Metakaolin - waste glass geopolymers. The influence of hardening conditions on mechanical performances

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Abstract. The development of new ecological materials for the construction field represents a sustainable solution for waste management as long as their properties are comparable with those of traditional materials in terms of strengths, durability, corrosion resistance etc. Considering the large amount of glass wastes that are generated (e.g. technical waste glass derived from industrial activities) a sustainable approach is to recycle them in new products. To this purpose, metakaolin-waste glass geopolymers were obtained by using 10% technical glass powder and 90% metakaolin, activated with alkaline solutions of NaOH 8M and 12M. After 24 hours of hardening in certain conditions (cured for 2 hours at 60°C respectively 90 °C in covered moulds and up to 24 hours at room temperature) the geopolymer specimens were subjected to thermal treatments at temperatures up to 700°C, in order to establish the influence of hardening conditions on mechanical performances. The transformations which occur in the geopolymer matrix during the hardening process were studied by SEM analyses and x-ray diffraction. The results showed that a higher treatment temperature improves the mechanical resistance.

1. Introduction
Geopolymer materials are considered a new class of inorganic binders, with low CO₂ emission, as they result through polymerization chemical reaction between an alkaline activator (alkali hydroxide, sulphate, carbonate or silicate) and aluminosilicate rich materials. The geopolymer structure is an amorphous or a low crystalline 3D network, depending on the temperature of polymerization, consisting of SiO₄ and AlO₄ tetrahedral units, alternately linked by oxygen atoms [1].

Geopolymers with an amorphous structure can be obtained by heat treatment at temperatures of up to 90 °C, while the treatments at higher temperatures lead to formation of geopolymer with crystalline structure like zeolites [2, 3].

The performances and structure of geopolymers are in relation with several factors of which the aluminosilicate oxides sources, Si/Al ratio, alkaline activator type and concentration, solid / liquid ratio and curing conditions are most referred. The presence of crystalline compounds as nepheline (NaAlSiO₄), jadeite (NaAlSi₂O₆), and albite (NaAlSi₃O₈) were observed in high heat-treated samples of Na-based geopolymers [4, 5]. De Silva et al. [6] emphasised that the geopolymer properties could be influenced by any minor changes in the available Si and Al concentrations, during synthesis. The
influence of solid to liquid ratio (s/l) was studied in correlation with SiO$_2$/Na$_2$O ratio. Lin et al. [7] reported that metakaolin based geopolymers activated with a mixture of NaOH / sodium silicate with SiO$_2$/Na$_2$O of 0.8 and s/l ratio of 0.4 encountered after 1 day of curing the lowest strengths while those prepared with s/l ratio of 0.8 and SiO$_2$/Na$_2$O = 2 reached the highest.

The numerous studies has demonstrated that the source of alumina and silicate oxides could be represented by a various powder materials of which the most commonly used being metakaolin, fly ash and granulated blast furnace slag [8-10]. However, several wastes (e.g. glass, mud) can be also used as long as they provide reactive silica and / or alumina [11-13].

The embedment of different glass waste in geopolymer materials is supposed to be proper as the glass waste comes with supplementary reactive silicon and alkali oxides (Na$_2$O or K$_2$O), which could reduce the demand of alkaline activator. Moreover, the fine glass powder could exert “filler effect” on the geopolymer structure [11].

The paper brings usefully information regarding the metakaolin based geopolymers with a content of 10% glass waste activated with NaOH 8M and 12M. The hardening processes of geopolymer mortars were enhanced by thermal treatments at 150, 400, 600 and 700°C. After heat treatments the geopolymers specimens were mechanically tested.

The hardening processes and the formed compounds were highlighted on pastes specimens, by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) coupled with EDX.

2. Experimental conditions

The metakaolin-waste glass geopolymers (MKGG) were prepared by using as solid components a commercial metakaolin powder (MK, with Ssp BET = 2.7 m$^2$/g) as source of alumina and silica and a glass powder (GP) as supplementary silica source, in a mix proportion of MK: GP – 90:10 (% mass percentages).

The glass powder was obtained by milling the recycled laboratory glass (broken or out of use), until a Blaine specific surface area of 3995 cm$^2$/g. The chemical composition of both MK and GP powders was determined by X-ray Fluorescence (XRF), using a Rigaku Supermini spectrometer, the results being presented in Table 1.

| Material | Oxide composition (w.t. %) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | SO$_3$ | P$_2$O$_5$ | BaO | Na$_2$O | K$_2$O | Cl |
|----------|----------------------------|--------|-------------|-------------|-----|-----|--------|-----------|-----|--------|-------|----|
| Metakaolin |                            | 54.1   | 29.7        | 0.4         | 2.25| 0.66| 0.06   | 0.3       | 2   | 10.5   | 1.5   | 0.02 |
| Glass    |                            | 83.3   | 4.77        | 0.1         | 0.6 | -   | -      | -         | -   | 2.4    | 7.5   | 1.0 |

The alkaline activator was NaOH 8M and 12M aqueous solution, at a liquid to solid ratio of 0.3. In order to study the influence of hardening conditions on mechanical performances, mortars with binder to sand ratio of 0.33 were prepared, casted in cubic molds (25×25×25mm) and compacted for 2 minutes.

The MKGG specimens, activated with NaOH 12M aqueous solution, were cured at 60°C for two hours in covered molds with plastic foil and subsequently for 24 hours at room temperature, while the MKGG samples activated with NaOH 8M, were cured at 90°C for two hours.

After demolding all the mortar specimens of MKGG were heat treated at temperatures of 150, 400, 600 and 700°C and mechanically tested to compression.

Crystalline phases were analyzed by x-ray diffraction (XRD, D8 Advance Bruker equipped with Powder Diffraction Database) and the effect of treatment temperature on the geopolymer’s microstructure was investigated using scanning electron microscopy (SEM, SU70 Hitachi) coupled with energy dispersive spectroscopy (EDS).
For this purposes MKGG pastes obtained and cured in the same conditions as mortar specimens were prepared.

3. Results and discussions

3.1 Mechanical performances
The performances of alkali activated metakaolin-based geopolymers are not only influenced by the chemical composition, dosage of raw materials and concentration of alkaline activator but also by the curing conditions during early-age polymerization process. The influence of curing temperature and alkaline activator on the compressive strengths (Cs) of MKGG geopolymers are presented in Figure 1.

![Figure 1. Compressive strengths of MKGG’s activated with NaOH 8M and NaOH 12M, heat treated up to 700°.](image)

As it can be seen for all the MKGG specimens the compressive strengths increase proportionally with the treatment temperature. At a lower temperature (150°C) the MKGG’s compressive strengths are small (do not exceed 9 MPa) due to the water removal from MK which determines internal cracks. For the 400°C treatment the Cs’ values remain relative constant for both types of specimens as compared to the 150 °C. The values decrease around 600°C due to the α to β quartz phase transformation and increase again around 700°C due to the sintering process, reaching the maximum value of 16 MPa in case of MKGG alkalinized with NaOH 8M. The concentration of alkaline activator also influences the Cs’ values. Thus, the compressive strengths decrease with increasing of NaOH concentration. These results could be explained by a delay in the geopolymerization process determined by a high concentration of activator which hinders the species dissociation and ions mobility and stability [14]. Additionally, the Na content of GP could induce an increase of non–uniform reaction products (e.g. hydrosodalite – nonstoichiometric solid solutions) resulting in a reduction of the gel resistance. Therefore, for the MKGG, a low concentration of alkaline activator could be sufficient to obtain good mechanical properties, especially in the conditions presented above.

3.2 Microstructural characteristics
The XRD spectra for the two MKGG geopolymer specimens are given in Figure 2 and 3. For the samples which recorded the highest compressive strengths, namely the MKGG activated with 8M NaOH solution and treated at 700°C, the XRD spectrum is also presented.
The MK pattern shows a broad peak characteristic of amorphous material with some crystalline phases of kaolinite, microcline and quartz (Figure 2). The XRD pattern of MKGG-150, activated with 8M NaOH solution, was found to have several additional interferences indicating the formation of certain crystalline phases. Thus, the most intense reflections correspond to the hydrosodalite zeolites compounds formed by interactions between alkaline activator and aluminum silicates from MK. Another crystalline compound identified on MKGG-150 pattern, also present at higher temperatures, is walstromite ($\text{BaCa}_2(\text{Si}_3\text{O}_9)$). Its formation could be enhanced by a more reduced NaOH
concentration which favors the dissociation of some Ba ions from glass waste and their link in new products during the polycondensation reactions. The thermal treatment at 700°C shows that the nepheline (Na₂O·Al₂O₃·2SiO₂) represents the main crystalline phase of which abundance determines increased mechanical strengths.

A more concentrate alkaline activator influence the crystallinity degree of MKGG specimens as well as theirs mineralogy (Figure 3). Thus, for the MKGG-150 specimen with 12M NaOH activator, some differences occur on the XRD pattern meaning that the walstromite compound is not formed. This could be explained by a steric agglomeration caused by the hydrosodalite formed in abundance in these different chemical conditions despite of copolymerization reaction of the SiO₄ and AlO₄ tetraedrical units, available for geopolymer network structuring. The thermal treatment at 600°C highlight the nepheline compound as main crystalline phase (Figure 3), although at the same temperature the MKGG-600 specimen with 8M NaOH activator is more crystalline.

![Figure 4. SEM images of MKGG activated with NaOH 12 M and heat-treated at 150°C (a and b), 400°C (c and d) and 600°C (e and f).](image)

The microstructure of MKGG’s is definitely influenced by the different heat treatments applied for specimens hardening and also by the alkaline activator concentration. Thus, the microstructures of the geopolymer synthetized using NaOH 12M are presented in Figure 4. The heat treatment at 150 °C lead to an amorphous geopolymer network formation in which abundant spherical clusters of hydrosodalite are grown (Figure 4 a and b). The detail from Figure 4b represents the EDS spectrum obtained on the spherical crystals grains confirming, through the present elements Si, Al, Na and O, the hydrosodalite formation. The increasing of temperature treatment up to 400 °C enhance the polymerization process and the metakaolin reactivity. However, the abundant spherical clusters of
Hydrosodalite (Figure 4 c and d) represent a forward steric barrier for the development of geopolymer network. On the SEM micrographs corresponding to specimen heat-treated at 600°C (Figure 4 e and f), besides of small amounts of hydrosodalite can also be observed the hexagonal crystalline formations corresponding to nepheline compound (Na$_2$O·Al$_2$O$_3$·2SiO$_2$), identified on XRD pattern too.

Figure 5. SEM images of MKGG activated with NaOH 8 M and heat-treated at 150°C (a and b), 600°C (c and d) and 700°C (e and f).

The microstructures of geopolymer activated with 8M NaOH are presented in Figure 5. The specimens heat-treated at 150 °C present hydrosodalite, unreacted MK and glass grains (Figure 5a and b). The SEM images of geopolymers heat-treated at 600 °C (Figure 5c and d) evidence a porous crystalline 3D microstructure, consisting of associated fine grains of hexagonal nepheline, like zeolites. An increasing of treatment temperature up to 700 °C determines a free of pores structures more compacted do to the sintering process (Figure 5e and f). The major crystalline phases are represented by nepheline crystals, whose kinetic reaction are favored by low NaOH concentrations (8M).

4. Conclusions
The effect of thermal treatment on both compressive strength and microstructure developed by metakaolin - waste glass geopolymers activated with 8M and 12M NaOH solution was investigated and the following conclusions can be deduced:

− the compressive strengths increase proportionally with the treatment temperature. At a lower temperature the MKGG’s compressive strengths are small due to the water removal from MK.
generating micro-cracks. The 700ºC favours the sintering process determining a more compact ceramized bulk which reach a maximum value of 16 MPa in case of MKGG alkalized with NaOH 8M;
– the XRD patterns indicate development of certain crystalline phases which are different depending on both treatment temperature and the alkaline activator concentration. Thus, at lower temperature the most intense reflections correspond to the hydrosodalite zeolites compounds while the higher temperature determine the nepheline formation which give the mechanical resistance;
– the heat treatment at 150 ºC lead to an amorphous geopolymer network formation in which abundant spherical clusters of hydrosodalite are grown. At 700 ºC, the geopolymer’s structures becomes free of pores and compacted by sintering in which the major crystalline formations is nepheline, whose reaction kinetic is favoured by the NaOH concentration (8M).

5. References
[1] Davidovits J 1991 *J. Thermal Analysis* 37 1633
[2] Koloušek D, Brus J, Urbanova M, Andertova J, Hulinsky V and Vorel 2007 *J. Mater. Sci.* 42 9267
[3] Grutzeck M, Kwan S and DiCola M 2004 *Cem. Concr. Res.* 34 949
[4] Rahier H, Wastials J, Biesemans M, Willem R, Van Assche G and Van Mele B 2007 *J. Mater. Sci. Sci.* 42 2982
[5] Barbosa V and Mac Kenzie K 2003 *Mater Res Bull* 36 319
[6] Da Silva P, Sagoe-Crenstil K and V. Sirivivathanon 2007 *Cem. Concr. Res.* 37 512
[7] Lin K-L, Shiu H-S, Shie J-L, Cheng T-W and Hwang C-L 2012 *Constr. Build. Mater.* 36 501
[8] Pascual A B, Tognonvi M and Tagnit-Hamou A 2014 *Int. J. Res. Eng. Technol.* 3 15
[9] Toniolo N, Rincón A, Roether J, Ercole P, Bernardo E and Boccaccini A 2018 *Constr. Build. Mater.,* 188 1077
[10] INCDPM Bucharest, Obtaining different environmental friendly composite materials by using secondary raw materials, *Research Programme NUCLEU—MEVAS*, Bucharest, 2017
[11] Moncea A M, Badanoiu A, Georgescu M and Stoleriu S 2013 *Mater. and Str.* 46 2135
[12] Ascensão G, Seabra M P, Aguiar J B and Labrincha J A 2017 *J. Clean. Prod.* 148 23
[13] Novais R M, Ascensão G, Seabra M P and Labrincha J A 2016 *Waste Manage.* 52 245
[14] Kuenzel C, Grover L M, Vandeperre L, Boccaccini A R and Cheeseman C R 2013 *J Eur Ceram Soc.* 33 251

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