FLY ASH-GEOPOLYMER COMPOSITE OBTAINED BY ADDITION OF RECYCLED POST-CONSUMER PACKAGING BOTTLE

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ABSTRACT: The experiment described in this paper is part of the series of worldwide investigation of the influence of different types of alumina-silicate waste on properties of geopolymer concrete. The work originality consists in the choice of recycled post-consumer green packaging bottle as a partial substitute for fly ash, unlike recent results known from the literature of the use of brown glass waste powder or in a mixture of coloured glass. The results showed that the replacement of 18 % of the initial fly ash content is an optimal solution to increase the compression and flexural strength of the geopolymer concrete both after 7 days of storage and after 28 days. In this case, the compression resistance values reached 34.8 and 46.0 MPa, respectively and the flexural resistance values were 5.9 and 8.9 MPa, respectively. Further increasing the proportion of green glass up to 30 % contributed to a surplus of concrete strength, but to a very small extent, reaching a maximum of 34.9 and 47.0 MPa and respectively, 6.0 and 9.1 MPa.

KEYWORDS: geopolymer concrete, fly ash, green residual glass, compression resistance, flexure resistance.

1. INTRODUCTION

One of the main current challenges of world research imposed by the need to protect the environment and avoid climate change is, since the end of the 20th century, the reduction of carbon dioxide (CO_2) emissions as a greenhouse gas into the atmosphere.

An important source of greenhouse gases has been identified as the global industrial activity of cement production, which emits into the atmosphere around 7 % of the entire amount of CO_2 produced in the world [1, 2]. Despite the essential role of Portland cement as a binder in the construction sector, used intensively for over 100 years in modern concrete manufacturing recipes, the European Commission has established a firm plan to reduce the economic activities that generate this gas type and search for new solutions of replacing products with this risk factor for the environment [3].

In this way, in the last decades, numerous studies aimed at the creation of new products with appropriate abilities and one of the methods adopted is the large-scale recycling of waste resulting from both production activities and other sources typical of the civilized world.

The damage to the protective ozone layer of the planet due to the emission of greenhouse gases into the atmosphere temporarily coincides with the expansion of landfills containing various wastes with negative implications on the health of soils, underground and surface waters, etc. [4].

In the last decade of the last millennium, a remarkable scientific contribution by the French researcher J. Davidovits opened new perspectives in the field of making cementitious materials different from the well-known Portland cement, but suitable for the manufacture of construction concrete, based on the activation in an alkaline liquid environment of silica and alumina-rich wastes. Numerous alumina-silicate materials resulted as by-products from different production activities in metallurgy, energy, mining, etc. were recycled through the partial or total disposal of existing landfills. The new type of material manufactured by the general method mentioned above was called geopolymer. Davidovits and his team of researchers patented between 1994-2022 several versions of geopolymer different by their particularities [5-11], the new type of material, friendly to the environment and achievable in much more cost-effective conditions, being accepted by the world scientific world. Currently, the development of the geopolymerization process of alumina-silicate waste in an alkaline environment is the concern of numerous researcher teams from different countries, whose contributions will certainly lead to positioning geopolymers among the materials of the future, especially in the construction sector. According to the results obtained so far, the main alumina-silicate raw materials used in the geopolymerization process are: coal fly ash resulting from coal burning in thermal power plants [12, 13] and granulated blast furnace slag technologically obtained in the pig iron manufacturing process [14, 15]. Also, the main natural alumina-silicate material is metakaolin [16]. All these resources have a high degree of availability worldwide.

The current paper aimed at the use of recycled residual glass powder from post-consumer packaging bottles in the starting mix for the manufacture of geopolymer concrete.

Research on the use of glass waste in traditional concretes as a partial substitute (up to 60 %) of coarse aggregate is already known. The use of coloured residual glass allowed to reach the highest compression resistance (over 40 MPa). Density of the fresh concrete decreased, while the flexural and compression strength increased visibly. 10 % residual glass as a substitute for fine aggregate led to the most pronounced increase in the value of the compression resistance of concrete. Growing the replacement ratio of fine aggregate by more than 20 % had an unfavourable effect on the concrete strength value, which started to decrease [17].

According to the work [18], the use of glass waste in the manufacture of traditional concrete improves its properties, the waste being applied in various forms: powder, fine aggregate, or coarse aggregate. However, the concrete quality can be affected by the addition of glass. The optimal solution proposed in this paper was the addition of glass powder to the mix by partially replacing the cement and adding the proportion of glass as coarse aggregate (up to 20 %). The observed effects were the increase of resistance to compression, flexure, and breaking. The strength and durability characteristics decreased corresponding to glass proportions of above 20 %.

In general, according to the literature, the results of using glass waste in the composition of traditional concrete are quite contradictory, especially on the optimal proportion of the added waste. Regarding the chemical composition of the residual glass, it seems that the use of coloured glass mixtures or only brown glass [17] contributes to obtaining the highest values of the compressive strength of concrete.

Recent research on the incorporation of residual glass particles in the fly ash-geopolymer concrete composition [4] aimed at the partial substitution of coal fly ash from the usually used composition with up to 30 % brown glass waste. Also, different ranges of glass particle size values were tested (from 0.1-40 µm to 0-1.2 mm). According to the experimental results, the indicated proportion of glass addition was between 20-30 % and the average value of the glass grain size was 550 µm. Thus, the compressive strength increased by about 80 %, while the flexural strength decreased compared to the values corresponding to the unmodified geopolymer. It was observed that there is no correlation between the two types of mechanical resistance.

In another recent work [19], recycled glass waste was used to replace fine aggregate (sand) in proportions between 7.5-22.5 %. The preparation of the geopolymer concrete specimens was carried out by their immersing in 2 % H_2SO_4 solution and respectively, 5 % $MgSO_4$ solution and then heating them at high temperatures (200-800 ℃) for 1.5 hours. The results showed that the workability was improved with the increase of glass powder addition. By using the proportion of 22.5 % glass, the curing of samples treated with $MgSO_4$ solution at ambient temperature for 120 storage days led to decreasing the resistance by 1.16 %. The samples immersed in H_2SO_4 solution lost 1.83 % of their initial resistance.

In the work presented below, fly ash-geopolymer concrete was prepared by incorporating recycled green residual glass from post-consumer drinking bottle (soda-lime glass type). Unlike the type of glass used predominantly as waste (brown or coloured mixture) both in the case of traditional concrete manufacturing and in the case of geopolymer concrete manufacturing [4], the colour of the recycled glass chosen for this experiment was green, having in its composition chromic oxide (Cr_2O_3) used for the industrial manufacture of emerald green glass. The test followed the effects of adding the residual green glass on the mechano-physical and heat properties of the geopolymer concrete as well as determining the influence of glass particle size on the geopolymer concrete properties.

2. METHODS AND MATERIALS

2.1 Methods

There are known methods of manufacturing geopolymer concrete by sintering the powder mixture at high temperatures (up to 900 ℃), obtaining porous structures with relatively lower density. These methods have the disadvantage of quite high energy consumption, even in the case of the use of non-conventional heating with electromagnetic waves (microwaves), a procedure developed on a small-scale in the last 6-7 years by the Romanian company Daily Sourcing & Research characterized by lower energy consumption [20].

Generally, the method for the production of geopolymer concrete is based on the use of alumina-silicate waste activated in alkaline liquid medium obtained by combining aqueous solutions of NaOH (or KOH) dissolved in deionized water (hydroxide concentration being between 4M-16M) and sodium (or potassium) silicate solution also known as ”water glass”. Preparing the liquid component, i.e. the alkaline activator, was carried out at least 24 hours before the solid component preparation by stirring the mentioned solutions. The solid component of the mix, usually composed of coal fly ash, granulated furnace slag, and possible other additions such as rice husk ash, silica fume, materials recovered from building demolition, glass waste powder, etc., is mixed in a container separately from the alkaline activator. After obtaining the homogenization of the solid mixture, the alkaline activator is slowly poured over it and the two phases are mixed using different mixing methods, until a paste is obtained that is poured into cubic and rectangular moulds. The paste hardening is performed either at room temperature or by heating in an electric oven at low temperatures (50-80 °C) for 24 hours. After the fresh material has hardened, it is removed from the moulds and the specimens are stored at room temperature for 7 and 28 days before carrying out the measurements for determining their physical, mechanical, thermal, and morphological features. A technological example in this sense is shown in [21]. Concretely, in the current paper, coal fly ash and recycled post-consumer bottle glass were alumina-silicate materials used in this experiment. NaOH and Na_2SiO_3 were adopted as components of the alkaline activator and the concentration of NaOH in solution was 10M. The temperature chosen for hardening the paste in the oven was 75 °C maintained for 24 hours.

2.2 Materials

The originality of the choice of the type of glass waste consisted in the adoption of recycled post-consumer green packaging glass. The analysis of the chemical composition of glass carried out at the Metallurgical Research Institute Bucharest (Romania) showed the existence of 70.5 % SiO_2, 3.8 % Al_2O_3, 5 % Fe_2O_3, 0.9 % Cr_2O_3, 0.4 % MgO, iron, chromium and manganese oxides being colouring chromophore oxides. The residual glass was mechanical processed through grinding in a ball mill in Bilmetal Industry Company in Popesti-Leordeni (Romania). Glass particle dimensions were selected by sieving in the range of 35-86 µm.

Fly ash (class F type) characterized by low composition of CaO (3.6 %) was supplied by the Romanian Paroseni thermal power plant approximately 7 years ago. This type of coal fly ash has been recommended by the geopolymer inventor (J. Davidovits) as suitable for developing the polymerization reaction in the alkaline environment. The chemical composition of fly ash included 49.8 % SiO_2, 23.5 % Al_2O_3, 6.1 % Fe_2O_3, 3.6 % CaO, 3,1 % MgO, 4.0 % K_2O, 1.6 % Na_2O, and 1.1 % TiO_2. The initial grain size of the ash was under 200 µm, requiring its supplementary grinding. Using a laboratory grinding equipment the fly ash size was reduced below 70 µm.

Initially, the maximum proportion of fly ash was 18.4 wt. % in the mixture for preparing the fly ash-geopolymer concrete including also the fine aggregate (quartz sand), the coarse aggregate (gravel), the alkaline activator, and water added. The green residual glass was added to the starting mixture in variable proportions between 18-30 % of the content of fly ash, which was thus progressively reduced. The other components of the mixture were river sand with the role of fine aggregate with a grain size below 1.5 mm and gravel with the role of coarse aggregate with a grain size of less than 5 mm. The alkaline activator was composed from 10M NaOH and Na_2SO_3 (38 % concentration), the Na_2SO_3/NaOH ratio being kept constant at 2.25. Four experimental versions of geopolymer concrete were designed, whose composition is shown in Table 1.

Table 1. Composition of experimental versions of geopolymer concrete

Composition ($kg \cdot m^{-3}$)	**Version 1**	**Version 2**	**Version 3**	**Version 4**
Fly ash	450	369	342	315
Green glass powder	-	81	108	135
Fine aggregate (river sand)	850	850	850	850
Coarse aggregate (gravel)	950	950	950	950
10M NaOH	60	60	60	60
Na_2SiO_3	135	135	135	135
Water added	70	70	70	70

2.3 Investigation methods used for determining sample features

Examining the geopolymer concrete was performed both regarding the workability of the fresh material as well as regarding the mechano-physical and microstructural characteristics. Workability was identified using Abram’ cone (EN 12350-2: 2006). The denseness was determined by Archimedes’ method based on the water-intrusion method (ASTM D792-20). The compression resistance was investigated through the method provided by EN 12390-3: 2001 on the cubic specimen, while the flexural resistance was measured on the rectangular specimen by applying the three-point bend test (SR EN ISO 14125: 2000). Modulus of elasticity was measured according to ASTM C469-02e1. The water uptake was examined through the immersing method of specimen under water (ASTM D570). The microstructural particularities of specimens were identified with Biological Microscope model MT5000, 1000 x magnification.

3. RESULTS AND DISCUSSION

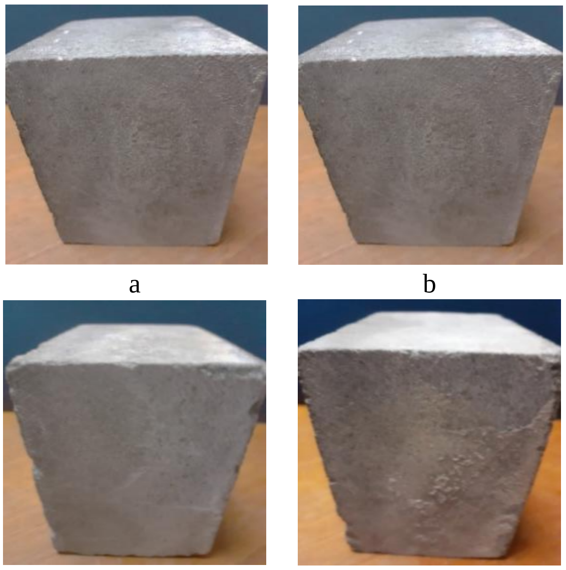
3.1 Results

The application of the Abram's cone test for slump flow showed the satisfactory level of the fresh concrete workability, under the conditions that the slump flow values fell within the range of 179-213 mm (Table 2).

Table 2. Abram's cone test for slump flow

Version	**No.1**	**No.2**	**No.3**	**No.4**
Slump flow (mm)	213	203	192	179

Images of the geopolymer concrete sample aspect are shown in Figure 1.



a b

c d

Figure 1. Images of the geopolymer concrete specimen appearance
a – version 1; b – version 2; c – version 3; d – version 4.

The external appearance of specimens made in the four experimental versions did not differ significantly, thus determining their mechano-physical and microstructural features constitutes the essential method of differentiating the samples.

The main characteristics of geopolymer concrete specimens are presented in Table 3.

Table 3. Main characteristics of the geopolymer concrete specimens

Characteristic	**Version 1**	**Version 2**	**Version 3**	**Version 4**
Denseness ($kg \cdot m^{-3}$)	2423	2435	2449	2462
Compression resistance (MPa) - after 7 days - after 28 days	29.9 42.4	34.8 46.0	34.9 46.9	34.9 47.0
Flexural resistance (MPa) - after 7 days - after 28 days	4.6 7.1	5.9 8.9	5.9 9.0	6.0 9.1
Modulus of elasticity (GPa)	30.7	29.0	27.5	20.1
Water uptake (%)	3.2	3.4	3.0	3.5

According to the data in Table 3, with the decrease in the coal fly ash proportion and its partial replacement with ground green glass waste, the denseness of the geopolymer concrete follows an increasing trend from 2423 to 2462 $kg \cdot m^{-3}$.

Testing the compression resistance at earl age (after 7 days) showed that the geopolymer reached the value of 29.9 MPa and then 34.8 MPa in the case of versions 1 and 2, in which the proportion of residual glass is zero and respectively, 18 % of the fly ash content, after that the increase in resistance becomes negligible up to 30 % addition of glass from the ash content.

A similar trend of the strength evolution of geopolymer concrete depending on the increase in the replacement degree of fly ash with green glass waste also recorded the flexural resistance both at earl age (after 7 days) and at the end of the curing process (after 28 days).

Modulus of elasticity was disadvantaged by the reduction of initial fly ash proportion and replacing with green glass powder, the modulus value decreasing from 30.7 GPa in the reference case (version 1) to 29.0 GPa in the case of replacing with 18 % green glass (version 2) and then, up to 20.1 GPa corresponding to version 4 with 30 % green glass.

Water uptake did not significantly influenced by the change of mixture composition, the ratio of water absorbed by the geopolymer concrete falling within the range of 3.0-3.5 %.

Figure 2 presents the microstructural aspect of the four geopolymer specimens corresponding to the green glass/fly ash ratio.

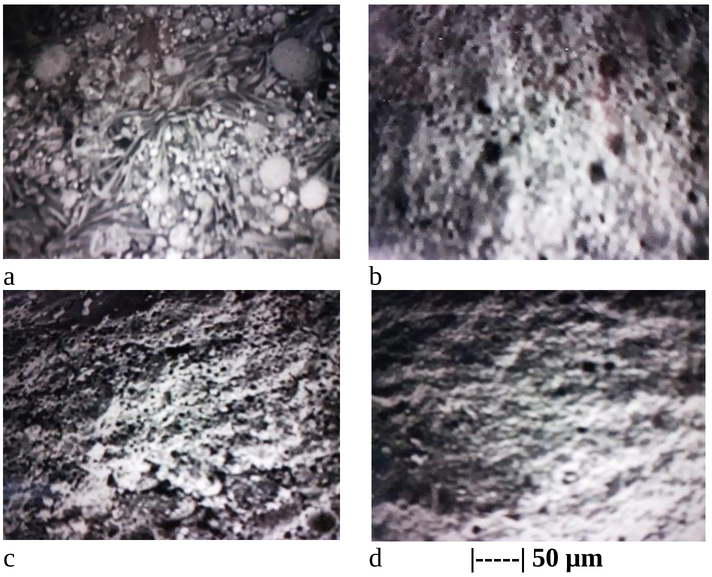


Figure 2. Microstructural appearance of geopolymer specimens
a – version 1; b – version 2; c – version 3; d – version 4.

According to Figure 2, in images (a) and (b) corresponding to versions 1 and 2 the structure specific to materials based on fly ash is visible. In images (c) and (d) these features are blurred.

3.2 Discussion

Few articles recently published in the literature have presented testing recycled residual glass introduced into the composition of geopolymer composites. The glass was used either as a partial substitute for fly ash or granulated blast furnace slag or a partial substitute for fine aggregate, aiming at the possibility of increasing the mechanical resistance of the geopolymer as well as other changes in its characteristics. The glass type tried in the mentioned experiments was brown glass or a mixture of coloured glasses and the results showed that an increase in the compression strength was identified at glass ratios around 20-25 %, after which its value showed a decreasing tendency compared to the initial one.

The current paper has continued these scientific investigations regarding the use of residual glass to improve the properties of geopolymer concrete, adopting green glass waste as a partial substitute for fly ash.

The role of residual glass in composition of the starting mixture for the manufacture of geopolymer concrete was determined after measuring its compression strength. Increases of 8.5 % compared to the initial resistance (for 18 % glass replacing ash), 10.6 % (for 24 % glass), and 10.8 % (for 30 % glass) were obtained. A slightly higher increase was recorded in the case of flexural strength: 9.9 % (for the addition of 18 % glass), 11.3 % (for the addition of 24 % glass), and 11.3 % (for the addition of 30 % glass).

4. CONCLUSION

The objective of this work was to test the use of green residual glass as a partial substitute for fly ash in the alumina-silicate cementitious mixture for preparing the geopolymer concrete. The research aimed at the continuation of recent investigations in the literature on the possibility of improving the characteristics of geopolymer composites due to the incorporation of ground glass. The addition of green glass waste replacing 18-30 % of the amount of fly ash led to an increase in the compression and flexural resistance by 8.5 % and 9.9 % respectively, compared to the reference values in the case of the addition of 18 %. Increasing the proportion of green glass up to 30 %, the mechanical resistance values increased further, but at a very low rate.

5. REFERENCES

1. Gibbs, M.J., Soyka, P., Conneely, D., CO_2 emissions from cement production, in Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, *Intergovernmental Panel on Climate Change*, Geneva, Switzerland, pp. 175-182, (2000).
2. Khaiyum, M.Z., Sarker, S., Kabir, G., Evaluation of carbon emission factors in the cement industry: An emerging economy context, *Sustainability*, MDPI, Tsai, W-H. (acad. ed.), Vol. 15, No. 21, (2023). https://doi.org/10.3390/su152115407
3. Ćirović, M.D., Risk analysis of the European Union 2030 greenhouse gas emission target compliance, *International Journal of Global*

Warming, Vol. 16, No. 1, pp. 64-85, (2018). https://doi.org/10.1504/IJGW.2018.10015566

4. Ziejewska, C., Grela, A., Hebda, M., Influence of waste glass particle size on the physico-mechanical properties and porosity of foamed geopolymer composites based on coal fly ash, *Materials*, MDPI, Shi, X. (acad. ed.), Vol. 16, No. 5, (2023). https://doi.org/10.3390/ma16052044
5. Davidovits, J., Davidovits, M., Davidovits, N., *Process for obtaining a geopolymeric alumino-silicate and products thus obtained*, US Patent no. 5342595, (1994).
6. Davidovits, J., *Method for obtaining a geopolymeric binder allowing to stabilize, solidify and consolidate toxic or waste materials*, US Patent no. 5349118, (1994).
7. Davidovits, J., Davidovits, M., Davidovits, N., *Geopolymeric fluoro-alumino-silicate binder and process for obtaining it*, US Patent no. 5352427, (1994).
8. Davidovits, J., Davidovits, M., Davidovits, N., *Alkaline alumino-silicate geopolymeric matrix for composite materials with fiber reinforcement and method for obtaining same*, UP Patent no. 5798307, (1998).
9. Davidovits, J., Davidovits, R., *Poly(sialate-disiloxo)-based geopolymeric cement and production method thereof*, US Patent no. 7229491, (2007).
10. Davidovits, J., Davidovits, R., Davidovits, M., *Geopolymeric cement based on fly ash and harmless to use*, US Patent no. 8202362, (2012).
11. Davidovits, M., Davidovits, J., Batut-Rollin, M., *Composite material comprising a fibrous reinforcement and a poly(phospho-sialate) geopolymer matrix and associated manufacturing method*, US Patent no. 11299425, (2022).
12. Qaidi, S., Hajm, H.M., Abed, S.M., Ahmed, H.U., Al-Dughaishi, H., Al-Lawati, J., Sabri, M.M., Alkhatib, F., Milad, A., Fly ash-based geopolymer composites: A review of the compressive strength and microstructure analysis, *Materials (Basel)*, MDPI, Khan, M., Bouclé, J. (eds.), Vol. 15, No. 20, (2022). https://doi.org/10.3390/ma15207098
13. Kumar Yadav, V., Hiraman Fulekar, M., Advances in methods for recovery of ferrous, alumina, and silica nanoparticles from fly ash waste, *Ceramics*, MDPI, Vol. 3, No. 3, pp. 384-420, (2020). https://doi.org/10.3390/ceramics3030034
14. Singh, V.K., Srivastava, G., Development of a sustain, nable geopolymer using blast furnace slag and lithium hydroxide, *Sustainable Materials and Technologies*, Elsevier, Vol. 40, (2024). https://doi.org/10.1016/j.susmat.2024.e00934
15. Sawarkar, P.G., Pote, A., Murmu, A.L., Properties of blast furnace slag geopolymer concrete, *Materials Today: Proceedings*, (2023) (available online). https://doi.org/10.1016/j.matpr2023.03.179
16. Grela, A., Lach, M., Bajda, T., Mikula, J., Hebda, M., Characterization of the products obtained from alkaline conversion of tuff and metakaolin, *Journal of Thermal Analysis and* Calorimetry, Springer Link, Vol. 133, pp. 217-226, (2018).
17. Rani, G.Y., Krishna, T.J., Murali, K., Strength studies on effect of glass waste in concrete, *Materials Today: Proceedings*, Vol. 46, Part 17, pp. 8817-8821, (2021). https://doi.org/10.1016/j.matpr2023.04.328
18. Manzoor, A., Kumar, E.Y., Sharma, L., Comparison of partially replaced concrete by waste glass with control concrete, *Materials Today: Proceedings*, Vol. 68, Part 4, pp. 1129-1134, (2022). https://doi.org/10.1016/j.matpr2022.09.092
19. Tahwia, A.M., Heniegal, A.M., Abdellatief, M., Tayeh, B.A., Elrahman, M.A., Properties of ultra-high performance geopolymer concrete incorporating recycled waste glass, *Case Studies in Construction Materials*, Elsevier, Vol. 17, (2022).
20. Paunescu, L., Ioana, A., Volceanov, E., Paunescu, B.V., Nonconventional ecological and low-energy consumption technique to produce high-strength geopolymer composite based on residual materials as a new type of construction material, *Nonconventional Technologies Review*, Vol. 27, No. 1, pp. 32-38, (2023).
21. Ng, H., Heah, C., Mold Mustafa Al Bakri, A., Ng, Y., Ridho, B., Study of fly ash geopolymer and fly ash/slag geopolymer in term of physical and mechanical properties, *European Journal of Materials Science and Engineering*, Vol. 5, No. 4, pp. 187-198, (2020). https://doi.org/10.36868/ejmse.2020.05.04.187