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Binary alkali activated systems obtained by the valorisation of two industrial wastes

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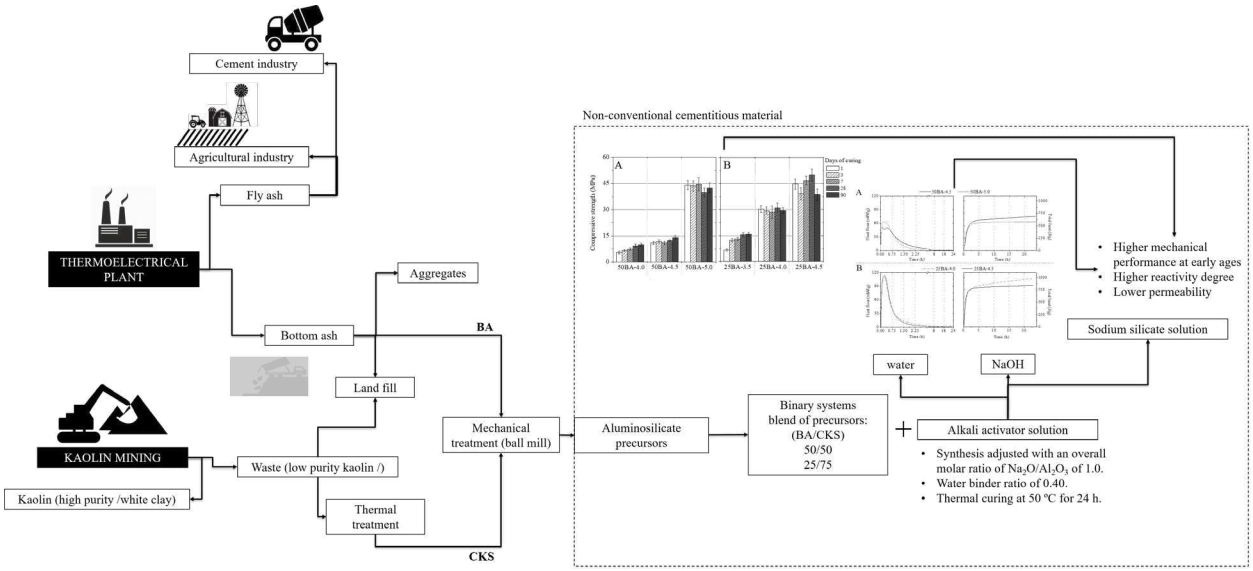
Abstract

This paper assesses the use and potential valorisation of two industrial wastes generated at large scale in Brazil, which are currently disposed in landfills, as raw materials for the production of geopolymers. Specifically, a kaolinitic sludge from the mining industry (CKS), and a bottom ash (BA) generated during coal combustion in a thermal power station, were used as aluminosilicate precursors in geopolymer synthesis. The geopolymers were synthesised at 50 °C, with a Na_2O/Al_2O_3 molar ratio of 1.0, and different SiO_2/Al_2O_3 molar ratios adjusted by the different mix proportions between precursors and by manipulating the content of the soluble silicate solution used as the activator. The mechanical strength and reaction products formed during the geopolymerisation process were assessed up to 90 days of curing by compressive strength and the assessment of some microstructural features. To understand the behaviour of these materials in use and to correlate this to microstructural properties, mortar samples were produced and assessed for compressive strength, flexural strength and water sorption by capillarity. The use of CKS as the main component of the precursor blend provides a geopolymer with better mechanical properties due to its higher reactivity, when compared to the BA. The content of soluble silicates in the alkali activator plays an important role during geopolymerisation, improving the mechanical properties due to formation of a more cross-linked and denser structure. The mortars show a compressive strength higher than 55 MPa after 28 days and low water absorption by capillarity, which is associated with a refined pore structure. This elucidates the feasibility of valorising these industrial residues as precursors for geopolymer cements when the mix proportion and synthesis conditions are adjusted and optimised.

Keywords: Bottom ash, calcinated kaolin sludge, geopolymers, waste valorisation.

Graphical abstract



Statement of novelty

This research was undertaken in order to assess the potential use of two industrial wastes, including: a calcined kaolinitic sludge (from the mining industry) and bottom ash (from a thermoelectrical industry) as precursors to produce geopolymers. This valorisation reduces the environmental damage associated with generating enormous quantities of these materials and their current disposition in landfill. The materials have different physicochemical properties, as well as reactivity, which influences the mechanical and microstructural properties of the geopolymer formed. The high reactivity of the kaolinitic precursor provides higher strength but requires a large amount of activator, on the other way, the inclusion of bottom ash, which has lower reactivity reduce the mechanical performance. The use of these materials as precursors for geopolymers gives value to non-valorised wastes.

1. Introduction

National and international regulations and policies, and increasing recognition of the need to live sustainably across all sectors of society, have promoted interest in decreasing the total volume of waste produced and thus to improve the sustainability of solid waste management in the industrial sector. Therefore, there is a strong move toward viewing waste as a resource that can be recycled and recovered. The valorisation of industrial wastes through re-use, recycling, or energy recovery has a significant environmental, economic and social benefit due to the reduction of areas used for landfill disposal, reduction of pollution caused by the contamination of soil, ground water and greenhouse gas emissions, reduction of consumption of fossil fuels, as well as the generation of new jobs. Although solid waste management was not included explicitly in the Millennium Development Goals (MDGs) and their indicators [1], there nonetheless exists a clear link, where better and more efficient waste management offer better opportunities for income generation.

The present article demonstrates the potential for valorisation of two different wastes generated by a power station plant and by the mining of kaolin, which are currently disposed in landfill without any added value. The first residue assessed here is a product generated by the combustion of coal in a power station plant. Coal combustion produces ~40% of global electricity and it is estimated that more than 778 Mt/y of wastes and by-products are generated [2, 3]. However, the environmental impact of coal ashes when disposed in landfills is becoming more widely known. The erosion, dispersal, leaching, and atmospheric transport of the ashes may spread contaminants into natural aquatic and terrestrial systems, causing water and soil contamination, biodiversity loss, and environmental degradation [4–7]. Recycling of coal ashes can be a feasible alternative to disposal with significant economic and environmental benefits.

Among the various different coal combustion by-products (CCPs), fly ash (FA) can be considered the most important due to its importance within the cement production market, considering its physicochemical features and the large quantities generated (~80% of total CCPs). Bottom ash (BA), which is the second most important CCP, is defined as the larger and heavier particles that are accumulated in the bottom of the boiler or furnace during coal combustion. BA has a low rate of reuse as a value-added by-product (46% and 39% in the EU and the US, respectively) [8, 9]. The BA that is not suitable for the cement industry (in blended cements or as a feed for clinker production) and then can be used as structural fill, in mining applications, as a road sub-base, or in snow and ice controller [10, 11]. Taking into account the large volume of this material that is currently disposed in landfill, and the new regulations requiring its safer disposal [12], BA management has become an economical and environmental concern for electricity generators. In the search for a more efficient pathway to reuse, BA has been also assessed as a mineral admixture in Portland-blended cements, and its pozzolanic reactivity can be improved through mechanical treatment for size reduction [13]. However, the generally low reactivity, low density, and high porosity of BA have been the main barriers to its use as a supplementary cementitious material (SCM).

There do exist some reports related to the use of BA as a raw material for the production of non-conventional cementitious binders, including alkali-activated cements or geopolymers [14–18]. Geopolymers are a type of cement produced by chemical activation of an aluminosilicate precursor by a highly alkaline reagent in order to obtain a material with cementitious properties. Geopolymers are often described as offering low energy consumption and low CO_2 emissions when compared with Portland cement, while enabling valorisation of high-volume industrial wastes or by-products [19, 20]. The relatively low reactivity of BA can yield geopolymers with lower mechanical performance than those based on FA [15]. However, the performance of BA-based systems can be improved through the application of mechanical treatment [18], and/or the inclusion of a secondary precursor with higher reactivity [21].

Taking into account the low reactivity of the BA used in this study [22–24], a waste derived from the kaolin mining industry was assessed as a secondary precursor: a rejected kaolinitic clay sludge, which is generated during the whitening and adjustment of the particle size distribution in wet processes for kaolin purification. Brazil is now the fifth-largest global producer of kaolin, reaching almost 2 Mt/year [25], which leads to generation of ~0.5 Mt/year of kaolin sludge and with a stockpile of approximately 10 Mt [26]. This residue is classified as an inorganic and inert material, class II, according to the Brazilian standards [27], and a non-hazardous material by the U.S. Environmental Protection Agency (EPA). In its production, kaolin is dispersed in water and screened for removal of coarser particles (> 44 μm). The slurry thus obtained is centrifuged to separate the kaolin into particle size fractions, which are then whitened. Finally, the kaolin is dewatered by filtration and then dried. The mineral matter rejected is in the form of a coarse-grained kaolin sludge, which is mainly disposed in large artificial basins [28, 29].

The sludge contains mainly kaolinite, with some of quartz and anatase [26]. This high content of kaolinite offers the potential for valuable use after its controlled thermal treatment, where a material with high pozzolanic reactivity and

high reactivity degree can be obtained [30–32]. The high content of SiO_2 and Al_2O_3, as well as the high reactivity of the calcined kaolin sludge (CKS), highlights a potential alternative route for its reuse as a raw material for the production of alkali-activated cements [33, 34]. Although commercial metakaolin (MK) has been one of the most used aluminosilicate precursors in geopolymer synthesis, the high cost of high purity kaolinite clays represents a barrier to large-scale production of MK geopolymer-based products [19].

In this way, the correct mix proportions between this two industrial wastes and activator can allow the use of these materials as precursors to produce geopolymers. The CKS requires a high-water consumption due its particles plate-shape morphology, however presents higher reactivity. The thermal treatment of the kaolin sludge, which is done in order to increase its reactivity, contributes significantly to its cost production due to the energy involved to achieve temperatures close to 700 ºC. On the other hand, even though the BA exhibits lower reactivity; its high stock (or availability) and considering that high temperature treatments are not required, elucidates its potential for its valorisation. As these materials present specific properties, it is necessary to understand some microstructural features and mechanical properties to evaluate their performance as precursors for the synthesis of blended alkali-activated-type binders. In this sense, the development of non-conventional cements offers alternative pathways for the valorisation of kaolin mining wastes and bottom ash, which are available in large volumes and currently landfilled.

This paper assesses the use of these two industrial wastes for producing binary geopolymers based on different BA/CKS blends and mix design parameters. The chemistry and microstructural features of the reaction products formed were assessed through isothermal calorimetry (IC), thermogravimetric analysis (TGA), X-ray diffractometry (XRD) and Fourier transformed infrared spectroscopy (FTIR), in conjunction with determination of compressive strength and mass transport properties.

2. Experimental programme

2.1. Materials

A bottom ash from a coal power station in Triunfo (RS), Brazil, and a waste kaolin sludge derived from the kaolin mining industry from Pará (Brazil), were used in this study. The bottom ash was sieved to 100% passing 300 μm, and then ball milled for 1 h. The final material showed a mean particle size of 17.4 μm with a d_{90} of 36.4 μm and a specific surface area, determined by the Brunauer-Emmett-Teller (BET) method, of 5.21 m^2/g. The kaolin sludge was calcined at 750 ºC for 1 h and then milled in a ball mill for 1 h. The calcined kaolin sludge (CKS) exhibited a mean particle size of 11.0 μm and a BET specific surface area of 19.7 m^2/g. The chemical compositions of the aluminosilicate sources are shown in Table 1. The higher specific surface of the CKS is related to the presence of layered particles, when compared to the BA.

Table 1. Chemical composition of raw materials, as determined by X-ray fluorescence.

	Bottom ash (CP)	Calcined kaolin sludge (CKS)
SiO_2	62.9	59.5
Al_2O_3	18.2	32.9
Fe_2O_3	9.0	2.7
K_2O	2.0	0.1
MgO	0.2	-
MnO	0.1	-
TiO_2	1.7	2.0
P_2O_5	0.2	0.4
SO_3	0.6	0.1
CaO	2.6	0.2
ZrO_2	0.2	0.1
Loss on ignition (950 °C)	2.2	2.0

The alkali activator was produced using NaOH pellets of analytical grade (~99%) and a sodium silicate solution composed of 26.5 wt.% SiO_2, 10.6 wt.% Na_2O and 62.9 wt.% H_2O, supplied by Sigma Aldrich. The NaOH and the sodium silicate solution were blended to achieve the required overall molar ratio for each mix design.

2.2. Sample preparation

The geopolymer pastes were formulated with CKS/BA ratios of 75/25, 50/50, and 0/100, in each case with an overall Na_2O/Al_2O_3 molar ratio of 1.0, and the dose of sodium silicate was adjusted to give an overall SiO_2/Al_2O_3 molar ratio for each sample as specified in Table 2. The geopolymers were produced with a water/binder (w/b) ratio of 0.40, where 'binder' here refers to the sum of the solid precursor and the anhydrous fraction of the alkali activator. The pastes were mixed mechanically for 6 minutes and then cast into 20 mm cubic plastic moulds, and then vibrated for one minute. The samples were cured at 50 ºC for 24 h with a relative humidity (RH) of 90%, then stored in a sealed plastic container at ~25 ºC and RH>90% until testing. The mix designs of the geopolymers produced are shown in Table .

Table 2- Mix designs and material constituents of the geopolymer samples produced.

Mix ID	CKS/BA ratio	Overall molar ratio			Material constituents (g)				
		Na_2O/Al_2O_3	SiO_2/Al_2O_3	water/ binder	CKS	BA	Sodium silicate	NaOH	Extra water
100BA-5.9	0/100	1	5.9	0.40	0	100	0	15.9	40.6
100BA-7.0	0/100	1	7.0	0.40	0	100	46.7	8.8	15.3
50BA-4.0	50/50	1	4.0	0.40	50	50	0.0	22.9	49.2
50BA-4.5	50/50	1	4.5	0.40	50	50	32.0	18.6	32.1
50BA-5.0	50/50	1	5.0	0.40	50	50	64.5	14.1	14.7
25BA-3.5	75/25	1	3.5	0.40	75	25	0.0	20.1	48.0
25BA-4.0	75/25	1	4.0	0.40	75	25	24.5	16.7	34.9
25BA-4.5	75/25	1	4.5	0.40	75	25	52.9	12.8	19.7

Standard siliceous sand (ABNT NBR 7214:2015, [35]) with a fineness modulus of 2.5 and a maximum particle size of 1.2 mm was used as the aggregate to prepare the mortars, which were formulated with a precursor:sand ratio of 1:3. The fresh mortar was cast in prismatic moulds of 40×40×160 mm, vibrated mechanically for 2 min and cured under the same conditions described above for paste samples.

2.3. Tests conducted

2.3.1 Pastes

The chemical reaction of alkali-activation to form the geopolymer cements was monitored through isothermal calorimetry using a TAM air microcalorimeter (TA Instruments) with a sensitivity of ± 20 μW. The temperature was set to 50 ºC, to match the temperature of the curing process. The precursors (BA and CKS) and the alkali activator solution were pre-heated separately within the equipment for 45 min prior to the mixing. The mixtures were prepared by mixing all constituents for 2 minutes inside the calorimeter. To enable a completely homogeneous fresh mixture under these mixing conditions, the w/b ratio was adjusted to 0.50 for these tests; all other mix design parameters were as shown in Table 2. The heat release was followed for 24 h.

The compressive strength was assessed for 5 cubic paste samples of 20 mm up to 450 days of curing, using a universal testing machine (EMIC) with a displacement rate of 0.5 mm/min. For the tests after 3, 28, and 90 days of curing, the samples used to determine compressive strength were collected after crushing, milled, washed with isopropanol, filtered and then dried at ~50 ºC for 20 min. The samples were stored in a vacuumed container until microstructural characterisation. The reaction products were assessed through the following tests:

- X-ray diffraction (XRD), using a Siemens D5000 diffractometer with Cu Kα radiation, a scanning speed of 0.5 º/min and a step size of 0.020º, for a 2θ range between 7 and 70 degrees.

- Thermogravimetry with mass spectroscopy (TGA-MS), using a Perkin Elmer TGA 4000 coupled with a Hiden Analytical mass spectrometer. The samples were heated to 1000 ºC with a heating rate of 10 ºC/min using alumina crucibles, and nitrogen as a purge gas (100 mL/min). The mass spectrometer was programmed for the detection of H_2O and CO_2 signals.

- Fourier transform infrared (FTIR) spectroscopy, in a Perkin Elmer FTIR spectrometer using the KBr pellet technique. The measurements were recorded in absorbance mode from 2500 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.3.2 Mortars

Key properties of mortars were evaluated to start the study of these precursors in an applicable material, and allow the analysis of properties associated with microstructure. The workability of fresh mortars was assessed with the testing protocol of the Brazilian standard NBR 13276 [36], and the compressive and flexural strength tests were performed following the procedure of NBR 13279 [37] after 1, 7 and 28 days. Water capillary suction was tested for samples after 28 days of curing based on the protocol NBR 15259 [38], in which water is allowed to pass into a dried sample through capillary suction, and the mass of the sample is monitored as a function of time.

3. Results and discussion

3.1. Isothermal calorimetry

Fig. **1** shows the heat released during geopolymerisation for the binary systems. The binary systems with a higher content of BA (50BA, in Fig. **1**B) exhibit two peaks during the initial 45 min of reaction, and the content of sodium silicate has a strong effect on the heat released. Taking into account that internal mixing inside the calorimeter was used in this study, and the mix components were all thermally equilibrated prior to the start of the experiments, the data collected at this very early age can be considered more reliable than is the case when the more common external mixing protocol is used. At a lower content of soluble silicate (50BA-4.5) there are two distinguishable peaks located at 5 and 24 min, with a maximum intensity of 51 mW/g. The geopolymerisation process is exothermic due to the dissolution of the aluminosilicate precursors, oligomer formation, gelation and further gel reordering [39]. In this sense, the first peak can be attributed to the dissolution of the precursors (BA/CKS) and release of silicate and aluminate monomers. The second and broader peak corresponds to the formation of aluminosilicate oligomers and the subsequent precipitation of an amorphous gel product (geopolymer) [40]. At a higher content of soluble silicate (50BA-5.0) the maximum rate of heat released increased to 63 mW/g and the second peak is less distinct. This indicates that the presence of a higher content of dissolved silicate species, which are supplied by the alkali activator, speed up the reaction due to faster polycondensation with the monomeric aluminate species released during the dissolution of the precursors. As an example, in Fig. **1B** the 50BA-5.0 showed a total heat release of 166 J/g at 24 h of reaction, which is ~20% lower than 50BA-4.5. Regardless of the CKS content, the total heat released is higher in systems with lower SiO_2/Al_2O_3 ratios, which indicates that the reaction is retarded and requires more time. This phenomenon was observed in a previous study using CKS as main precursor [35] and can be attributed to the aluminosilicate gel film formed, which envelops the dissolving particles and consequently reduces the rate of reaction. The increased content of SiO_2 was achieved through a higher content of bottom ash in the binary precursors system, as well as by the addition of soluble sodium silicate. Due to the lower reactivity of bottom ash, the increase in SiO_2 is more effective when the sodium silicate in the activator is increased.

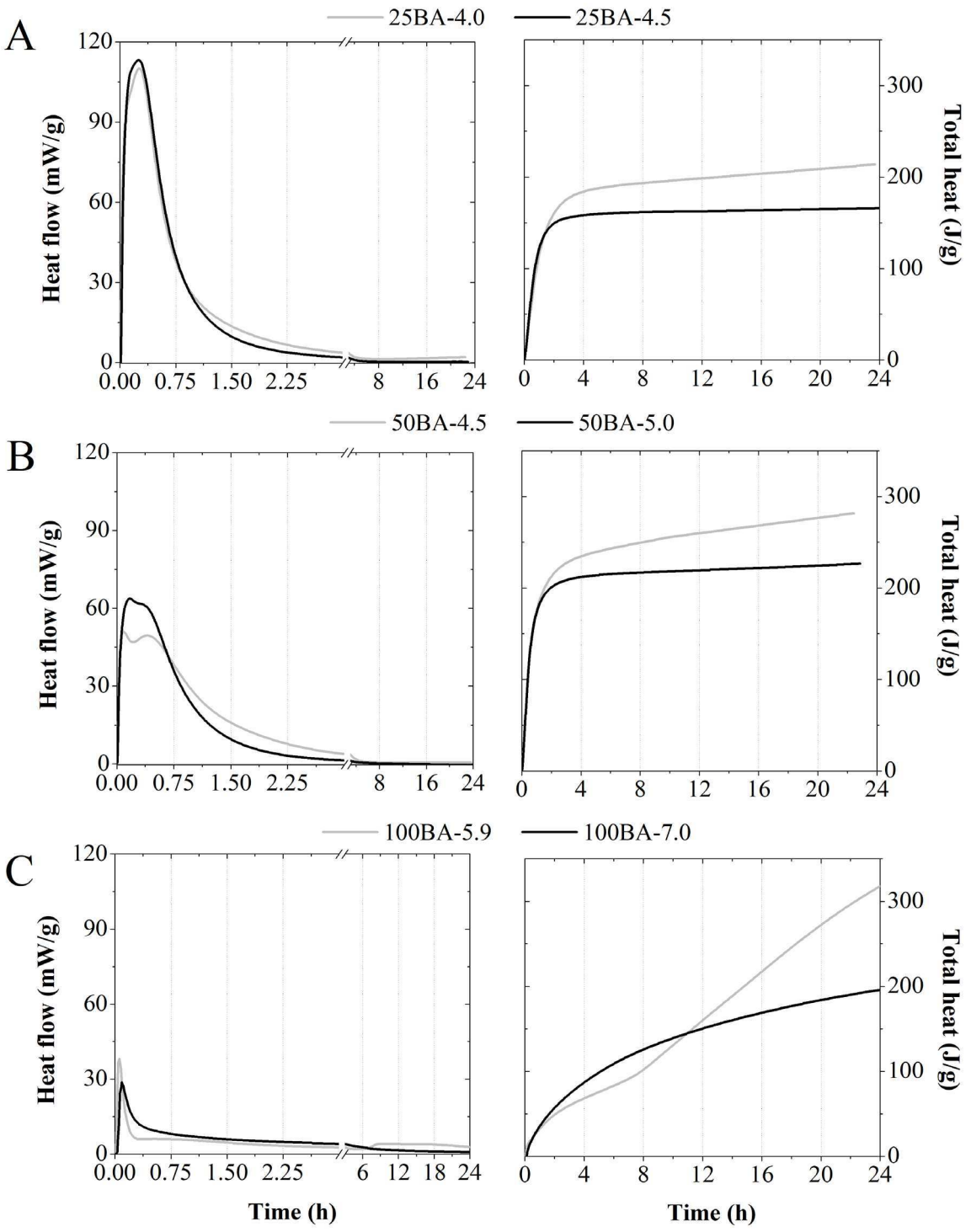


Fig. 1 Isothermal calorimetry data for the geopolymers as marked (sample IDs from Table 3) A. BA/CKS: 25/75; B. BA/CKS:50/50 and C. BA:100/00. In each part, the left-hand plot shows the heat flow with the time axis expanded by a factor of 10 in the early stages of the reaction, and the right-hand plot shows the cumulative heat release with a linear time axis.

The presence of CKS, which has higher reactivity [34], modifies the kinetics of geopolymerisation so that a single and more intense peak of heat release is identified at 15 min (Fig. **1**B). Therefore, as the content of CKS increases from 50 wt.% to 75 wt.% (for the systems 50BA and 25BA, respectively), a higher maximum of heat evolution is reached, and earlier, and a narrower single exotherm is identified. Likewise, the cumulative heat released also increased with higher contents of CKS. The higher content of Al_2O_3 in the CKS increases the release of aluminate monomers in the 25/75 BA/CKS blends. The higher heat release during the dissolution of the CKS can be attributed

to the high specific surface area of the particles, as well as the presence of an amorphous and highly strained layer structure in kaolinitic clays after thermal treatment [40, 41].

Under the activation conditions used, the dissolution of the BA is much lower than that of CKS due to the lower content of amorphous (or more reactive) phases; the crystalline phases present in the BA (see XRD analysis below) do not participate to a significant extent in the reactions [42]. The maximum heat released by the systems based on BA (Fig. **1**C) is up to three times lower, when compared to the binary systems. The use of a blend of highly reactive and less reactive materials led to overlap between the dissolution and polycondensation processes [34].

3.2. Compressive strength of pastes

The mechanical performance of the materials produced is strongly influenced by the content of soluble silicate (which defines the overall SiO_2/Al_2O_3 molar ratio for each precursor blend), as well as the BA/CKS ratio (Fig. 2). The bottom ash geopolymers system 100BA-5.9, which is activated by NaOH, presents an increasing compressive strength during the curing time, with a value of 26.7 MPa at 90 days of curing. The addition of sodium silicate, in 100BA-7.0, provides higher mechanical performance (~44 MPa at 90 days). The blend 50BA-4.0, which has the lowest SiO_2/Al_2O_3 molar ratio (and was produced with a NaOH-based activator) had a compressive strength lower than 10 MPa regardless of the duration of curing. However, this low mechanical performance can be improved by either using an alkali activator with higher content of soluble silicate, or by the inclusion of more CKS. In this sense, 50BA-5.0, with a silicate activator giving an SiO_2/Al_2O_3 molar ratio of 5.0, had a compressive strength up to 4 times higher than 50BA-4.0. Likewise, the adjustment of the BA/CKS ratio in the precursor to 25/75 (higher content of CKS) with an SiO_2/Al_2O_3 molar ratio of 4.0 (25BA-4.0) gave a compressive strength up to 2.8 times higher than that of 50BA-4.0. Similar behavior is also identified in the pastes with an SiO_2/Al_2O_3 molar ratio of 4.5; 25BA-4.5 had a compressive strength up to four times higher than 50BA-4.5. According to previous studies, the CKS-based systems produced using NaOH as activator exhibited compressive strengths lower than 20 MPa even after 90 days of curing [34]. This value is considerably lower than for the corresponding BA-based systems, whose compressive strength at 90 days of curing is close to 30 MPa.

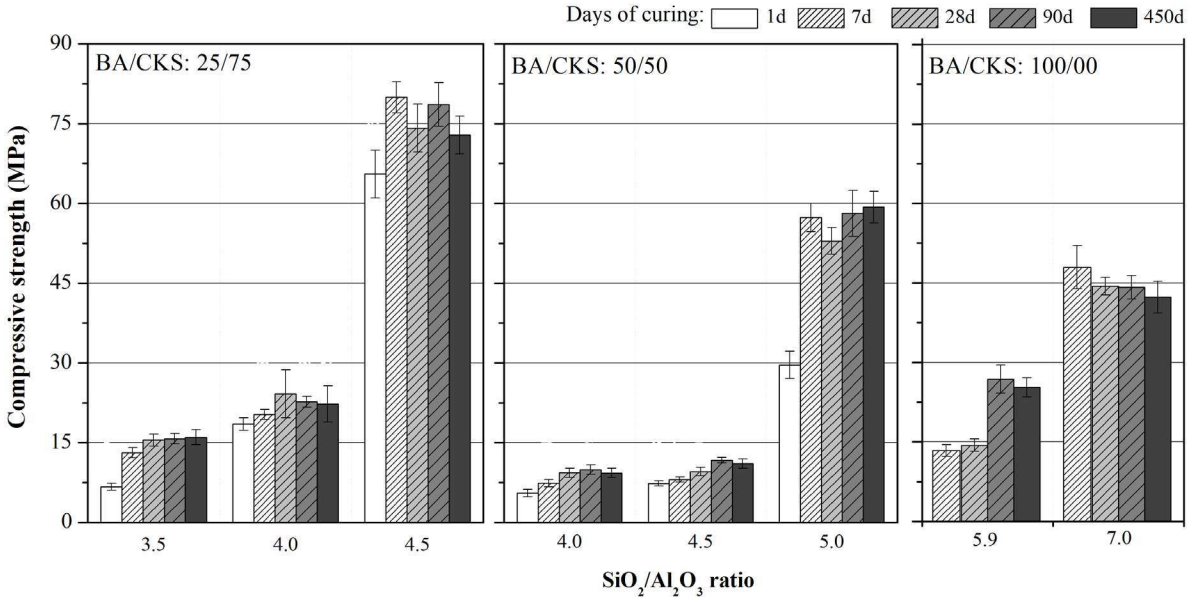
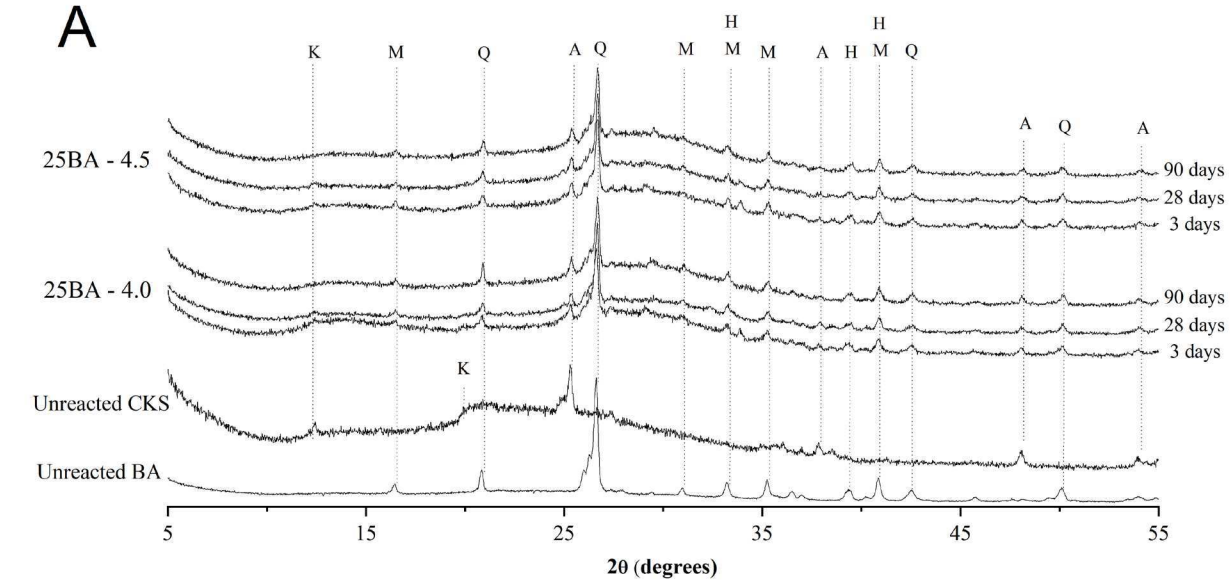


Fig. 2 Compressive strength of the geopolymers with different BA/CKS ratios as marked. Errors bars indicate standard deviation.

From these data, there does not exist a direct and proportional relation between the total heat released and the compressive strength. The higher values of total heat do not indicate the formation of stronger and more cross-linked microstructure. For example, although 25BA-4.5 showed lower total heat release when compared with 25BA-4.0 (**Fig. 1**a), it also had the highest compressive strength after 1 days of curing. The pastes that achieved high compressive strength (> 25 MPa) also showed a significant standard deviation in the results, which makes unclear the behavior between different durations of curing.

3.3. Binder characterisation

Fig. **3** shows the X-ray diffractograms of the unreacted precursors (BA and CKS) and the geopolymers after 3, 28 and 90 days of curing. The crystalline phases present in the BA and CKS, including mullite ($Al_6Si_2O_{13}$, Pattern Diffraction File, PDF# 01-083-1881), hematite (Fe_2O_3, PDF# 01-079-0007), quartz (SiO_2, PDF# 01-088-2302), and anatase (TiO_2, PDF# 00-021-1272) are identified in all samples regardless the synthesis conditions or age of curing. The presence of well-defined peaks and the lower intensity of the amorphous hump in the BA corroborates its lower reactivity, which is also identified through the lower mechanical performance and lower heat release observed for the geopolymer produced with this precursor. On the other hand, the CKS shows an intense amorphous hump, with few traces of the remaining kaolinite ($Al_2Si_2O_5(OH)_4$, PDF# 01-078-2109). The pronounced amorphous hump shown by the CKS in the 2θ range between 20 and 30° 2θ decreases and shifts to higher angles after alkali-activation, which can be attributed to the formation of aluminosilicate gels [34, 43]. The X-ray diffractograms of all pastes studied are quite similar, regardless of the activator composition and BA/CKS ratio, and no crystalline zeolite phases were identified as reaction products, even after 90 days of curing. The patterns for the systems with a BA/CKS ratio of 50/50 showed a higher amorphous hump between 25 and 35° 2θ, related to the gels which can be related to the higher heat released during the first 24 hours due to a more extended formation of the geopolymeric gel, which is also consistent with the mechanical strength previously reported. Sodium carbonate (Na_2CO_3; PDF# 01-086-0312) was identified in the sample 50BA-4.5 due to reaction of the sodium-rich pore solution with the atmospheric CO_2 during either curing or handling.



K - Kaolinite; A - Anatase; M - Mullite; H - Hematite; Q - Quartz

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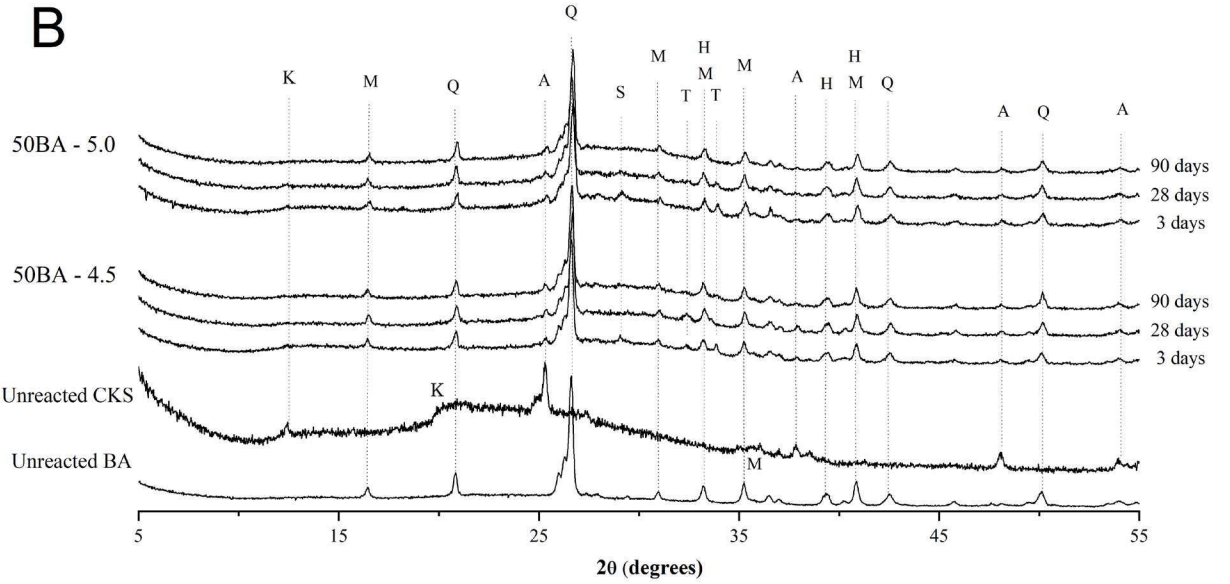

K - Kaolinite; A - Anatase; M - Mullite; H - Hematite; Q - Quartz; T - Trona; Sodium silicate

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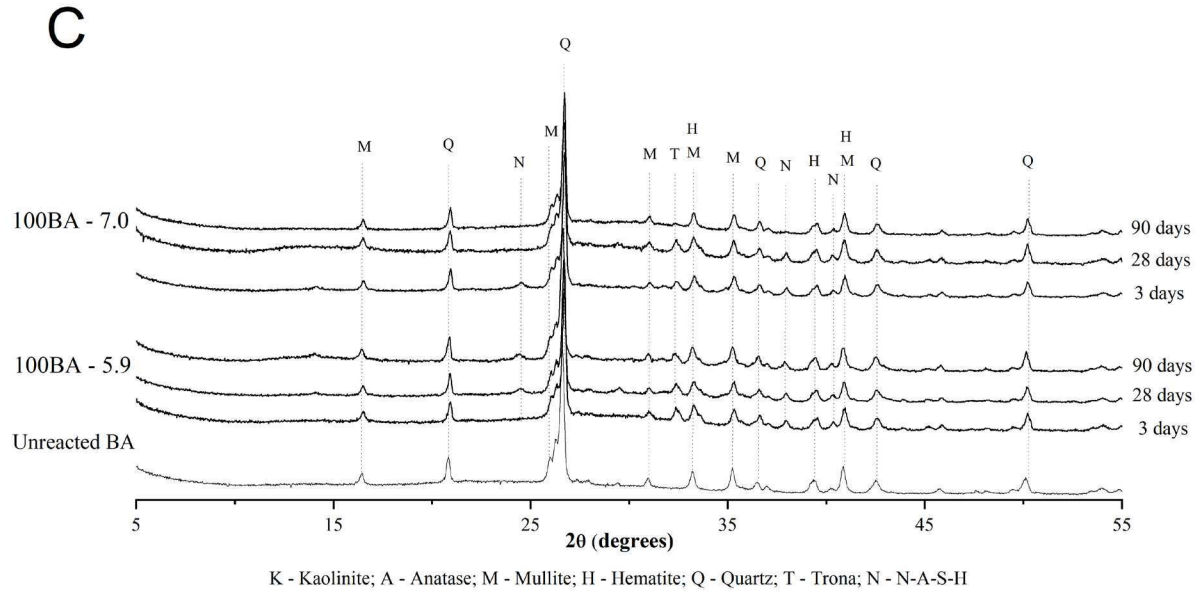

Fig. 3 X-ray diffractograms of the unreacted precursors, and of the geopolymers at different ages of curing. A. BA/CKS: 25/75; B. BA/CKS:50/50; and C. BA/CKS:100/00.

Fig 4. to Fig. 6 show the thermogravimetric analysis and accompanying MS spectra for masses of CO_2 (40 g/mol) and H_2O (18 g/mol), for the geopolymers with different BA/CKS ratios up to 90 days of curing. The DTG curves each exhibit a strong peak between 25-250 ºC, which is attributed to the loss of trapped water from the gel pore structure, and the water physically bound to the reaction products. There are no significant differences in the temperature of the main peak in the DTG curves among the samples assessed, which indicates that these water environments are similar in all samples. The geopolymers with a BA/CKS ratio of 25/75 (Fig. 4) have a lower total mass loss when compared with the ratio 50/50 (Fig. 5), which is attributed to a more extensive formation of reaction products. The mass spectroscopy also shows the release of water, whose highest signal was detected between 105 and 120 °C. At higher temperature (400-500 °C) the water present as hydroxyl groups in the aluminosilicate framework is released [44]. These results confirm that most of the water in the geopolymeric system is present as free or adsorbed water, with little chemically bound as hydroxyl groups.

The water released by the geopolymer with a BA/CKS ratio of 25/75 and an SiO_2/Al_2O_3 molar ratio of 4.5 was lower when compared to the corresponding systems produced with a higher content of soluble silicates (SiO_2/Al_2O_3 molar ratio of 5.0), which can be linked to differences in the quantity of gel formed. These results are consistent with the lower mechanical performance exhibited by 50BA-4.5 compared to 50BA-5.0. For the systems with a BA/CKS ratio of 25/75 (Fig. 6), no significant differences in the total mass loss were identified regardless of the SiO_2/Al_2O_3 ratio, despite the very notable difference in strength between 25BA-4.5 and the other pastes at this BA/CKS ratio (Figure 2).

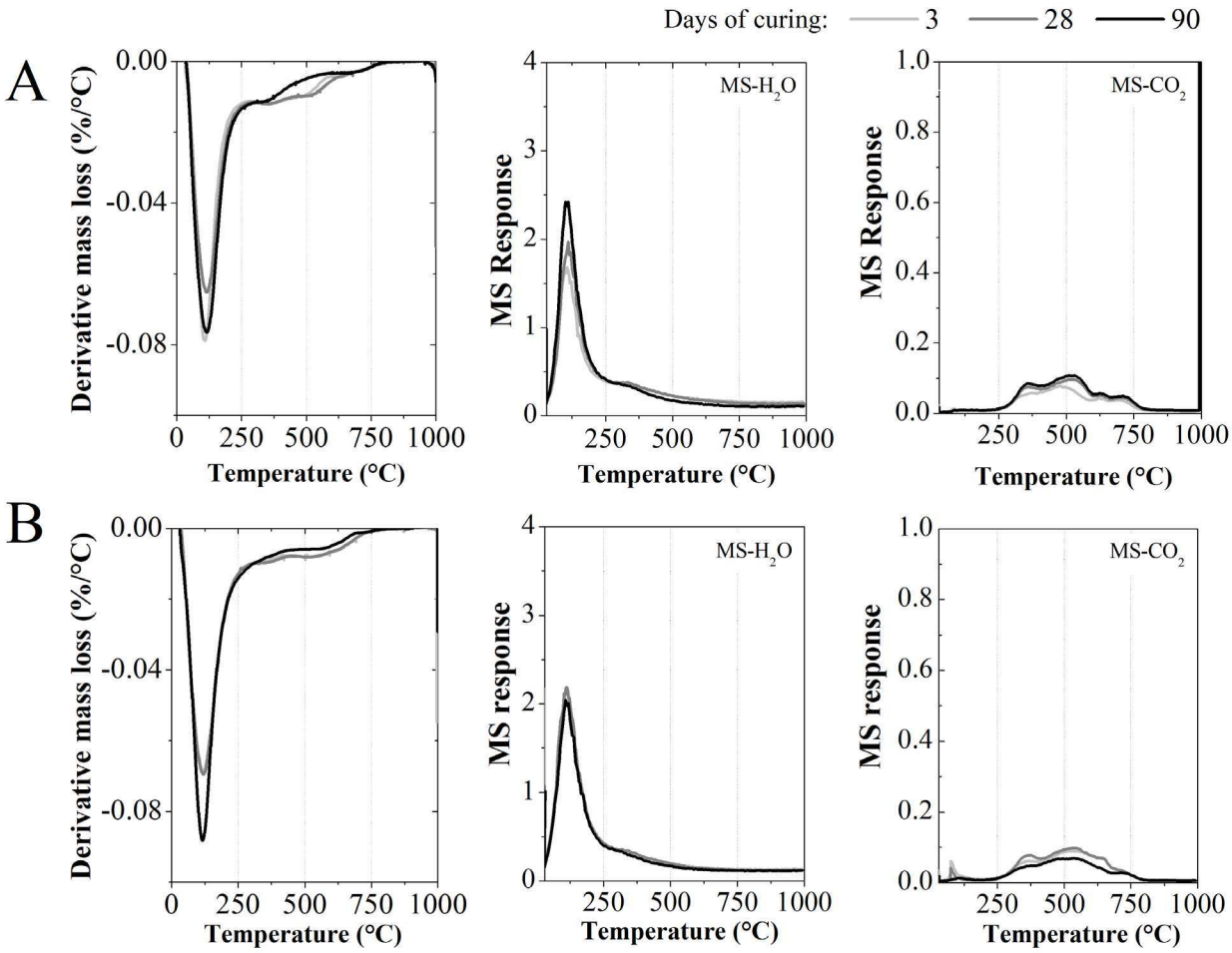

Fig 4 Differential thermogravimetric curves (DTG), and water and carbon dioxide mass spectroscopy (MS) results for the geopolymers produced with a BA/CKS ratio of 25/75 at different SiO_2/Al_2O_3 molar ratios: A, 4.0; and B, 4.5.

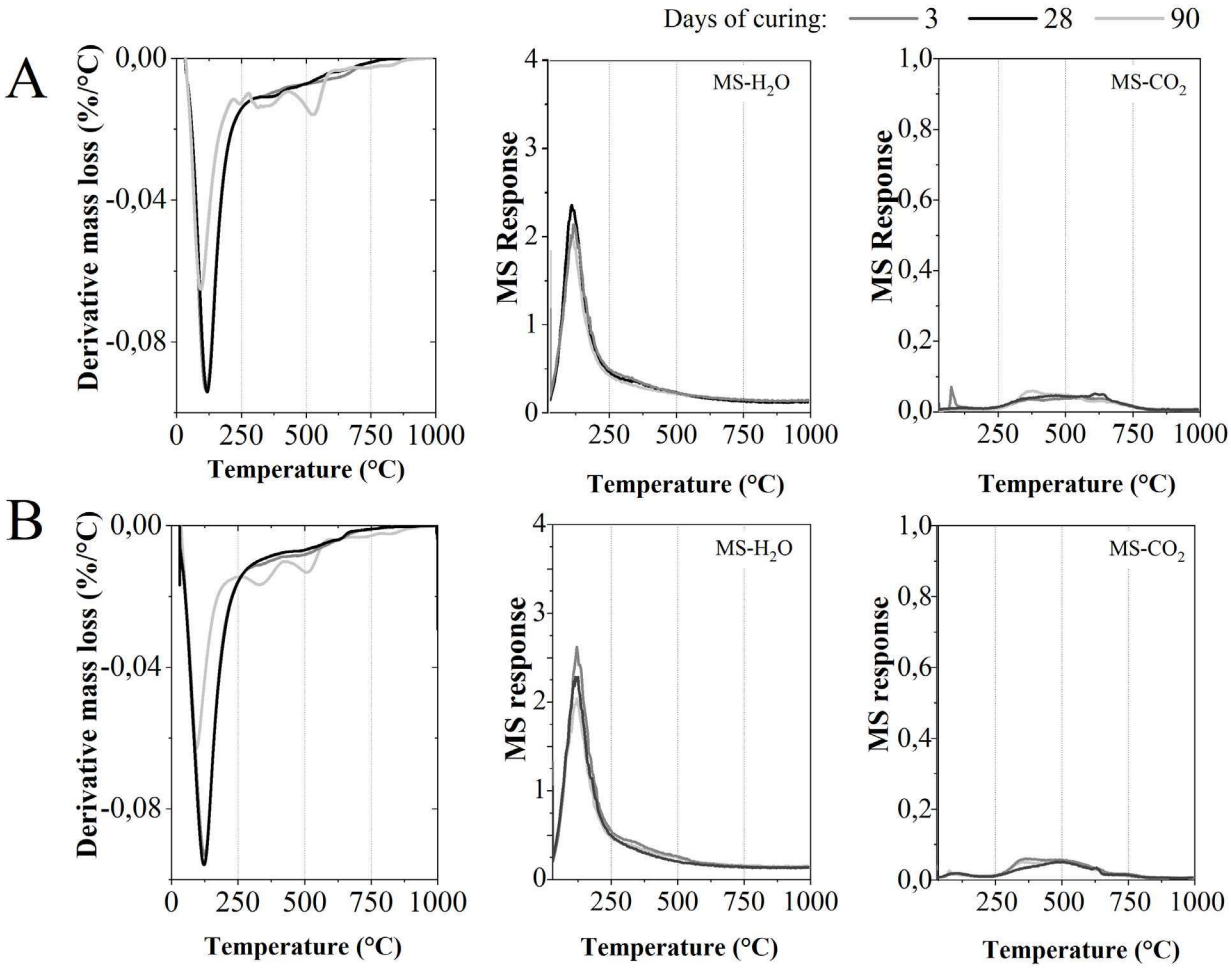

Fig. 5 Differential thermogravimetric curves (DTG), and water and carbon dioxide mass spectroscopy (MS) results for the geopolymers produced with a BA/CKS ratio of 50/50 at different SiO_2/Al_2O_3 molar ratios: A, 4.5; and B, 5.0.

The release of CO_2 detected by the mass spectroscopy showed two stages, the first one with a peak between 70 and 90 °C, followed by a broader and more intense signal located between 350 and 700 °C. The signal identified at lower temperatures can be attributed to the thermal conversion of minor alkali carbonates formed due to carbonation of the sample during handling and storage. The second signal can be attributed to the thermal decomposition of different calcium carbonates-containing products with low crystallinity (not identified in the X-ray diffractograms). The content of carbonates is slightly higher as the content of BA is increased, as this is the precursor that supplied Ca into the system, and can also indicate an excessive amount of activator that can lead to the carbonation of the Na^+. These results are also consistent with the peak with a low intensity identified between 600 and 750 °C in the DTG curves.

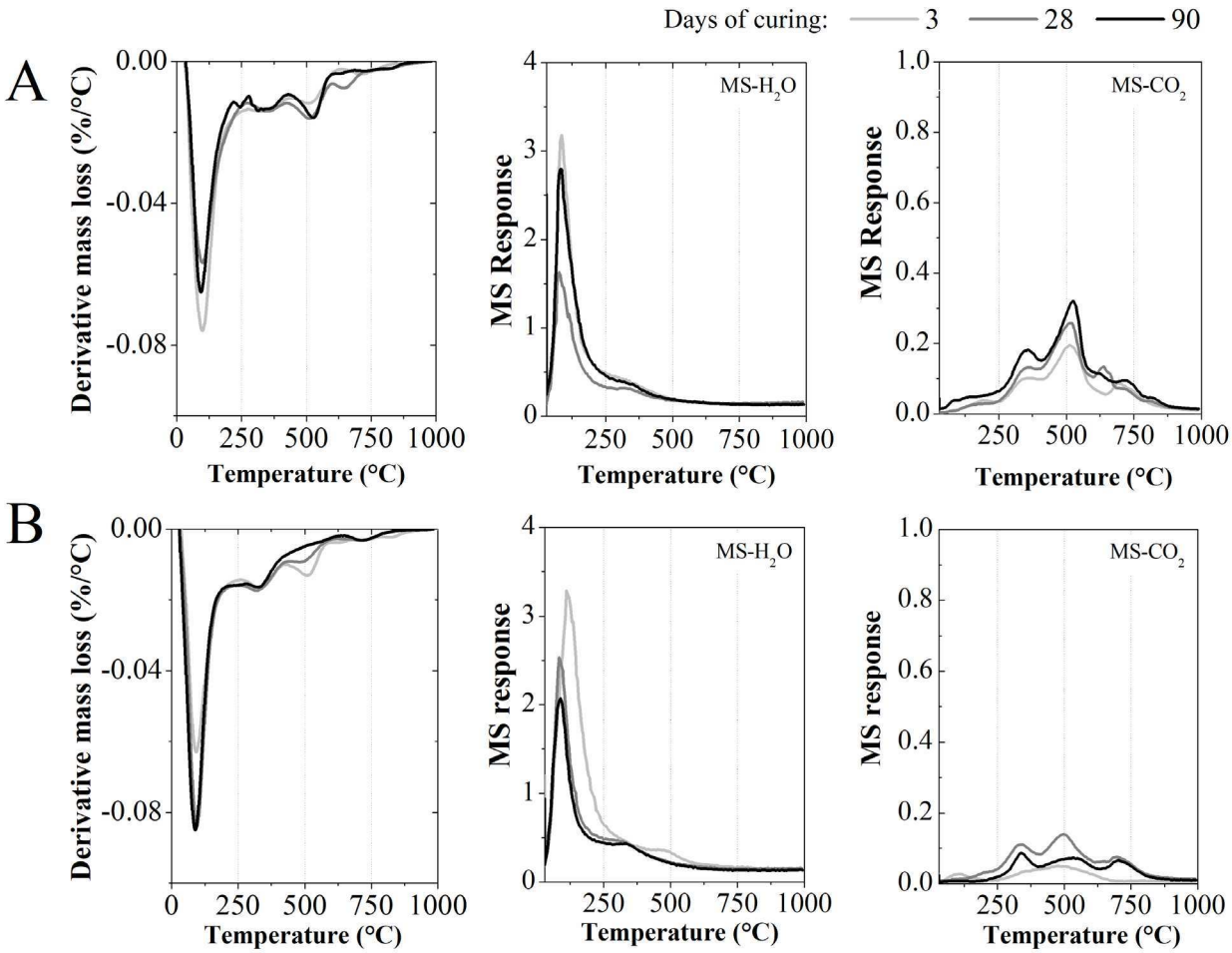

Fig. 6 Differential thermogravimetric curves (DTG), and water and carbon dioxide mass spectroscopy (MS) results for the geopolymers produced with a BA/CKS ratio of 100/0 at different SiO_2/Al_2O_3 molar ratios: A, 5.9; and B, 7.0.

3.4. Mortars

The paste mix designs of the geopolymers with BA/CKS ratios of 50/50 and 25/75 with SiO_2/Al_2O_3 molar ratios of 5.0 and 4.5, respectively, which showed the highest compressive strength results in the paste mixtures (Fig. 2) were used for the production of mortars. Fig. 7 shows the workability of the fresh mixtures, and the compressive and flexural strengths of the geopolymeric mortars assessed after 3, 7 and 28 days of curing. The 50BA-5.0 mortar exhibited a higher workability than 25BA-4.5, which is attributed to the lower content of CKS. As observed in a previous paper [35], the morphology of CKS is a plate-like particle structure with high surface area and high reactivity, and these properties tend to increase the water demand [45]. The high content of soluble silicate in the alkali activator also reduced the workability of the fresh mixture, which is related to the higher viscosity of alkali activator solutions with high SiO_2/Na_2O molar ratio [46].

The compressive strengths of the mortars are consistent with the results presented above for pastes, where 25BA-4.5 exhibited the highest mechanical performance. After 28 days of curing both mortars showed compressive strength values higher than 50 MPa, which elucidates the high degree of valorisation that is achieved for the waste materials here. The mortars also showed a clear evolution in the strength development, so that at 28 days the compressive strength of these mortars are up to ~40% higher than the corresponding systems at earlier ages. In this sense, the inclusion of the sand as a fine aggregate removed the loss of compressive strength due to shrinkage-related processes that was identified in the results in pastes (Fig. 2). Sand particles act as a reinforcement which also provides dimensional stability [47]. However, it is not clear why the flexural strengths of both mortars show the opposite behavior and appear to regress from 7 to 28 days.

Table 2 Compressive strength and flexural for the geopolymers mortars

Mortar ID	Flow of fresh mortars, NBR 13276 [36] (mm)	Age (days)	Compressive strength		Flexural strength	
			MPa	SD	MPa	SD
25BA-4.5	174	7	49.9	7.1	9.3	0.5
		28	58.3	7.3	7.2	0.7
50BA-5.0	182	7	34.8	3.5	6.5	0.2
		28	47.6	6.6	6.7	0.9

SD: Standard deviation among 6 samples

Capillary sorptivity curves obtained for the mortars after 28 days of curing are shown in Fig. **7**. The low sorptivity, associated with a low pore volume and a refined pore structure, is desirable from a durability point of view. According to NBR 15259:2005 [38], the kinetics of the water sorption can be described by a capillary absorption coefficient calculated from the values obtained after 10 and 90 min. Following this calculation procedure, mortars 25BA-4.5 and 50BA-5.0 had capillary coefficients of 3.39 and 4.45 $g/dm^2 \cdot min^{1/2}$, respectively. The water absorption after 24 h is similar between the two mortars, but the relative rates of the water sorption in the two samples indicate a denser pore structure with a higher tortuosity for 25BA-4.5, which is consistent with the higher mechanical strength of this mortar.

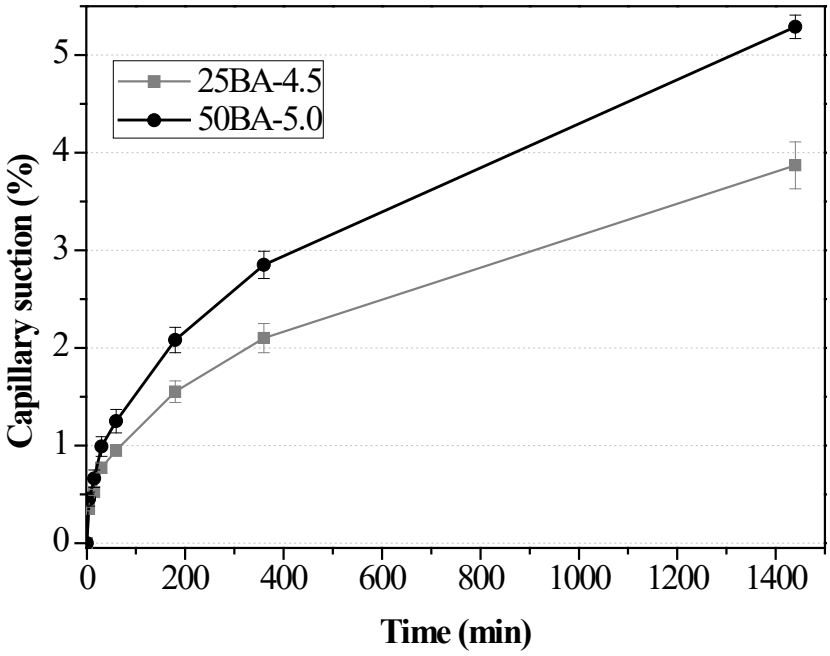

Fig. 7 Capillary sorptivity of geopolymer mortars after 28 days of curing.

The results of compressive strength and porosity determination are clearly related to microstructural properties. The higher compressive strength is also observed in the systems produced with higher alkali activator dose based on sodium silicate, which is aligned with the behavior identified in the pastes. The porosity is reduced by the presence of sodium silicate in the alkali activator, which is also associated with the higher amount of gel formed during the geopolymerisation, where the most reactive blend of precursors shows a lower water absorption when compared to the less reactive blend precursor system. These results indicate that these precursors (CKS and BA) are promising materials to be used in geopolymers at large scale.

4. Conclusions

Coal bottom ash (BA) and calcined kaolin sludge (CKS) can be valorised as precursors for blended geopolymer pastes and mortars. The partial replacement of BA by CKS increases the average reactivity of the precursor blend, and thus also the heat released during geopolymerisation and improve the workability when using the same amount of water. The inclusion of an optimum content of silicate soluble increases the compressive strength very significantly, and materials with attractive mechanical performance can be obtained across a wide range of BA/CKS ratios. The results reported in the present study elucidate that the presence of soluble silicates in the alkali activator, and the inclusion of a higher content of a precursor with high reactivity, play a significant role in determining the mechanical performance of a geopolymer material. The disordered aluminosilicate gel structure that gives strength to the binders can also be tailored to give relatively low capillary uptake coefficients, and the paste mix designs generated in this work can be scaled to give mortars with desirable mechanical performance. The results also elucidate that the understanding of synthesis optimisation through the adjustment of the alkali activator composition and dosage is a useful way to increase the potential valorisation of those industrial wastes that exhibit lower reactivity. Therefore, the geopolymerisation of some industrial wastes can be considered an interesting pathway for their reuse, and more detailed studies (such as real environmental impact, durability, application and cost) are required for the large-scale inclusion of this new material within the industry.

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