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HIGH-TEMPERATURE, RESISTANT, ARGILLITE-BASED, ALKALI-ACTIVATED MATERIALS WITH IMPROVED POST-THERMAL TREATMENT MECHANICAL STRENGTH

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Abstract—Fire resistance performance is one of the most important requirements in geological storage conditions in order to improve the resistance of storage packages to high thermal constraints (in the case of a fire for example). With the need to develop new fire-resistant materials, the aim of the present study was to develop fire-resistant geopolymer binders based on Callovo-Oxfordian (COx) argillite. Two types of kaolin with different degrees of purity were mixed with argillite in various proportions. These mixtures were calcined at 600 or 750°C. In order to assess the fire resistance of activated materials, thermal treatment at 1000°C was performed. The compressive strength and mineralogical composition of the samples were investigated before and after heat treatment. The results showed that the addition of argillite improved significantly the thermomechanical properties of kaolin-based geopolymers containing impurities, especially the mixture containing 67% argillite and calcined at 750°C. This phenomenon was not observed for the pure-kaolin geopolymer. Improvement of fire resistance was due to the formation in situ of leucite and zeolite-type phases ($KAlSi_2O_6$ and $KAlSiO_4$) and of wollastonite ($CaSiO_3$) at high temperature, which is linked to the Ca available in the raw materials.

Keywords—Callovo-Oxfordian argillite (COx) · Carbonate · Geopolymer · Kaolin · Thermal resistance · Thermomechanical properties

INTRODUCTION

Fire resistance is an important property required in numerous applications. Geopolymer materials are characterized by high thermal stability which is generally related to the solidification of melted phases and/or the formation of thermally stable crystalline phases (Davidovits 1991; Duxson 2006). These three-dimensional amorphous binders result from the activation of an aluminosilicate source with an alkaline solution (Davidovits 1991). They can be synthesized from various aluminosilicate materials such as metakaolins, common clays, fly ash, blast furnace slags, etc. (Duxson 2006; Buchward et al. 2009a; Yao et al. 2009; Autef et al. 2013).

According to the literature, the fire resistance of these materials can either be from viscous sintering and pore collapse (Duxson 2006) or due to the formation of thermally stable crystalline phases (Cheng and Chiu 2003; Fernandez-Jimenez et al. 2008). The thermal behavior of a Na-based geopolymer which was characterized by its dehydration at a temperature below 400°C and the crystallization of the geopolymer network to nepheline between 850 and 950°C was studied by Buchwald et al. (2009b). The recrystallization of K-based geopolymers to feldspars, leucite, and kalsilite at a temperature of 1000°C was demonstrated by Barbosa and MacKenzie (2003), whereas other authors have studied the thermal behavior of geopolymers based on aluminosilicate sources containing carbonates. For example, the thermal behavior of fly ash and metakaolin has been studied by Zhang et al. (2014) who showed that an increase in fly ash content led to better mechanical properties after thermal treatment because of less mass loss and sintering reactions of un-reacted fly ash at high temperatures. Likewise, the thermal behavior of metakaolin and materials based on granulated blast furnace slag was studied by Bernal et al. (2011) who showed that incorporation of slag enhances mechanical strength after thermal treatment. The addition of a Ca-rich aluminosilicate substance can, therefore, improve the thermal resistance of the resulting alkali-activated materials. In fact, in alkali-activated materials, alkaline-earth carbonates such as calcite and dolomite could play the role of fillers (Azim et al. 2016). The decomposition of alkaline earth carbonates at temperature leads to the presence of alkaline earth oxides. Depending on the Ca content and activating solution concentration, reactive calcium oxide may either lead to the formation of Si–O–Ca bonds in competition with Si–O–Al bonds resulting from the polycondensation reaction (Peyne et al. 2017) or react with the dissolved silicate to form a C–S–H gel (Calcium Silicate Hydrate) coexisting with an aluminosilicate gel (Yip et al. 2005; Lodeiro et al. 2013). At higher temperature, calcium oxide could react with silica to form wollastonite, which is a

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thermally stable phase (Yu et al. 1999; Gharzouni et al. 2018).

The Callovo-Oxfordian argillite is composed of 52% clay minerals (interstratified illite-smectite, illite, kaolinite, and chlorite), 26% carbonate (calcite and dolomite), and 17% quartz (Montes et al. 2004). Recent studies (Gharzouni et al. 2017; Dupuy et al. 2018a) have demonstrated that raw argillite was not reactive enough to be alkali-activated and needs to be treated thermally first. Obtaining a consolidated material based on thermally treated argillite with a compressive strength of ~26 MPa after 28 days is possible (Dupuy et al. 2018a),

The thermal behavior of geopolymers based on a mix of argillite and kaolin has not been studied previously, so the objective of the present study was to evaluate the thermal behavior of various mixtures of raw argillite and kaolins. In order to understand the effect of carbonate decomposition on thermal resistance, further objectives were: to calcine the various mixtures at two temperatures, 600 and 750°C, which should either conserve or decompose the carbonates; to test the compressive strengths of the consolidated materials before and after thermal treatment; and to assess the structural changes using X-ray diffraction (XRD), thermal analysis, and dilatometry.

MATERIALS AND METHODS

Materials

Three aluminosilicate sources: two types of kaolin (KI [obtained from AGS, Clérac, France] and K5 [obtained from Argeco Développement, Fumel, France]) and argillite (referred to here as A25, and obtained from ANDRA, Châtenay-Malabry, France), were used as raw materials. Their main physicochemical characteristics (Table 1) showed that KI consisted mostly of silica and alumina while K5 contained traces of calcite (Gharzouni 2016). A significant amount of Ca was present in the argillite compared to KI and K5 (Gharzouni et al. 2017; Dupuy et al. 2018a). The mean particle diameter (Gharzouni 2016) of KI was 5 μm and this was consistent with its high water demand (Gharzouni 2016) of 798 μL/g. K5 and A25 both had similar water demands (530 and 535 μL/g, respectively) with approximately the same particle size (20 and 26 μm, respectively). The water demand corresponds to the volume of water that can be adsorbed by 1 g of powder before saturation. Previous studies (Autef et al. 2013; Gharzouni 2016) have shown that small particle size and large water-demand values are indicators of aluminosilcate source reactivity in an alkaline medium. A commercial K silicate solution (obtained from Woellner GmbH, Ludwigshafen, Germany) with a Si/K molar ratio of 1.7 and water content of 79% was used. The activation solution was prepared by dissolving KOH pellets (obtained from CABOT GmbH, Rheinfelden, Germany) in this commercial solution. The activation solution, labeled S, had a Si/K molar ratio of 0.58.

Sample Preparation

Each kaolin was mixed with the argillite at various proportions and calcined at 600 or 750°C for 4 h. The homogenization of mixtures was performed for 4 h using a roller mixer. The nomenclature adopted to identify samples was as in this example: $(KY_{1-x}A25_x)^T$, where KY refers to the type of kaolin used; A25 represents the raw Callovo-Oxfordian argillite (COx); x and T indicate the mass fraction of A25 and the calcination temperature (600 or 750°C), respectively.

The procedure for preparing geopolymers was as follows. The activation solution was prepared; then, one of the aluminosilicate mixtures described above was added to achieve a solid/liquid ratio of 1.28. This mixture was stirred for ~5 min, then poured into a closed mold and held at room temperature until consolidation was established. Samples were labeled as in the following example: $S(KY_{1-x}A25_x)^T$, where S refers to the silicate solution and $(KY_{1-x}A25_x)^T$ to the aluminosicate mixture. For example, the $S(K5_{0.33}A25_{0.67})^{750}$ sample was prepared by mixing the activation solution (S) with the aluminosilicate source consisting of 33% kaolin K5 and 67% argillite (A25) calcined at 750°C. In order to characterize the fire resistance of samples after 7 days of consolidation, they were heated to 1000°C for various characterization tests.

Characterization Techniques

X-ray diffraction experiments were performed using a Bruker-D8 Advance instrument (Bruker, Billerica, Massachusetts, USA) which operates with Bragg-Brentano geometry and a CuK$\alpha_1\alpha_2$ target. The geopolymer samples were ground finely and packed against a flat surface (glass slide) and placed onto the goniometer sample holder. Data were recorded over the range 10–50°2θ with an angular step size of 0.019°2θ and a counting time of 172.8 s per step. Phase identification was done using the Joint Committee Powder Diffraction Standard (JCPDS) reference database.

Aluminosilicate powders were calcined in a cell oven (Ceradel Model C9DLSP, Limoges, France) at a heating rate of 5°C/min up to 600 or 750°C for 4 h in an air atmosphere, then cooled. High-temperature stability of

Table 1. Chemical and physical characteristics of the aluminosilicate sources used.

Aluminosilicate source	Chemical composition (wt.%)										D_{50} (μm) (± 3 μm)	Water demand (μL/g) (± 30 μL/g)
	SiO_2	Al_2O_3	MgO	CaO	Na_2O+K_2O	TiO_2	Fe_2O_3	P_2O_5+ MnO	S	LOI (1000°C)		
A25	48.68	13.41	2.50	10.73	3.80	0.72	4.51	0.10	0.83	14.70	26	535
KI	42.84	36.5	–	–	–		–	–	–	20.66	5	798
K5	55.48	32.69	–	1.11	–	1.11	0.55	–	–	9.05	20	530

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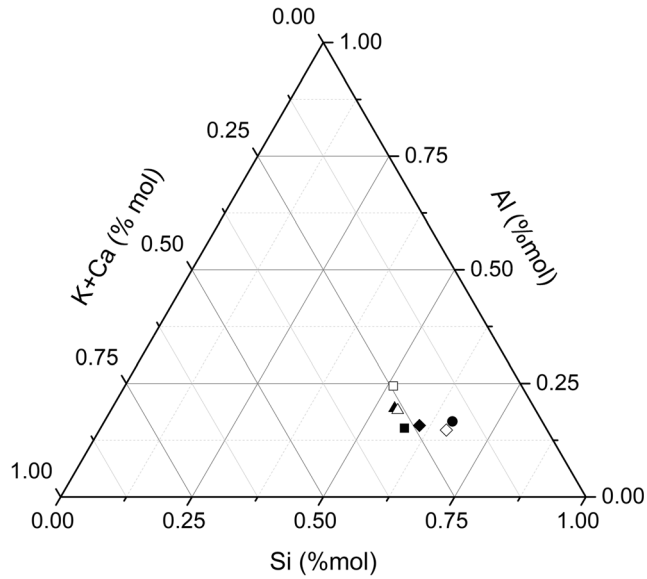


Fig. 1. Chemical composition of the (□) SKI, (●) SK5, (■) SA25, (○) $SKI_{0.67}A25_{0.33}$, (Δ) $SKI_{0.33}A25_{0.67}$, (◆) $SK5_{0.33}A25_{0.67}$, and (•) $SK5_{0.67}A25_{0.33}$ samples in the Si-Al-K+Ca/O ternary diagram.

the geopolymers was evaluated by heating the samples at a rate of 5°C/min to 1000°C, holding for 15 min, then cooling naturally.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using a TA Instrument SDT Q600 (TA Instruments, New Castle, Delaware, USA).

Table 2. Photos and density of the various samples (Ø = 15 mm) before and after thermal treatment at 1000°C.

Sample	Before thermal treatment	After thermal treatment	
		No resistance	Resistance
SKI			
$SKI_{0.33}A25_{0.67}$			
$SKI_{0.67}A25_{0.33}$			
SA25			
$SK5_{0.33}A25_{0.67}$	 **1.85 g/cm³**		 **1.60 g/cm³**
$SK5_{0.67}A25_{0.33}$	 **1.89 g/cm³**		 **2.20 g/cm³**
SK5	 **1.82 g/cm³**		 **2.30 g/cm³**

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Measurements were carried out under dry air flow (100 mL/min) in a platinum crucible. About 30 mg of crushed sample was heated to 1100°C at a rate of 5°C/min and with a dwell time of 15 min.

Compressive strength tests were carried out at room temperature on untreated and heated samples using an Instron 5969 testing machine (Instron, Elancourt, France). Measurements were performed on five cylindrical samples ($d/H = 0.5$, where diameter d = 15 mm and height H = 30 mm) after 7 days of curing in a closed polystyrene mold at room temperature. The compressive strength value was expressed in MPa and corresponded to the average value of at least five measurements.

Dilatometric measurements were performed in air with a vertical dilatometer (Setsys, Setaram Instrumentation, Caluire, France). The cylindrical samples ($d/H = 0.625$, where d = 5 mm and H = 8 mm) were placed between two platinum/alumina holders during the analysis, and a correction was applied to remove the contribution of the device/holders. Samples were heated to 900°C at a rate of 5°C/min in an air atmosphere and cooled at a rate of 20°C/min.

RESULTS AND DISCUSSION

Effect of Kaolin Purity on the Thermal Behavior

After calcination at 600 or 750°C, mixtures $(KY_{1-x}A25_x)^T$ were activated using a K silicate solution. The 14 samples were plotted in the Si–Al–(K+Ca) ternary diagram (Fig. 1). Samples based on KI were richer in Al than those based on K5 and A25. Samples based on K5 contained more SiO_2, however. The substitution of kaolin by argillite increased the Ca content and decreased the Al content. The consolidated materials obtained were heated to 1000°C. The photos of the various samples $S(KY_{1-x}A25_x)^{600}$ before and after thermal treatment at 1000°C (Table 2) reflected various thermal behaviors:

(1) Samples characterized by the presence of cracks, melted phases, or significant shrinkage exhibited no resistance to thermal treatment (SKI^{600}, $SA25^{600}$, $S(KI_{0.67}A25_{0.33})^{600}$, $S(KI_{0.33}A25_{0.67})^{600}$, SKI^{750}, and $S(KI_{0.33}A25_{0.67})^{750}$).
(2) The rest of the samples exhibited good resistance to thermal treatment, with no major physical change other than minor shrinkage.

These first results proved that the thermal behavior depended essentially on the nature of the aluminosilicate source. In fact, regardless of calcination temperature, the use of a pure kaolin (KI) or argillite (A25) or a mixture of both did not favor thermal resistance. Nevertheless, samples based on kaolin (K5) or mixtures of kaolin (K5) and argillite (A25) showed good thermal resistance. During the calcination phase, the carbonates decomposed to oxides and favored the solid-state reactions (Dupuy et al. 2018a). For the same calcination temperature of 600°C, the kaolin purity appeared to influence significantly the fire-resistance properties of the consolidated materials, demonstrating that K5 exhibited better synergy with argillite (A25) than KI to produce thermally resistant materials because of its greater proportion of impurity. The various geopolymers $S(K5_{1-x}A25_x)^T$ were characterized before and after 1000°C.

Influence of Thermal Treatment on Mechanical and Structural Properties

To develop fire-resistant geopolymers, characterization has been focused on K5- and A25-based materials only ($S(K5_{1-x}A25_x)^T$). In order to understand the thermal behavior of the geopolymers, thermal analysis, compressive strength tests, and XRD analysis were performed. The TGA and DTA curves of $S(K5_{0.33}A25_{0.67})^{600}$ and $S(K5_{0.33}A25_{0.67})^{750}$ samples (Fig. 2) can be divided into four parts, each one corresponding to a characteristic weight loss.

The first two major weight losses observed were at 25–50°C and 50–200°C and are attributed to free and adsorbed water, respectively (Perera et al. 2005). The weight loss noted between 300 and 600°C is either related to the decomposition of $Ca(OH)_2$ and $Mg(OH)_2$ (L'vov et al. 1998; Chatterjee and Lahiri 2014) and/or structural water resulting from dehydroxylation of the clay minerals (Buchwald et al. 2009a, b). Indeed, the decomposition of calcite and dolomite initially present in the argillite leads to the presence of CaO and MgO, respectively, which can react easily with the humidity from air to form $Ca(OH)_2$ and $Mg(OH)_2$. The weight loss at 600–1000°C could also be due to the decomposition of carbonate-based compounds (Foldvari 2011) and the structural water of the geopolymer material. The two samples exhibited similar curves

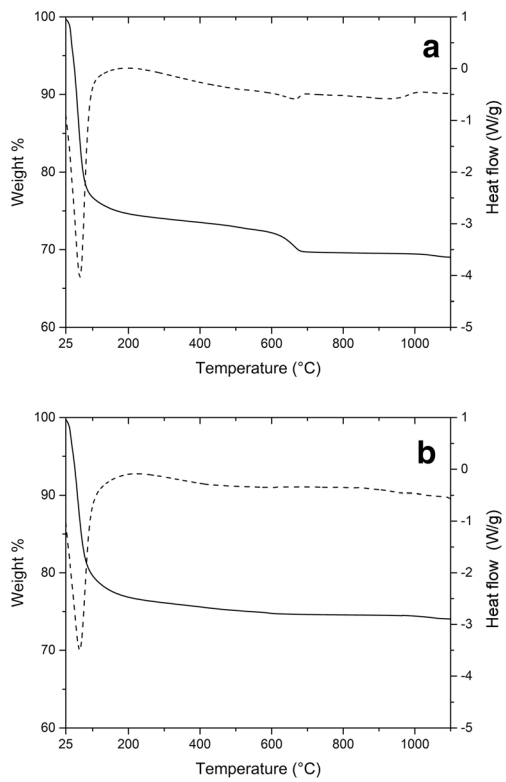


Fig. 2. Thermal curves (DTA-TGA) of **a** $S(K5_{0.33}A_{0.67})^{600}$ and **b** $S(K5_{0.33}A_{0.67})^{750}$ (weight loss (—) and heat flow (- - - -)).

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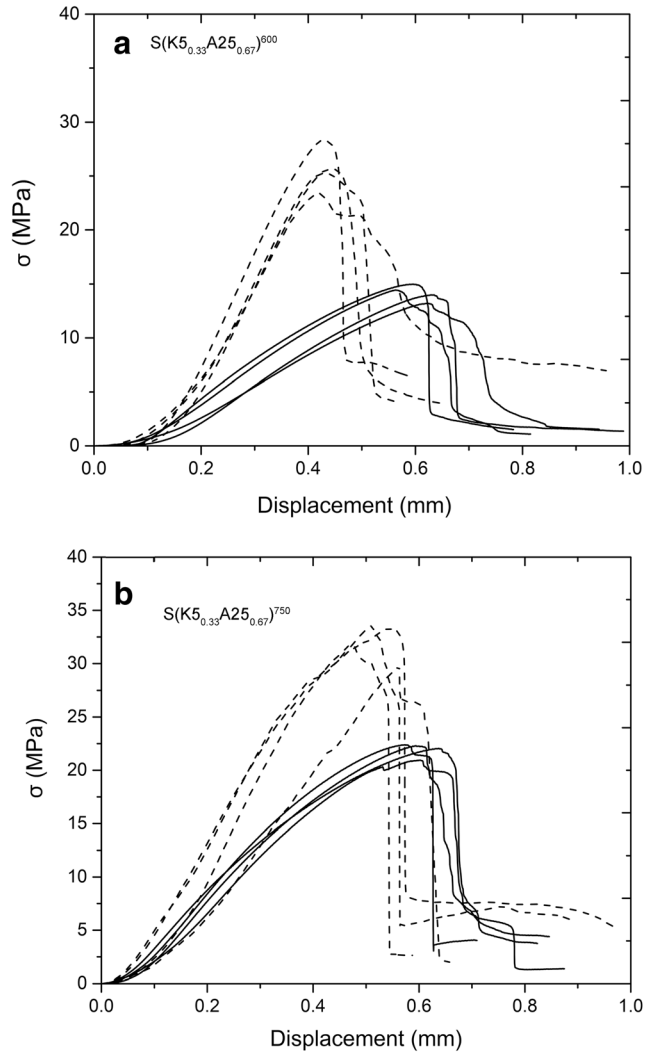


Fig. 3. Evolution of the compressive strength curve as a function of the displacement before (—) and after (- - - -) thermal treatment of **a** $S(K5_{0.33}A25_{0.67})^{600}$ and **b** $S(K5_{0.33}A25_{0.67})^{750}$ samples.

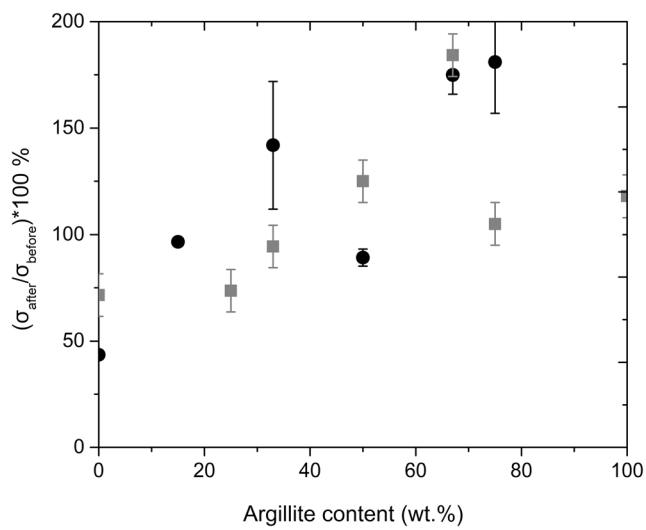


Fig. 4. Value of $(\sigma_{after}/\sigma_{before})\times100$ for the geopolymers $S(K5_{1-x}A25_x)^T$ as a function of argillite content for calcination temperatures of (•) 600 and (■) 750°C.

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except the weight loss at 600°C differed from that at 750°C in the case of sample $S(K5_{0.33}A25_{0.67})^{600}$ due to the decomposition of carbonates.

An example of compressive strength curves of both untreated and thermally treated samples $S(K5_{0.33}A25_{0.67})^{600}$ and $S(K5_{0.33}A25_{0.67})^{750}$ (Fig. 3) revealed that, before heat treatment, sample $S(K5_{0.33}A25_{0.67})^{750}$ exhibited greater compressive strength than sample $S(K5_{0.33}A25_{0.67})^{600}$ (22 and 15 MPa, respectively). Moreover, the compressive strength curves for both calcination temperatures (600 and 750°C) exhibited the linear variation characteristic of an elastic regime (Trindale et al. 2017; Dupuy et al. 2018b; Wang et al. 2019). After heat treatment, the compressive strength increased to 27 and 35 MPa for samples $S(K5_{0.33}A25_{0.67})^{600}$ and $S(K5_{0.33}A25_{0.67})^{750}$, respectively.

In order to quantify the gain or loss of mechanical performance after thermal treatment, the ratios between the compressive strength after and before heat treatement for all samples $((\sigma_{after}/\sigma_{before})\times100)$ for both calcination temperatures was compared (Fig. 4). For a calcination temperature of 600°C, the ratio increased to 1.37 for a 33% argillite content, then decreased to 0.84 for the sample with 50% argillite. This ratio then increased to 1.81 for an argillite content of 75%. For a calcination temperature of 750°C, the compressive strength ratio increased with the increase in argillite content from 0.70 to 1.90 then decreased from 1.90 to 0.72 for 75% argillite content. According to these results, the composition with 67% argillite is optimal ($\sigma\times1.8$). The results for calcination at this temperature were more homogeneous than for 600°C. The calcination temperature, therefore, affects the physical properties of the material significantly, especially its fire resistance. The difference between the two calcination temperatures was probably due to the nature of Ca-based compounds in the calcined raw material. Previous work (Chatterjee and Lahiri 2014) found that the calcite ($CaCO_3$) present in the raw argillite remained in the material after calcination at 600°C, while, after calcination at 750°C, almost all calcite was transformed to lime (CaO).

In order to explain further the mechanical behavior after thermal treatment, XRD characterization was performed. The XRD pattern of sample $S(K5_{0.67}A25_{0.33})^{600}$ (Fig. 5) revealed that the argillite (A25) contained impurities such as dehydroxylated muscovite ($KAl_3Si_3O_{11}$) and calcite or other minerals such as arcanite that could have formed during alkali activation (Dupuy et al. 2018b). After thermal treatment, the intensity of $KAl_3Si_3O_{11}$ peaks decreased considerably in favor of the appearance of the zeolite-type phase (anorthitic K-Al silicate, $KAlSiO_4$) (Smith and Tuttle 1957; Kremenovic et al. 2013). This phase can be formed from the dehydroxylated muscovite ($KAl_3Si_3O_{11}$) and the K present in the amorphous phase of the geopolymer network (Dupuy et al. 2018b). Wollastonite peaks ($CaSiO_3$) appeared and were related to solid reactions between SiO_2 and Ca released by carbonate decomposition (Yu et al. 1999).

The XRD patterns of sample $S(K5_{0.33}A25_{0.67})^{600}$ showed the same phases as $S(K5_{0.67}A25_{0.33})^{600}$ but with greater intensity due to the larger argillite content. Patterns of sample $S(K5_{0.5}A25_{0.5})^{600}$ showed the same phases as $S(K5_{0.67}A25_{0.33})^{600}$ and $S(K5_{0.33}A25_{0.67})^{600}$ with the

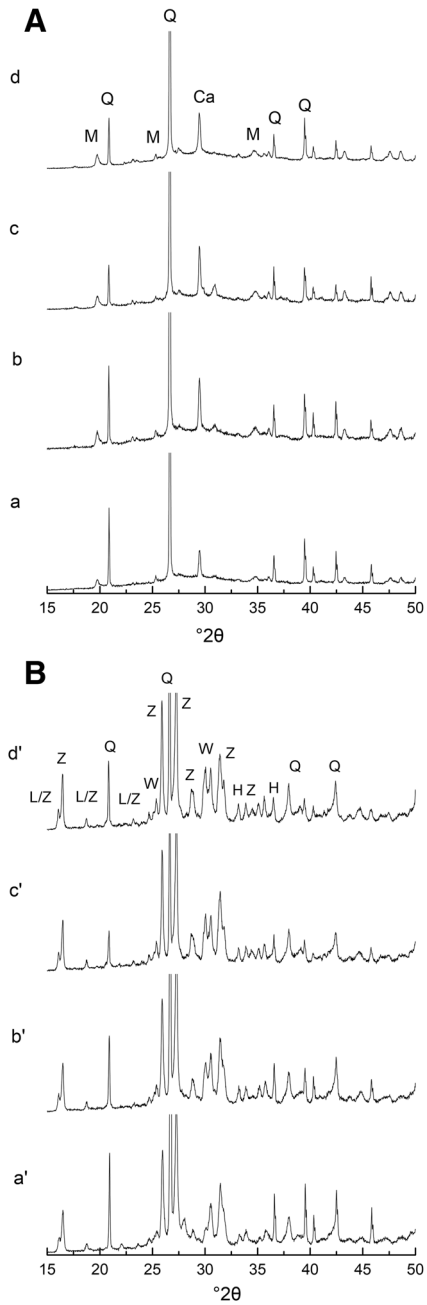


Fig. 5. XRD patterns of the $S(K5_{0.67}A25_{0.33})^{600}$, $S(K5_{0.5}A25_{0.5})^{600}$, $S(K5_{0.33}A25_{0.67})^{600}$, and $S(K5_{0.33}A25_{0.67})^{750}$ samples before **A** (a,b,c,d) and after **B** (a′,b′,c′,d′) thermal treatment, respectively (Z: zeolite, L: leucite-type, M: muscovite, Q: quartz, Ca: calcite, W: wollastonite, D: Diopside, H: hematite).

appearance of krotite ($CaAl_2O_4$). Samples based on mixtures calcined at 750°C ($S(K5_{0.33}A25_{0.67})^{750}$) revealed the same phases as samples based on mixtures calcined at 600°C but with greater intensities due to the increased availability of reactive Ca from the total carbonate decomposition at 750°C and reaction with the other available species from the viscous flow (Chatterjee and Lahiri 2014). As a consequence, XRD

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analysis revealed interactions between the available species leading to the crystallization of various phases (zeolite-type phase, $KAlSiO_4$, and wollastonite, $CaSiO_3$) which are responsible for the improvement in the mechanical strength after heat treatment. In fact, greater amounts of impurities in K5 and A25 led to an in situ formation of new phases, stable at high temperatures, such as wollastonite and zeolite-type phases. Similar results were obtained by Rovnanik and Safrankova (2016) who proved that, for fly ash-based geopolymers, fusion of the fly ash occurs and thermally stable new phases are formed, such as albite and nepheline, at high temperature.

Effect of Carbonates on the Thermal Behavior

In order to explain the mechanical behavior after thermal treatment and especially the decrease in the compressive strength of sample $S(K5_{0.5}A25_{0.5})^{600}$ after thermal treatment at 1000°C, the raw materials were studied further with a focus on $(K5_xA25_{1-x})^T$ with $x = 0.33$, 0.5, and 0.67, and $T = 600$ and 750°C. For this, thermal analysis (DTA-DTG) was performed on the various raw mixtures (Fig. 6). Dilatometry measurements of consolidated materials based on the mixtures $S(K5_{0.5}A25_{0.5})^{600}$ and $S(K5_{0.5}A25_{0.5})^{750}$ were examined (Fig. 7). At 600°C (Fig. 6), four weight losses were detected. The first (1) was attributed to the release of adsorbed and free water. (2) The minor weight loss observed between 300 and 450°C was due to $Mg(OH)_2$ decomposition (Dupuy et al. 2018a). This weight loss can be explained by the decomposition of a small proportion of the dolomite, initially present in argillite, at 600°C in the various mixtures. (3) The third weight loss, between 450 and 600°C, was due to dehydroxylation of kaolinite and the clay minerals in the argillite. (4) Finally, the major weight loss between 600 and 800°C, which increases with increases in argillite content, is associated with carbonate (especially calcite) decomposition (Dupuy et al. 2018a). At 750°C (Fig. 6), the same weight losses were distinguished but with different percentages. A larger weight loss at 300–450°C was observed in the case of the $(K5_{0.5}A25_{0.5})^{750}$ mixture than in the other two, indicating a larger amount of $M(OH)_2$ where M = Ca or Mg and, therefore, more carbonate decomposition. More carbonate decomposition in the case of this mixture seems to be explained by the presence of a eutectic in the $CaCO_3$–$MgCO_3$ binary (Shatskiy et al. 2016), thereby promoting decomposition and favoring solid reaction between the various species. The various species reacted with the silicate solution to form a geopolymer, therefore. During the thermal treatment, all these species were reactive and could react to form wollastonite, which was responsible for the increase in the compressive strength. This behavior was notable in the dilatometry curve of sample $(K5_{0.5}A25_{0.5})^{750}$ (Fig. 7). The first shrinkage (1) at <300°C was due to the loss of water contained in the porous network (Autef et al. 2016). The second shrinkage (2) at 750°C was due to viscous flow. Then, (3) a delay in shrinkage was observed in relation to the formation of a crystalline phase based on SiO_2 decreasing the amount of viscous flow. This phase could be wollastonite because its formation was observed at ~900°C in several systems (Swamy and Dubrovinsky 1997; Karamanov and Pelino 2008). In the case of the sample based on raw materials calcined at 600°C, the carbonate compounds were not decomposed (Fig. 6) and, thus, acted as reinforcements in the

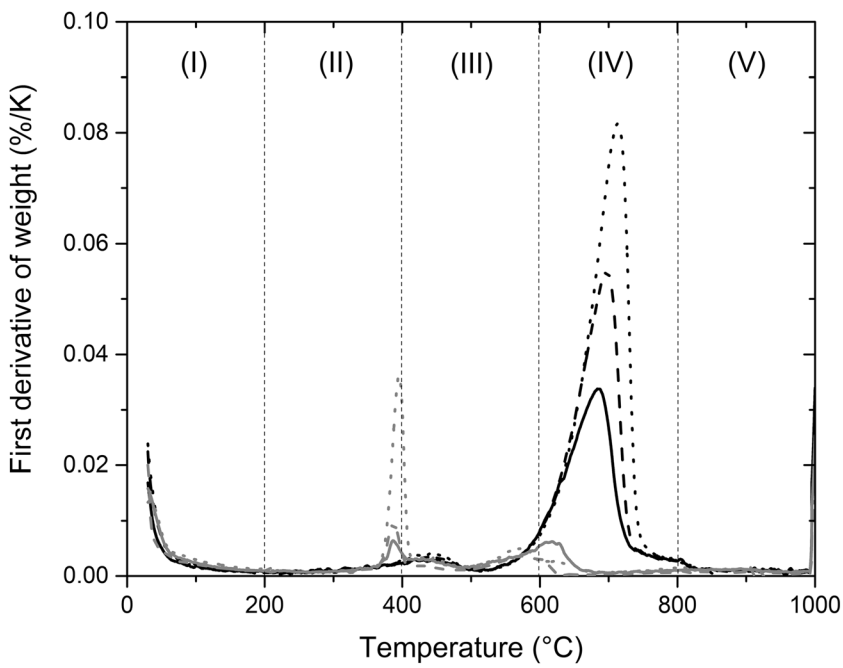


Fig. 6. Derivative of weight loss (thermal analysis) of (—) $K5_{0.67}A25_{0.33}$, (- - - -) $K5_{0.5}A25_{0.5}$, and (…) $K5_{0.33}A25_{0.67}$ mixtures calcined at 600 (black) and 750°C (gray).

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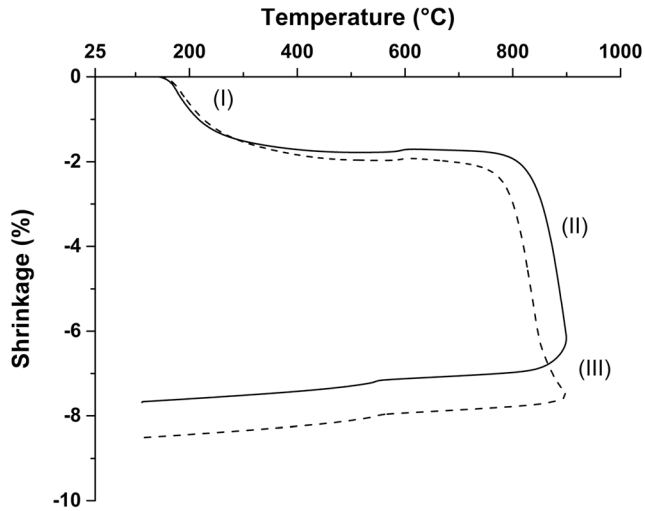


Fig. 7. Dilatometric curves of (—) $S(K5_{0.5}A25_{0.5})^{600}$ and (- - - -) $S(K5_{0.5}A25_{0.5})^{750}$ samples.

geopolymer matrix and were able to react during the thermal treatment at 1000°C. For sample $S(K5_{0.5}A25_{0.5})^{600}$, this was characteristic of a sintering observed at 850°C (Fig. 7) without the appearance of the wollastonite. In this case, the decomposition of carbonate species in the presence of Al species issued from metakaolin was able to form the krotite phase (Miranda-Hernandez et al. 2018) noted in the XRD patterns. This formation was possible due to the presence of some viscous flow in the system SiO_2–CaO–Al_2O_3 (Hamann et al. 2018).

Finally, for the $S(K5_xA25_{1-x})^{750}$ samples, evolution of the mechanical strength ratio (from 71 to 184%) was in accordance with the increase in pH (from 9.8 to 11.7; see Supplementary Material) confirming the presence of reactive Ca available for reaction with the silicates at high temperature to form wollastonite. For the $S(K5_{0.5}A25_{0.5})^{600}$ samples, the decrease in mechanical strength after heat treatment at 1000°C was explained by the appearance of a liquid phase which prevented the formation of in situ carbonated silicate phases responsible for the formation of the wollastonite. The Ca and Al available formed preferentially a calcium aluminate. Thus, the mechanical behavior after heat treatment depended heavily on the carbonate decomposition.

SUMMARY AND CONCLUSIONS

The present study aimed to develop fire-resistant argillite-based geopolymers and, more precisely, to conserve or even improve the mechanical strength of post-thermal treatment materials. To achieve this objective, two types of kaolin with different degrees of purity were mixed with raw argillite in variable proportions. After grinding and mixing, the resulting blends were calcined at 600 or 750°C and then mixed with a K silicate solution to obtain consolidated materials. In order to assess the fire resistance of the activated materials, a thermal treatment at 1000°C was performed. Compressive strength and mineralogical compositions of the samples before and after heat treatment were investigated. The mixture of argillite and kaolin contained impurities and, at both calcination temperatures, exhibited an improvement in mechanical strength after thermal treatment. The best results were obtained (σ×1.8) for the composition based on the mixture composed of 67% argillite. Geopolymer synthesized from the pure kaolin mix failed to improve the mechanical properties. The presence of impurities and of alkaline earth carbonates, in particular, improved the mechanical properties at all temperatures. This result can be explained by in situ formation of thermally resistant crystalline phases such as zeolite-type and wollastonite phases with increase in temperature. Two mechanisms were identified in the present study, depending on the calcination temperature of the aluminosilicate source:

(1) In the case of the sample based on raw materials calcined at 600°C, the carbonate compounds were not decomposed; they could simultaneously act as a reinforcement in a geopolymer matrix and react during thermal treatment at 1000°C.
(2) For samples based on raw materials calcined at 750°C, the presence of reactive Ca enabled reaction at high temperature with the silicates to form a mechanical reinforcement such as wollastonite.

Finally, the mechanical behavior of a geopolymer after heat treatment was intimately related to available carbonates. The composition of the aluminosilicate sources (and especially impurities) and calcination temperature may influence directly the fire-resistant properties of geopolymers. A calcination temperature of 750°C for a mixture of argillite and kaolin was found to be optimal in obtaining fire-resistant geopolymer materials.

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