capable of 12 megapixels was used to capture macro images of foamed glasses under ambient light.

## 3. Results and Discussion

### 3.1. Crystallographic Analysis

The crystallography of starting materials is very essential that affect the resultant material properties of foamed glasses due to the fact that amorphous structure provide lower thermal conductivity which leads to obtain, for instance, better insulation building materials. According to the XRD analysis given in Fig. 1, the ferrochromium slag is mainly amorphous while several crystalline phases including sergeevite (calcium magnesium carbonate hydroxide hydrate), magnesiochromite and donathite (iron magnesium chromium oxide) formed. The crystal phase of sergeevite can somehow be occurred due to rapid cooling of ferrochromium slag whilst magnesiochromite and donathite, as a group of spinel, can be formed in consequence of eventual low cooling [19].

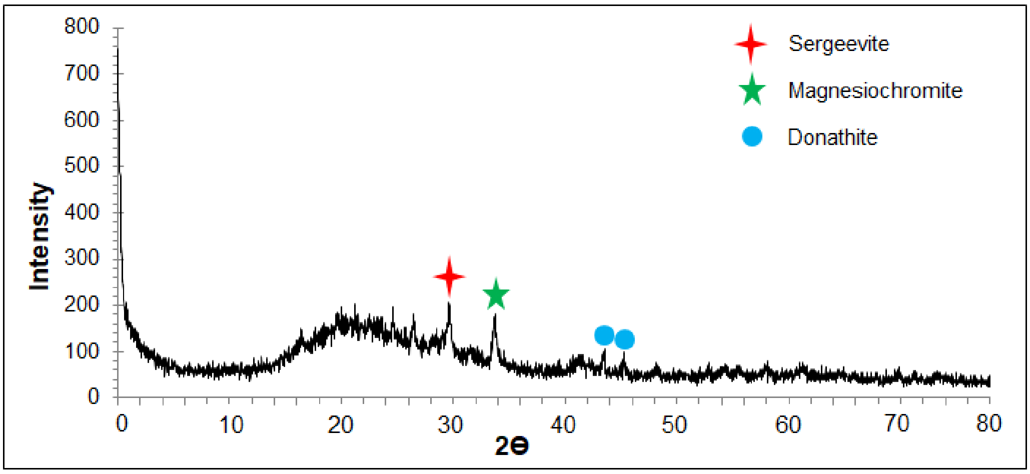

Fig. 1. X-Ray Diffraction Pattern of Ferrochromium Slag.

### 3.2. Thermal Analysis

The thermal analysis conducted on flint container glass waste was given in Fig. 2. From the mass change curve, it indicated that a slight weight loss, 0.67%, occurred due to the burning of organic impurities present in the waste. Moreover, it can be deduced that the endothermic peak at 612 °C can be referred as quartz transformation while the endothermic peak at 1012 °C is meant to starting of glass melting.

The thermal analysis performed on ferrochromium slags was shown in Fig. 3. In weight loss curve, it can be seen that 13.83% mass change occurred. From 20 to 200 °C, nearly 5% of weight loss was caused by physical water and some organics whereas other volatiles like carbonates were decomposed from 400 to 1450 °C. From the DSC curve, the first peak at 170 °C, can be attributed to the physical water loss as well as moisture on the ferrochromium slag. The second and third peaks at 510 °C and 790 °C reflects exothermic and endothermic processes, respectively. Afterward, there occurred almost no reaction from 800 to 925 °C, and then decomposition of various species, occurrence of minor phases as well as partial melting of the ferrochromium slag components took place.

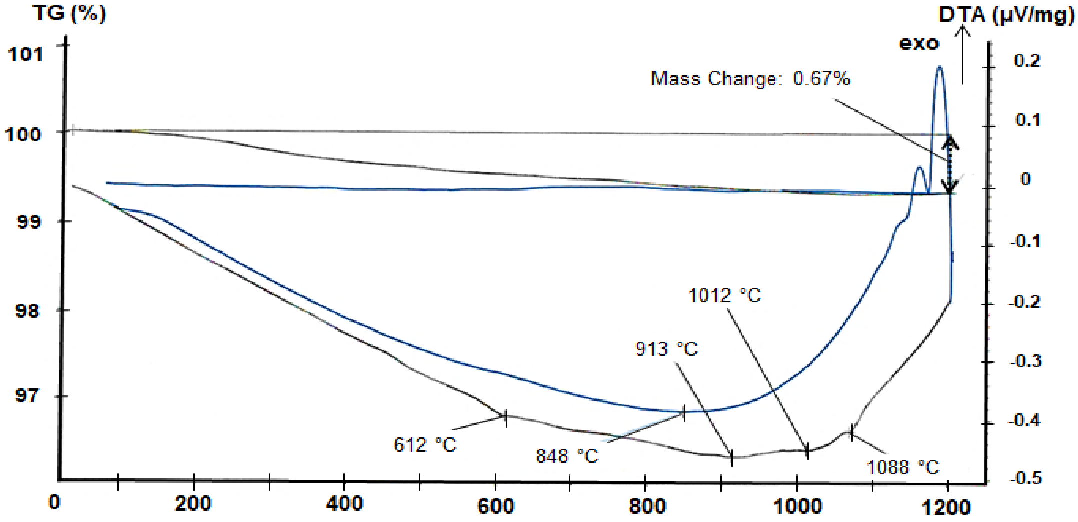

Fig. 2. TG&DTA analysis of flint container glass waste.

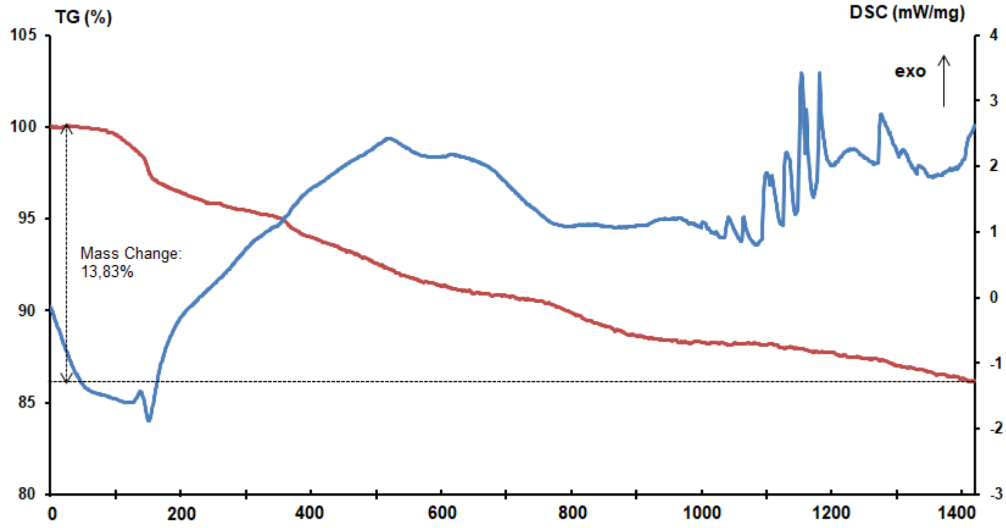

Fig. 3. TG&DSC analysis of ferrochromium slags.

### 3.3. Physical Analysis

The foamed glass samples were successfully produced and revealed in Fig. 4 and Fig. 5. As can be appreciated from the figures that a good expansion was achieved compared to the initial pellet (Ø as 27-mm and height as 10-mm). That is to say, almost three times higher expansion was obtained. However, as the amount of ferrochromium in foam glass is increased the foaming ability is unfavorably affected.

Fig. 4. The top-view of foamed glass samples produced (from left to right: S1, S2 and S3).

Fig. 5. The front-view of foamed glass samples produced (from left to right: S1, S2 and S3).

The results of bulk density (g/cm$^3$) and porosity (%) measurements are given in Fig. 6. According to Fig. 6, the bulk density values were found as 0.365, 0.405 and 0.569 g/cm$^3$ for S1, S2,and S3 samples, respectively. The bulk density values are low enough to meet the lightweight demand. However, as the amount of ferrochromium slag is increased in foamed glass, from S1 to S3, the bulk density value increases. This is because the crystalline phases of ferrochromium slags like magnesiochromite or donathite inhibit the expansion of foamed glass. The optimum content of ferrochromium slags, therefore, can be attained as a maximum 20 wt.%. For porosity aspects of foamed glasses, 84, 81 and 74 % values were obtained for S1, S2,and S3 samples, respectively. As the content of ferrochromium slag is increased in foamed glass, from S1 to S3, the porosity percentages are diminished. As inversely correlated with bulk density, porosity percentages are decreased due to inefficient expansion characteristics of crystalline phases held by ferrochromium slags. As known well, the higher the porosity percentage of foamed glass, the lower the bulk density values obtained which lead to have lightweight properties. Hence, the amount of ferrochromium slags in foamed glass lowering than 20 wt% provides lower bulk density with higher porosity aspects in this study.

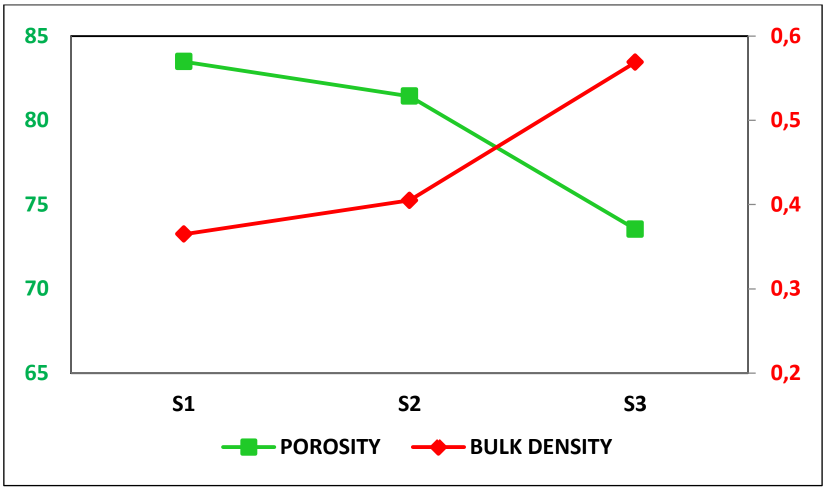

Fig. 6. The results of bulk density and porosity measurements.

The water absorption (%) and compressive strength (MPa) results are shown in Fig. 7. As can be seen from Fig. 7 that both water absorption and compressive strength are increased as the content of ferrochromium slags are introduced into foamed glasses. Namely, 12, 25 and 71 % of water absorption were obtained whereas 1.48, 1.25 and 1.19 MPa were measured for S1, S2, and S3 samples, respectively. For instance, to gain better heat insulation properties, closed pores should be included in foamed glasses rather than opened pores. In this case, since water absorption percentages are increasing by adding ferrochromium slags the opened pores are being created in the structure which deteriorates heat insulation property. On the other hand, relatively high mechanical property is desired from insulation material. At this point, increasing amounts of ferrochromium slag ensured to obtain higher compressive strengths in the produced samples. The reason behind this increment can be expressed as crystalline phases from ferrochromium slags. As a result, this study showed that the addition of ferrochromium was limited to some extent that closed pores could form with a 20 wt%.

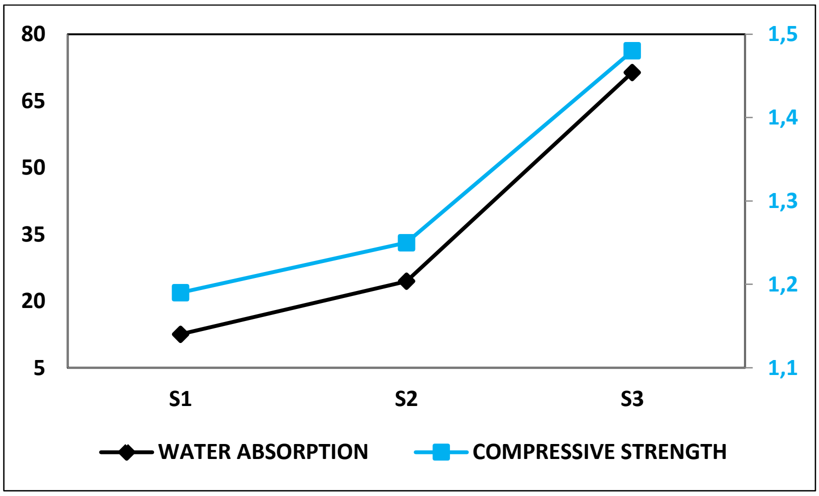

Fig. 7. The results of water absorption and compressive strength measurements.

Bulk density values lowering than that of liquid media used conclude up with floating samples. In this study, since bulk density values are very lower than that of demineralized water the foamed glass samples float on the water surface as given in Fig. 8. Even though water absorption percentages are relatively high the produced samples continued to float in water.

Fig. 8. Floating foamed glass samples in demineralised water (from left to right: S1, S2 and S3).

### 3.4. Macrostructure Images

After conducting the above mentioned analysis, the macrostructure images were captured as seen in Fig. 9. In all images, red circled areas revealed inhomogeneous regions as well as non-uniform pore distributions. From images of "a" to "c", meaning that S1 to S3, the pore sizes started to get bigger while non-uniformity in pore distribution occurred. In addition to this, opened pores were generated as ferrochromium slag content was increased from S1 to S3. Most particularly, S2 and S3 foamed glass samples had approximately 6 mm pore sizes in the side of the surface. This phenomenon is also proved by Fig. 4 that several swelling pores can sharply be seen. For the obtainment of well-distributed closed pores in foamed glasses, the study showed that a maximum of 10 wt% of ferrochromium can be introduced with respect to macrostructural images.

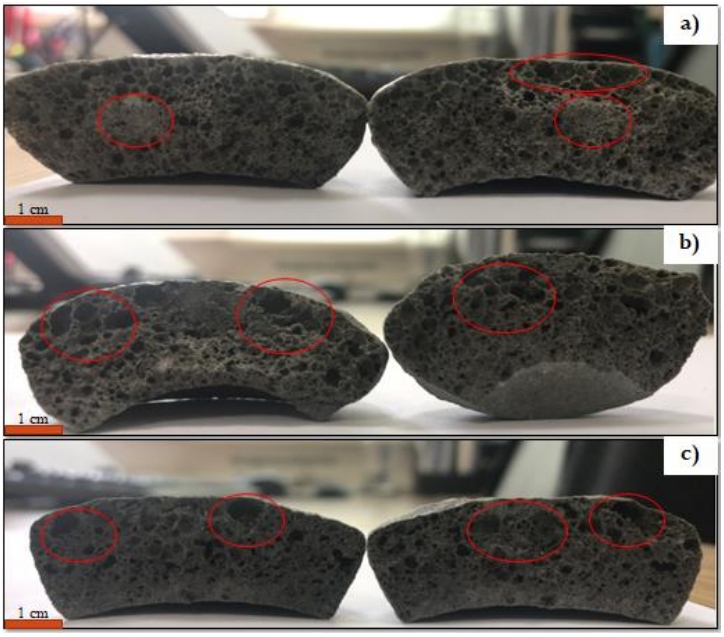

Fig. 9. Macro images of foamed glasses produced (from top to bottom: a); S1, b); S2 and c); S3).

### 3.5. A comparison with other studies

To make sense of the findings of the present study, Table 2 comprises the results of a number of studies included in literature as well as a commercially available product. As can be seen that various solid waste materials were utilized to produce foamed glasses. Although types of solid waste used and foaming agents differ from each other the results are pretty much comparable. That is, H. Yin et al. found out reasonable bulk density values as 0.22 to 0.42 g/cm$^3$ while obtaining relatively low compressive strength. On the other hand, M. Zhu et al. come up with satisfying consequences for both bulk density and compression strength whereas Kahina et al. reached up to 0.60 to 1.10 g/cm$^3$ bulk densities. More essentially, a commercially available product of Foamglas® has superior properties like very low bulk density values with notably porosity percentages combined with favorable mechanical strengths. Nevertheless, the present study has a promising aspect and serve as a basis for advances in waste-derived products.

Table 2. A comparison of the present study and other studies & commercially available product (N/A: Not Available Information).

| **Reference Study** | **Our Study** | **Foamglas®** [20], [21] | **Kahina C. et al.** [9] | **H. Yin et al.** [10] | **M. Zhu et al.** [11] | **Z. Li et al.** [22] | **L. Ding et al.** [12] |
|---|---|---|---|---|---|---|---|
| **Type of waste glass** | *Container* | SodaLime | Float | SodaLime | Container | Waterglass | E-glass |
| **Type of solid wastes** | *Ferrochromium slags* | N/A | Bricks & Clay | Iron tailings | Fly Ashes | Coal Gangue | Blast furnace slag |
| **Foaming Agent** | *Glycerol* | Carbon Black | $CaCO_3$ | SiC | $CaCO_3$ | $CaCO_3$ | $CaCO_3$ |
| **Foaming Conditions** | *850 °C*<br>*30 min* | N/A | 850 °C<br>15 - 30 min | 810-860°C<br>30 min | 600-800 °C<br>45 min | 1120 °C<br>60 min | 950 °C<br>120 min |
| **Porosity (%)** | *73 - 83* | 85 - 95 | N/A | 82 - 92 | N/A | 69 - 73 | N/A |
| **Bulk density (g/cm³)** | *0,36 – 0,56* | 0,10 – 0,30 | 0,60 - 1,10 | 0,22 – 0,42 | 0,46 | 0,59- 0,68 | 0,79 |
| **Compressive Strength (MPa)** | *1,2 – 1,5* | 0,40 – 6,00 | N/A | 0,53 | 5 | N/A | N/A |

## 4. Conclusion

The fabrication of foamed glass samples by valorization of ferrochromium slags and flint container glass waste were successfully achieved. With the help of this, the accumulation of those wastes in the environment can effectively be prevented. The addition of ferrochromium slags in foamed glasses showed an increase in bulk density, compressive strength and water absorption whereas a decrease in porosity. However, the limit of adding 20 wt% is promising for obtaining lightweight properties with homogeneously distributed pores combined with relatively high compressive strength.

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