# Proving the role of boron in the structure of fly-ash/borosilicate glass based geopolymers

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ABSTRACT

A spectroscopic investigation was carried out in order to determine the boron evolution into the structure of fly-ash based geopolymers, integrated with borosilicate glass coming from pharmaceutical waste. Fourier transformed infra-red (FTIR) spectroscopy was used to define the type of bonds after geopolymerization. Various solid-state nuclear magnetic resonance (MAS-NMR) measurements were instrumental to evaluate the extent of network formation in the structure and to compare the type of environments among the geopolymerization products and the source materials. ^{11}B NMR conducted firstly on a pure borosilicate glass sample and then on a geopolymeric sample evidenced a variation of the chemical shifts of the pattern, proving that boron oxide ($B_2O_3$) initially dissolved and then took part in polycondensation reactions. FTIR spectroscopy showed the characteristic peaks of a geopolymeric product, also proving that the effectiveness of the reaction was not affected by incorporation of boron.

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## 1. Introduction

Geopolymers are well-suited materials to abate $CO_2$ emission coming from the Portland cement production [1], and then replace them, in the near future, in buildings and other applications [2,3]. The cost of production of geopolymers is the only weakness, but the use of industrial wastes as raw materials could provide a valid solution to this problem, as demonstrated by the successful incorporation of fly-ash, a by-product of thermal power plants, vitrified residues of waste incineration and waste glasses [4–6]. In particular, fly-ash is known to yield geopolymers of appreciable mechanical properties compared to those made of metakaolin [1,3,7,8]. Puertas et al. [9], in addition, showed the possible synergy of fly-ash and recycled glass in waste-derived geopolymers.

In this paper we present, for the first time, the introduction of recycled borosilicate glass (BSG) for geopolymer production. BSG is actually a glass residue, since it derives from dismantled pharmaceutical vials and cannot be reused in the manufacturing of the original articles [10]. Owing to the specific chemical composition (BSG is an "alumino-boro-silicate"), however, it is conceived that BSG can provide the key components of zeolitic networks for geopolymer production, such as amorphous silica and alumina

[11], as well as boria ($B_2O_3$), which may replace $Al_2O_3$ [12] and contribute to the polycondensation process. In this study, solid–state MAS NMR spectroscopy [13,14] was used to assess the extent of boron oxide incorporation in the structure of fly-ash based geopolymers, comparing the pattern of the original borosilicate glass with those of the geopolymers, in order to define the connectivity of the microstructure. FTIR spectroscopy was utilized to define the degree of polymerization [15,16].

## 2. Materials and methods

Fly-ash from a Bohemian thermal power plant (Počerady power plant, North Bohemia, Czech Republic) was used as the aluminosilicate source. Recycled BSG cullet (Kimble/Kontes, Vineland, NJ) powder was added and then mixed by hand with the fly ash, in a proportion of 70% fly-ash and 30% BSG in weight. NaOH (Sigma Aldrich, ACS reagent, 97%, pellets) solution (13 M) was added to the mixture with a total liquid to solid weight ratio of 0.5. The slurry was stirred for 5 min to homogenize and then, it was cast in cylindrical rubber moulds, and cured in oven at 85 °C for 24 h in a highly wet environment (RH = 99%). The samples were demoulded and left at ambient temperature for 48 h prior to testing.

Relative density of as-prepared samples was calculated to be 0.7 (theoretical density of 2.078 g/cm$^3$ and real density of 1.44 g/cm$^3$).

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Methodology of preparation were selected according to the literature [9,17]. FTIR spectra were collected by using a Nicolet 6700 FTIR spectrometer in the range between 4000 and 400 cm$^{-1}$. Moreover, the analyses were conducted on pellets composed of 0.2 g of potassium bromide and 0.002 g of geopolymer.

$^{11}$B, $^{27}$Al and $^{29}$Si NMR spectra were obtained using a Bruker Avance-500 spectrometer (USA). The rotation frequency of 10 kHz was used for $^{27}$Al and $^{29}$Si, 14 kHz was used for $^{11}$B. Recycle delay of 5 s was used for $^{11}$B, 2 s for $^{27}$Al and 20 s for $^{29}$Si. $^{29}$Si NMR spectra were deconvoluted in the sum of the single chemical shifts, using the DMfit software [9]. The admitted error was calculated to be about ±1 ppm.

## 3. Results and discussion

Fig. 1 shows the FTIR spectra for both fly-ash and geopolymer samples. In the original fly-ash, an absorption band, detected at around 1085 cm$^{-1}$, may be attributed to the stretching vibration of the T—O—T bond, where T refers to Si or Al elements. Concerning the fly-ash, it is possible to distinguish the bands at 465 cm$^{-1}$, 555 cm$^{-1}$ and 779 cm$^{-1}$ associated with T—O bending vibrations, double ring linkages and symmetrical vibration of tetrahedral groups (TO$_4$), respectively [15]. Geopolymer spectra shows only a shoulder at 550 cm$^{-1}$ and 770 cm$^{-1}$. Interestingly, the band at 820 cm$^{-1}$ is detectable, denoting the stretching vibration of the tetrahedral BO$_4$ [18], which highlights boron incorporation in the network. The FTIR patterns show total compliance with the literature [15,16], so the geopolymerization was not macroscopically affected by boron uptake. The bands located at 1460 cm$^{-1}$, 1644 cm$^{-1}$ are associated with atmospheric carbonation and H—O—H bending vibration; all the remaining peaks (from 2400 cm$^{-1}$ to 3600 cm$^{-1}$) are linked to vibrational evidences due to the presence of water [1].

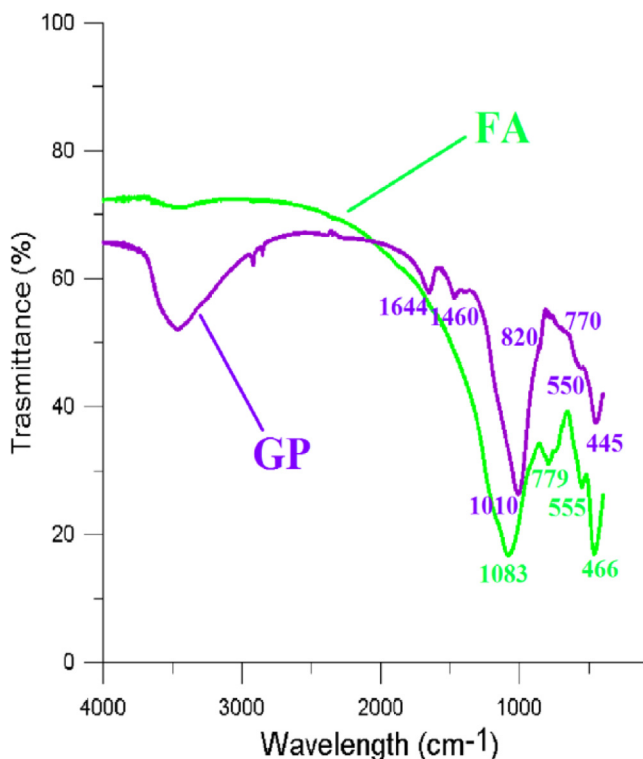The $^{27}$Al NMR plots, for both fly-ash and geopolymer samples, are given in Fig. 2a. Relevant chemical shifts are detected at about 0 ppm, related to octahedral aluminum, and at 58 ppm, corresponding to a mix of tetrahedral and dipyramidal aluminum [13]. Fly-ash is characterized by an even intensity of both chemical shifts, whilst the geopolymer sample exhibits much higher intensity at 58 ppm, i.e. the octahedral aluminum rearranged in the tetrahedral coordination. Fig. 3 shows the $^{29}$Si NMR deconvolution for both the fly-ash and the geopolymer samples. The figure also reports a list of the chemical shifts and values of the percentage area covered by a single signal, quantifying the concentration of the detected phase. In fly-ash, the spectra reveals signals at −84 ppm, −95 ppm, −104 ppm and −110 ppm, which are associated with an aluminosilicate glass phase [9,13]. It is noticed that the unit attributed to −104 ppm exhibits the widest area. The peak at −88 ppm occurs due to the presence of the crystalline unit Q$_3$(3Al) in mullite. The denotation of the units is referenced according to Oh et al. [13]. The peaks located at −114 ppm and −118 ppm are attributed to the crystalline silica Q$_4$(0Al) unit. The most intense signals are those attributed to the glassy phases, i.e. the reactive phase, which implies a significant reactivity of the fly-ash. The geopolymer spectra (Fig. 3) displays peaks at −88 ppm, −92.5 ppm, −98.1 ppm, −104 ppm and −110 ppm associated with tridimensional cross-linked silicate units in different aluminum environments, i.e. Q$_4$(4Al), Q$_4$(3Al), Q$_4$(2Al), Q$_4$(1Al) and Q$_4$(0Al) respectively. Q$_4$(4,2,1Al) are the most intense in the spectra, which means that there was an appreciable replacement of aluminum inside the network. The signal at −115 ppm is related to some unreacted crystalline silica from the fly-ash [9,13].

Both $^{11}$B NMR spectra of BSG and geopolymer samples are reported in Fig. 2b. $^{11}$B NMR of the BSG shows two chemical shifts: 1 ppm attributed to tetrahedral coordinated borate (BO$_4$), 11 ppm associated with trigonal coordinated borate (BO$_3$) [14]. In the geopolymer spectra, a change in difference between the two peaks is evident: while the BO$_4$ chemical shift is still intense, the BO$_3$ is almost depleted, demonstrating that the trigonal boron dissolved and rearranged in a tetrahedral structure, i.e. the configuration in zeolitic gels (geopolymeric structures). These results prove the boron uptake in the geopolymer structure. An $^{11}$B NMR analysis conducted on geopolymer treated with borate salts has been carried out, showing similar results, as reported in literature [19]. In particular, B takes part to the geopolymerization, forming polymeric chains with Si, and then partially replacing the Al in its function. This, finally, improves the connectivity of the structure in favor of a more stable 3-D cross-linked network. This structure refinement implies better mechanical properties [5]. Preliminary compressive test showed an average value of 45 MPa, which, considering the relative density, means an improvement of 25% in respect to the literature [9,20].

## 4. Conclusions

FTIR and NMR spectroscopies were used to investigate the structure of fly-ash and borosilicate based geopolymers, and to define the role of boron in geopolymerization reactions. FTIR spectroscopy showed a characteristic absorption band attributed to the stretching modes of tetrahedral boron ions, whose tetrahedral configuration is compatible to the reaction product of geopolymerization. $^{27}$Al NMR and $^{29}$Si NMR spectra were instrumental in understanding the extent of the reaction. 11B NMR spectroscopies evidenced a change of the trigonal boron (BO$_3$) inside the BSG in favor of a quasi-total tetrahedral boron configuration (BO$_4$). Thanks to these results, it was inferred that boron is part of the geopolymeric structure, replacing the Si in the network, similarly to the role played by aluminum.
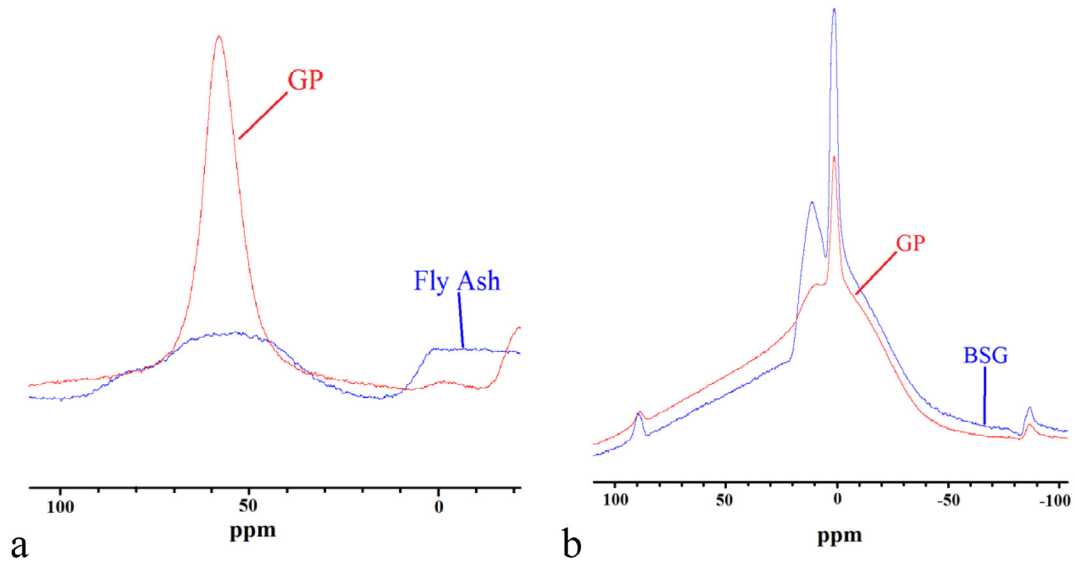


**Fig. 1.** FTIR spectra for fly-ash (FA) and geopolymer (GP). The peaks are discussed in the text.

**Fig. 2.** a) $^{27}Al$ NMR spectra of fly-ash vs $^{27}Al$ NMR of the geopolymer (GP). b) $^{11}B$ NMR spectra of the BSG vs $^{11}B$ NMR spectra of the geopolymer (GP).
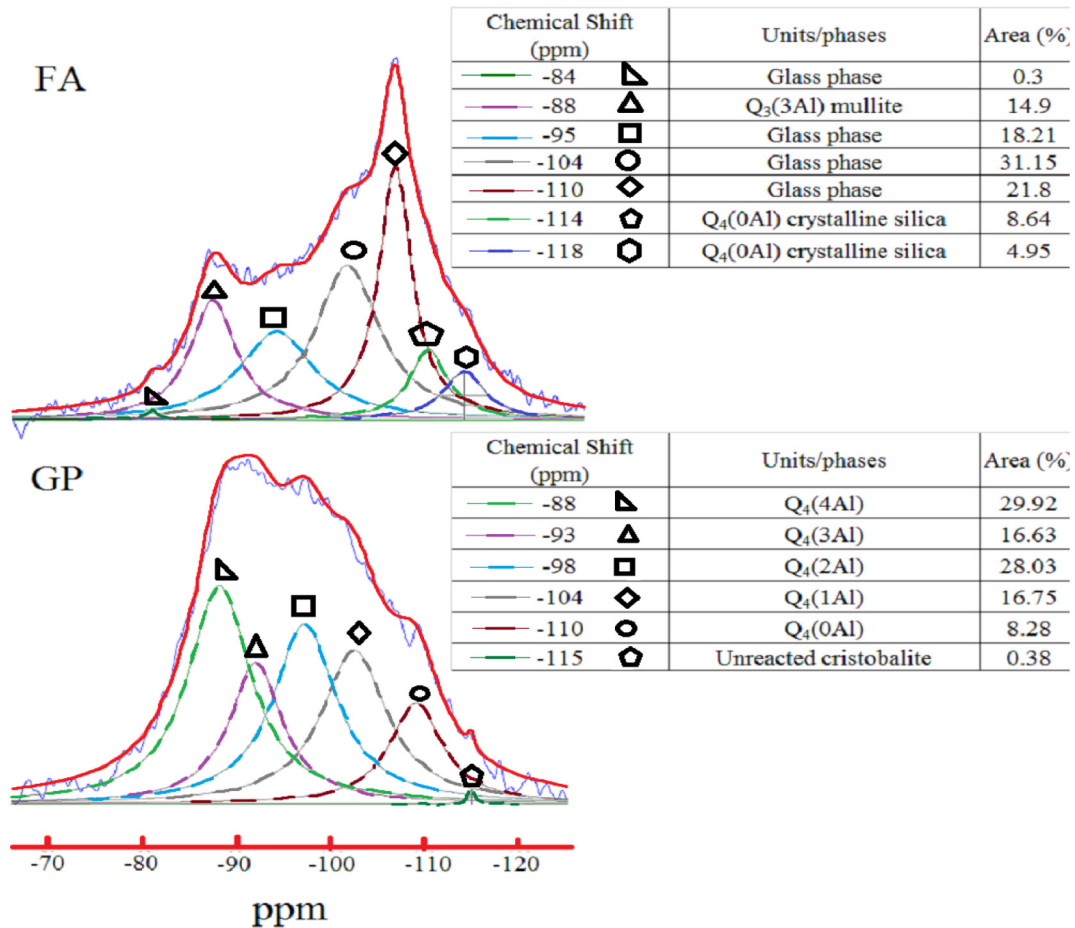


| Chemical Shift (ppm) | | Units/phases | Area (%) |
|---|---|---|---|
| −84 | ◺ | Glass phase | 0.3 |
| −88 | △ | $Q_3$(3Al) mullite | 14.9 |
| −95 | ☐ | Glass phase | 18.21 |
| −104 | ⬭ | Glass phase | 31.15 |
| −110 | ◇ | Glass phase | 21.8 |
| −114 | ⬠ | $Q_4$(0Al) crystalline silica | 8.64 |
| −118 | ⬡ | $Q_4$(0Al) crystalline silica | 4.95 |

| Chemical Shift (ppm) | | Units/phases | Area (%) |
|---|---|---|---|
| −88 | ◺ | $Q_4$(4Al) | 29.92 |
| −93 | △ | $Q_4$(3Al) | 16.63 |
| −98 | ☐ | $Q_4$(2Al) | 28.03 |
| −104 | ◇ | $Q_4$(1Al) | 16.75 |
| −110 | ⬭ | $Q_4$(0Al) | 8.28 |
| −115 | ⬠ | Unreacted cristobalite | 0.38 |

**Fig. 3.** Deconvoluted $^{29}Si$ NMR spectra of the fly-ash (FA) and geopolymer (GP) samples.

## Acknowledgements

## References

[1] E. Arioz, Ö. Arioz, Ö.M. Koç, Int. J. Chem. Eng. Appl. 4 (2013) 4–7.
[2] A. Palomo, P. Krivenko, I. Garcia-Lodeiro, E. Kavalerova, O. Maltseva, A. Fernandez-Jimenez, Mater. Construcción. 64 (2014) 1–23.
[3] X.Y. Zhuang, L. Chen, S. Komarneni, C.H. Zhou, D.S. Tong, H.M. Yang, W.H. Yu, H. Wang, J. Clean. Prod. 125 (2016) 253–267.
[4] M. Torres-Carrasco, C. Rodríguez-Puertas, M. Del Mar Alonso, F. Puertas, Bol. La Soc. Esp. Ceram. Y Vidr. 54 (2015) 45–57.
[5] F. Puertas, M. Torres-Carrasco, Cem. Concr. Res. 57 (2014) 95–104.
[6] I. Kourti, D.A. Rani, D. Deegan, A.R. Boccaccini, C.R. Cheeseman, J. Hazard. Mater. 176 (2010) 704–709.
[7] M.M.A.B. Abdullah, L. Jamaludin, K. Hussin, M. Bnhussain, C.M.R. Ghazali, M.I. Ahmad, Int. J. Mol. Sci. 13 (2012) 4388–4395.
[8] A. Bhowmick, S. Ghosh, Int. J. Civil Str. Eng. 3 (2012) 168–177.
[9] M. Torres-Carrasco, F. Puertas, J. Clean. Prod. 90 (2015) 397–408.
[10] R.K. Chinnam, A.R. Boccaccini, E. Bernardo, H. Epstein, Int. J. Appl. Ceram. Technol. 12 (2015) E19–E27.
[11] A. Palomo, A. Fernández-Jiménez, Proc. World Coal Ash Conference (2011) 1–14.
[12] A. Fernández-Jiménez, A. Palomo, I. Sobrados, J. Sanz, Microporous Mesoporous Mater. 91 (2006) 111–119.
[13] J.E. Oh, Y. Jun, Y. Jeong, Cem. Concr. Compos. 50 (2014) 16–26.
[14] S. Sen, Z. Xu, J. Stebbins, J. Non Cryst. Solids 226 (1998) 29–40.
[15] A. Fernández-Jiménez, A. Palomo, Microporous Mesoporous Mater. 86 (2005) 207–214.
[16] T.E.M. Edx, H. Xu, J.S.J. Van Deventer, Cem. Concr. Res. 32 (2002) 1705–1716.
[17] V. Fernández, U. López, R. Vítreos, U.E. Industriales, 2 394 979, 2013, pp. 14.
[18] S.Y. Marzouk, R. Seoudi, D.A. Said, M.S. Mabrouk, Opt. Mater. (Amst) (2013).
[19] C. Nicholson, B. Murray, World Congress Geopolymer, Saint-Quentin, 2005.
[20] Y. Luna-Galiano, A. Cornejo, C. Leiva, L.F. Vilches, Mat. De Constr. 69 (2015).