

Conference Paper

Low Temperature Glass Sintering Based on Silico Sodium Resins

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Abstract

By using silicate inorganic binders and glass waste it is possible to mould technical and artistic elements which later can be compacted by means of low temperature, and subsequently apply the sintering trough high temperature processing, which is generally lower than current melting glass processes, close to 1250 °C. The experimental phase established thermal ranges from 600°C to 750°C, a fact that allows for an effective sintering temperature (of around 650°C/18 hours). The mixtures and proportions for this experiment were fixed including ethyl silicate as a fluidizer in mixtures, as well as the size of glass grains. The results indicate good compaction of the samples after the initial phase (80°C/24h), allowing proper handling without alterations in samples edges. During heating treatment, mechanical resistance increases gradually (600-750°C), although the volume of porosity was inversely proportional. According to the matrix vs grain size relationship, the partial fusion of both materials is evident in the rounding of the glass grains as well as the resin bonds joined between them. The resins appeared in a homogenous fashion, covering and gluing the grains, a development which improves the joining of sintered samples. Samples with a mixture of sodium silicate and ethyl silicate resins experienced less melting between grains due to a lower volume of fluxing elements, which means a lower percentage volume of sodium (Na). This study concludes that a sintering process for new vitreous composites could be carried out between 650°C and 700°C, offering the opportunity for a substantial reduction in the amount of energy required to produce industrial glass.

Keywords: Water-glass, glass recycling, low temperature

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1. Introduction

For restoring glass heritage parts, as well as for producing new elements with technical and artistic value is required a great methodological effort. The method proposed in this research paper allows simplification of methodologies, reduction of energy costs and recyclability of waste materials. Producing new glasses with this way need the use of liquid binder made of sodium silicate, sodium hydroxide as catalyst and shards glass as

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aggregate got from bottles, colored/colorless, of calcium sodium glass. All this is based on geopolymer production concept [1–5].

In [6] is confirmed that there is a potential for lowering the costs associated with the alkaline activator that can also contribute to recycling more waste materials. Furthermore [7, 8] investigated the potential for recycling waste glass as a partial replacement material for the alkali-activator, and found that soluble silica from the waste glass formed part of the gel in the geopolymerisation reaction.

According to [9–11], the use of waste as a source of silica in the production of sodium silicate as a substitute for commercial sodium silicates contributes significantly to reducing the environmental impact and lowering the carbon footprint of alkaline cements production and with the optimum mixture selected, it is possible to fabricate pieces that exhibits promising physical and mechanical properties and could be increased with a more technically process.

As a novelty, this research pretend to obtain new glasses can be used in restorative applications for architectural heritage, as well as in technical and artistic applications, getting high simplification in the production processes and significant lowering of melting-sintering temperature.

2. Experimental

Raw materials used, were aggregates of glass and silicon and sodium binder. Glass shards (from colour amber beer bottles) were granulometry classified which sizes close to 2,5 mm. Sodium silicate binder (80/60%) was catalyzed with 20% sodium hydroxide (Figure 1), adding in one case 20% ethyl silicate diluent, all according to proportions shown (Table 1).

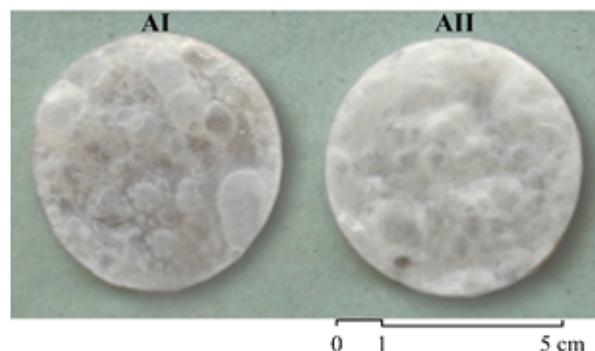


Figure 1: Binder samples (AI, AII according Table 1) with curing at 90 °C/24 h. 'Author's own work'.

Samples were prepared from a mixture of crushed glass with sodium silicate binder in percent of 80/20, according to the characteristics of two binders used in table 1 (binders

TABLE 1: Percent of sodium silicate binder, catalyst and diluent for AI and All cases. 'Author's own work'.

	Binder (%)	Diluent (%)	Catalyst (%)
	Sodium silicate Na ₂ SiO ₃	Estel 1000 (C ₂ H ₅ O) ₄ Si	NaOH water dilution
AI	80		20
All	60	20	20

AI and All) and according to granulometry shown (Table 2). Therefore two groups of samples (PSI and PSII) were obtained based on binder mixtures (AI and All).

TABLE 2: Grain size distribution of glass aggregates for samples studied. 'Author's own work'.

	Size range (mm) / percent			
	2.5->1.25	1.25->0.80	0.80->0.25	<0.25
PSI PSII	40	25	25	10

Afterwards homogeneous raw materials mixing, samples were cured in polyethylene plastic mould in an oven at 90°C for 24 h (Figure 2).

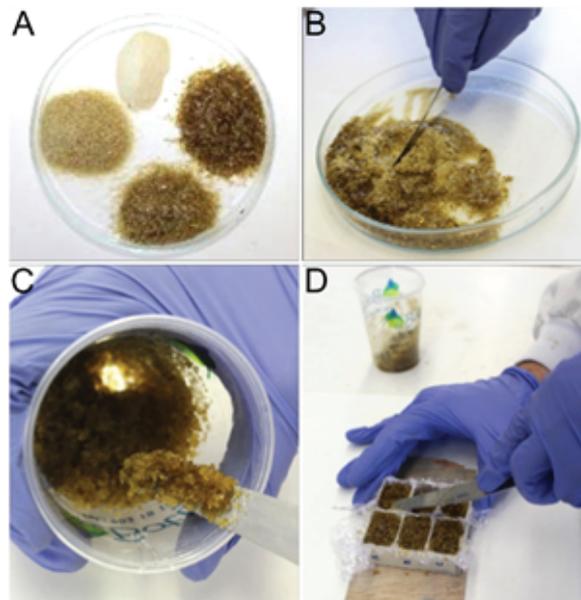


Figure 2: Grain sizes, mixing and curing samples process. 'Author's own work'.

In addition samples were then exposed to sintering temperatures in ranges of 600 to 750°C during 14 hours, for determining the best partial melting temperature. The heating curves are those shown (Figure 3).

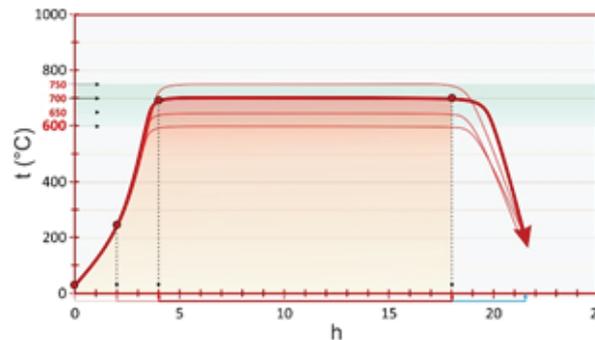


Figure 3: Thermal paths (t / h) for sintering samples from 600 to 750 °C. 'Author's own work'.

2.1. Experimental techniques

Chemical analysis (x-ray fluorescence, FRX) of glass aggregates and binder. It was done by a sequential spectrometer of dispersive wavelength with x-ray generator of 4 KW (PHILIPS Magix Pro-PW-2440).

Characterization of thermal properties of binder and glass aggregates from the study of their dilatometric curves (it was done with a differential dilatometer Netzsch Gerätebau 402EP model). It measures linear expansion coefficient α and Glass transition temperature (T_g).

Morphological study and chemical analysis of samples were done by Scanning Electron Microscope (SEM) high resolution GEMINI (FESEM) CARL ZEISS (CIC-UGR), equipped with system of Chemist-EDX analysis.

3. Results and Discussion

Macroscopic study of samples (PSI and PSII) set and sintered in a generic way, both are shown (Figure 4), highlighting that both cases have proper compaction.

The chemical analysis of raw materials indicate similarity according to silica content between binders and aggregates of recycled glass amber bottles, being main differences the percentages of chromophores oxides (Table 3). It means that used materials have chemical affinity and do not have incompatibilities for sintering process.

According to the thermal behaviour of binder and aggregate, the values concerning maximum temperature, linear expansion coefficient and thermal vitreous transition temperature are very similar (Table 4).

In relation to results from scanning electron microscopy (Figures 5, 6, 7, 8 & 9) several aspects are detected: samples cured at 90°C/24h (Figure 5), have a good bonding between inorganic polymer and glass grains. The glass grains show sharp edges.

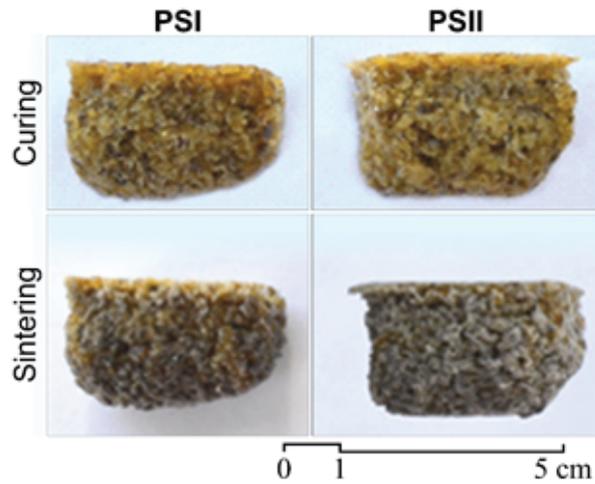


Figure 4: Macroscopic image of cured samples (upper) with geopolymers at 90°C/24 h, and thermally sintered at 650°C/14h (down). 'Author's own work'.

TABLE 3: Chemical analysis (% weight) by XRF spectrometry of binder, diluent/ binder and recycling glass. 'Author's own work'.

Oxides %	Binder Na ₂ SiO ₃	Binder/Diluent (C ₂ H ₅ O) ₄ Si	Amber glass
SiO ₂	76.70	99.91	72,60
Na ₂ O	21.10	0.02	13,40
Al ₂ O ₃	1.06		1,74
MgO	0.08	0.03	2,22
K ₂ O	1.14		0,87
Fe ₂ O ₃	0.03		0,30
CaO	0.02		9,80
SO ₃	0.08	0.02	0,05
TiO ₂	0.02		
P ₂ O ₅	0.01	0.04	
(ppm)			
Cl	929	840	
Zr	78	43	
Cr	58		6000
Ni	42	40	
Cu	23	19	
Br	11		
Sn		2950	

On the other hand, the samples fired to thermal compaction (600°C/14h) have glass grains with rounding due to the effect of temperature (Figure 6). This detail is observed

TABLE 4: Thermal values of raw materials getting from their dilatometry curves. 'Author's own work'.

	Binder Na ₂ SiO ₃	Binder/Diluent (C ₂ H ₅ O) ₄ Si	Amber glass
Max. Test temperature (°C)	659	671	663
Linear expansion coefficient α ($\times 10^{-6}$ K ⁻¹)	8.80	9.05	9.37
Temperatura de transición vítrea Tg (°C)	574	579	575

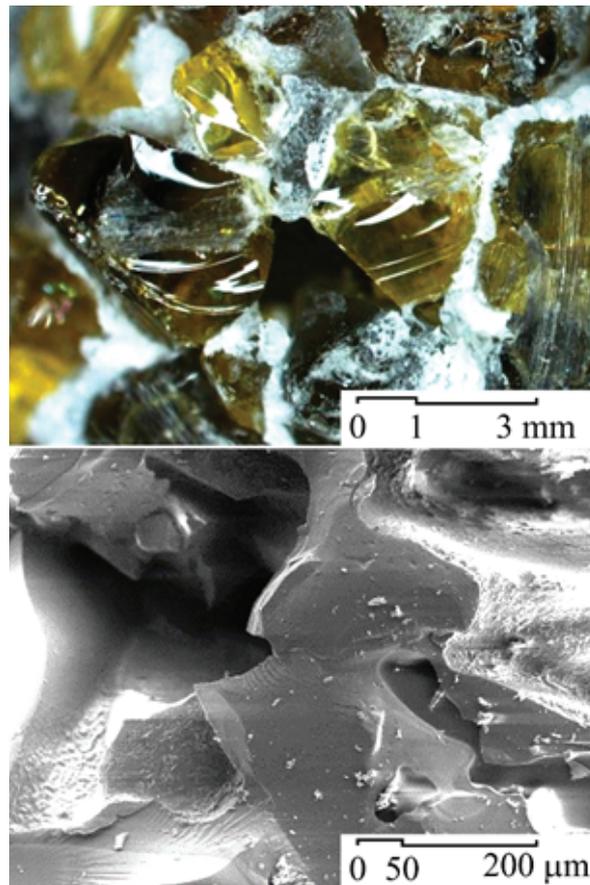


Figure 5: Cured glass mortar at 90°C/24h with macroscopic and SEM detail. The aggregate grains show sharp edges, the binder coats, fills and adheres the grains and pores. 'Author's own work'.

in the SEM image (down), while at macroscopic level the fragments remain sharp edges (upper), fact which means that sintering is very emerging and soft.

At 650 ° C / 14h, macroscopic results show sintering and rounding of glass grains, as well as a compaction of new materials and inorganic resin (Figure 7).

In the following SEM image is allow check the increasing rounding of glass grains and melting of binder. Red dot line and red arrows (Figure 8 down) suggest contacting areas between different elements that forming new glasses. The presence of neo-formed crystallizations in the binder is also highlighted for thermal range of 650°C/14h.

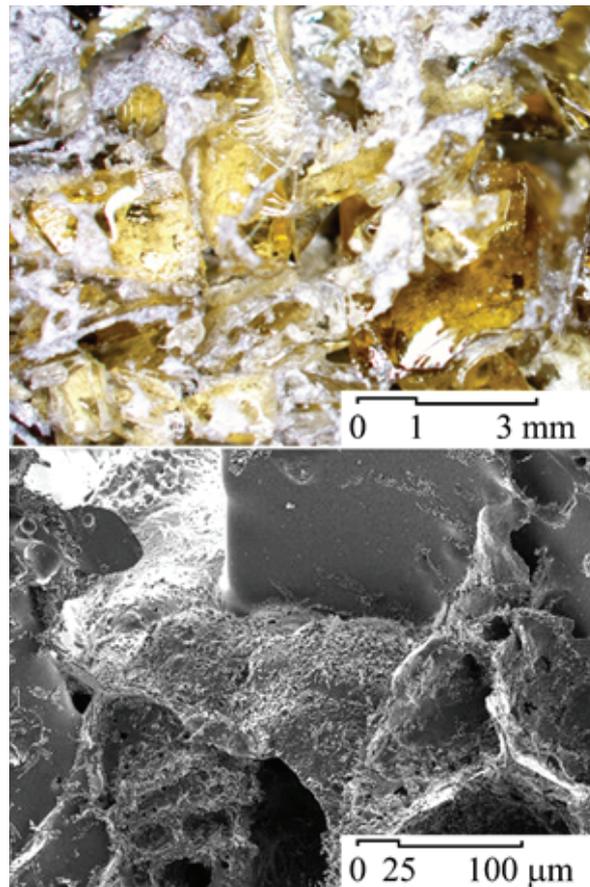


Figure 6: Sintered glass mortar at 600°C/14h with macroscopic and SEM detail. The aggregate grains show low rounding in comparison with binder showing porous due to removal of solvent. 'Author's own work'.

In the case of materials with temperatures of 700-750 °C/14 h, the sintering indicators are very high due to melting processes between aggregates and binder (Figure 8). Important fusions are observed between binders and glass aggregate grains (light blue area with red and blue dot lines). Also small bubbles trapped in vitreous matrix, from gases elimination during sintering, are also observed.

In addition, for these temperatures recrystallizations are formed due to devitrification during cooling and tempering process of new glasses (Figure 9). The case shown corresponds to a crystalline neoforming made of residual Fe from the raw material amber glass.

The new materials sintered at different temperatures have different melting degree, fact what can be checked by variation of volume (Figure 10). In this way, sintered materials have positive variations in their volumes for range of 600°C/14h, and negative variations (contraction) from 650 °C onwards. This fact indicates the minimum sintering temperature for these kind of products.

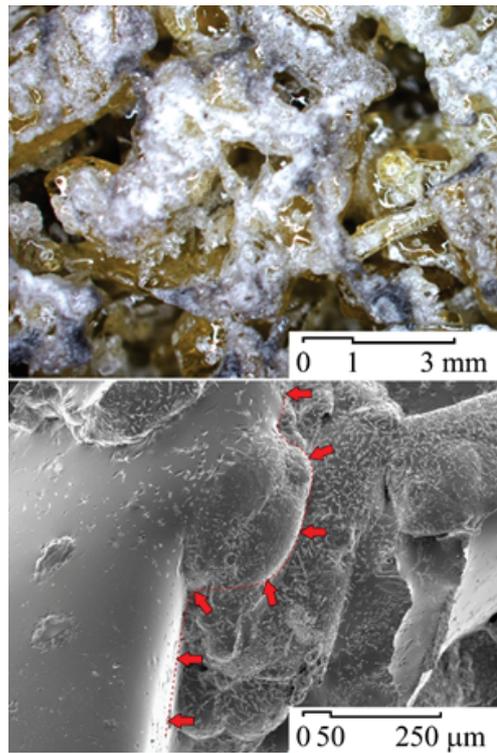


Figure 7: Sintered glass mortar at 650°C/14h with macroscopic and SEM detail. The aggregate grains are very rounded and partially melted (line and red arrows). The binder is also melted with sodium recrystallizations. 'Author's own work'.

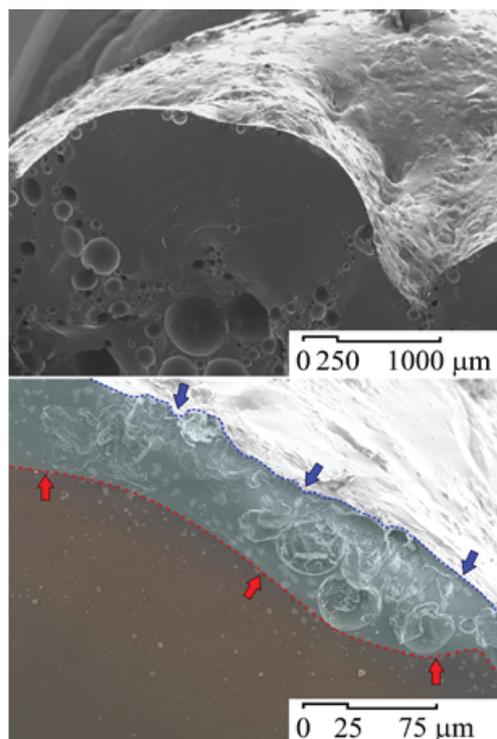


Figure 8: Sintered glass mortar at 700°C/14h with SEM detail. Upper image shows small bubbles trapped in vitreous matrix. Down image shows the blue area indicates melting between the binder and glasses grains. 'Author's own work'.

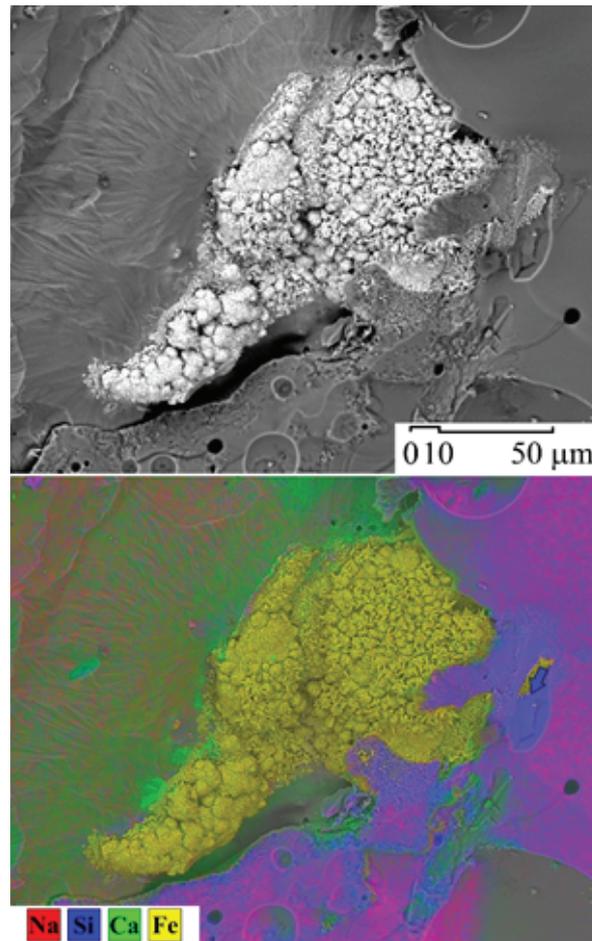


Figure 9: Detail of neo-crystallization of Fe in samples subjected to sintering at 700 ° C / 14h (top image). Bottom image shows map of chemical distribution for Na, Si, Ca and Fe. 'Author's own work'.

As indicated, the sintering indicators are high in the case of materials with temperatures of 700-750 ° C / 14 h, mainly due to the fusion processes between the aggregates and the binder. This fact is confirmed by volumetric contraction, close to 20% and 45% respectively (Figure 10, ranges 700-750°C), and SEM images (Figures 8 and 9).

4. Conclusions

Obtaining compounds compacted at low temperature (90°C/24h) has great advantages to produce materials of great usefulness and durability. The savings in technical processes and materials is very high, and can be treated and machined with warranty from 24 hours of its preparation.

These materials constitute a true substitute for expensive processes, such as the preparation of hot glass. These new products improve technical properties and ease of use that are organic polymers (e. g. epoxy or polyester). Products mechanically finished

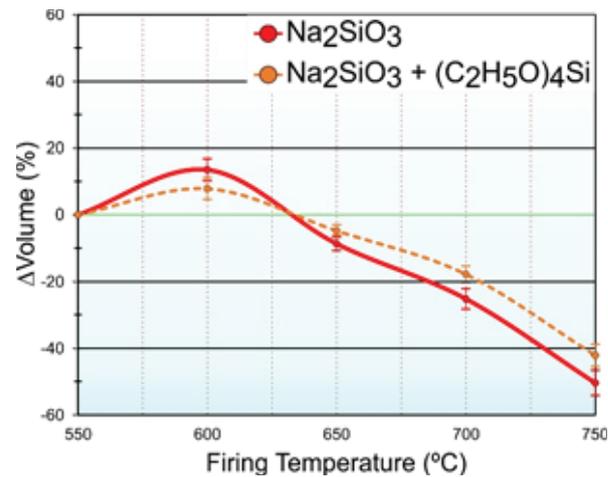


Figure 10: Change in volume depending on the sintering temperature of glasses agglomerated with sodium silicate (red line) and sodium silicate + ethyl silicate (orange line). 'Author's own work'.

after low temperature compaction can be finished by further sintering with heating at temperatures above 600 °C.

However, there are small differences between the materials what constitute the glasses, fact what can facilitate sintering at a lower temperature, below 700°C, as has been checked in our study. On the other hand, lower linear expansion value of binder will prevent the appearance of cracks during cooling of the new manufactured materials.

On contrary, if manufactured products with high sintering are needed, heating at 700 ° C, or higher is very proper, although it means significant volumetric contractions (greater than 40%).

Finally, the addition of ethyl silicate, (C₂H₅O)₄Si, as binder/diluent in mixtures gives fluidity and plasticity to the agglomeration process, favouring cold workability of mixtures. However greater proportionality of Si in the mixtures with respect to sodium fluxes, result a higher temperature for better sintering.

Acknowledgments

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References

- [1] Provis, L. and van Deventer, J.S.J. (eds.) (2009). *Geopolymers: Structures, Processing, Properties and Industrial Applications*. (Cambridge: Woodhead Publishing).
- [2] van Deventer, J.S.J., Provis, L., and Duxson, P. (2012). Technical and commercial progress in the adoption of geopolymer cement. *Miner. Eng.*, vol. 29, pp. 9-104.
- [3] Turner, L. and Collins. F. (2013). Carbon dioxide equivalent (CO₂-e) emissions: A comparison between geopolymer and OPC cement concrete. *Const. & Build. Mat.*, vol. 43, 125-130
- [4] Villegas, M. A., *et al.* (2017) *The glass sculpture*. (Granada: University of Granada), p.350.
- [5] Sáez-Pérez, M.P., *et al.* (2019). New low temperature glass composites from glasses recycling, applied for architectural conservation. 4th International Conference on Technological Innovation in Building 6-8 March 2019, Madrid, pp. 260-262
- [6] Mohajerani, A., *et al.* (2019). Recycling waste materials in geopolymer concrete. *Clean Techn Environ Policy* vol. 21, pp. 493–515.
- [7] Rashidian-Dezfouli, H., and Rangaraju, P.R. (2017). Comparison of strength and durability characteristics of a geopolymer produced from fly ash, ground glass fiber and glass powder. *Materiales de Construcción*, vol. 67, <http://dx.doi.org/10.3989/mc.2017.05416>
- [8] Torres-Carrasco, M., and Puertas, F. (2015). Waste glass in the geopolymer preparation. Mechanical and microstructural characterisation, *J. Clean. Product.*, vol. 90, pp. 397–408.
- [9] Rivera, J.F., *et al.* (2018). Novel use of waste glass powder: Production of geopolymeric tiles. *Advanced Powder Technology* vol. 29 pp. 3448-3454.
- [10] Puertas, F., Torres-Carrasco, M., and Alonso, M.M., (2015). *Handbook of Alkali-Activated Cements, Mortars and Concretes*. (Paris: Elsevier).
- [11] Torres-Carrasco, M., Palomo, J.G., and Puertas, F. (2014). Disoluciones de silicato sódico procedentes del tratamiento de residuos vítreos. *Estudio estadístico*, *Materiales de Construcción*, vol. 64, issue 14, <https://doi.org/10.3989/mc.2014.05213>.