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Fire Resistant Geopolymers Based on Several Clays Mixtures

Ameni Gharzouni, Clément Alizé and Sylvie Rossignol

Abstract

This chapter aims to highlight the effect of clay mixture mineral composition and alkali concentration of potassium alkaline solutions on the thermal behavior of geopolymer materials. For this, three mixtures composed of kaolin (pure, impure kaolin or mixture of both), calcium carbonate, sand and potassium feldspar and three potassium alkaline silicate solutions with different concentrations were used (5, 6 and 7 mol.L^{-1}). At first, the effect of rotary calcination parameters at 750°C such as the dwell time (30, 60, 120 and 180 min) and weight powder (100, 400 and 500 g) was investigated. It was demonstrated that the kaolin dehydroxylation is quasi complete (> 90%) and do not significantly depend on the dwell time and powder weight. Whereas the carbonate decomposition degree increases with the increase of dwell time and the decrease of powder weight but still not complete (<80%). These differences influence the feasibility of consolidated materials. Indeed, a flash setting occurs for samples based mixtures with high calcium carbonate decomposition degree (> 50%) and low wettability values (500 μL/g) for the three used alkaline solutions. The thermal behavior at 1000°C depends on the chemical composition of the aluminosilicate source and the concentration of alkaline solution. A conservation of the compressive strength at 43 MPa after thermal treatment at 1000°C of geopolymers based on mixture of pure and impure kaolin and a low potassium concentration solution (5 mol.L^{-1}) was evidenced.

Keywords: geopolymers, kaolin, rotary oven, thermal properties, compressive strength

1. Introduction

Thermal resistance is an essential property for different applications. Inorganic refractory materials are generally used. However, the preparation of these materials requires high-temperature solid state reactions [1]. As an alternative, geopolymer materials, synthetized at low temperature (less than 100°C), are known to have good thermal stability. The term geopolymer was introduced by Davidovits [2] to design amorphous three-dimensional materials resulting from the activation of an aluminosilicate source by an alkaline solution [3]. They are generally synthesized from metakaolin [4, 5] or other more abundant and low-cost clays or industrial co-products [6, 7]. The thermal stability of metakaolin based geopolymers is due to the densification resulting from viscous sintering and pore network collapse [8]. The effect of calcium on the thermal behavior was also highlighted [9]. It was proven that the addition of low amount of calcium increases the densification temperature and improves the mechanical strength after thermal treatment. Dupuy et al. [10],

have shown that geopolymers based on argillite (mainly composed of interlayered illite/smectite and 22% of calcite) exhibit a good thermal resistance that depends on the argillite calcination process. Indeed, a higher resistance is obtained for furnace-calcined argillite compared to flash calcined one due to the complete dehydroxylation of clay minerals and decomposition of carbonates. Tognonvi et al., [11] have also shown that the addition of argillite improved significantly the thermomechanical properties of kaolin-based geopolymers due to the in-situ formation of wollastonite, leucite and zeolite-type phases. Rashad and Zeedan [12] found that for fly ash based materials, the concentration of the activator had a significant effect on and residual strength after heating. As the concentration of the activator increases, the initial strength compressive strength increases. However, as the concentration of the activator increases, the residual compressive strength after firing decreases. Barbosa et al. [13], have also evidenced the crystallization of feldspar, kalsilite and leucite at 1000°C in potassium based gopolymers. Consequently, the mineralogy and thermal treatment of the used aluminosilicate is an important parameter controlling the thermal behavior of geopolymers. Raw clays contains naturally clay minerals, carbonate and feldspar. Calcium carbonate decomposes between 600 and 800°C into free lime and carbon dioxide. However, depending on the relative humidity, the produced CaO can react with H_2O to form $Ca(OH)_2$ [14]. The carbonate thermal decomposition depends on different parameters such as the nature and crystalline structure, the sample weight, the particle size, the purge gas... [15]. Furthermore, the calcination process can also influence the carbonate decomposition. For example, it was demonstrated that the limestone calcination in a pilot-scale rotary kiln calcination depends essentially on heat transfer and feed rate, whereas rotational speed and inclination angle are less important [16]. The calcination process have also an important role on the chemical, physical and structural properties of clays. San Nicolas et al. [17] have undertaken a comparative study between rotary and flash calcinations of kaolin and have shown that the method of thermal treatment influences the physical properties of resulting metakaolins and therefore and their reactivity for geopolymer synthesis. That is why it is necessary to understand the effect of mixture of kaolin, calcite and feldspar. The interaction between kaolinite and calcite upon thermal treatment was also studied [18, 19]. It was evidenced that calcite decomposition was influenced by the ratio of kaolinite to calcite, the CO_2 flow rate, the mixing, the heating rate and the volatiles during the dehydroxylation of kaolinite.

To understand the thermal behavior of geopolymer based on clays, it is necessary to understand the role played by each constituent of the clay. Thus, fundamental research on clay mixtures should be undertaken. The objective of this study is to exacerbate the effect of rotary furnace on the physical and chemical properties of clay mixtures and on the thermal behavior at 1000°C of the resulting geopolymers.

2. Effect of rotary furnace on clay mixtures properties

Three clay mixtures, named F1, F2 and F3, were studied as detailed in **Table 1**. They are composed of 40 wt. % of kaolin (pure and/or impure kaolin), 15% of calcium carbonate, 35% of sand and 10% of potassium feldspar. The difference between the two kaolins is the purity. In fact, impure kaolin has a Si/Al molar ratio of 1.44 and contains mo quartz, calcite and hematite. However, the pure metakaolin has a Si/Al molar ratio equal to 1. The mixtures were thermally treated at 750°C in a laboratory-scale rotary furnace (HTR 11/150 + 301 controller, Carbolite Gero) with different parameters. The dwell time was varied at 30, 60, 120 and 180 min. Furthermore, for the same dwell time of 60 min, the powder weight was

Constituent (wt. %)	Mixtures		
	F1	F2	F3
Pure kaolin	40	0	20
Impure kaolin	0	40	20
Calcium carbonate	15		
Sand	35		
Feldspar	10		

Table 1.
Nomenclature and the weight percentage of each constituent of the mixtures.

varied at 100, 400 and 500 g. The effect of these parameters on the calcined powder was investigated.

2.1 Dehydroxylation and carbonate decomposition degree

Thermal analysis (DTA-TGA) were performed on raw and calcined mixtures. An example of the obtained curves for raw F1 mixture is plotted in **Figure 1**. Three endothermic pics accompanied with three weight losses are observed in the temperature ranges 30–200°C, 400–600°C and 600–800°C. The first one is attributed to the release of adsorbed and free water [20]. The second weight loss between 400 and 600°C corresponds to the dehydroxylation of kaolin [21]. The weight loss, between 600 and 800°C, is due to the decomposition of calcium carbonate [22]. The comparison between the raw and calcined mixtures permits to calculate the kaolin dehydroxylation degree or the calcium carbonate degree (A) as Eq. (1)

$$A = 1 - \frac{m2}{m1} \times 100 \qquad (1)$$

where, m2 is the mass fraction of the residual hydroxyl groups or CO_2 in the calcined mixture and m1 is the mass fraction of the hydroxyl groups or CO_2 in the raw mixture.

In order to understand the effect of dwell time and powder weight, the kaolin dehydroxylation degree and the carbonate decomposition rate were plotted in function of the dwell time in **Figure 2A**. No significant change of the dehydroxylation degree can be observed in function of the dwell time (**Figure 2A.a**). Regardless of the mixture, the dehydroxylation degree varies between 92 and 99% revealing a quasi-complete dehydroxylation of kaolin. However, lower values of carbonate decomposition degree and varying in function of the dwell time are noticed (**Figure 2A.b**). In general, the decomposition degree increases with the increase of the dwell time. For F1 mixture, the decomposition degree increases from 32 to 49% at 30 and 180 min, respectively. F2 mixture shows the highest decomposition degree of 80% after 180 min. F3 mixture exhibits similar results as F1 mixture with a decomposition degree of 50% after 180 min.

Consequently, the kaolin dehydroxylation is quasi-complete whatever the dwell time. However, depending on the mixture, the carbonate decomposition is partial and increases for longer dwell time. This result reveals than more energy is needed for calcium carbonate decomposition.

Similarly, the kaolin dehydroxylation degree and the calcium carbonate decomposition degree were plotted in function of the powder weight in **Figure 2B**. The
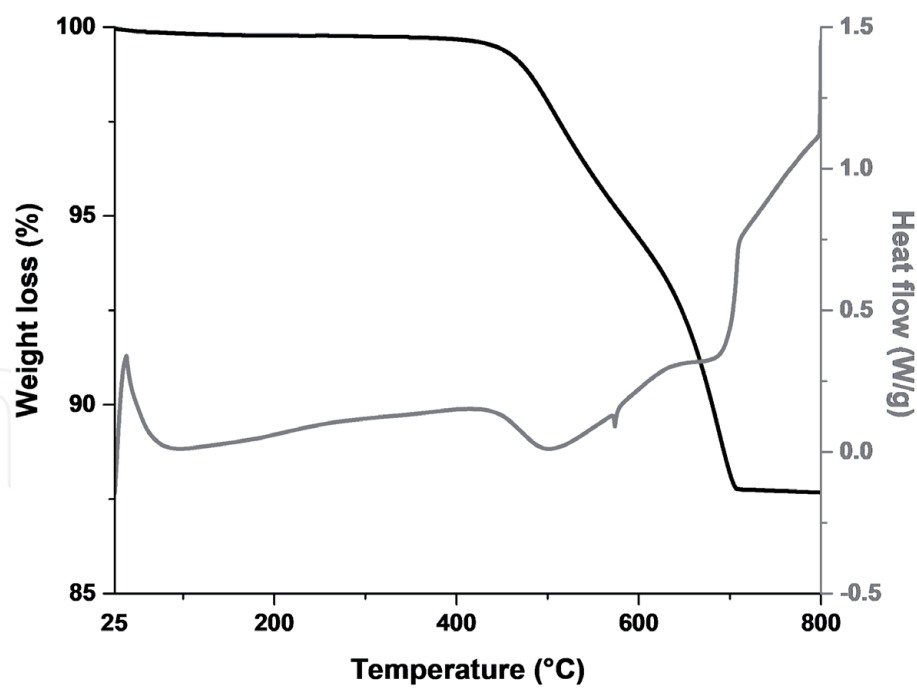
Figure 1.
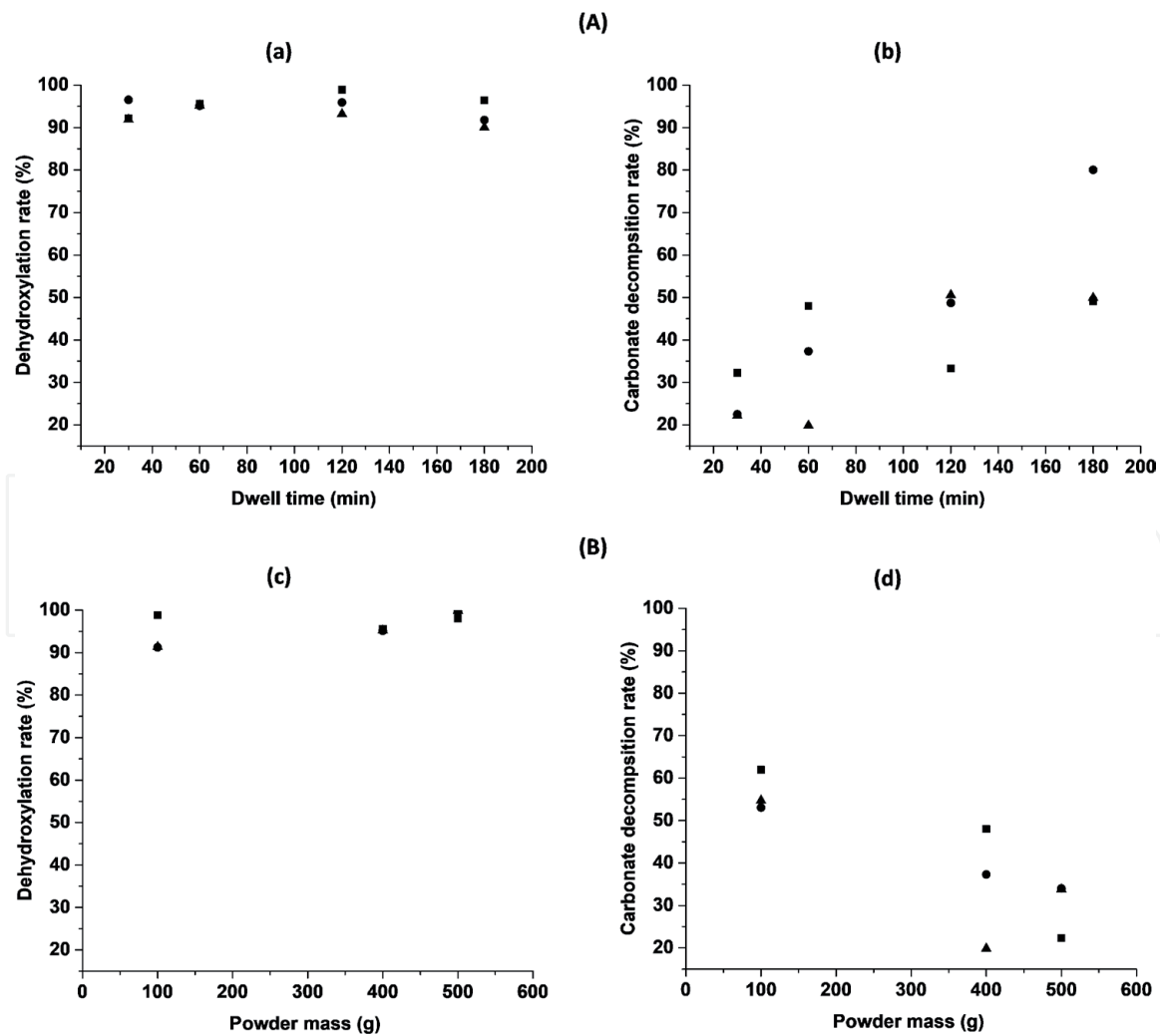*Thermal curves (—) weight loss and (—) heat flow of raw F1 mixture.*

Figure 2.
Evolution of (a, c) kaolin dehydroxylation and (b, d) carbonate decomposition degrees in function of the (A) dwell time and (B) powder mass for ■ F1 ● F2 and ▲ F3 calcined mixtures.

dehydroxylation degree values are very high, similar and varying between 91 and 99% (**Figure 2B.a**). A more significant difference can be observed in the carbonate decomposition degree. Indeed, it decreases with the increase of powder weight (**Figure 2B.b**). For F1 mixture, it decreases from 61 to 22% for 100 and 500 g, respectively. F2 and F3 mixtures show similar result with a decrease from 53 to 33% for 100 and 500 g, respectively. Consequently, the smaller powder weight, the higher decomposition degree. This result is in accordance with literature [23, 24].

Thus, the rotary thermal treatment parameters and more precisely the dwell time and the powder weight influence the calcium carbonate decomposition in kaolin and carbonate mixtures. Indeed, it increases with the increase of dwell time and the decrease of powder weight but remains not complete.

2.2 Wettability value

No significant differences were detected in the particle size of the different powders. Indeed, the median diameter is equal to 9, 60 and 60 µm for F1, F2 and F3 mixtures respectively, regardless if the used calcination parameters. So, a focus
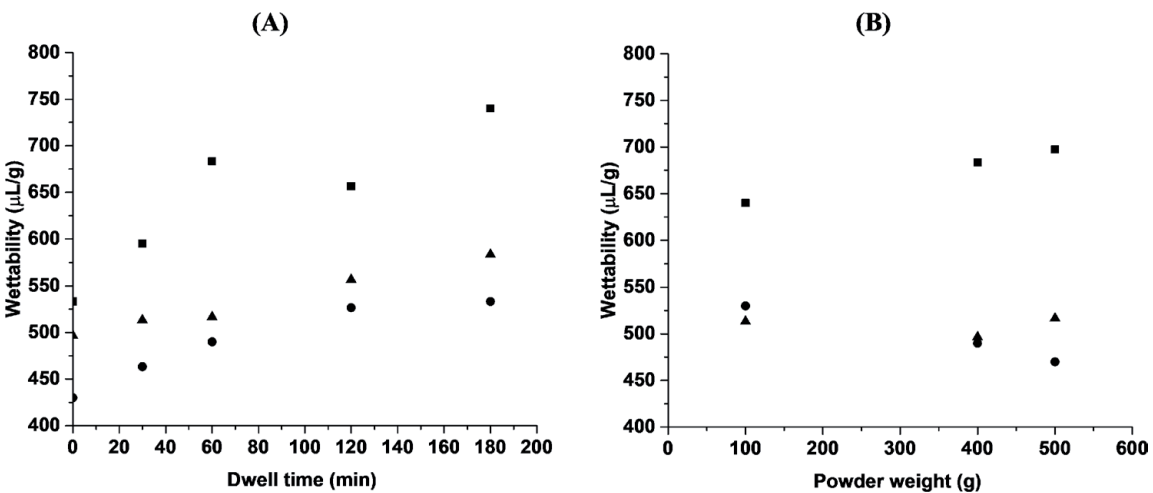

Figure 3.
Evolution of wettability values in function of the (A) dwell time and (B) powder mass for ■ F1 ● F2 and ▲ F3 calcined mixtures.
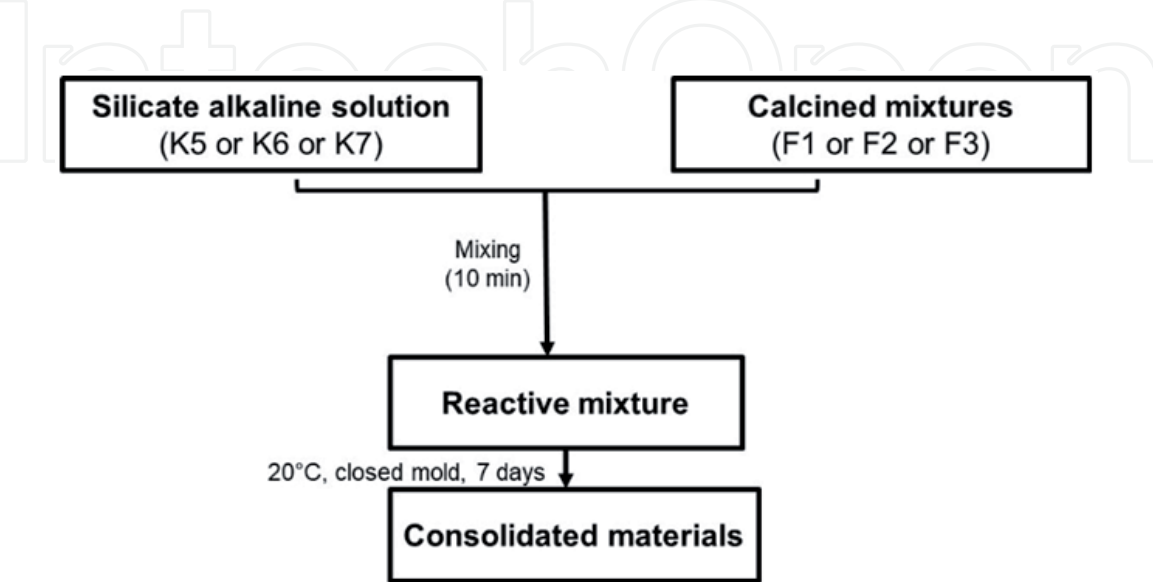

Figure 4.
Protocol of geopolymer sample preparation.

has been put on the wettability value which is an indicator of the aluminosilicate reactivity for geopolymer synthesis [5]. It corresponds to the volume of water that can be adsorbed by one gram of powder until saturation. In order to determine the calcination parameters effect, the wettability values were also plotted in function of the dwell time and the powder weight in **Figure 3**. At first the raw mixtures have different wettability values (533, 430 and 497 μL/g for F1, F2 and F3 mixtures respectively. Whatever the mixture, the wettability values increase with the increase of dwell time. The highest values are obtained for F1 mixture due to the higher purity of the used kaolin (740, 533 and 583 μL/g for F1, F2 and F3 mixtures, respectively). Less impact can be observed of the powder weight on the wettability values (**Figure 3B**). Quite similar values are observed whatever the mixture for the different powder weight. Thus, the wettability values are more sensitive to the dwell time and the chemical composition of the initial mixtures. Consequently, rotary calcination parameters induces differences in chemical composition and properties of the clay mixtures. This fact will induce different reactivity in alkaline media (**Figure 4**).

3. Thermal properties evaluation of geopolymer materials

3.1 Feasibility of geopolymer materials

Feasibility tests of consolidated materials were carried out for all the studied mixtures. Sample were prepared by mixing calcined mixtures with three potassium alkaline solution with different potassium activation solution with different concentration (5, 6 and 7 mol.L^{-1}). The samples were cast in closed polysterene mold and kept at room temperature. Examples of the visual aspect of the different obtained samples are presented in **Figure 5**. Whatever the used solution, samples exhibit either flash setting (hardening after few seconds of mixing before total homogenization of the mixture) (**Figure 5A**) or a consolidated appearance and a reddich color due to the initial color of the used kaolin containing hematite [25] (**Figure 5B**). The flash setting seems to be only linked to the calcined mixtures and not to the used alkaline solution. That is why the feasibility of consolidated materials was plotted in function of the properties of the calcined mixtures i.e. the wettability value and the calcium carbonate decomposition degree in **Figure 6**. For F1 mixture, whatever the dwell time, the samples are feasible. This is due to low carbonate decomposition degree <49% and high wettability values (> 600 μL/g). For F2 mixture, for a dwell time exceeding 60 min, a flash setting is observed. It corresponds to high carbonate decomposition degree exceeding 40% and a wettability
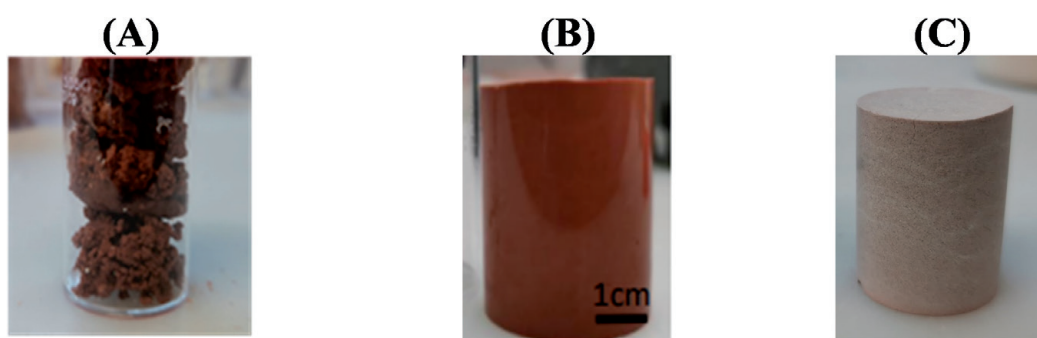

(A)   **(B)**   **(C)**

Figure 5.
Example of (A) flash consolidated sample (S1F2, dwell time = 180 min) and consolidated sample (S3F2, dwell time = 30 min) (B) before and (C) after thermal resistance at 1000°C.
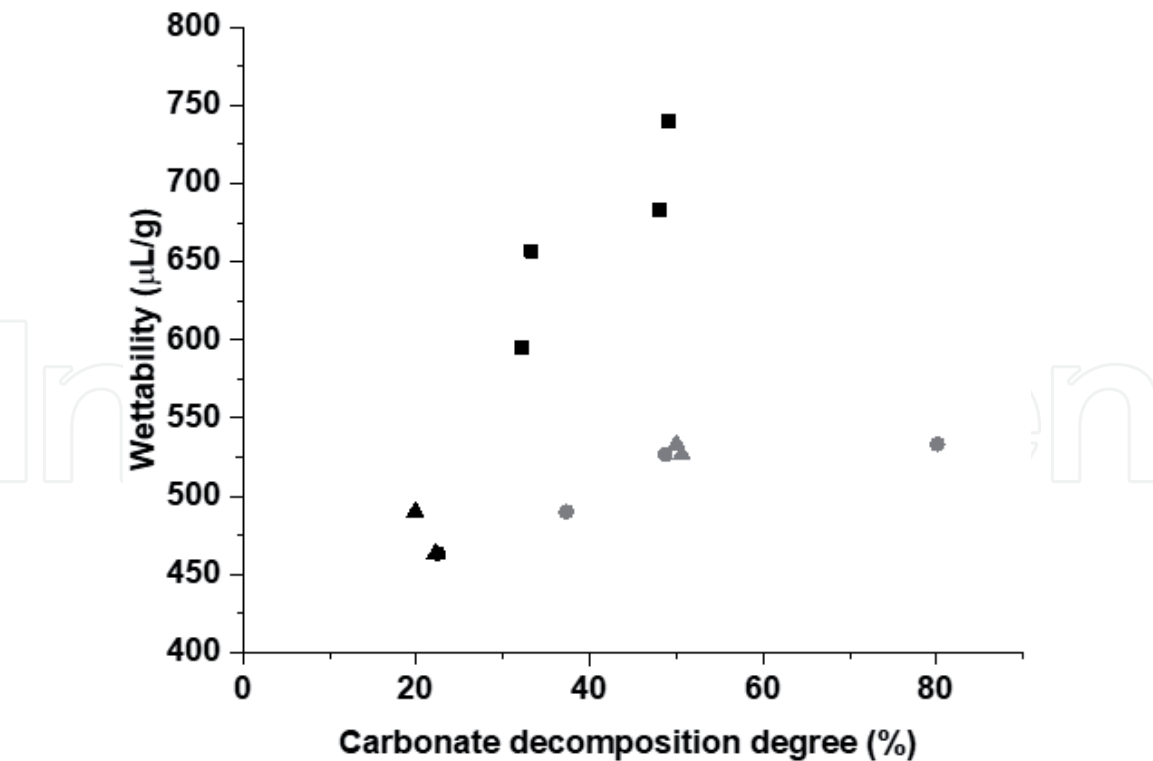
Figure 6.
Feasibility of consolidated materials in function of the wettability value and the calcium carbonate decomposition degree of the different calcined mixture for ■ *F1* ● *F2 and* ▲ *F3 mixtures (grey: flash setting).*

value from 500 μL/g. Concerning F3 mixture, flash setting is obtained from a dwell time of 120 and 180 min corresponding to carbonate decomposition degree of 50% and a wettability values about 500 μL/g.

To sum up, flash setting occurred for mixtures with high calcium carbonate decomposition degree (>50%) and low wettability values about 500 μL/g. This result is in accordance with literature where flash setting was generally associated with high "CaO" content [26, 27].

3.2 Thermo-mechanical properties

In the following section, only the thermal behavior of the sample based on mixture with a dwell time of 30 min (no flash setting) with the different alkaline solutions was evaluated. Samples were heated at 1000°C during 1 hour in an oven. An example of the visual aspect of the thermally treated geopolymer is presented in **Figure 5**. C. It is shown a color lightening and no cracks. The samples were subjected to compression tests before and after thermal resistance at 1000°C. The obtained compressive strength values are given in **Table 2**. Before thermal treatment, the highest compressive strength values are obtained with K7 solution (from 47 to 54 MPa for K7F1 and K7F2, respectively). This fact can be explained by the higher reactivity of this solution due to its higher alkali concentration permitting to favor the geopolymer reaction and to reinforce the final structure [28]. After thermal treatment, with K6 and K7 solution, whatever the mixture, a decrease of the compressive strength is noticed especially with F1 mixture (based on pure kaolin) showing a drastic decrease from 30 to 3 MPa and from 46 to 20 MPa with F2 and F3 mixtures, respectively. With K5 solution, a decrease of compressive strength is obtained for F1 and F2 mixtures. However, the mechanical strength are conserved using F3 mixture (43 MPa). The reduction in strength is due to the dehydration of the geopolymer matrix creating internal stress, weakening the structure [29].

Sample	σ before thermal resistance (MPa)	σ after thermal resistance (MPa)
K5 F1	39	22
K5 F2	39	26
K5 F3	43	43
K6F1	30	3
K6 F2	42	28
K6 F3	38	20
K7 F1	47	20
K7 F2	54	46
K7 F3	49	24

Table 2.
Compressive strength value before and after thermal resistance at 1000°C.

Consequently, the compressive strength are governed by the reactivity of the alkaline solution. However, after thermal treatment, the compressive strength depend on the chemical composition of the aluminosilicate source.

3.3 Structural investigation

In order to explain the different mechanical behaviour and for more accurate information on the structural change of the samples after thermal treatment at 1000°C, XRD characterization was performed. Examples of XRD patterns for K7F1 ($\sigma_{after\ 1000°C}/\sigma_{before\ 1000°C}$ = 0.5), K7F2 ($\sigma_{after\ 1000°C}/\sigma_{before\ 1000°C}$ = 0.9) and K5F3 ($\sigma_{after\ 1000°C}/\sigma_{before\ 1000°C}$ = 1), before and after thermal resistance are presented in **Figure** 7. Before thermal treatment, similar phases are observed such as quartz, orthoclase and residual calcite. Impurities such as hematite are detected in F2 and F3 based samples and are due to the used kaolin. After thermal treatment, the patterns evidence the persistence of quartz and orthoclase and the formation of new crystalline phases such as leucite $K(AlSi_2O_6)$ [30], kalsilite ($KAlSiO_4$), potassium aluminium silicate ($KAl(SiO_4)$) and wollastonite ($CaSiO_3$) [31]. In fact, the amorphous phase crystallizes to form potassium aluminum silicate $KAl(SiO_4)$, kalsilite and leucite. Calcium reacts from silica of the amorphous phase to form wollastonite. These phases are refractory and are the origin of the thermal resistance of the samples [32, 33]. More leucite seems to be formed in detriment of kalsilite in K5F3 and K7F2 compared to K7F1 sample. This due to higher Si/Al ratio of this sample. Indeed, the formation of leucite is favored at higher Si/Al molar ratio [13]. This fact can explain the conservation of mechanical strength for this sample.

In summary, the thermal treatment at 1000°C leads to the formation of crystalline phases which depend on the initial chemical composition of the mixture. To correlate the thermal behaviour to the chemical composition, the compressive strength ratio ($\sigma_{after\ 1000°C}/\sigma_{before\ 1000°C}$) was plotted in function of the molar ratio (nCa + nSi)/nK in **Figure 8**. It is demonstrated that the compressive strength ratio increases from 0.1 to 1 with the increase of the molar ratio (nCa + nSi)/nK from 1 to 1.6. Indeed, the increase of this molar ratio means the increase of the availability of calcium and silica able to form crystalline phases at high temperature. The decrease of the potassium concentration seems also to favor the thermal resistance. Consequently, the thermos-mechanical behavior is related to the structural changes after thermal treatment which is intimately linked with the initial chemical composition of the used precursors.
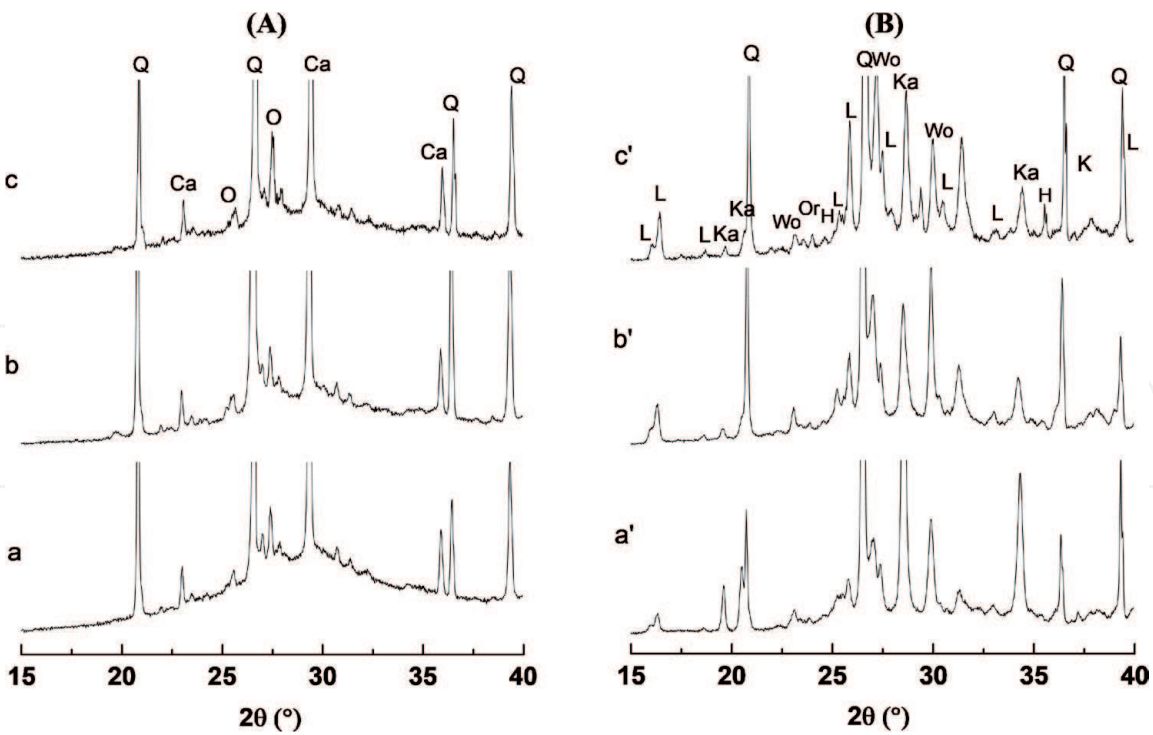
Figure 7.
XRD patterns of geopolymers (a, a') K7F1, (b, b') K7F2 and (c, c') K5F3, before (A) and after (B) thermal resistance at 1000°C (Q-quartz (01-070-3755), Ca-calcite (00-005-0586), A-anatase (00-021-1272), L-leucite (04-013-2099), Wo-wollastonite (00-043-1460), Ka-kalsilite (00-066-0070), Or-orthoclase (04-009-3610).
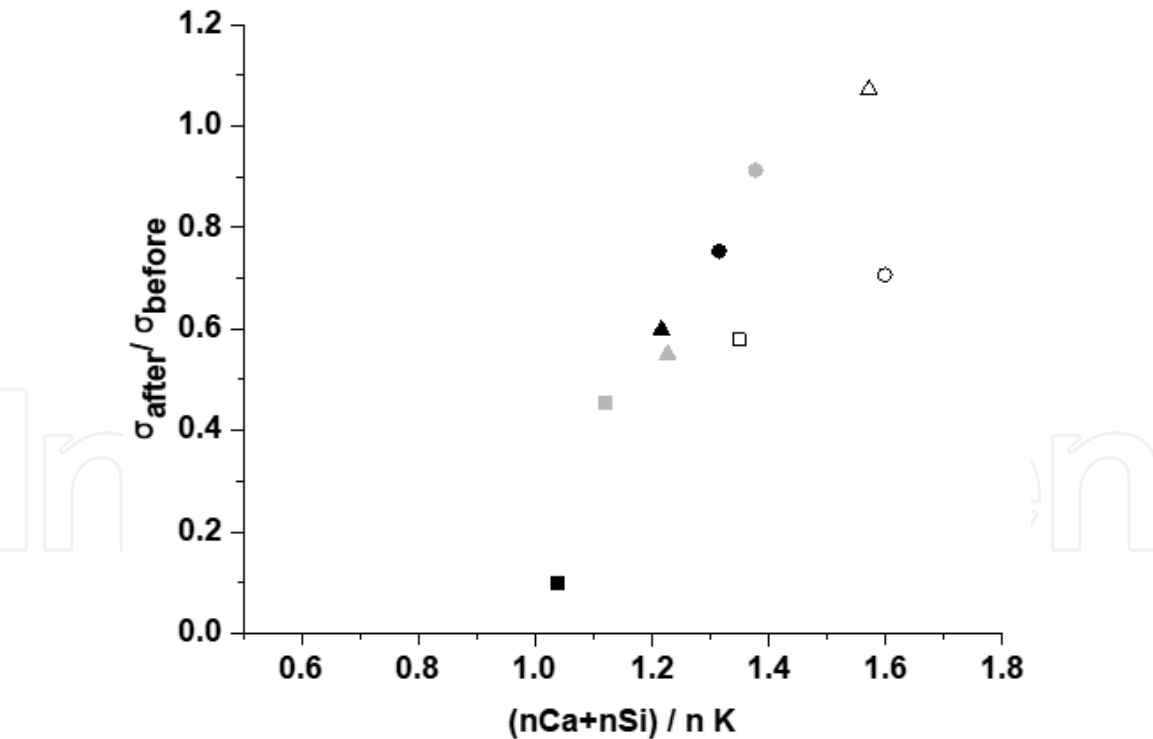

Figure 8.
Evolution of the compressive strength ratio (σ after thermal resistance/ σ before thermal resistance) in function of the molar ratio (nCa+nSi)/nK for ■ F1 ● F2 and ▲ F3 mixtures with K5 (empty), K6 (black) and K7 (grey).

4. Conclusion

The objective of this study is to evaluate the thermal behavior of geopolymer materials based on different clay mixtures and potassium alkaline solution with different concentrations. Three clay mixtures composed of 40 wt. % of kaolin (pure or

impure kaolin or mixture of both), 15% of calcium carbonate, 35% of sand and 10% of potassium feldspar, were studied. At first, the effect calcination parameters at 750°C in a rotary furnace was investigated. Indeed, the effect of dwell time (30, 60, 120 and 180 min) and weight powder (100, 400 and 500 g) on the kaolin dehydroxylation and the calcium carbonate decomposition degrees. It was shown that the kaolin dehydroxylation is quasi complete (> 90%) and varies very slightly with the dwell time and powder weight. However, more significant changes are observed for the carbonate decomposition degree which it increases with the increase of dwell time and the decrease of powder weight but still not complete (from 50 to 80%) even after 180 min of dwell time at 750°C. Consolidated materials were prepared based on the different mixtures and alkaline solutions with different concentrations (5, 6 and 7 mol.L^{-1}). A problem of flash setting has been encountered and was due to the properties of the calcined mixtures (high calcium carbonate decomposition degree (> 50%) and low wettability values about 500 μL/g) and not the used alkaline solution. The thermal behavior at 1000°C of the sample based on mixture with a dwell time of 30 min with the different alkaline solutions was evaluated. Before thermal treatment, the highest compressive strength were obtained for the highest alkali concentration of the used solution (54 MPa). However, after thermal treatment, the compressive strength depend on the chemical composition of the aluminosilicate source. A general decrease of the mechanical strength was observed a drastic decrease was obtained with mixture based on pure kaolin. A slight decrease for sample based on impure kaolin. A conservation of the compressive strength with mixture based on mixture of pure and impure kaolin. Formation of new crystalline refractory phases such as leucite, kalsilite, potassium aluminium silicate and wollastonite was evidenced. Thus, in order to obtain thermal resistant materials with conservation or increase of residual strength after 1000°C, it is recommended to use a low concentrated potassium alkaline solution and an aluminosilicate rich of calcium.

Conflict of interest

The authors declare no conflict of interest.

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