

Activation of Metakaolin/Slag Blends Using Alkaline Solutions Based on Chemically Modified Silica Fume and Rice Husk Ash

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Abstract This study describes the use of alkaline silicate solutions produced by mixing silica fume (SF) or rice husk ash (RHA) with aqueous NaOH, as alternative silica-based activators for metakaolin (MK)/slag (GBFS) blended binders. Pastes prepared with these activators show similar trends in mechanical strength development as a function of activation conditions compared with the pastes obtained using commercial silicate solutions as activator. All activating solutions promote higher compressive strength development with increased contents of GBFS in the binders, which promotes the coexistence of aluminosilicate reaction products along with calcium silicate hydrate gel. Higher-silica binding systems prefer a higher GBFS content for optimal strength development compared to those with a lower overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. SF-derived activators give reaction products which are very similar to those obtained using commercial silicate solutions, as a consequence of the high reactivity of this precursor, supplying high concentrations of Si to the systems since the early stages of reaction. RHA-derived activators appear to have

slightly delayed Si availability due to the less-reactive character of this precursor, which influences the relative rates of formation of the two types of gel in blended systems. These results show that activation of GBFS/MK blends with by-product derived silicate-based activators can generate mechanical strengths and structures comparable to those obtained using commercial silicate solutions.

Keywords Alkali-activation · Granulated blast furnace slag · Metakaolin · Sodium silicate · Silica fume · Rice husk ash

Introduction

Alkali-activated binders (also referred as to ‘geopolymers’) are produced from an aluminosilicate source mixed with an alkaline solution, which promotes the dissolution of the silicate and aluminate species present in the precursor, and their consequent polycondensation to form a material with good mechanical performance [1]. These binders exhibit technological and ecological advantages in comparison with ordinary Portland cement (OPC), and the industrial use of geopolymer concretes in the production of high performance building materials is expanding [2]. Different alkaline solutions based on alkali metal hydroxides, carbonates and silicates have been used over the past decades for the production of alkali-activated binders [3]. A strong dependence on the nature of the alkaline activator in the structural and mechanical development of these binders has been identified throughout the literature.

Sodium silicate has been extensively used in the activation of aluminosilicate precursors such as granulated blast furnace slag (GBFS), metakaolin (MK), fly ash and others. This has been identified as the activator which

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generally promotes the highest mechanical strength development along with a reduced permeability, which is associated with a stable and densified structure [4–8]. However, the use of sodium silicate markedly increases the embodied energy and CO₂ emissions associated with alkali-activated-based binders [9, 10], as a consequence of its manufacturing process which involves the calcination of sodium carbonate (Na₂CO₃) and quartz sand (SiO₂) at temperatures between 1,400 and 1,500°C. This process generates CO₂ as a decomposition product, and also leads to emissions from the fuel required to achieve the high-temperature conditions [11]. This has promoted the development of alternative activators with a view towards increased sustainability.

Živica and Rowseková [12–15] have conducted several studies on modified silica fume (silica fume + NaOH), identifying the great potential of this solution in the production of high performance activated slag binders. Similar results have been obtained by the authors [16] in the activation of fly ash using modified nanosilica. These facts suggest that the combination of alkalis with highly amorphous Si-containing precursors can be successfully used as alternative activators in the production of geopolymer binders based on a range of aluminosilicate components. A point of interest is that this is not limited to silica fume, which is a by-product but a moderately high-value one due to its purity, but also includes the use and valorization of alternative, low-value silica-rich wastes, such as rice husk ash.

The rice husk is the hard coating of the rice grain, and is composed of minerals that need to be removed for human consumption. This by-product is usually used as a fuel in a boiler in the rice mill or in a small electricity generating plant, or as a fertilizer for agriculture. The combustion of this husk generates high volumes of ash, varying from 13 to 29 wt% depending on the variety of the rice, the climate, and the geographic location where it is produced [17, 18]. The rice husk ash (RHA) is largely composed of silica (87–97 wt%) with small amounts of inorganic salts, making it a sustainable source of Si for several applications [17, 18]. The use of RHA as a mineral admixture combined with Portland cement in the production of high performance binders has increased over the past decades, as a consequence of its similarities to silica fume (SF) in terms of the high content of reactive SiO₂ and a very high specific surface area [19, 20], when produced under appropriate conditions. RHA has been also used as a component in the production of alkali-activated binders [21, 22], as a raw material for the preparation of Si-rich zeolites [23–25] and recently, as a precursor for the production of soluble sodium silicates [26, 27]. This makes RHA an attractive candidate for the preparation of Si-rich alkaline solutions that can be used in alkali-activation processes.

Under proper activation conditions, activated MK/GBFS blends develop a structure mainly composed of coexisting alkali aluminosilicate (‘geopolymer’) gel and Al-substituted calcium silicate hydrate (C–S–H) gel. This provides performance advantages in terms of permeability and durability, and promotes an improved mechanical strength when compared with geopolymers solely based on MK [28–34]. This paper assesses the feasibility of producing geopolymer binders based on silicate-activated MK/GBFS blends, using alternative activators produced from chemically modified Si-rich precursors such as SF and RHA. The reaction products are analyzed for compressive strength, along with structural characterization by infrared spectroscopy and thermogravimetry.

Experimental Procedure

Materials

The primary raw material used in this study is a metakaolin (MK) produced in the laboratory by calcination of a Colombian kaolin containing minor quartz and dickite impurities [33]. 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 d₅₀ of 12.2 µm and 10% of particles finer than 4 µm. A highly amorphous granulated blast furnace slag (GBFS) from the Colombian factory *Acerías Paz del Río* was also used. Its specific gravity was 2,900 kg/m³ and Blaine fineness 399 m²/kg. The particle size range, determined through laser granulometry, was 0.1–74 µm, with a d₅₀ of 15 µm. The chemical compositions of these raw materials are shown in Table 1, where the basicity coefficient ($K_b = \text{CaO} + \text{MgO}/\text{SiO}_2 + \text{Al}_2\text{O}_3$) and the quality coefficient ($\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3/\text{SiO}_2 + \text{TiO}_2$) determined for the GBFS were 1.01 and 1.92, respectively.

Alkali activation of these precursors was carried out using three different activators:

Table 1 Compositions of the MK and GBFS used, from X-ray fluorescence analysis

Component (mass % as oxide)	MK	GBFS
SiO ₂	50.72	32.29
Al ₂ O ₃	44.63	16.25
CaO	2.69	42.45
Fe ₂ O ₃	–	2.35
MgO	–	2.87
Other	0.94	1.88
LOI	1.02	1.91

LOI is loss on ignition at 1,000°C

- A *commercial sodium silicate (SS)* solution with a chemical composition of 32.4 wt% SiO₂, 13.5 wt% Na₂O and 54.1 wt% water, and a solution modulus ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$) of 2.4. Pellets of NaOH analytical grade (99.9%) were added to the SS in order to reach the desired Na₂O/Al₂O₃ ratios.
- An *alkali silica fume activator (SFA)* prepared with a commercial densified silica fume (Sikafume®), with a particle size of range of 1–500 μm, with a d₅₀ of 64.1 μm determined by laser granulometry without ultrasonic dispersion, and containing 95.51 wt% SiO₂ [35], and NaOH analytical grade (99.9%) in order to obtain the desired molar ratio. The SF and NaOH were mixed for 10 min, and sealed in plastic containers immersed in a water bath at room temperature (25°C) for 24 h before use, to allow the silica fume particles time to dissolve before mixing with the aluminosilicate components.
- An *alkali rice husk ash activator (RHAA)* prepared with a rice husk ash and NaOH analytical grade (99.9%). The RHA was produced by burning rice husk material at 600°C in air in a laboratory furnace for 2 h, and ground in a ball mill to obtain a particle size distribution between 1 and 60 μm with a d₅₀ of 9.2 μm. These conditions have been determined in previous studies as being suitable in order to obtain a highly reactive pozzolan from this particular source of rice husks [36, 37]. The content of amorphous silica in the final RHA was 68%, with an unburnt carbon content of less than 2%. The RHA and NaOH were mixed under the same conditions mentioned above for SFA, considering only the content of reactive (amorphous) silica in the RHA in calculating this value.

Sample Preparation and Tests Conducted

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) SiO₂/Al₂O₃ molar ratios of 3.0 (mix GP-1) and 3.8 (mix GP-9), and a constant overall Na₂O/SiO₂ ratio of 0.25. The quantity of water in the alkali activator was adjusted to achieve an H₂O_{total}/Na₂O ratio of 12. The mix designs are given in Table 2.

These activation conditions have been identified as enabling MK-based geopolymer systems [38] and alkali-activated MK/GBFS blends using commercial silicate solutions [34] to reach high compressive strengths while retaining acceptable workability. The fresh pastes were mixed for 12 min, poured into cylindrical molds, and vibrated for 5 min to reach a homogeneous distribution in the mold and remove entrained air. Samples were kept sealed in the molds under ambient conditions (25–30°C)

for 24 h, 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 before testing.

The compressive strength was assessed by testing cylindrical paste 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 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 analyzed using a thermogravimeter SDT-Q600 in a nitrogen atmosphere, from 25 to 1,100°C at a heating rate of 10°C/min. Fourier transform infrared (FTIR) spectroscopy was conducted via the KBr pellet technique, using a Shimadzu FTIR 8400 instrument, scanning from 2,000 to 400 cm⁻¹.

Results and Discussion

Compressive Strength

Reference pastes prepared with SS formulated with a SiO₂/Al₂O₃ ratio of 3.0 (GP1) present no significant differences in mechanical strength with the incorporation of GBFS up to 40% (Fig. 1a), as the main structure of these MK/GBFS blends is dominated by aluminosilicate type products (geopolymer gel) [34]. On the other hand, addition of 60% of GBFS promotes the highest compressive strength values reported for this set of samples, being twice the compressive strength obtained for MK-based geopolymers. This is coherent with the structural differences observed with respect to the mixes formulated with lower contents of GBFS [34], suggesting that an increased content of calcium in the systems is favoring the formation of Ca-rich phases such as the Al-substituted C–S–H gels typically observed in alkali-activated slag binders [32, 33, 39, 40].

The compressive strength of the MK-based geopolymer with SiO₂/Al₂O₃ = 3.8 is 15 MPa (Fig. 1b), less than half of that of the corresponding sample with SiO₂/Al₂O₃ = 3.0. This is attributed to the excess of silicate, related to higher SiO₂/Al₂O₃ ratios here, as the extent of polymerization of the silica in solution is high and its rate of reaction is therefore slower than is required for optimal strength development in systems dominated by MK [41].

The addition of 20% GBFS to the GP-9 samples shows approximately a doubling in compressive strength compared to the MK-based samples (Fig. 1b), which can be attributed to the reaction of the Ca supplied by the GBFS with some of the excess silicate present, to form additional

Table 2 Mix designs of geopolymer samples tested

Geopolymer	GBFS/(GBFS + MK) ratio	MK	GBFS	SS	SF	RHA	NaOH	H ₂ O	w/b ^a
GP-1	0.0	100	0	86.9	–	–	11.1	23.9	0.47
	0.2	80	20	67.3	–	–	11.2	25.5	0.44
	0.4	60	40	47.7	–	–	11.3	27.1	0.40
	0.6	40	60	28.2	–	–	11.3	28.6	0.35
	0.8	20	80	8.6	–	–	11.4	30.2	0.30
	0.0	100	0	–	29.5	–	26.3	70.9	0.46
	0.2	80	20	–	22.8	–	22.9	61.9	0.42
	0.4	60	40	–	16.2	–	19.6	52.9	0.39
	0.6	40	60	–	9.6	–	16.2	43.9	0.35
	0.8	20	80	–	2.9	–	12.9	34.8	0.30
	0.0	100	0	–	–	41.4	26.3	70.9	0.42
	0.2	80	20	–	–	32.1	22.9	61.9	0.40
	0.4	60	40	–	–	22.7	19.6	52.9	0.37
	0.6	40	60	–	–	13.4	16.2	43.9	0.34
	0.8	20	80	–	–	4.1	12.9	34.8	0.30
GP-9	0.0	100	0	151.7	–	–	6.8	7.8	0.51
	0.2	80	20	123.9	–	–	7.5	11.4	0.48
	0.4	60	40	96.1	–	–	8.1	15.0	0.44
	0.6	40	60	68.3	–	–	8.7	18.6	0.40
	0.8	20	80	40.4	–	–	9.3	22.2	0.35
	0.0	100	0	–	51.5	–	33.3	89.8	0.49
	0.2	80	20	–	42.0	–	29.0	78.4	0.46
	0.4	60	40	–	32.6	–	24.8	67.0	0.43
	0.6	40	60	–	23.2	–	20.6	55.5	0.39
	0.8	20	80	–	13.7	–	16.3	44.1	0.34
	0.0	100	0	–	–	72.3	33.3	89.8	0.44
	0.2	80	20	–	–	59.0	29.0	78.4	0.42
	0.4	60	40	–	–	45.8	24.8	67.0	0.39
	0.6	40	60	–	–	32.5	20.6	55.5	0.36
	0.8	20	80	–	–	19.3	16.3	44.1	0.33

^a Calculated considering the total water and the total solids (precursor + anhydrous activator)

strength-giving gel. The samples activated with the commercial sodium silicate with 20% GBFS, which present similar structural characteristics to those solely based on MK [30], also show a notable reduction in strength when moving from $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$ to 3.8, but to a lesser extent than the MK-only mixes. The increased incorporation of GBFS in the mixes generally leads to higher compressive strength. 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 $\text{Ca}(\text{OH})_2$ solubility equilibrium to favor the dissolution of calcium from the slag, promoting the subsequent formation of stable calcium-containing gel phases [34]. This effect is due specifically to the presence of Ca, and is quite distinct from the detrimental effect of excess Si in the MK-based geopolymers which contain no Ca. The highest

strength (but also the highest variability in strength) in these sample sets is observed with 60% GBFS at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$; the optimal GBFS content at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.8$ is higher, consistent with the increased tendency towards C–(A)–S–H formation in the presence of higher concentrations of dissolved silica.

The modified silica fume derived activator promotes similar 7-day compressive strengths in specimens with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$ (Fig. 1a), when compared with the reference samples activated with commercial sodium silicate. However, it is important to note that when using the silica fume based activator a higher variability (displayed in Fig. 1 as an increased standard deviation) in compressive strength is observed. Some of the samples assessed present mean compressive strengths comparable to, or even higher than, the reference samples produced with commercial

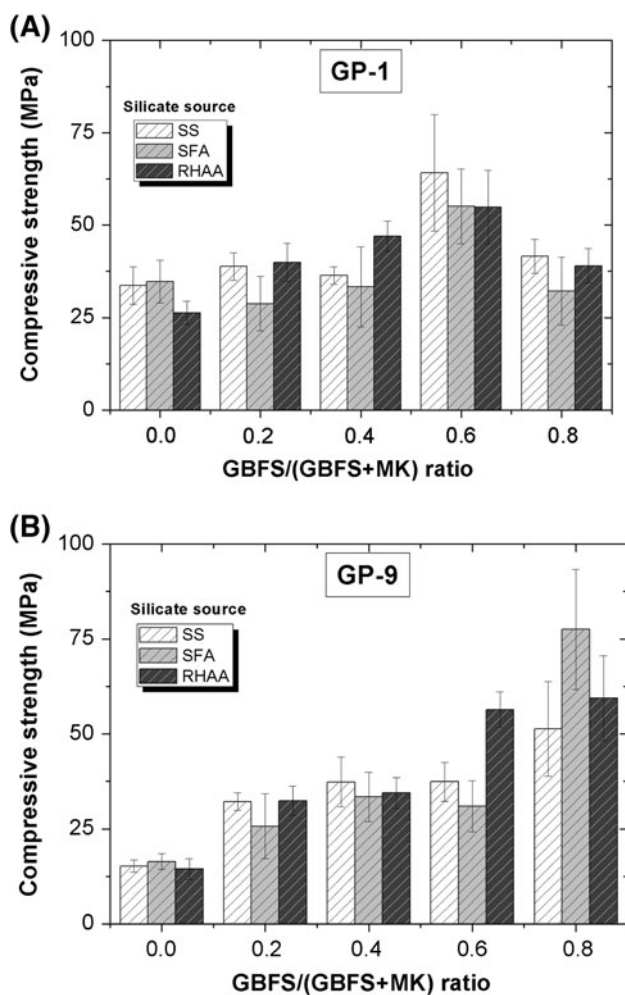


Fig. 1 Seven-day compressive strengths of MK/GBFS blends activated with commercial sodium silicate solution (SS), chemically modified silica fume (SFA), and chemically modified rice husk ash (RHAA). Error bars correspond to one standard deviation. GP-1 samples (a) have $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$, GP-9 samples (b) have $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.8$

sodium silicate activator, while those produced with higher GBFS content generally have lower mean strengths—but the differences cannot be considered significant in a statistical sense. The increased variability in the binders activated with the modified silica fume may potentially be attributed to an increased brittleness exhibited by the binders activated with modified silica fume, although any possible reasons for such behavior are unclear.

Samples formulated with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (GP9) activated with the silica fume derived activator also tend to present (Fig. 1b) a slight reduction in the mean compressive strength and an increased variability, compared with the reference samples activated with commercial sodium silicate; again, the effect is small and potentially not statistically significant when considering the standard deviations associated with the data. However, the exception to this trend is for pastes formulated with

increased contents of GBFS (80%), which exhibit remarkable increments in the compressive strength when compared with pastes activated by commercial sodium silicate and containing the same amount of GBFS. This is consistent with the reports of Živica et al. [12, 13], and the trends identified in a previous study [42], where the use of silica fume derived activators in binders based solely on GBFS was seen to promote the formation of a highly densified structure (mainly composed of C-(A)-S-H gel), and consequently enhanced compressive strength.

The MK-based geopolymers prepared with the RHA-derived activator with an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.0 (GP1-RHA; Fig. 1a) exhibit a slight reduction in compressive strength compared with the MK-only specimens activated with commercial sodium silicate and modified silica fume. However, addition of 20 or 40% GBFS brings an increase in mechanical strength relative to the reference samples; the specimens with 60 or 80% GBFS have strengths which are slightly lower than the strengths of the reference samples. The pastes prepared with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.8 (GP9; Fig. 1b) and low amounts of GBFS (>40%) also show similar strengths to the reference specimens; however, a remarkable increment (up to 20 MPa) in the compressive strength is observed when the content of slag increases to 60 and 80%. The strengths reported for the GP9 specimens with a GBFS/(GBFS + MK) ratio of 0.6 are notably higher than for the comparable samples prepared with commercial sodium silicate and modified silica fume; however, analysis of trends in the data at 80% slag across the three activator types is complicated by the greater variability in the strengths reported at this GBFS content; although the average compressive strengths are slightly higher for specimens activated with silica fume based activator, followed for those prepared with rice husk ash activator and commercial sodium silicate.

The effect in the mechanical strengths of activated MK/GBFS blends using the alternative activators, compared with those observed in reference pastes activated with SS, is likely to be determined by the different rates of release of silicate in these systems in the early stages of geopolymerization. This directly influences the structural characteristics of the binders, and consequently their compressive strengths [43, 44]. In pastes activated with RHA-derived activators, it is expected that there will be lower dissolved silica content in the solutions compared with commercial silicate solutions, as a consequence of partial dissolution of some of the amorphous (and thus potentially reactive) phases present in the by-product, during the 24 h allowed for the equilibration of the solutions. The presence of these remnant, partially dissolved silica particles would be expected to slow down the availability of SiO_2 in the system, leading to a slightly lower mechanical strength development.

The growth of both the aluminosilicate and calcium silicate type gels formed in these systems will also be strongly affected by the availability of Al species during the initial period of reaction [45]. In binders solely based on GBFS activated with the silica fume activator, more crystalline and Al-rich reaction products, compared with those obtained in pastes activated with commercial sodium silicate, have previously been identified [46]. The fact that similar trends in compressive strength development in MK/GBFS blends are reported for both commercial sodium silicate and modified silica fume activated pastes suggests that the 24-h equilibration time used here was sufficient to dissolve the SF particles and render the Si available in the early period of reaction. However, this was not the case for pastes activated with the RHA derived activator due to the partial crystallinity of the RHA, which leads to the later availability of the Si from this activating solution.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra of the raw materials and the reactive silica sources used for the preparation of the alternative activators are given in Fig. 2. The spectrum of the anhydrous GBFS presents vibration modes at 999 cm^{-1} characteristic of T–O (where T is Si or Al) bonds of tetrahedral silicates, at 876 cm^{-1} likely related to the asymmetric stretching vibration of Al–O of AlO_4 groups, and at 710 cm^{-1} attributed to the bending vibration mode of the Al–O–Si bonds. These three bands also correspond to those observed in gehlenite [47], which has been identified by X-ray diffraction in this source of GBFS in previous studies [33]. A band at $1,438\text{ cm}^{-1}$ associated with the asymmetric vibration mode of the O–C–O bonds in carbonates is also

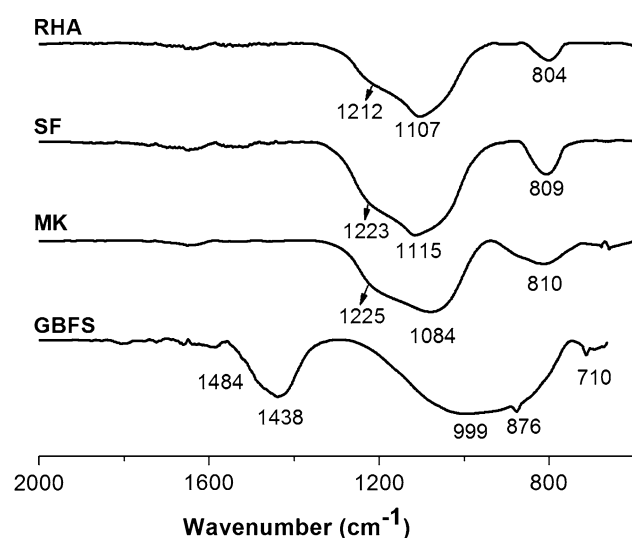


Fig. 2 Fourier transform infrared spectra of the raw materials used for the preparation of the binders and activators

observed. This is coherent with the partial carbonation identified in this raw material [33] as a consequence of weathering during storage.

The spectrum of MK presents a broad band at $1,115\text{ cm}^{-1}$ linked to disorder induced by the dehydroxylation of kaolin and formation of amorphous structures. This is also observed in the vibration mode at 810 cm^{-1} which is associated with Al–O bonds of tetrahedral Al [48, 49]. The FTIR spectra of SF and RHA are very similar, exhibiting a broad band around $\sim 1,110\text{ cm}^{-1}$ associated with the asymmetric stretching of Si–O–Si bonds, along with a vibration mode at $\sim 809\text{ cm}^{-1}$ attributed to the symmetric stretching of Si–O–Si bonds of amorphous SiO_2 [49].

The spectra of activated MK/GBFS blends with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$ exhibit (Fig. 3) a vibration band between $1,643$ and $1,651\text{ cm}^{-1}$ associated with the bending modes of H–OH bonds of water molecules associated with the reaction products. Increased contents of GBFS also lead to the growth of the carbonate band as discussed above, showing that the carbonates identified in this raw material do not react significantly under alkaline activation conditions.

The main band between 900 and $1,200\text{ cm}^{-1}$ is assigned to the asymmetric stretching vibration of Si–O–T bands, where T is tetrahedral silicon or aluminum. These specific frequencies are characteristic of unreacted silica ($\sim 1,100\text{ cm}^{-1}$) and the newly formed aluminosilicate type gels expected in geopolymers ($950\text{--}1,020\text{ cm}^{-1}$). MK-based specimens activated with SS show a high intensity band at 1010 cm^{-1} attributed to a highly crosslinked geopolymer gel framework, along with the formation of a band at 860 cm^{-1} assigned to the asymmetric stretching vibration mode of AlO_4 sites, and one at 719 cm^{-1} assigned to the symmetric stretching vibrations of the Si–O–Si(Al) bridges [51]. The band at 535 cm^{-1} is attributed to the symmetric stretching of Al–O–Si and the one at 473 cm^{-1} to the bending of Si–O–Si and O–Si–O bonds [50].

The inclusion of GBFS, and most specifically its role in supplying soluble Ca^{2+} ions, leads to a shift of the main band towards a lower wavenumber, suggesting structural changes associated with reduced polymerization of the gels, along with the potential inclusion of Ca in the structure. It has been reported [28–34] that the activation of MK in the presence of calcium promotes the simultaneous formation of C–(A)–S–H and N–A–S–(H) type gels. The formation of alkali-substituted phases such as N–(C)–A–S–H is also possible, as previously reported in GBFS-rich activated GBFS/MK blends [31–33] and in synthetic cementitious gels [52]. In these systems, the Ca^{2+} is believed to be 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 more commonly fill this role

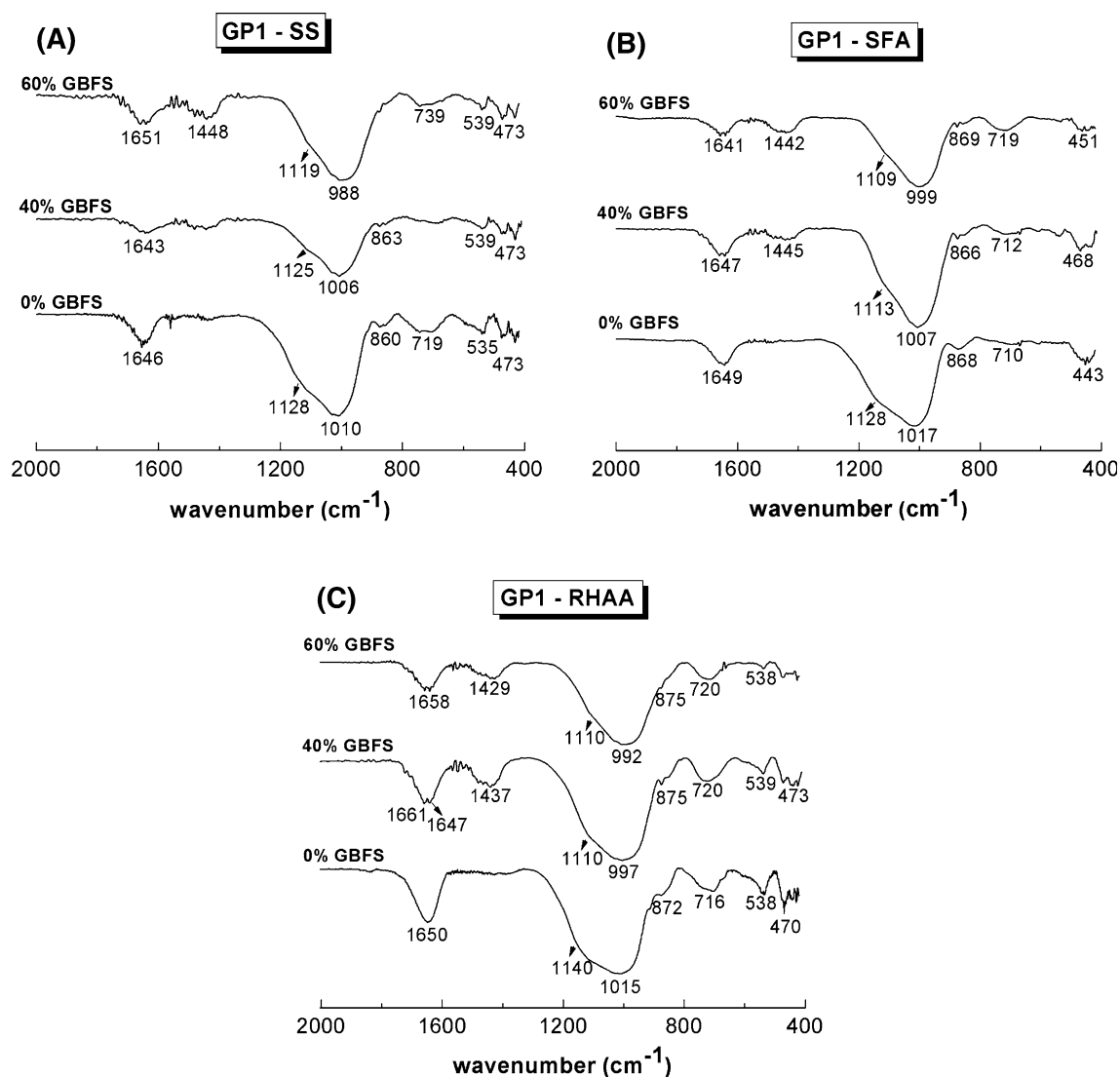


Fig. 3 Fourier transform infrared spectra of pastes of MK/GBFS blends with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$ as a function of the content of GBFS: **a** activated with commercial sodium silicate (SS), **b** activated with the

SF-based activator (SFA), **c** activated with the RHA-based activator (RHAA)

[53, 54]. This is coherent with the shift of the symmetric stretching vibrations of the Si–O–(Si,Al) bridges to higher wavenumber (from 719 to 739 cm^{-1}) with increased contents of GBFS, which suggests the modification of the aluminosilicate framework compared with solely MK-based geopolymers as a consequence of cation substitution in the non-framework sites.

Specimens without slag prepared with the SF-based and RHA-based activators present similar vibrational modes to those identified in samples prepared with SS. In these mixes, the Si–O–T band is located at slightly higher wavenumber (1,017 cm^{-1} for silica fume based activators, 1,015 cm^{-1} for rice husk ash activators), exhibiting a broader shoulder (at 1,128 or 1,140 cm^{-1}), than was reported for the commercial sodium silicate-activated mix. This is consistent with the presence of some unreacted Si

from the waste-derived activators, particularly in the systems using the rice husk ash activator, which contains a significant quantity of unreactive crystalline silica contributing to this peak. Increasing addition of GBFS in these systems again promotes the shifting of the Si–O–T band towards lower wavenumbers, consistent with the inclusion of higher contents of calcium in aluminosilicate type gel, as identified in systems activated with the commercial activator.

Thermogravimetry

MK-based geopolymers and those containing 60% GBFS, activated with commercial sodium silicate and rice husk ash activator, were selected for further analysis by thermogravimetry (Fig. 4). The total mass loss of samples

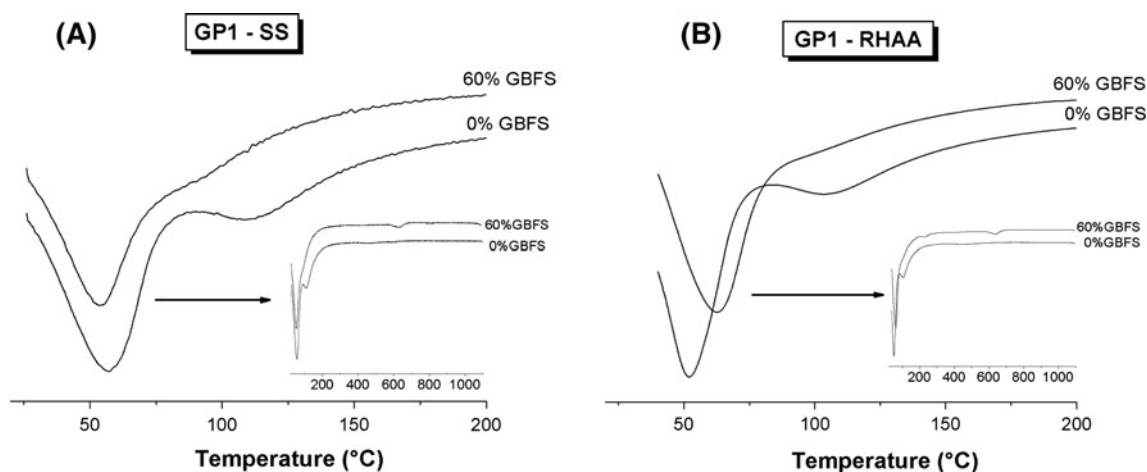


Fig. 4 DTG traces for alkali silicate-activated MK/GBFS blends, each with an overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.0, as function of the type of activator used: **a** commercial sodium silicate (SS), and **b** rice husk ash based activator (RHAA)

based solely on MK was 28.2 and 30.9% when pastes were prepared with commercial sodium silicate and rice husk ash derived activator, respectively. A slight reduction in the total mass loss, to 25.8 and 29.2% respectively, is identified in specimens including 60% GBFS, due to the binding of some additional water in C–S–H type gels. A previous study of activated MK/GBFS blends [34] revealed that the strong weight loss peak identified at $\sim 52^\circ\text{C}$ in the differential thermogravimetry (DTG) traces of pastes activated with commercial sodium silicate can be assigned to the loss of the freely evaporable water which is present in large pores in the aluminosilicate type product (geopolymer gel) which dominates these systems in the absence of GBFS [55].

The second, smaller peak identifiable at $\sim 107^\circ\text{C}$ indicates the presence of water in environments resembling its environment in zeolites or feldspathoids in these binders, as reported for MK-geopolymers [56]. Pastes activated with the rice husk-derived activator present a slightly sharper and higher intensity low temperature peak (52°C) compared with the binders prepared with commercial sodium silicate, which may indicate the formation of reaction products with higher contents of freely evaporable water. A similar effect is identified in the peak at $\sim 107^\circ\text{C}$, likely indicating the formation of more distinct local structural environments for physically sorbed water in the gel phases in these binders than when activating with commercial sodium silicate.

Adding 60% GBFS to samples activated with the rice husk ash-derived activator causes a shift towards higher temperatures ($\sim 63^\circ\text{C}$) of the distinct minimum of the first weight loss peak when compared with pastes activated with sodium silicate, which is attributed to the incorporation of Ca in the geopolymer gel, as previously identified in the

FTIR results. A remarkable reduction in the intensity of the peak at $\sim 107^\circ\text{C}$ in samples activated with both commercial sodium silicate and rice husk ash-based activators is identified with the inclusion of 60% GBFS. This is coherent with the increased availability of Ca in the systems as a consequence of the dissolution of the GBFS, suppressing the formation of zeolite type products. A third peak of low intensity is also observed at 229°C in rice husk ash-activated specimens, which is associated with products with water more tightly bonded to the structure than in geopolymer gel, such as C–S–H gel [57]. The peaks slightly above 600°C in both of the slag-containing samples are due to the decomposition of the calcium carbonates present, as identified in FTIR [32, 33].

Conclusions

This study has shown that it is possible to valorize rice husk ash through its use as a silica source for the synthesis of activating solutions for use in the formulation of alkali-activated slag/metakaolin binders, through dissolution of the silica-rich waste material into a concentrated sodium hydroxide solution. The binders synthesized using rice husk ash-derived activators present mechanical performance which is in general comparable to those synthesized from commercial silicate solutions or silica fume, except at high slag/metakaolin ratios where the delayed availability of silica due to the incomplete initial dissolution of the rice husk ash particles can lead to higher 7-day strengths by supplying silica later in the reaction process. The nanostructures of the binders synthesized from the three activators are all very similar, as measured by infrared spectroscopy and thermogravimetry. The potential for use

of rice husk ash in this application both provides a means of valorizing this waste product, and also presents opportunities for the further reduction of the environmental impact of alkali-activated binder technology by avoiding the need to calcine the silica along with the alkali source in commercial production of waterglass.

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