

Article

One-Part Alkali-Activated Pastes and Mortars Prepared with Metakaolin and Biomass Ash

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Received: 23 July 2020; Accepted: 11 August 2020; Published: 13 August 2020



Abstract: Common alkali-activated materials (AAMs) are usually manufactured with highly alkaline solutions. However, alkaline solutions are dangerous for workers who must wear gloves, masks, and glasses when handling them. This issue makes common (or two-part) AAMs not user-friendly and problematic for bulk production if no safety procedures are followed. In this paper, the possibility of manufacturing alkali-activated pastes and mortars without alkaline solution is investigated. These innovative one-part AAMs have been prepared with metakaolin as the aluminosilicate precursor, potassium-rich biomass ash as the alkaline activator, and water. AAMs have been prepared by varying the K/Al molar ratio: pastes have been studied in terms of reaction kinetics, through isothermal calorimetry, and mortars have been tested in terms of mechanical compressive strength. Results show that the K/Al molar ratio governs both the reaction kinetics and the mechanical strength of these innovative materials. The highest compressive strength is obtained when the K/Al ratio is equal to 2.5 and the water/solid ratio is equal to 0.49. If biomass ash is heated at 700 °C to decompose the calcium carbonate, its reactivity and the final compressive strength increase.

Keywords: one-part geopolymers; geopolymer; alkali-activated materials; metakaolin; biomass ash; isothermal calorimetry; compressive strength

1. Introduction

Conventional alkali-activated materials (AAMs) can also be referred to as “two-part” AAMs. If AAMs are prepared with aluminosilicates with a SiO₂ + Al₂O₃ content higher than 80 wt.% and a low CaO content, such as class F fly ash and metakaolin, they belong to the sub-class of geopolymers [1]. AAMs are synthesized by activation of a powdered aluminosilicate precursor (e.g., metakaolin, fly ash, and blast furnace slag) and a highly alkaline activator. The alkaline solutions (NaOH, KOH and Na_xSiO_(2+x/2) with x usually between two and four) are categorized as corrosive and must be handled with gloves, masks, and glasses. This issue, together with the formation of a sticky and thick paste, make them not user-friendly and problematic for bulk production if no safety procedures are followed.

During the last 20 years, researchers have tried to obtain a novel type of AAM that can be prepared without using dangerous alkaline solutions. They started to refer to them as one-part or “just add water” AAMs (or geopolymers), to mimic the preparation of common Portland cement-based materials. In synthesis, they consist of a ready-to-use reactive powder, that can form a solid material with good mechanical properties just by the addition of water.

Even though this research field started two decades ago, there are very few studies regarding the preparation and properties of one-part AAMs/geopolymers. Moreover, as for “two-part” AAMs,

different types of aluminosilicate precursors and activators are used, thus the properties of the final products depend on the characteristics and reactivity of the initial raw materials [2]. The most common precursor is fly ash (FA) from coal combustion either alone or coupled with ground granulated blast furnace slag (GGBFS) [3–6]. The latter is commonly added as calcium-rich precursor for AAMs to improve the reactivity of low-calcium fly ash [7]. Other aluminosilicate materials used for AAM's preparation are clay minerals. However, as for "two-part" AAMs, they require calcination to be reactive in alkali-activation [8,9]. Moreover the plate-like shape and the high surface area of their particles increase water demand [10], resulting in hardened materials with high total porosity [11]. The most studied aluminosilicate source used for AAM preparation is metakaolin (MK), which is the dehydroxylated form of kaolin. Other clayey materials include metabentonite [12], albite (a sodium feldspar, often one of the main components in mine tailings) [13], potash feldspar, pyrophyllite, and natural zeolite [14]. Moreover, other natural or by-product aluminosilicate precursors have been used in AAM production, such as volcanic ash [15], red mud [16], geothermal silica [17]; however, the most suitable precursor for one-part mixes depends on materials' local availability [18] since the environmental impact rapidly increases with transportation distance [19]. As well as precursors, different types of activators have also been used in the preparation of one-part AAMs, such as sodium aluminate, sodium silicate, sodium sulfate, sodium carbonate, and sodium silicate pentahydrate [20].

Biomass ash (BA) is a material obtained by thermal treatment of biomasses. It can be generated by burning wood, agricultural wastes, grasses or even algae. Normally, it can be used as fertilizer in agriculture if it does not contain harmful compounds, otherwise it should be landfilled; therefore, a more high-value recovery is necessary. A solution can be the use of BA in one-part AAM preparation. Depending on the starting material, BA can be rich in silicon, calcium or potassium oxides, which makes it a good candidate for one-part AAMs both as a precursor and activator. Obviously, different sources of biomass provide for BA different phases and chemical compositions; in particular, those generated by the thermal treatment of wood are rich in calcium, whereas herbal ashes contain mainly silicon and potassium [21].

Sturm et al. [22] produced one-part geopolymers with BA as the precursor, by mixing rice husk ash, a silica-rich by-product obtained by calcination of rice husk at temperatures up to 800 °C, and anhydrous sodium aluminate with water at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.5$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$ molar ratios. They cured specimens in an oven at 80 °C and 80% relative humidity (RH) for different curing periods. They found that just 24 h curing is necessary to produce materials with a compressive strength of 30 MPa. The elevated mechanical properties of this type of one-part geopolymer were found to be related to the high degree of reaction of the silica and the absence of crystalline products (zeolites).

Other authors used BA as the activator, without thermal pretreatment. For example, Hassan et al. [23] prepared white one-part AAMs by mixing dry powders at different $\text{NaOH}/\text{CaCO}_3$ molar ratios, composed of a calcium-rich wood biomass ash and NaOH, with diatomite, a siliceous sedimentary rock, and water. The obtained specimens were cured at 23 ± 2 °C and $99 \pm 1\%$ RH. The authors found that by decreasing the $\text{NaOH}/\text{CaCO}_3$ molar ratio of the dry activator, the compressive strength of the hardened one-part AAMs increased and the porosity decreased up to a certain limit; then the trend inverted for lower molar ratios. The highest compressive strength after 28 days of curing, 48 MPa, was obtained by one-part pastes manufactured with a $\text{NaOH}/\text{CaCO}_3$ molar ratio of 0.5 and was probably that high due to the nucleating sites and filling effects of CaCO_3 . Peys et al. [24] studied the possibility of using different types of potassium-rich BA as the alkaline activator to synthesize metakaolin-based one-part inorganic polymers. They found that a higher reactivity was obtained by maize cob ashes mixed with water and metakaolin with an ash/metakaolin (a/m) weight ratio of 0.9. Mortars were prepared with different a/m ratios, pressed at 59 MPa and cured with different procedures. The highest compressive strength (around 40 MPa) was obtained after pre-curing specimens at 20 °C for 24 h and then heating them at 80 °C for 48 h. Baló et al. [25] produced one-part inorganic polymers with raw materials coming from Africa (Cameroon), by mixing metakaolin with a potassium-rich BA as the alkaline activator obtained by combusting cotton shells. Cotton shell ash was used as it

is, and after calcination at 850 °C to improve its reactivity. They studied the evolution of hydration kinetics and compressive strength by varying the K/Al molar ratio of pastes and mortars. Moreover, they also compared the compressive strength of specimens only poured and vibrated with that of specimens with a lower water content but pressed at 7.9 MPa. They found that for both types of specimens, compressive strength values were increased by increasing the K/Al molar ratio. Moreover, when specimens were produced with pure cotton shell ash, one-part inorganic polymer mortars reached the highest compressive strength at a value of K/Al = 4; in the case of calcined cotton shell ash, the maximum compressive strength was obtained with a K/Al ratio of five, regardless of if poured and vibrated or compressed.

The aim of this paper was to produce one-part alkali-activated pastes and mortars manufactured by adding only water to metakaolin and biomass ash coming from Europe, in order to see if the results obtained by Balo et al. [25] can be reproduced by using different raw materials. The one-part alkali-activated mixtures produced in the present work were not subjected to compression, used instead for brick production, in order to evaluate if it is possible to manufacture a construction material that can be just poured in molds or applied as it is at the construction site without any additional treatment. Moreover, in the present experimentation a BA coming from wood has been used instead of one coming from agricultural waste. This wood BA, to the best of our knowledge, has never been used as the sole alkaline activator in the preparation of one-part alkali-activated materials. Metakaolin was used as the aluminosilicate precursor and BA was used as the alkaline activator. Pastes were prepared by maintaining the water/solid ratio constant and by varying the K/Al molar ratio. To dissolve the aluminosilicate precursors and initiate the reaction, Ke et al. [16] reported that good activators for one-part AAMs should have a pH higher than 11, thus the pH of our BA in the amount of water to be used was measured. The reaction kinetics of binders was studied by isothermal micro-calorimetry. The mechanical strength was investigated through compression tests on mortars manufactured by varying both the K/Al molar ratio and the water/solid ratio in specimens both only poured and vibrated. Moreover, the possibility of heating biomass ash to decompose carbonates and increase its reactivity, thus mortar's mechanical strength, was investigated.

2. Experimental Program

In the following sections, materials and methods will be presented. The raw materials characteristics and equipment used will be reported in the "Raw materials characterization" section. In the "Preparation and characterization of pastes" section, the preliminary study on pastes with various K/Al molar ratios is reported by providing their mix design and the calorimetric analysis in order to study the reaction kinetics and the reactivity of pastes. In the "Preparation and characterization of mortars" sub-paragraph, some selected K/Al molar ratios have been chosen to prepare one-part alkali-activated mortars, here, the mix design of mortars has been reported and mechanical and morphological tests have been performed in order to study if the K/Al molar ratio influences the properties of hardened mixtures.

2.1. Raw Materials Characterization

As the aluminosilicate precursor, metakaolin (Figure 1a) was synthesized by heating at 700 °C; a kaolin originating from UK and provided by Imerys Minerals Ltd (Paris, France) was used. The chemical and mineralogical compositions of the kaolin are given in Tables 1 and 2, respectively. The kaolinite and the metakaolinite used in this experimentation are the same used in Peys et al. [24], and the chemical and mineralogical compositions can be found also in their work. As the alkaline activator, a biomass ash (Figure 1b) was chosen. It originated from the Roodenhuyse power plant located in Belgium, which uses wood for electricity generation. Being obtained from wood, the chemical composition shows that the biomass ash is mainly constituted by calcium and potassium oxides (Table 1). The chemical analysis of kaolin and biomass ash was performed by means of semi-quantitative wavelength dispersive X-ray fluorescence (XRF) spectrometry by means of a Philips spectrometer,

model PW 2400. The X-ray diffraction (XRD) analysis of kaolin was performed using a Philips PW 1830 diffractometer.

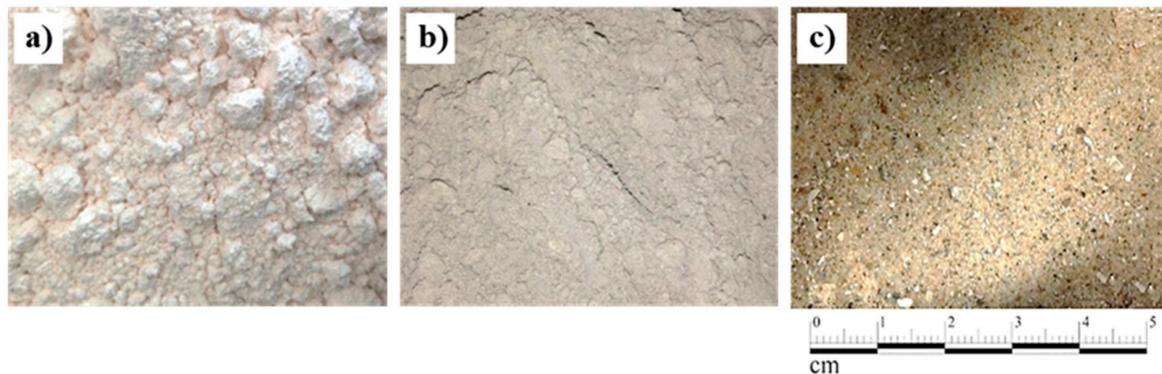


Figure 1. Visual aspect of (a) metakaolin, (b) biomass ash, and (c) river sand.

Table 1. Chemical composition (wt%) of kaolin and biomass ash measured by X-ray fluorescence (XRF).

Material	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	SO ₃	Fe ₂ O ₃	MgO	MnO	Cl	Na ₂ O
Kaolin	51.0	34.0	-	3.0	-	1.0	<1.0	-	-	-
Biomass ash	9.0	1.7	46.1	20.9	10.7	3.6	3.7	1.8	<1.0	<1.0

Table 2. Mineralogical composition (wt%) of kaolin measured by XRD.

Kaolinite	2:1 Clays	K-Feldspar	Quartz
68	21	8	3

The morphology of metakaolin and biomass ash, analyzed by Scanning Electron Microscopy (SEM) in a Philips FEG–ESEM XL30 electron microscope on carbon-coated samples, is reported in Figure 2 and shows the typical plate-like structure of metakaolin and the spherical morphology of biomass ash. The specific density of metakaolin and biomass ash measured with a gas pycnometer was 2.50 g/cm³ and 2.25 g/cm³, respectively.

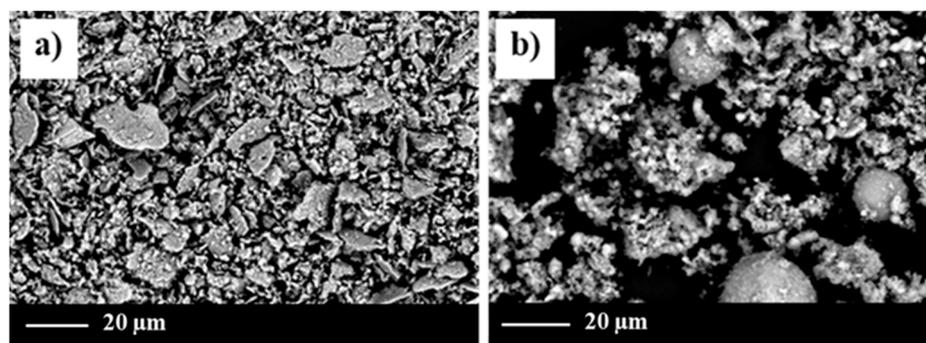


Figure 2. SEM images of (a) metakaolin and (b) biomass ash.

The pH of the biomass ash was measured by a HANNA instruments pH-meter by putting 0.5 g of ash in 5 g of distilled water, as reported in the literature [24,25]. In the present study, the biomass ash has a pH of 12.5, which is higher than the threshold reported in the literature and makes biomass ash a good candidate for producing one-part AAMs.

Thermogravimetric analysis (TGA) of metakaolin and biomass ash was carried out by heating samples in nitrogen atmosphere up to 1000 °C with a heating rate of 20 °C/min using a Q5000IR

Thermogravimetric analyzer, TA Instruments. Results obtained by TGA are reported in Figure 3. Concerning metakaolin, a constant mass loss around 2% of the initial mass is registered after 900 °C. The very low reduction of metakaolin mass is related to the calcination process at 700 °C to which the starting kaolin has been already submitted ensuring the largest mass loss occurred prior to this test. On the other hand, the biomass ash is subjected to different mass losses at different increasing temperatures. The first one, very limited and of about 1%, occurs around 100 °C and is caused by the evaporation of water. This is the water adsorbed by the ash when it is stored at environmental conditions, as in the present study. The second one around 350–400 °C is very small, less than 0.5%, and it is probably related to the oxidation of the lignin and cellulose that remained in the ash [26–28]. After 400 °C, a mass increase was recorded probably related to the oxidation of FeO to Fe₂O₃ [29]. Instead, the mass losses observed at temperatures over 600 °C are related to the decomposition of both calcium and potassium carbonates [30]. The former is huge, it occurs in the range of 650–900 °C and it is predominantly due to the decomposition of CaCO₃. The latter, occurring beyond 900 °C, is smaller than the previous one and it is related to the decomposition of K₂CO₃ and calcium and magnesium sulfate.

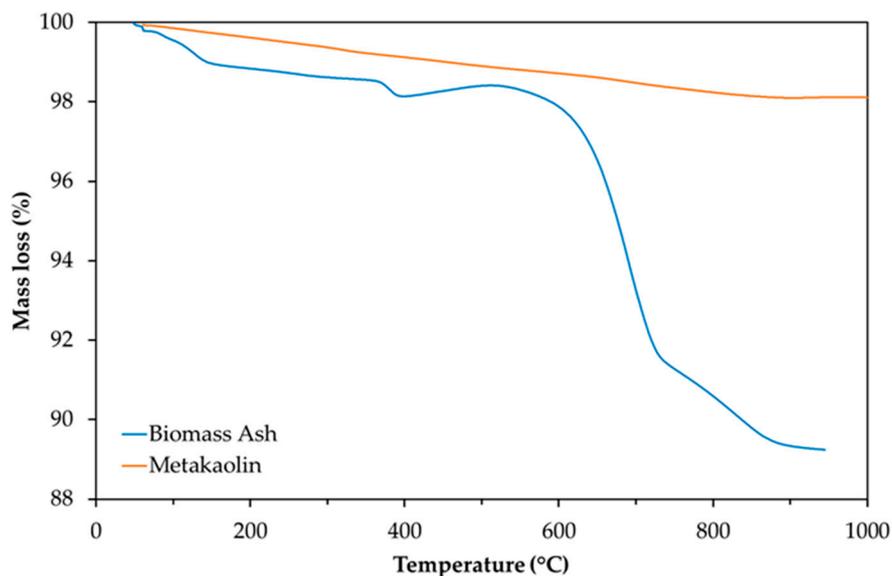


Figure 3. Thermogravimetric analysis (TGA) of metakaolin and biomass ash.

Results obtained by TGA encouraged us to heat the biomass ash at 700 °C in order to decompose calcium carbonate and therefore to make the biomass ash more reactive. The formation of the carbonate happened during storage. This shows that it might be important to store the BA in a closed environment to prevent any carbonation.

To prepare mortars, common river sand (Figure 1c) with maximum diameter of 2 mm and density of 2.65 g/cm³ was used.

2.2. Preparation and Characterization of Pastes

2.2.1. Mix Proportion of Pastes

One-part alkali-activated pastes were manufactured at the same water/solid (w/s) ratio equal to 0.56 by weight, by varying the quantity of biomass ash and metakaolin in order to obtain different K/Al molar ratios ranging from 0.50 to 3.00 with a step of 0.50. These pastes were labeled as “ASH_MK_X.XX”, where “X.XX” represents the K/Al molar ratio, thus a paste with K/Al = 0.50 is referred to as ASH_MK_0.50.

As reference, two additional mixtures with the same w/s ratio of 0.56 were manufactured. The former was prepared with biomass ash and water, to investigate the rate of biomass ash dissolution, and was labeled as “ASH_H2O”; the latter was a two-part reference alkali-activated paste labeled as “MK_KOH_1.00” and prepared with metakaolin and KOH solution (prepared by dissolving KOH pellets in water) at a K/Al molar ratio of 1.00. Paste compositions are reported in Table 3.

Table 3. Paste compositions for isothermal micro-calorimetry.

Paste	Biomass Ash (g)	Metakaolin (g)	H ₂ O (g)	KOH Pellets (g)	w/s ¹	K/Al
MK_KOH_1.00	-	1.43	1.08	0.49	0.56	1.00
ASH_H2O	4.00	-	2.24	-	0.56	-
ASH_MK_0.50	1.00	1.43	1.36	-	0.56	0.50
ASH_MK_1.00	2.00	1.43	1.94	-	0.56	1.00
ASH_MK_1.25	2.50	1.43	2.23	-	0.56	1.25
ASH_MK_1.50	3.00	1.43	2.48	-	0.56	1.50
ASH_MK_1.75	3.50	1.43	2.76	-	0.56	1.75
ASH_MK_2.00	4.00	1.43	3.04	-	0.56	2.00
ASH_MK_2.50	5.00	1.43	3.60	-	0.56	2.50
ASH_MK_3.00	6.00	1.43	4.16	-	0.56	3.00

¹ in w/s ratio, solid is the sum of biomass ash and metakaolin.

2.2.2. Reaction Kinetics of Pastes

To investigate the heat evolution as a function of time, pastes were analyzed with a TAM Air (TA Instruments) isothermal micro-calorimeter at T = 25 °C. MK_KOH_1.00 and ASH_H2O samples were analyzed for 130 h, whereas all the other one-part alkali-activated pastes for 60 h.

2.3. Preparation and Characterization of Mortars

2.3.1. Mix Proportion of Mortars

After having analyzed the reaction kinetics of pastes, some selected K/Al molar ratios were used to prepare one-part alkali-activated mortars with the same aggregate/metakaolin weight ratio equal to 3.0 and two different w/s ratios equal to 0.65 and 0.49. Sand was used in saturated surface dry (s.s.d.) condition, which is reached when sand absorbs water in an amount of 2% with respect to its weight. Mortars were manufactured also with biomass ash heated at 700 °C in order to decompose carbonates and increase its reactivity (see Section 3.1). Mortars prepared with biomass ash were labeled as “ASH_MK_X.X” or “ASH_MK_X.Xb”, where “X.X” represents the K/Al molar ratio and “b” represents the w/s ratio equal to 0.49, so that a mortar with K/Al = 1.5 is referred to as ASH_MK_1.5, if prepared with a w/s ratio of 0.65, or ASH_MK_1.5b, if prepared with a w/s ratio of 0.49. Mortars prepared with the heated biomass ash were labeled as “HASH_MK_X.X” where “X.X” represents the K/Al molar ratio.

Mortar mixes are reported in Table 4.

Table 4. One-part alkali-activated mortars composition (g/L).

Mortar	Biomass Ash (g/L)	Heated Biomass Ash (g/L)	Metakaolin (g/L)	H ₂ O (g/L)	Sand (g/L)	w/s ¹	K/Al
ASH_MK_0.5	237	-	339	375	1018	0.65	0.50
ASH_MK_1.0	377	-	269	420	808	0.65	1.00
ASH_MK_1.5	469	-	223	450	670	0.65	1.50
ASH_MK_1.5b	527	-	251	381	753	0.49	1.50
ASH_MK_2.5b	661	-	189	417	567	0.49	2.50
HASH_MK_1.0	-	377	269	420	808	0.65	1.00
HASH_MK_1.5	-	469	223	450	670	0.65	1.50

¹ in w/s ratio, solid is the sum of biomass ash and metakaolin.

Mortar batches were prepared by mixing powdered materials together, namely biomass ash, metakaolin and sand, for 2 min and then water was added and mixed for 5 min. Afterwards, mortars were poured and vibrated in cylindrical molds with 35 mm diameter and 70 mm height to perform mechanical tests.

Mortars were cured at $T = 20\text{ }^{\circ}\text{C}$ and a relative humidity (RH) of 100%, ensured by covering the molds with a plastic foil, for 24 h. Then, they were demolded and cured in an oven at $T = 70\text{ }^{\circ}\text{C}$ for 24 h to speed up the curing process.

2.3.2. Water Stability of Mortars

Prior to performing mechanical tests, the hardened mortars were studied in terms of water stability, by putting crushed specimens in water. Results demonstrate that the one-part alkali-activated mortars obtained from this study do not dissolve in water after 3 months of immersion (Figure 4).



Figure 4. Water stability of one-part alkali activated mortars after 3 months of immersion.

2.3.3. Hardened Properties of Mortars

After curing, specimens were left to cool down for 2 h, then they were weighed to calculate their hardened density (ρ) and then three specimens per composition were characterized by mechanical tests. The compressive strength (R_c) was calculated with Equation (1), according to [31]:

$$R_c = f_c / 0.83 \quad (1)$$

where: R_c , cubic compressive strength (N/mm^2); 0.83, correction factor to calculate the cubic compressive strength from cylindrical compressive strength of a cylinder with height/diameter = 2; f_c , cylindrical compressive strength (N/mm^2).

Finally, microstructural analyses were carried out on crushed mortar specimens with a Phenom Pro desktop scanning electron microscope (SEM).

3. Results and Discussion

3.1. Characterization of Pastes

Results obtained by isothermal micro-calorimetry are reported in Figure 5.

All the samples studied in this experimentation show that the reaction kinetics involves two reaction stages, which are found also in common geopolymers: dissolution and polymerization [32,33]. These two stages were also found in [24,25] for one-part inorganic polymers. The first one, related to the exothermic dissolution of alkali salts and breakdown of metakaolinite [25], immediately starts when the sample is mixed with water. In the present mixtures, the dissolution stage is represented by the initial decreasing part of the curves. On the other hand, the peak attributed to the polymerization reactions occurred at different times depending on the sample composition. When the pure biomass

ash was put in water (ASH_H2O) a second exotherm was observed around 3–4 h, but the exact origin was not studied. In order to compare the reaction to a better-known system, KOH was selected as a simple “model” activator. Upon dissolving the ash in water, K^+ and OH^- ions were formed which justifies the choice. When metakaolin was mixed with the KOH solution (MK_KOH_1.00) the peak maximum was reached after 20 h (Figure 5). In one-part alkali-activated pastes, however, the maximum of the polymerization occurred after 10 h (Figure 5). In these pastes, by increasing the K/Al molar ratio, the rate of heat released also increased and the reaction continued for a longer period. The two-part alkali-activated paste MK_KOH_1.00 shows a slower reaction, which continued even after 5 days (130 h—end of test), with respect to the other pastes for which the main part of the reaction lasted around 60 h (Figure 5).

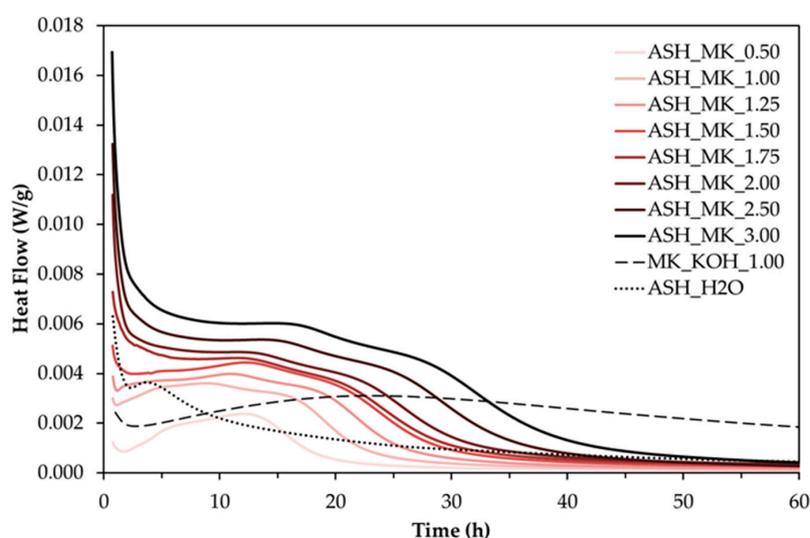


Figure 5. Heat flow development of pastes up to 60 h at $T = 25\text{ }^{\circ}\text{C}$.

By integrating the heat flow during the first 60 h of test, the reaction enthalpy as a function of K/Al molar ratio can be calculated (Figure 6). The sample prepared with pure biomass ash and water released a total enthalpy of -45.9 J/g , whereas the two-part paste MK_KOH_1.00 developed a total enthalpy equal to -90.2 J/g , after 60 h. On the other hand, analyzing the results obtained by one-part alkali-activated pastes it was found that by increasing the amount of biomass ash, hence the K/Al ratio, the reaction enthalpy also increased up to a maximum value obtained by the paste with K/Al = 2.50, which was equal to -63.5 J/g . This result means that the stoichiometric value was reached, close to a K/Al molar ratio equal to 2.50. The maximum reaction enthalpy obtained by ASH_MK_2.50 could also mean that this paste is the one with the highest mechanical properties. It is worthy to note that the initial line did not go through zero because of the dissolution enthalpy of the ash in water, which might be different in presence of metakaolinite. Moreover, the samples were not prepared inside the calorimeter, but materials were mixed outside and then put in the instrument; therefore, the heat flow registered at the beginning of the test and thus the calculated reaction enthalpy were slightly different from the real ones.

At the same K/Al molar ratio equal to 1.00, the two-part paste MK_KOH_1.00 had a reaction enthalpy 30% higher than that of the one-part alkali-activated paste ASH_MK_1.00. This result means that at the same K/Al molar ratio, a much lower amount of metakaolin reacted in the one-part system compared to that of the two-part system. It is probable that not all the K in the ash was available for the reaction, or that some side reactions occurred. This needs further investigation.

The relationship between heat flow and reaction enthalpy of one-part alkali-activated pastes and potassium-rich biomass ash content was also studied in other papers [24,25], where two different potassium-rich biomass ashes coming from agricultural wastes were used. Peys et al. [24] found that

when maize cob ash is added to metakaolin to produce inorganic polymers the reaction enthalpy follows a linear trend by increasing the ash to metakaolin mass ratio from 0.3 to 0.9. However, the reaction enthalpy obtained in their study is much higher than that found in the present study, because of the higher reactivity of maize cob ash compared to that of biomass ash used in the present experimentation. As reported by authors in [24], different biomass ashes have different reactivities, in fact they found that maize cob ash is more reactive than maize stalk ash, giving the higher reaction extent and thus higher reaction enthalpy of the former compared to the latter. Baló et al. [25] found instead that when cotton shell ash is used as the alkaline activator in metakaolin-based inorganic polymers, the reaction enthalpy increases up to a certain K/Al molar ratio and then slightly decreases, as found by authors in the present study where biomass ash coming from wood combustion was used. Moreover, they found that this trend was maintained also when cotton shell ash is calcined at 850 °C; however, the K/Al molar ratio that provided the highest reaction enthalpy was lower than that of cotton shell ash used as it is.

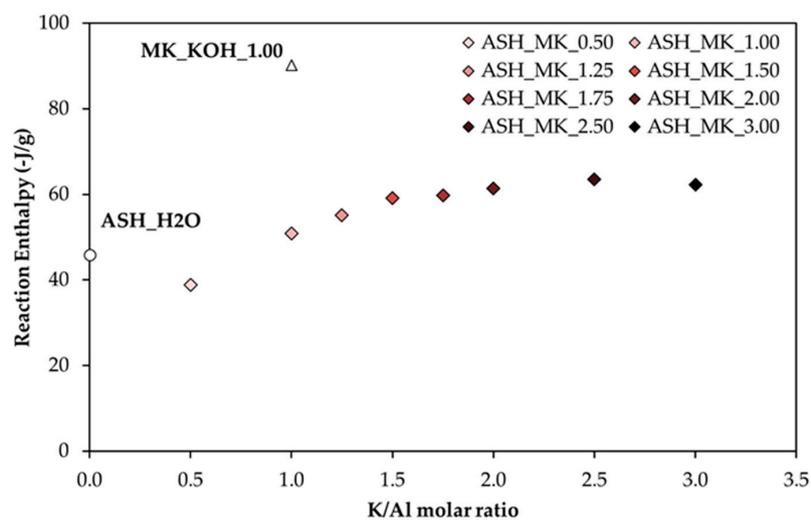


Figure 6. Relation between K/Al molar ratio and reaction enthalpy of mixtures after 60 h of testing.

3.2. Characterization of Mortars

By increasing the K/Al molar ratio, thus increasing the biomass ash quantity in place of metakaolin, the workability of one-part alkali-activated mortars increased considerably. Therefore, it was not possible to maintain the w/s ratio constant at 0.65 for mortars with a K/Al molar ratio above 1.5 and when K/Al molar ratios equal to 1.5 and 2.5 were adopted, the w/s ratio was lowered up to 0.49. This effect was found also by Candamano et al. [34], who prepared two-part alkali-activated mortars by partially replacing metakaolin with forest biomass ash. They suggested that the increased workability of mixtures containing a higher content of biomass ash was caused by the higher dissolution rate of metakaolin related to the increased alkalinity of the mixture. This process was confirmed by calorimetric analysis; in fact, by increasing the K/Al molar ratio of pastes also the dissolution rate increased (Figure 5). On top of that, metakaolinite needed more water to obtain workability than for instance fly ash or a blast furnace slag. The dissolution of metakaolin, together with the spherical shape of biomass ash particles used in this study, and their lower water uptake, caused the increase in workability of the studied one-part AAMs.

Results obtained by one-part alkali-activated mortars in terms of hardened density and compressive strength are reported in Table 5. In general, all manufactured mortars showed similar ρ values, which range around 1.57 and 1.63 g/cm³ regardless of their composition. In the literature [34], it is reported that by maintaining the w/b ratio, curing method, curing time, and drying conditions constant, the increased replacement level of metakaolin with biomass ash causes an increased porosity; however, in the compositions prepared in this experimentation, this effect was not so evident.

Table 5. Hardened density (ρ) and compressive strength (R_c) of one-part alkali-activated mortars.

Paste	ρ (g/cm ³)	R_c (N/mm ²)
ASH_MK_0.5	1.57	1.6
ASH_MK_1.0	1.57	1.7
ASH_MK_1.5	1.48	1.8
ASH_MK_1.5b	1.58	3.4
ASH_MK_2.5b	1.63	3.7
HASH_MK_1.0	1.59	1.7
HASH_MK_1.5	1.62	2.3

Concerning the compressive strength of one-part alkali-activated mortars manufactured with the unheated biomass ash, it was quite evident that R_c values were very low. The mortar manufactured with the lower K/Al molar ratio equal to 0.5 had a R_c value equal to 1.6 MPa. The increase in K/Al molar ratio to 1.0 and to 1.5 caused a slight increase in compressive strength to 1.7 and 1.8 MPa, which were 6% and 13% higher than 1.6 MPa. Even though the mortar manufactured with K/Al molar ratio of 1.5 was less dense, thus more porous, than that with a K/Al ratio of 0.5, it showed a higher compressive strength, meaning that the extent of reaction in dissolution and polymerization of materials was slightly higher. By decreasing the w/s ratio from 0.65 to 0.49 at the same K/Al molar ratio of 1.5, the compressive strength of one-part alkali-activated mortars increased up to 3.4 MPa, which was 89% higher than 1.8 MPa. Moreover, a further increase in compressive strength was registered at the same w/s ratio of 0.49 by increasing the K/Al molar ratio from 1.5 to 2.5. In fact, the ASH_MK_2.5b mortar reached a R_c value of 3.7 MPa, which was 9% higher than 3.4 MPa. In traditional cement-based materials, the mechanical strength increases by decreasing the water/cement ratio, whereas in two-part alkali-activated matrices the mechanical strength increases both by decreasing the w/s ratio [11] and by increasing the alkalinity of the activating solution [35,36]. As for two-part AAMs, in one-part alkali-activated matrices, the reduced w/s ratio, at the same K/Al molar ratio, reduced the porosity of mortars. Moreover, the increased alkalinity given by the increase in K/Al molar ratio, thus the biomass ash content, at the same w/s ratio, increased the amount of reactive material and contributed to a higher densification of the matrix and reduction of porosity. This result was also found by Peys et al. [24] who reported an increase in inorganic polymers' compressive strength by modifying the ash/metakaolin mass ratio from 0.3 to 0.9. Moreover, this trend was found both with a maize cob ash and a maize stalk ash, even though the compressive strength is higher when maize cob ash is used, because of its higher reactivity. Baló et al. [25] manufactured one-part mortars at the same w/s ratio of the present study and equal to 0.56. They reported that when cotton shell ash is used an increase in compressive strength is found up to a maximum value (at K/Al molar ratio of 4) and then a decrease is registered for higher K/Al molar ratios.

One-part alkali-activated mortars manufactured with the heated biomass ash, instead, were prepared at the same w/s ratio of 0.65 by increasing the K/Al molar ratio. Unfortunately, it was not possible to go beyond a 1.5 molar ratio since the use of the heated biomass ash caused shorter setting time the higher the heated biomass ash content. Comparing the results obtained by mortars with the heated and unheated biomass ash, at the same w/s ratio of 0.65 and the same K/Al molar ratios, it was found that at 1.0 molar ratio, the heating of the material did not modify the mortar's compressive strength, whereas at a 1.5 molar ratio, the compressive strength of HASH_MK_1.5 mortar (2.3 MPa) was 28% higher than that of ASH_MK_1.5 mortar. This means that the thermal treatment of the biomass ash contributed also to an increase in their compressive strength. Therefore, the decomposition of calcium carbonate was beneficial for increasing the reactivity of the biomass ash used in this study. The higher compressive strength of one-part alkali-activated mixtures manufactured with calcined ash compared to those using a not-calcined one is reported also by Baló et al. [25]. Here, it is shown that calcined cotton shell ash provides to mortars a slightly higher compressive strength than cotton shell ash as it is. As in the present work, the authors reported that the calcination of ash increases its

reactivity which in turn increases the compressive strength of mortars manufactured with it. However, compressive strength values obtained by authors in [25] were higher than those obtained in the present work, this means that biomass ash obtained by wood combustion is less reactive than cotton shell ash whether it is calcined or not.

The morphological analysis of some selected one-part alkali-activated mortars investigated by SEM are reported in Figure 7. In the first three rows, mortars manufactured with unheated biomass ash and metakaolin with different K/Al molar ratios and w/s ratios are reported, whereas in the last row, the SEM images of one mortar prepared with the heated biomass ash are reported.

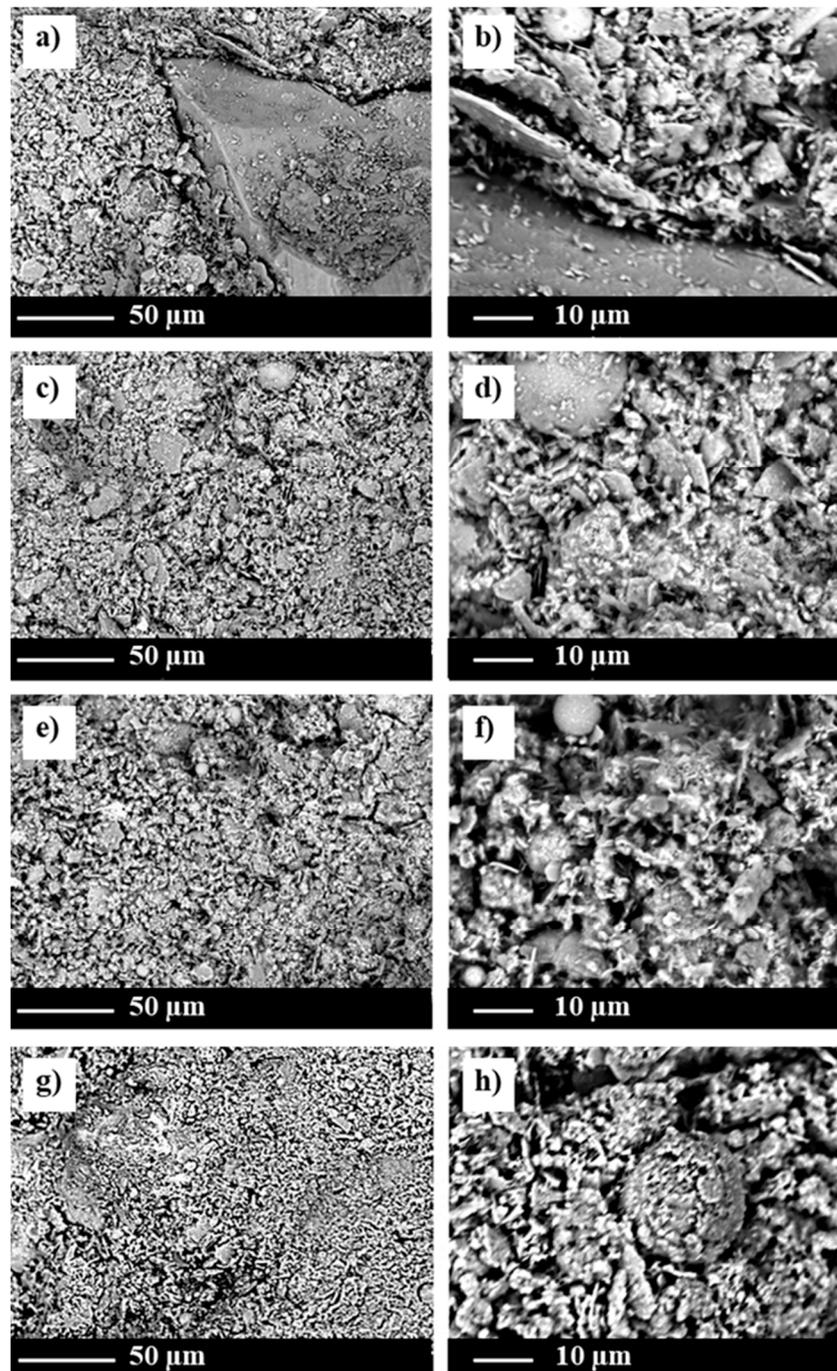


Figure 7. SEM images of one-part alkali activated mortars: (a) and (b) ASH_MK_0.5; (c) and (d) ASH_MK_1.5; (e) and (f) ASH_MK_2.5b; (g) and (h) HASH_MK_1.5.

Microstructures of mortars prepared with both heated and unheated ash at different ash/metakaolin ratio, hence K/Al molar ratio, seem not to differ very much. In all of them, metakaolin particles and biomass ash are visible, the former is characterized by plate-like shaped particles, whereas the latter is represented by cenospheres. Considering one-part alkali-activated mortars manufactured with the unheated biomass ash, a slight densification of the matrix is visible moving from ASH_MK_0.5 mortar (Figure 7a,b) and ASH_MK_1.5 (Figure 7c,d) to ASH_MK_2.5b (Figure 7e,f), since, in this last mortar, less metakaolin flakes are detectable and the surface appears smoother. This result is in good agreement with mechanical compressive strength results (Table 5), where the increase in K/Al molar ratio from 0.5 of ASH_MK_0.5 mortar to 2.5 of ASH_MK_2.5b together with the decrease in w/s ratio from 0.65 to 0.49 increased the mechanical strength of the material from 1.6 MPa to 3.7 MPa.

At the same K/Al molar ratio of 1.5, the heating of biomass ash seemed to increase the densification of the matrix and also to modify the surface of heated biomass ash, which appeared completely covered by small metakaolin flakes. This result is consistent with what was found by mechanical strength tests where the two one-part alkali-activated mortars prepared with the same w/s ratio of 0.65, namely ASH_MK_1.5 and HASH_MK_1.5, obtained a R_c value of 1.8 MPa and 2.3 MPa, respectively.

Results obtained by microstructural analysis confirmed what was found by mechanical tests where higher compressive strength values were registered for one-part alkali-activated mortars manufactured with both higher K/Al molar ratio and lower w/s ratio. Moreover, a slight increase in compressive strength can be obtained at the same K/Al molar ratio of 1.5 and w/s ratio of 0.65 by heating the biomass ash at 700 °C.

4. Conclusions

The possibility of manufacturing one-part alkali-activated pastes and mortars using metakaolin as the aluminosilicate precursor and potassium-rich biomass ash obtained by the combustion of wood as the powdered alkaline activator was investigated. In particular, the reaction kinetics of pastes and the mechanical strength of mortars were studied and related to the different K/Al molar ratio and water/solid ratios. Moreover, the possibility of heating biomass ash at 700 °C to decompose calcium carbonate in order to make it more reactive was investigated.

The results obtained show that mortar's compressive strength is low and ranges between 1.6 to 3.7 MPa. Moreover, it has been found that:

- the reactivity of the alkaline precursor (biomass ash) determines the strength development of the one-part alkali-activated material;
- by increasing the K/Al molar ratio, the reaction heat of one-part alkali-activated pastes increases up to a maximum value at K/Al of 2.5;
- the increase in K/Al molar ratio contributes also to increase the mechanical strength of one-part alkali-activated mortars, even though the compressive strength increases more if the w/s ratio decreases;
- the heating of biomass ash causes faster setting and is beneficial to increase the compressive strength of the final one-part alkali-activated mortar.

This experimentation highlighted that it is possible to manufacture one-part alkali-activated pastes and mortars by activating metakaolin with a powdered alkaline activator such as potassium-rich biomass ash. However, the mechanical properties highly depend on the starting raw materials. To increase the compressive strength of one-part AAMs, it is possible to increase the K/Al molar ratio, decrease the water/solid ratio and even thermally treat the biomass ash.

Author Contributions: Conceptualization, A.M., H.R. and F.T.; methodology A.M. and H.R.; software, H.R.; validation, A.M. and H.R.; formal analysis, A.M.; investigation, A.M.; resources, H.R.; data curation, A.M.; writing—original draft preparation, A.M.; writing—review and editing, A.M., H.R. and F.T.; visualization, A.M.; supervision, H.R. and F.T.; project administration, H.R.; funding acquisition, H.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding. The authors wish to thank Università Politecnica delle Marche for funding the 3-month period abroad during the PhD course of Eng. Alessandra Mobili, allowing the development of this research. The APC was waived.

Conflicts of Interest: The authors declare no conflict of interest.

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