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# Mechanical and thermal characterisation of geopolymers based on silicate-activated metakaolin/slag blends

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**Abstract** This article assesses the effect of mix design parameters on the compressive strength and thermal performance of alkali silicate-activated blends of metakaolin (MK) and granulated blast furnace slag (GBFS). A strong interrelationship between the effects of activator composition and the GBFS/(GBFS + MK) ratio is identified through statistical analysis of compressive strength data. Pastes formulated with higher $SiO_2/Al_2O_3$ molar ratios show improvements in mechanical strength with increasing GBFS addition, associated with the formation of a structure comprising coexisting aluminosilicate 'geopolymer' gel and Ca-rich Al-substituted silicate hydrate (C-(A)-S-H) reaction products. The inclusion of GBFS in MK-based geopolymers seems also to improve their performance when exposed to high temperatures, as higher residual compressive strengths are reported for these mixtures compared to solely MK-based systems. Only slight differences in shrinkage behaviour are observed at temperatures of up to 600 °C with the inclusion of GBFS; however, slag-blended pastes exhibit enhanced stability at temperatures exceeding 800 °C, as no variation in the compressive strength and no additional shrinkage are identified. These results suggest that nanostructural modifications are induced in the gel by the inclusion of GBFS into MK-based geopolymers, improving the overall performance of these materials.

## Introduction

The chemical reaction between an aluminosilicate source and an alkaline solution, when formulated in adequate proportions, produces a mechanically strong material referred to as an alkali-activated binder, or 'geopolymer' [1]. Metakaolin (MK)-based geopolymers have been widely studied over the past decades [2–4], but one of the main drawbacks of these binders is a tendency towards a large degree of drying shrinkage and cracking [5]. This is associated with the high water demand of the reacting mixes, as a consequence of the high surface area and particle shape of MK [6]. This affects the mechanical strength development and stability of these materials, which does not always compare well with the performance of other alkali-activated binders based on industrial by-products, such as granulated blast furnace slag (GBFS) or high-calcium fly ash (HCFA) which present lower cost and higher potential for large-scale industrial applications than MK. Other than the lower aspect ratio of the particles, the main difference between these precursors is the presence of calcium in the GBFS and HCFA, which leads to the development of a microstructure enriched in stable and high density phases such as C-S-H gels, which promotes high compressive strengths [7, 8].

The effect of calcium inclusion in geopolymers based on MK has been studied using different sources such as calcium hydroxide [9, 10], GBFS [10–17], natural calcium

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silicate materials [14], and carbonates [19, 20]. In general, an improvement in mechanical strength with the inclusion of calcium has been reported, as a consequence of a microstructure mainly composed of coexisting alkali aluminosilicate (‘geopolymer’) gel and Al-substituted calcium silicate hydrate (C-S-H) gel. For MK/GBFS blends, it has been identified that the mechanism of activation is highly dependent on both the alkalinity of the alkali activator and the ratio between MK and GBFS, which act together to control the rate of $Ca^{2+}$ dissolution and availability during the reaction [19]. Under lower alkalinity conditions, the dissolution of $Ca^{2+}$ from GBFS is promoted and consequently the formation of C-S-H type gels is favoured, leading to stable gel coexistence, but higher alkalinity tends to lead to $Ca(OH)_2$ precipitation rather than gel growth. These general observations are in good agreement with the specific structural details observed by Buchwald et al. [15] in blended GBFS-MK binders by nuclear magnetic resonance (NMR) spectroscopy, and by Bernal et al. [17, 18] using high-resolution X-ray diffractometry.

In order to assess the stability of both types of gels, and their interactions under different alkalinity conditions, studies have been carried out in synthetic mixes of both types of compounds [21]. It has been reported that the addition of alkalis to these synthetic gels induces modifications of the original C-S-H gel, promoting the formation of a C-N-S-H gel [22–24]. Similar mixed sodium-calcium silicate hydrate gels have been observed directly in alkali silicate-activated slag binders by Bernal et al. [17, 18], and are believed to improve the durability of alkali silicate-activated GBFS/MK blends when exposed to $CO_2$-rich environments [17].

Several studies have been reported regarding the performance at high temperatures of alkali-activated materials based individually on MK [2, 25–33] and GBFS [11, 34–37]. Those studies have found that alkali-activated systems, independent of the precursor used but particularly in the low-calcium ‘geopolymer’ systems, generally show a higher stability when exposed to high temperatures than ordinary Portland cement. This is attributed to the presence of a highly condensed binder gel, the low content of chemically bonded water in the alkali-activated gel products, and the absence of portlandite as a reaction product in the majority of systems. This means that alkali-activated binders can provide an attractive technological alternative to traditional cements in applications where stability at high temperatures is required. However, the effect of including GBFS in MK-based geopolymers, in terms of thermal performance, has not been reported in the literature. These blended systems are of interest due to their good mechanical performance, as well as the increased setting times compared to GBFS-only systems [18].

The purpose of this article is to remedy this deficit in the literature: geopolymers are produced with specified overall (activator + solid precursor) $SiO_2/Al_2O_3$ molar ratios, and different degrees of GBFS substitution for MK, according to a factorial experimental design. Performance at high temperatures is studied by exposing the specimens to temperatures up to 1000 °C, and then determining residual compressive strength and autogenous shrinkage. Thermogravimetry is also conducted for paste samples before and after exposure to elevated temperatures, to provide a better understanding of the relationship between the structure of the blended pastes and their performance.

## Experimental program

### Materials

The primary raw material used in this study is a MK produced in the laboratory by calcination of a Colombian kaolin containing minor quartz and dickite impurities [18]. Calcination was carried out at 700 °C in an air atmosphere, for 2 h. The particle size range of the MK was 1.8–100 µm, with a $d_{50}$ of 12.2 µm and 10% of particles finer than 4 µm. A highly amorphous GBFS from the Colombian factory *Acerías Paz del Río* was also used. Its specific gravity was 2900 kg/$m^3$ and Blaine fineness 399 $m^2$/kg. The particle size range, determined through laser granulometry, was 0.1–74 µm, with a $d_{50}$ of 15 µm. The chemical compositions of these raw materials are shown in Table 1, where the basicity coefficient ($K_b = CaO + MgO/SiO_2 + Al_2O_3$) and the quality coefficient ($CaO + MgO + Al_2O_3/SiO_2 + TiO_2$) determined for GBFS were 1.01 and 1.92, respectively.

Alkaline activating solutions of the desired composition were formulated by blending a commercial sodium silicate solution with 32.4 wt% $SiO_2$, 13.5 wt% $Na_2O$ and 54.1 wt% $H_2O$, and solid analytical-grade NaOH, to reach desired modulus values ($SiO_2/Na_2O$ molar ratio, denoted Ms) between 0.9 and 2.0.

**Table 1** Composition of the MK and GBFS used, from X-ray fluorescence analysis. LOI is loss on ignition at 1000 °C

| Component (mass % as oxide) | MK | GBFS |
|---|---|---|
| $SiO_2$ | 50.72 | 32.29 |
| $Al_2O_3$ | 44.63 | 16.25 |
| CaO | 2.69 | 42.45 |
| $Fe_2O_3$ | – | 2.35 |
| MgO | – | 2.87 |
| Other | 0.94 | 1.88 |
| LOI | 1.02 | 1.91 |

## Sample preparation and tests conducted

### *Samples without exposure to high temperatures*

The geopolymers were formulated with GBFS/(GBFS + MK) ratios of 0.0, 0.2, 0.4, 0.6 and 0.8. The alkali activator was formulated in order to obtain overall (activator + solid precursor) $SiO_2/Al_2O_3$ molar ratios of 3.0, 3.4, 3.8 and 4.0 and a constant $Na_2O/SiO_2$ ratio of 0.25. The quantity of water in the alkali activator was adjusted to achieve a $H_2O/Na_2O$ ratio of 12. These activation conditions have been identified as enabling MK-based geopolymer systems to reach high compressive strengths while retaining acceptable workability [38]. The fresh pastes were mixed, poured into cylindrical moulds, and vibrated for 5 min to reach a homogeneous distribution in the mould and remove entrained air. Samples were kept in the moulds for the first 24 h and then exposed to thermal curing at 60 °C and >90% relative humidity for 24 h. Subsequently, the samples were stored at ambient temperature (25–30 °C) and 90% relative humidity for 7 days.

The compressive strength was assessed by testing cylindrical samples of 30 mm (diameter) × 60 mm (height), using a universal testing instrument (ELE International) at a displacement rate of 1 mm/min. Sample ends were flattened and made parallel using coarse sandpaper before testing. Each reported value corresponds to the average of 5–7 measurements. The statistical analysis of the effect of formulation conditions on the compressive strength of alkali-activated MK/GBFS blends was carried out using a full fixed factorial 4 × 5 experimental design. The factors analysed were the $SiO_2/Al_2O_3$ molar ratio and the GBFS/(GBFS + MK) ratio, as described in Table 2.

Variance analysis (ANOVA) and post-ANOVA tests (Tukey probe) of the compressive strength results were conducted using the software package Minitab 15, in order to determine the significance and effect of each factor assessed. The ANOVA examination of the factorial experimental design is based on the fact that the total sum of squares (TSS) can be divided into the sum of squares of the factors studied, their interaction, and the error. The $p$ values obtained for each factor contributing to the TSS and obtained from the ANOVA establish the significance level of each factor and its interactions in the response variable (i.e., compressive strength). Here, a significance level of 95% was fixed, so that a $p$ value lower than 0.05 indicates that the factor or interaction has a statistically significant effect on the compressive strength.

**Table 2** Factors and levels analysed through the factorial experimental design

| Factor | Levels |
|---|---|
| GBFS/(GBFS + MK) ratio | 0.0, 0.2, 0.4, 0.6, and 0.8 |
| $SiO_2/Al_2O_3$ molar ratio | 3.0, 3.4, 3.8, and 4.0 |

The mixes exhibiting the highest compressive strength, for each GBFS/(GBFS + MK) ratio, were milled and sieved to pass a 0.074 mm sieve, and then analysed using a thermogravimeter SDT-Q600 in a nitrogen atmosphere, from 25 to 1100 °C at a heating rate of 10 °C/min.

### *Samples exposed to high temperatures*

Thermal performance was assessed in geopolymers formulated with an overall (activator + solid precursor) $SiO_2/Al_2O_3$ molar ratio of 3.0, GBFS/(GBFS + MK) ratios of 0.0 and 0.2, and constant $H_2O/Na_2O$ and $Na_2O/SiO_2$ ratios of 12 and 0.25, respectively. These formulation conditions were selected with the aim of producing blended geopolymers rich in MK and with satisfactory mechanical performance. Samples were produced as described above.

The specimens were heated in a furnace at temperatures of 200, 400, 600, and 1000 °C, with a heating rate of 1 °C/min, a hold time of 2 h, and then cooled inside the furnace to 25 °C, to avoid thermal shock and potential cracking of the samples. The heating conditions were established taking into account the low thermal conductivity of the geopolymer samples ($\lambda \approx 0.44$ W/m K) [39]. After thermal exposure, residual compressive strength and volumetric contraction were determined. Additional thermogravimetric analysis of samples exposed to high temperatures was conducted, under the same testing conditions as described above.

# Results and discussion

## Characterisation of silicate-activated metakaolin/slag blends

### *Compressive strength*

The addition of GBFS to MK-based geopolymers leads to an increase in compressive strength (Fig. 1), compared with reference samples produced using MK as the sole precursor. This effect is more evident in geopolymers formulated with $SiO_2/Al_2O_3$ ratios of 3.8 and 4.0, where the samples with 80% GBFS exhibited compressive strength values up to five times higher than the samples without GBFS. However, the beneficial effects of GBFS addition are less marked at lower $SiO_2/Al_2O_3$ ratios. Excess slag addition at the lowest $SiO_2/Al_2O_3$ ratio tested (i.e., with the use of the most alkaline activator among the samples tested) leads to a decrease in strength beyond 60% GBFS, which was not observed when more Si-rich activators were used. Binders with a GBFS/

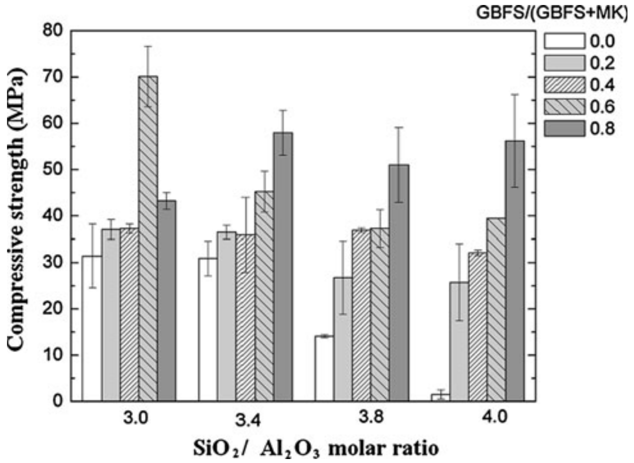


**Fig. 1** Compressive strengths of geopolymers produced by silicate activation of MK/GBFS blends, as a function of the overall $SiO_2/Al_2O_3$ molar ratio. Data shown are the mean of 5−7 replicate measurements; *error bars* represent one standard deviation

(GBFS + MK) ratio of 0.8 formulated with $SiO_2/Al_2O_3$ ratios between 3.4 and 4.0 showed the highest compressive strengths among the samples analysed here, reaching values up to 60 MPa. This is consistent with the strength data previously reported for pastes [18], mortars [17], and concretes [40] at this GBFS/(GBFS + MK) ratio and with higher Ms activators. Pure GBFS systems were not formulated in this investigation due to the excessive alkalinity required to reach the selected $SiO_2/Al_2O_3$ and $Na_2O/SiO_2$ ratios. It is also notable that the lowest compressive strength values observed for any of the samples including GBFS are around 30 MPa, regardless of the activation conditions.

An increase in the $SiO_2/Al_2O_3$ ratio in the blended MK/GBFS systems here causes a reduction in the compressive strength of all of the primarily geopolymer systems (systems with GBFS contents below 80%, Fig. 1), similar to the well-known trends observed in geopolymers based solely on MK at overall $SiO_2/Al_2O_3$ ratios greater than 3.0 [38, 41]. An excess of silicates, associated with higher $SiO_2/Al_2O_3$ ratios here, is known to lead to a reduction in the compressive strength of MK-rich geopolymers [41], as the extent of polymerisation of the silica is high and its rate of reaction is therefore slower than is required for optimal strength development in systems dominated by MK. This is because the most active silicate species involved in MK dissolution is the silicate monomer, and this is only present at low concentrations in high-modulus silicate solutions [42].

However, this decrease in strength with increasing $SiO_2/Al_2O_3$ ratio is not observed in the more slag-rich systems, consistent with the literature for slag-only binders [17, 18]. Here, the dominant effect is not specifically related to the availability of silicate monomers, as dissolved silica plays a less active role in the dissolution of GBFS compared to MK. Instead, the presence of a higher concentration of soluble silica reduces the pH of the activating solution, and therefore also the free hydroxide concentration. This shifts the $Ca(OH)_2$ solubility equilibrium to favour the dissolution of calcium from the slag, promoting the subsequent formation of stable calcium-containing gel phases.

The enhancement of compressive strength of geopolymers based on MK by addition of small amounts of GBFS has also been observed by other authors [11–16], although no study spans the full range of binary systems as studied here. The addition of GBFS, and most specifically its role in supplying soluble $Ca^{2+}$ ions, plays an important role in determining the physical and mechanical properties of the blended systems. In blended pastes at high alkalinity conditions (low $SiO_2/Al_2O_3$ ratio), the geopolymeric product formed via MK activation is the main contributor to mechanical strength, as C-S-H phases are less stable under very high alkalinity [22, 43], and $Ca(OH)_2$ precipitation may take place instead of C-S-H formation, even when the concentration of dissolved $Ca^{2+}$ is low, due to the very high free hydroxide concentration [44]. However, at lower alkalinity, the presence of C-S-H gel formed via the activation of GBFS contributes significantly to the binder performance.

The compressive strength of geopolymer pastes is also a consequence of the chemical bonds involving the aluminosilicate gel formed, and the physico-chemical interactions that can occur between the geopolymeric gel and the unreacted particles [41]. It has been reported [9, 10, 45, 46] that the activation of MK in the presence of moderate to high concentrations of calcium can lead to the formation of C-S-H and C-A-S-H gels, along with geopolymer-type gel, under suitable activation conditions. In such systems, the $Ca^{2+}$ ions may also become associated with the Si-O-Al framework of the geopolymeric gel, contributing to balancing the negative charge associated with tetrahedral Al(III), in place of the alkali metal cations which usually fulfil this role [2, 43, 47].

Based on the results of ANOVA analysis (Table 3) with a degree of significance of 0.001, it is possible to identify a second-order interaction between the $SiO_2/Al_2O_3$ ratio and the GBFS/(GBFS + MK) ratio. This agrees well with the mechanistic arguments presented above, regarding the different roles of the silica supplied by the activating solution in the presence of different amounts of calcium, showing that this difference in the reaction mechanism as a function of activator alkalinity has a statistically significant impact on the compressive strength of the resulting binder.

Additionally, a Tukey probe ($p$ value $< 0.05$) was performed to determine whether there are statistically significant differences between the different combinations of activation conditions and GBFS substitution levels assessed in this study. The results reveal that from a statistical

**Table 3** ANOVA results for the compressive strength of geopolymers based on silicate-activated MK/GBFS blends ($R^2 = 0.934$)

| Source of variability | Sum of squares | F | p-value |
|---|---|---|---|
| Model | 7630 | 14.99 | – |
| $SiO_2/Al_2O_3$ molar ratio | 967 | 12.03 | 0.000 |
| GBFS/(GBFS + MK) ratio | 4970 | 46.37 | 0.000 |
| ($SiO_2/Al_2O_3$) × (GBFS/(GBFS + MK)) | 1694 | 5.27 | 0.001 |
| Error | 536 | – | – |
| Total | 8166 | – | – |

point of view there is not a significant difference in the strengths of each of the following sets of mixes:

- geopolymers with no GBFS at $SiO_2/Al_2O_3$ ratios of 3.8 and 4.0;
- geopolymers with no GBFS at $SiO_2/Al_2O_3$ ratio of 3.0 and 3.4;
- geopolymers with 60% GBFS at $SiO_2/Al_2O_3$ ratios of 3.4, 3.8, and 4.0.

This information is potentially valuable in designing formulations for MK/GBFS-blended geopolymers, enabling optimisation of the content of activator that needs to be included for a desired compressive strength based on other criteria including workability, setting time, and economics. For instance, alkali-activated GBFS systems have previously been shown [18] to give higher compressive strengths than those with GBFS/(GBFS + MK) ratios of 0.8 or 0.9, but the addition of MK has nonetheless been observed to be desirable in these systems due to the greater control of setting time, which is able to be obtained in the blended systems, while still achieving very acceptable mechanical performance.

*Thermogravimetry*

The sample set with the highest compressive strength was selected for further analysis by thermogravimetry: $SiO_2/Al_2O_3$ ratios of 3.0 for each GBFS/(GBFS + MK) ratio studied. From Fig. 2, it can be seen that all the specimens present the bulk of their weight loss at temperatures below 300 °C, but there are variations in the distinct minima of the low-temperature weight loss peaks for the samples with different contents of GBFS; this is particularly visible in the inset panel of Fig. 2. Considering the temperature of the minimum of the first weight loss peak for the lower slag samples (~58 °C), it is possible to identify that MK-based geopolymers and samples containing up to 40% of GBFS present a similar trend in weight loss. This indicates that the main structure of these MK/GBFS blends is dominated by aluminosilicate type products (geopolymer gel), which usually present high weight loss at low temperatures as a consequence of the freely evaporable water present in large pores in these gels [48]. The remainder of the water associated with these gels is present as tightly absorbed water in small pores, or as condensed hydroxyl groups on the surface of the gel [29, 30].

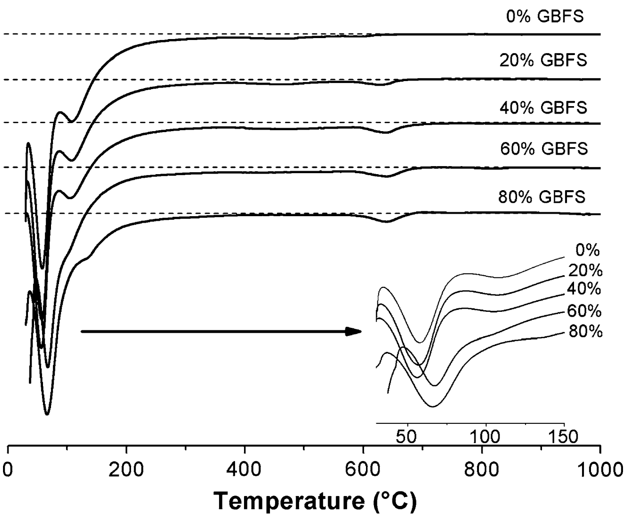


**Fig. 2** Differential thermograms (DTG; mass loss downwards, *dashed lines* represent zero for each data set) indicating the effect of the content of GBFS in alkali silicate-activated MK/GBFS blends

The identification of a second, low-intensity peak at ~107 °C is also observed, which is likely to be related to reaction products with water more tightly bonded to their structure than in geopolymeric gel. At this temperature, it is common to detect the start of the dehydration of zeolites and related structures (e.g. hydrosodalite) [49], and therefore, this small band is likely to indicate the formation of minor zeolite-type phases in these systems, as expected in MK-geopolymers, particularly when cured at slightly elevated temperature [50].

Increased contents of GBFS (60 or 80%) cause a shift to higher temperatures (~67 °C) of the distinct minimum of the first weight loss peak, suggesting differences in the structures of these samples which result in different dehydration characteristics. Specimens containing 60 or 80% of GBFS present a broader low-temperature pore water peak overlapping the ~107 °C peak, which is distinguishable as a shoulder in samples with 60% GBFS, but not at 80%. The formation of a low intensity peak at 140 °C in the sample with 80% GBFS can be attributed to the dehydration of a C-S-H gel [51], as this is the main reaction product identified in GBFS-rich blended binders [15–18].

This indicates that, under the alkalinity conditions assessed, an increase in the content of calcium available in the systems is favouring the formation of Ca-rich phases such as C-S-H gels with a high degree of Al substitution, as typically observed in alkali-activated slag binders [18, 52–55]. The shift in the low-temperature peak from ~58 to ~67 °C may be associated with the incorporation of Ca in the geopolymer gel, modifying its structure and favouring the formation of different phases such as N-(C)-A-S-H, as previously identified in activated GBFS/MK blends [17, 18] and synthetic gels [22], with the pore water slightly more strongly held in the gel than in a purer alkali aluminosilicate geopolymer gel.

The higher-temperature regions of the DTG plots in Fig. 2 are reasonably featureless, particularly at low slag content, with a gradual weight loss observed as the small quantity of chemically bound water (present as hydroxyl groups bonded to gel network Si and Al sites) is released. In samples containing GBFS, an additional peak is identified at temperatures between 590 and 690 °C, which is attributed to the presence of calcium carbonates of varying crystallinity. This has been observed in previous studies of alkali-activated slag using a similar precursor [17, 18] as a consequence of weathering of the slag before sample preparation. Considering that samples were cured and stored under controlled sealed conditions, a significant extent of carbonation is not expected to occur in the specimens assessed. Slight increments in the intensity of this band with the addition of more GBFS are consistent with this suggestion. None of the samples show significant weight loss above 700 °C.

## Effect of exposure to high temperatures of silicate-activated MK/GBFS blends

### *Residual compressive strength and shrinkage*

The samples with a $SiO_2/Al_2O_3$ ratio of 3.0, and 0 and 20% GBFS content, were selected for further analysis by thermal treatment, to determine the effect of low levels of slag addition on the thermal behaviour of a MK-based geopolymer. The compressive strengths of the geopolymer pastes decreased by as much as 35 MPa (Fig. 3) when samples were exposed to 200 °C and then cooled to room temperature for testing. This is coherent with the TGA results (Fig. 2), showing that the samples have lost a large fraction of their weight at this temperature. The materials also display a volumetric contraction of up to 15% (Fig. 4), as a consequence of the increased surface energy of the gel as water is released from its surface and small pores, which will cause the porous gel network to partially collapse [28, 29]. This is likely to induce microcracking, as observed in other Ca-rich alkali-activated cements exposed to high temperatures [36, 56], which may act as stress concentrators, reducing the loading capacity of the pastes.

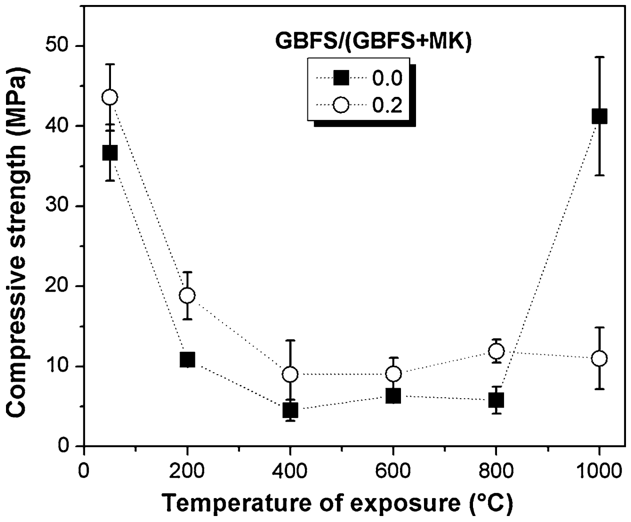


**Fig. 3** Compressive strengths of alkali silicate-activated MK/GBFS blends as a function of the temperature of exposure. Each value corresponds to the average of 5–7 measurements

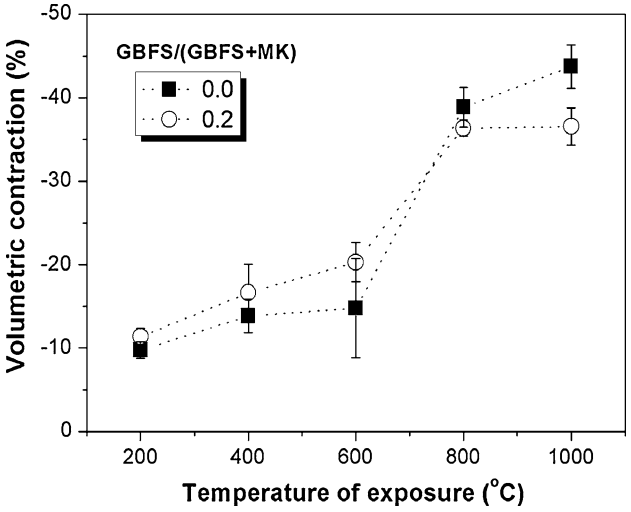


**Fig. 4** Volumetric contraction of alkali silicate-activated MK/GBFS blends under high temperature exposure. Each value reported corresponds to the average of 7 specimens, measured as the change in both diameter and height of the cylindrical samples

There is a slight further loss of strength between 200 and 400 °C, but any variations in the mechanical strength at temperatures between 400 and 600 °C are within the experimental uncertainty, which correlates well with the stability of the materials in this temperature range as identified by thermogravimetry (Fig. 2). Specimens containing 20% GBFS present a more marked decrease in compressive strength compared with unblended samples in this temperature range, which could be attributed to the dehydroxylation of Ca-containing products formed in these systems (possibly including C-S-H gel). This reduction in mechanical strength is also coherent with the greater extent of volumetric shrinkage detected at 600 °C in the blended pastes (Fig. 4).

On the other hand, the purely MK-based systems do gain strength after exposure at 1000 °C. This elevated temperature has led to structural reorganisation of the geopolymer gel, contributing to formation of a new structure exhibiting compressive strength comparable to that of unexposed samples. Duxson et al. [29, 30] identified that in MK-based geopolymers, exposure to this range of temperatures led to densification of the sample, comparable to a viscous sintering process, as the gel network softens and the interparticle spaces in the geopolymer gel collapse, as shown for these samples by the electron micrographs presented in Fig. 5. This is likely to enhance the post-heat treatment mechanical performance of the samples, as the softened gel regions then solidify to form a glassy structure upon cooling. However, this reaction leads to severe shrinkage of the samples as observed in Fig. 4, associated with the contraction of the silicate gel [57]. The severe shrinkage does start at a lower temperature than the strength gain, at 800 °C both the 0 and 20% GBFS samples (Fig. 4), which shows that the start of densification by viscous sintering precedes the development of a sufficient quantity of molten aluminosilicate to give sufficient glass formation for an increase in strength. It is also likely that there is some crystallisation of dense sodium aluminosilicate phases such as nepheline in this temperature range, as observed for comparable MK-based samples by Duxson et al. [58].

The onset of densification is also observed here for pastes with 20% GBFS, as seen by the markedly higher extent of shrinkage from 600 to 800 °C in this sample set in Fig. 4. However, the later increase in post-exposure mechanical strengths is not observed in these samples, meaning that any significant extent of melt formation must take place at a temperature exceeding 1000 °C. For alkali-activated slag binders, it has been reported [35] that samples synthesised with high-modulus activators exposed to temperatures of 1200 °C can exhibit increments in compressive strength of up to 40% compared with specimens before heating, which is associated with the formation of crystalline phases such as åkermanite and gehlenite. This indicates that higher temperatures of exposure might be required to induce structural changes in the more Ca-rich products formed in blended binders compared to the MK-only system. The geopolymer gel has been identified as the dominant reaction product in the 20% GBFS system, so it may be that the incorporation of small amounts of Ca into its structure leads to an increase in melting temperature. However, the use of lower-modulus activators in the alkali activation of GBFS led to complete failure of the samples at 1200 °C [36], showing the importance of silica in the formation of the glassy phases which result in the retention of significant residual strength after heat exposure.

An increase in $SiO_2/Al_2O_3$ ratio leads to reductions in the onset temperature of densification of MK-geopolymers, which may be associated at least in part with incomplete incorporation of aluminium from MK into the gel [48]. The incomplete reaction means that there are more free sodium cations present, because fewer are required to charge-balance framework Al sites, and the presence of excess alkalis reduces the glass transition temperature of aluminosilicates [29, 30]. Considering that all samples were formulated in order to reach constant overall $SiO_2/Al_2O_3$ molar ratios, the activating solution modulus used was lower for the samples which included GBFS. This might reduce the availability of soluble silicates at early ages of reaction, promoting the formation of a geopolymer gel with lower $SiO_2/Al_2O_3$ ratio than the gel which forms in the MK-only samples, consequently increasing the onset temperature of densification.

The results obtained here are not completely conclusive regarding the role of calcium in determining the thermal performance of activated MK/GBFS blends, because different factors such as variations in the porosity of the samples, which has not been analysed in this study, might also affect the behaviour at high temperatures of these binders. In this regard, Zhang et al. [59] analysed the effect of including GBFS into MK-based geopolymer matrices in terms of the permeability of the materials, identifying that the addition of GBFS reduces permeability, which is intrinsically related to the porosity of the binder. Molecular water held in finer pores will be removed from the sample at slightly higher temperatures, and so this observation is also consistent with the thermogravimetry data presented above.

### *Thermogravimetry*

Both the unexposed and exposed samples (after heating to 600 and 800 °C) were subjected to analysis by thermogravimetry. These data sets are plotted, along with the data for the unheated sample (as in Fig. 2), in Fig. 6. In unblended samples, after exposure to 600 °C or higher, the free water peak centred at ~60 °C is not observed, due to the evaporation of freely bonded water from the geopolymer gel during heating.

However, the growth of an asymmetric mass loss peak between 60 and 250 °C, centred at ~110 °C, is identified, and is attributed to the dehydration of the zeolite-like structures present in the aluminosilicate geopolymer gel. Upon initial heating to 600 °C, these structures were fully dehydrated, but did not undergo full structural collapse, meaning that they were able to become partially rehydrated during sample cooling and preparation for TGA analysis in

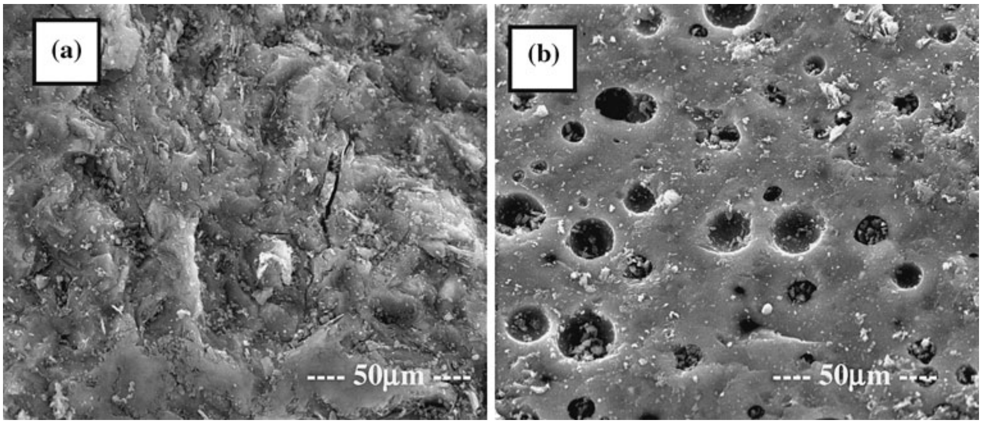
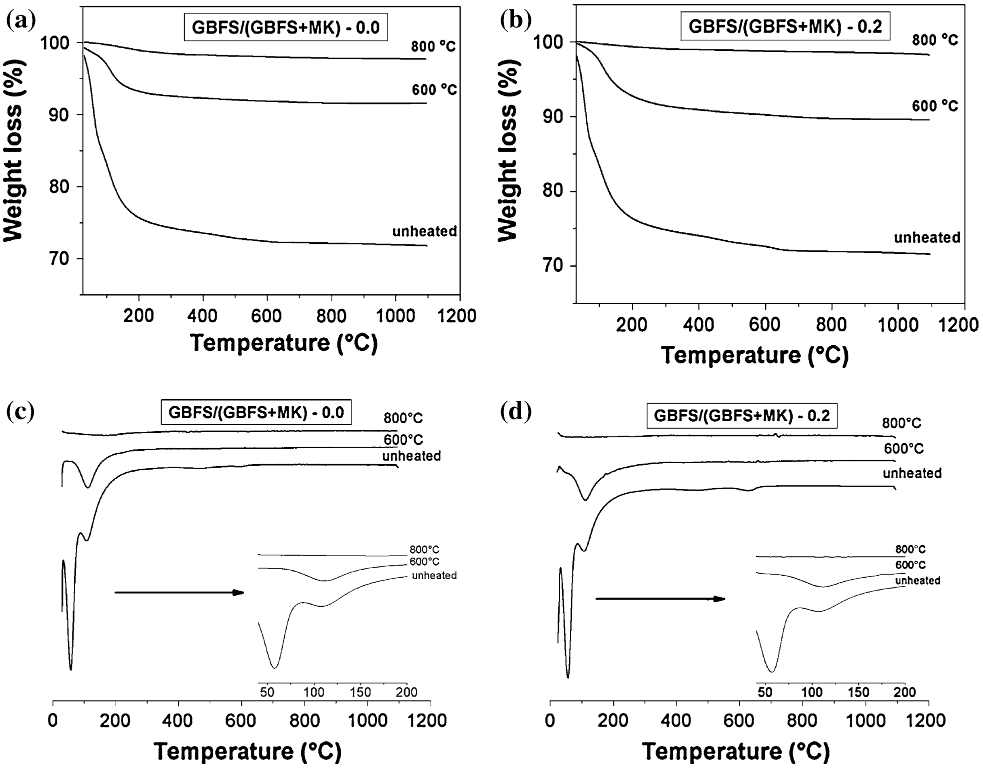


**Fig. 5** Representative scanning electronic micrographs (FEI QUANTA; 30 keV accelerating voltage) of MK based geopolymers formulated with a $SiO_2/Al_2O_3$ ratio of 3.0 after **a** 7 days of curing and **b** exposure to 1000°C

**Fig. 6** Thermograms and differential thermograms for **a**, **c** alkali silicate-activated MK, and **b**, **d** the MK/20%GBFS blend, each with an overall $SiO_2/Al_2O_3$ ratio of 3.0, where the samples had previously been exposed to elevated temperatures as marked



the humid ambient laboratory atmosphere. This peak is not identified in the DTG results of samples exposed at 800 °C, which is consistent with the high volumetric contraction exhibited at this temperature, suggesting that the variation in physico-mechanical properties of the MK-based geopolymers after exposure to temperatures higher than 600 °C is related to the collapse of the zeolite-like geopolymer gel structure and its contribution to the densification of the matrix.

Similar findings are observed in the blended samples. In this case, after exposure to 600 °C a small remnant quantity of more readily evaporable water (centred at ~60 °C), attributed to water in calcium-rich phases, is observed, along with a wider weight loss peak associated with zeolitic water (centred at ~110 °C). In samples exposed at 800 °C, these peaks again cannot be identified, in good agreement with the observations for the unblended samples, and also the high extent of volumetric contraction in these specimens. This further indicates that Ca-rich products are being formed in these samples, even when low percentages of GBFS are included in the matrix, and considering the widening of the band between ~71 and 310 °C, the results are coherent with the dehydration temperature range of a C-S-H gel [51]. As no further variation of the physico-mechanical properties of these pastes can be observed when they are exposed to higher temperatures (1000 °C), it can be proposed that the coexistence of the geopolymer and C-S-H gels modifies the mechanism of densification of the samples to be at least in part a crystallisation-led phenomenon, as identified for alkali-activated GBFS.

The results obtained here are also consistent with the data of Dombrowski et al. [60] regarding the effects of calcium addition on the thermal contraction and post-thermal treatment strength of fly ash-based geopolymers blended with different percentages of $Ca(OH)_2$. In that system, the addition of small amounts of $Ca(OH)_2$ increased the temperature at which full densification occurred, and also gave an enhancement in the strength of the samples after cooling to room temperature, consistent with the effect of calcium on the geopolymer gels here. However, the addition of a higher content of calcium, giving the formation of a more C-S-H based gel, led to a significant decrease in the post-exposure strength, and densification at a higher temperature, which is more consistent with the alkali-activated slag systems discussed in the literature [35, 36]. The 20% GBFS samples studied here fall between these two extremes, and so comparison with the literature for the end-member systems provides the ability to better understanding of the behaviour of these samples.

## Conclusions

Adding ground blast furnace slag to MK-based geopolymers while maintaining a constant overall $SiO_2/Al_2O_3$ ratio provides an improvement in mechanical properties. There is an optimum in strength at 60% slag addition for an overall $SiO_2/Al_2O_3$ ratio of 3.0, while strength increases monotonically with slag addition up to 80% for $SiO_2/Al_2O_3$ ratios of 3.4 or higher. An excessively high silica content is more detrimental to the performance of unblended MK geopolymers than it is in the presence of even as little as 20% GBFS; C-S-H-type gels are able to form at these higher $SiO_2/Al_2O_3$ ratios, while the alkalinity of the very high-silica systems is not sufficient to give satisfactory geopolymer gel formation. There is a strong interrelationship between $SiO_2/Al_2O_3$ ratio and slag content in determining the strength of blended geopolymers; these parameters are not independent of each other, meaning that an understanding of the chemistry controlling this interaction is necessary in the design of cost-effective, high-performance geopolymer mixes depending on the relative availabilities of the two types of precursors in a specific location.

Thermogravimetric analysis shows that the geopolymer gel structure is modified in the presence of calcium, including changes in the structure and the extent of zeolite formation, as identified by the nature of the low-temperature water loss peaks. The unblended MK system and the system with 20% slag show very similar extents of densification at 800–1000 °C; however, the unblended system shows a much higher residual strength upon cooling from 1000 °C to room temperature, indicating that the extent of glass formation from the geopolymer gel at 1000 °C is reduced by the incorporation of Ca into the gel, as a consequence of the formation of a C-S-H type gel that coexists with the aluminosilicate geopolymer gel.

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