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## **Effects of potassium-silicate, sands and carbonates concentrations on**

### **metakaolin-based geopolymers for high-temperature applications**

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**Abstract:** Geopolymers can be optimized to have interesting physical characteristics, which are influenced by the raw materials and additives utilized in their formulations. For this reason, various formulations of two metakaolin-based binders with filler additions of different natures, i.e., sands and carbonates, were tested. The aluminosilicate source used is a commercial metakaolin (Si/Al = 1.44). The feasibility of the consolidated samples and their thermal behaviors were evaluated. The viscosity tests of the fresh geopolymer pastes indicated that their setting times are controlled by their potassium concentrations. The evaluation of the thermal stabilities of consolidated samples was carried out before and after heat treatment at 1000 °C by means of compressive tests. Geopolymers with low potassium concentrations showed mechanical strengths that were 16% greater (37 to 43 MPa) than geopolymers with high potassium concentrations, both before and after heat treatment. The exposure to different conditions did not influence the final mechanical properties of the geopolymers. XRD analysis of the geopolymers was performed and the crystallization of kalsilite was found in samples high potassium concentrations. Different mechanisms during geopolymerization,

specifically the kinetic and thermodynamic mechanisms of geopolymers with high and low potassium concentrations, respectively, can explain the diverse mechanical responses of the geopolymers at room temperature, while the presence of kalsilite can explain the differences of geopolymers at high temperatures. Hence, it is possible to develop fire-resistant geopolymers by controlling the concentrations of potassium and fillers.

**Keywords:** carbonate; dolomite; geopolymer viscosity; sand; fire-resistant; kalsilite; leucite

## 1. Introduction

Materials have to have certain properties to be called fire-resistant, such as thermal stability and mechanical resistance once exposed to high temperatures, as well as chemical stability and resistance to heat decomposition [1,2]. Ceramic materials [3] are naturally able to bear heat. Geopolymers [4,5] are ceramic materials generally obtained through polycondensation reactions between an aluminosilicate source, such as either kaolinitic or metakaolin clays, and an alkaline solution that contains an alkaline-earth silicate, generally potassium or sodium. The properties of geopolymers are similar to those of common ceramics, such as chemical and thermal stability [6,7] and mechanical resistance. Moreover, their formulations can be manipulated to develop characteristics and properties that are useful for different applications. Different fillers can be added to geopolymer formulations to produce inexpensive ceramics with fire-resistant properties [8,9].

Potassium-based geopolymers have been observed to have great thermal stability, mainly due to the crystallization of kalsilite and/or leucite at high temperature as stated by V.F.F. Barbosa et al. [10]. K. Sakkas et al. [11] successfully produced a geopolymer based on potassium silicate, alumina and slag with excellent passive fire-resistant properties and low thermal conductivity. After being exposed to thermal loading with a peak temperature of 1380

°C, the K-based geopolymer specimens showed no damage or visible deformations. X-ray investigation showed the presence of leucite in these samples.

The use of sand in geopolymers was investigated in previous studies [12,13], underlining the enhancement of mechanical properties because of a higher solid-to-liquid ratio. Similar conclusions were stated by P. Kathirvel et al. [14], who also suggested that the increased mechanical performance of geopolymers with quartz powder/sand addition is probably due to the ability of fine aggregates to fill the voids of and densify geopolymer structures. Moreover, the presence of silicon ions resulting from the chemical attack of quartz by the alkaline solution during preparation could lead to geopolymer chains being more interconnected at higher quartz contents. The grains size of the quartz sand is also a key factor on the developing of mechanical strength, because of their packing ability. The research of Q. Wan et al. [15] highlighted that metakaolin-based geopolymers samples produced with quartz sand particles with sizes of 75-32  $\mu\text{m}$  showed a compressive strength of approximately 56 MPa. As Nodehi M. et al. [16] reviewed, quartz sand can be added to metakaolin-based geopolymers for the production of ultrahigh-performance geopolymer concrete with enhanced mechanical properties. When quartz sand is used as an inert filler, usually with particle sizes below 1.18 mm, it fills internal pores, which helps to withstand internal stresses.

Previous works [17,18] have shown that the addition of carbonates can significantly increase the mechanical properties and heat resistance of metakaolin-based geopolymers, mainly due to the reaction between free  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions with silica to form wollastonite, as stated by C. Dupuy et al. [19] and T.M. Tognonvi et al. [20]. A high carbonate content can translate into low shrinkage (approximately 6 to 8%) after heating from 600 to 1000 °C, as demonstrated by S. Petlitckaia et al. [21], leading to more thermally stable geopolymers. In fact, C.K. Yip et al. [22] observed that an addition of approximately 20% carbonates (calcite and/or dolomite) can improve the overall geopolymer compressive strength due to the

presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, which can play a significant role in the binding of the geopolymer gel phase with carbonate particle surfaces. The presence of both geopolymeric gel and calcium silicate hydrate gel in a matrix containing ground granulated blast furnace slag can be responsible for the improvement of the geopolymer mechanical strength. Based on previous works [23,24], dolomite was mainly used as a precursor and as fine inert filler in geopolymer formulations to increase their mechanical properties.

This paper aims to investigate the influences of different potassium concentrations and additives (quartz sands and carbonates) used in the formulations of metakaolin K-based geopolymers on thermal stability. Their influence will be first understood with regard to feasibility, viscosity and thermal stability, by means of compressive tests performed before and after heating. Then, XRD measurements will be used to highlight the presence of phases that exhibit different behaviors.

## **2. Materials and methods**

### **2.1. Raw materials and sample preparation**

The aluminosilicate source was metakaolin M5 (Argicem rosé, provided by Argeco, France). Potassium feldspar, provided by Kemmlitzer Kaolinwerke GmbH, was added to reproduce the typical composition of clays commonly used as aluminosilicate sources for geopolymers [26]. The fillers used were two different types of fine sands, the first referred as sablon (natural pH = 8.4, waste, Argeco, France) and the second as blansil (natural pH = 6.5, Sibelco, France), both containing quartz as the most present phase, and two carbonates, calcite ( $\text{CaCO}_3$ , natural pH = 8.3) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ , natural pH = 8.5), both obtained from Ceradel (France). Two different potassium silicate solutions were used:  $\text{K}^6$  ( $[\text{K}] = 6 \text{ mol/L}$ ,  $\text{SiO}_2/\text{H}_2\text{O} = 0.18$ ) and  $\text{K}^5$  ( $[\text{K}] = 5 \text{ mol/L}$ ,  $\text{SiO}_2/\text{H}_2\text{O} = 0.26$ ), provided by Wöllner, Germany. For the preparation of samples, metakaolin powder is mechanically stirred with an alkaline solution and other components by an overhead mixer for 5 minutes at 500 rpm or until

complete homogenization. Then, the paste was cast into a polystyrene mold that was then sealed for 7 days at room temperature until complete consolidation. To investigate the influence of the exposure to different environments on the mechanical properties, after being produced with a standard method, i.e., seven days in a mold (endogenous condition, 95% Hr), K<sup>5</sup>M5 (S/B)CD samples were exposed to different conditions for different periods of time at the same temperature of 20 °C, such as 7 days exposed to air at room conditions (50% Hr), 28 days in water (100% Hr), 35 days sealed in a bag (75% Hr) and 35 days sealed in their own mold (endogenous condition, 95% Hr).

The nomenclature adopted is to identify first the components of the formulation and then the different contents of additives. For instance, a sample labeled K<sup>5</sup>M5 SBCD was formulated with M5 metakaolin, K<sup>5</sup> silicate solutions, 10% M5 wt. of feldspar, 35% M5 wt. of sablon and blansil, 15% M5 wt. of calcium and dolomite. Samples with different ratios of fillers are indicated with labels displaying the division between the species involved. The weight percentages, referred to as the metakaolin mass, of the different formulations are given in Table 1.

## **2.2. Characterization techniques**

The heating program was performed in a static oven at a heating ramp of 5 °C/min to the target temperature of 1000 °C, then a dwelling step was maintained for 60 minutes, followed by a cooling ramp of 10 °C/min until the oven reached room temperature.

Viscosity tests were carried out on fresh pastes with a rotational Brookfield Viscometer DV2T coupled with a low shear, low viscosity cylindrical spindle LV-04 (64) while varying the rotational speed, starting at 100 rpm (for viscosity up to 6 Pa·s) and ending at 1 rpm (up to 600 Pa·s). Cylindrical polystyrene vessels ( $\varnothing = 28.00$  mm) were applied. Data were obtained performing a test every 10 minutes before reaction and every 5 minutes from its start. Between tests, pastes were kept sealed in cylindrical vessels and continuously stirred with a

roller mixer, to keep them homogenized. Viscosity analysis allows to determine two major parameters of geopolymer reactions: the initial viscosity  $\eta_0$  and the time of setting  $t_c$ , from which the paste begins to quickly react and then consolidate.

Uniaxial compression tests were performed on cylindrical samples with an aspect ratio of 2 ( $\varnothing = 15$  mm,  $h = 30$  mm) after 7 days at room temperature and after heating at 1000 °C. Instron 5969 with a load cell of 50 kN and a crosshead speed of 0.5 mm/min was used. The maximum compression strength  $\sigma_{max}$  was calculated by the means of seven samples for each composition and each temperature of treatment.

The acquisition of diffractograms was carried out on powdered samples before and after heat treatment with a Bruker-AXS D8 equipped with a copper anode ( $CuK\alpha = 1,5418 \text{ \AA}$ ) from 5° to 70° ( $2\theta$ ) with a 0.015° step with an acquisition time of 1 second. The crystalline phases were identified by comparison to a PDF (Powder Diffraction File) reference of ICDD (Internationale Center for Diffraction Data).

### **3. Results and discussion**

#### **3.1 Feasibility and thermal behavior**

The feasibilities of consolidated samples with different potassium silicate solutions ( $K^6$ , 6 and  $K^5$ , 5 mol/L) and different additives (sands, carbonates and the mix) were tested. All compounds can be easily made and are feasible with homogeneous aspects and the same brown–red color, regardless of their chemical composition, which is due to the presence of iron in the metakaolin used [<sup>27</sup>], as presented in Table 2. A visual inspection of the heat-treated samples shows that every formulation can withstand the heating program without severe cracking; each sample exhibits decreases in volume and total mass, as well as a change in color, from dark brown to white/light brown. This behavior was also seen in previous works [<sup>25,26</sup>]. The iron present in the metakaolin M5 gives the red color. The environment of Fe is crystallized hematite [<sup>27</sup>]. During heating at 1000°C, this phase disappears, because it

loses its crystallinity. The iron flows into the geopolymer viscous flow, changing its environment, thus the change in color [28]. The thermal behavior was evaluated with respect to volumetric shrinkage after heating at 1000 °C. Samples obtained with K<sup>6</sup> solution show an average volumetric shrinkage of approximately 23%. The addition of only sand in geopolymer compounds (K<sup>6</sup>M5 S, B and the mix SB) does not increase thermal stability, as these samples show volumetric variation greater than the values of K<sup>6</sup> geopolymers (respectively 26, 25 and 27%). This is probably due to the nature of the sands. Moreover, the addition of only carbonates (K<sup>6</sup>M5 C, D and CD together) decreases the thermal stability, with these samples showing greater volumetric shrinkage (22, 30 and 23%, respectively). The combination of different additives, namely, the use of sands and carbonates in the same formulation, seems to yield higher thermal stability. The sand- and carbonate-based geopolymers K<sup>6</sup>M5 BC, SCD, BCD and SBCD have volumetric variations of 20, 20, 19 and 21%, respectively, which are lower than the values of the K<sup>6</sup>-based mixtures. An explanation for this is that less filled samples have higher volumetric variations than the average of the other mixtures due to a lower presence of filler, which increases the liquid-to-solid ratio. On the other hand, mixtures obtained with K<sup>5</sup> solution demonstrate a similar trend but have a lower overall average value (17% volumetric shrinkage). For example, K<sup>5</sup>M5 SCD is observed to have a volumetric shrinkage of approximately 16%, which is lower than that of K<sup>6</sup>M5 SCD (21%). The K<sup>5</sup>M5 formulations result in better geopolymer thermal stabilities than the K<sup>6</sup>M5 formulations. As discussed later, different potassium concentrations of the silicate solution result in different reaction behaviors, which leads to different thermal stabilities. To obtain a better thermal performance, the mass ratios of the fillers, either sands and/or carbonates, of the K<sup>5</sup>M5 SBCD geopolymer were changed. K<sup>5</sup>M5 (SB)/(CD) and K<sup>5</sup>M5 (S/B)CD pastes were obtained with ratios of 28.5% wt. sand and 21.5% wt. carbonates (instead of 35% and 15%), and 25% sablon and 75% blansil (instead of a 50/50 ratio). The

average volumetric shrinkage after the heating program at 1000 °C is 15% for K<sup>5</sup>M5 SBCD-based geopolymers, which is lower than the 17% for K<sup>5</sup> and the 23% for K<sup>6</sup>-based geopolymers. Geopolymers obtained with K<sup>5</sup> solution are more thermally resistant and have lower volumetric shrinkage than K<sup>6</sup>-based geopolymers, and high contents of fillers lead to increases in thermal stabilities. Furthermore, changing the ratios between fillers in K<sup>5</sup>-based geopolymers enhances this property even more. Out of the first samples tested, only 10, shown in Table 2, demonstrate feasibility with higher thermal stability. Hence, the next characterization will be carried out on only these 10 formulations.

### **3.2 Viscosity data**

The viscosity test results are shown in Figure 1 (a), which compare the initial viscosities ( $\eta_0$ ) and starting consolidation times ( $t_c$ ) of the 10 formulations. Initial viscosity is the value of the viscosity in the first minutes of analysis. The geopolymerization reaction happens in two steps: first, a stabilization or very slight increase of the viscosity, when the oligomers are formed, and then, an exponential increase of the viscosity, which includes the formation of interconnections among oligomers that create a 3-D structure. The starting consolidation time is calculated as the point at which the two lines representing the first and second reaction steps come together. All formulations display similar time-dependent behaviors, as described in previous studies [29]. The K<sup>6</sup>M5 BC binder, for example, shows an initial viscosity of 0.86 Pa·s, which seems constant until exponential growth occurs after 98 minutes. The geopolymers of the K<sup>6</sup>-based series have different initial viscosities (0.86, 2.5, 0.95 and 1.56 Pa·s for BC, BCD, SCD and SBCD, respectively) and similar setting times (98, 54, 72 and 58 minutes for BC, BCD, SCD and SBCD, respectively). The K<sup>5</sup>-based geopolymers show similar initial viscosities (1.8, 3.14, 1.59, 2.44, 1.35 and 2.7 Pa·s for BC, BCD, SCD, SBCD, (S/B)CD and (SB)/(CD), respectively) and different setting times (250, 115, 144, 158, 223 and 270 minutes for BC, BCD, SCD, SBCD, (S/B)CD and (SB)/(CD), respectively). The

addition of different fillers and their combination affects the behavior and reaction rates of the mixtures. Dolomite increases the viscosity and reaction rate of the paste, whereas sablon, which is derived from the production of metakaolin M5, seems to have an effect on promoting the fast growth of the geopolymer network [30]. The combination of both dolomite and sablon dramatically increases these two parameters. On the other hand, the use of blansil in the mixture seems to decrease viscosity and slow the polymerization. The two different groups of geopolymers can be clearly distinguished, as the reaction rates of the formulations based on the K<sup>6</sup> solution are faster than those based on the K<sup>5</sup> solution. The K<sup>6</sup>-based mixtures show different initial viscosities and quicker starting reaction times, whereas the K<sup>5</sup> samples show slower reactions but higher average viscosities. The different behaviors are probably due to the different concentrations of potassium in the solutions used to produce the samples; K<sup>5</sup> has a lower potassium concentration than K<sup>6</sup> (5 and 6 mol/l, respectively). More specifically, the differences observed between the K<sup>5</sup>- and K<sup>6</sup>-based samples can be connected to the concentration of potassium. In the presence of a low concentration of potassium, the reactivity is lower [31], inducing higher setting times and an increase in viscosity. In the presence of a higher potassium concentration, the setting time is lower, and the various viscosities can be linked to the raw materials. In fact, the use of blansil, which has a weak pH value (6.5), induces a disturbance on the ionic force, delaying the setting time. The addition of carbonates (K<sup>6</sup>M5 BCD sample) with higher pH values (8.3. and 8.5) increases the overall pH value of the mixture, resulting in an increase in the reactivity and a consequent decrease in the setting time. The addition of sablon (pH =8.4) leads to the same behavior. Varying the concentration of potassium and the nature of the additives leads to the control of the viscosity and the reaction rates. Observing the differences in viscosities with respect to the alkali concentration and the natures of additives reveals differences in the reaction mechanisms and kinetics. This result may explain the different thermal behaviors. K<sup>6</sup>-based pastes have very rapid reactions

with the lowest setting times, which could translate into a kinetically driven reaction. On the other hand, K<sup>5</sup> has the slowest reactions, probably due to a thermodynamic mechanism.

### 3.3 Mechanical properties

The maximum compressive strengths ( $\sigma_{\max}$ ) of the 10 mixtures are reported in Figure 2 (b). All samples were observed to behave similarly when compressed, and the compressive strength curves (Figure 2 (a)) exhibited the linear variation characteristic of an elastic regime and the brittle behavior of ceramic materials [3]. K<sup>6</sup>M5 BC shows a compression strength of 47 MPa at room temperature, which is greater than that of the other K<sup>6</sup>M5-based geopolymers (38, 37 and 38 MPa for the SCD-, BCD- and SBCD-added K<sup>6</sup>M5 mixtures, respectively). On the other hand, K<sup>5</sup>M5 samples at room temperature have similar mechanical strengths of 46, 45, 50 and 37 MPa for BC-, SCD-, BCD- and SBCD-added geopolymers, respectively. Considering the error, the addition of fillers does not seem to affect the mechanical properties. However, the effect of the different potassium concentrations on the two silicate solutions is noticeable, as K<sup>5</sup> samples (Si/Al = 1.84) show greater average values than K<sup>6</sup> samples (Si/Al = 1.74) with regard to the compressive strength (44 and 40 MPa, respectively). A high potassium concentration induces the rapid formation of a metastable network, while a low potassium concentration yields the possibility of obtaining a better speciation equilibrium, which leads to a more polymerized network. Both data are in agreement with the higher mechanical properties of the K<sup>5</sup>-based samples, which are also due to the measured Si/Al = 1.84 [32,33]. Changing the ratio of the fillers of the K<sup>5</sup>M5 SBCD geopolymer seems to enhance its mechanical properties. These samples ((SB)/(CD) and (S/B)CD) show the same value of 55 MPa, which is greater than that of the reference (37 MPa for K<sup>5</sup>M5 SBCD). This phenomenon can be explained by an increase in the granular skeleton [34] that occurs when the ratios between sands and carbonates change. First, the addition of more fillers with lower granulometries, i.e., calcite and dolomite ( $D_{50} = 14$  and  $2 \mu\text{m}$ , respectively), in the (SB)/(CD)

sample leads to favored packaging, where grains can more efficiently fill the voids [16]. Second, the increased content of blansil in (S/B)CD modifies the speciation equilibrium. These compounds display a lower natural pH, favoring the dissolution of metakaolin and increasing their mechanical properties [35]. After thermal treatment at 1000 °C, all samples show a slight decrease in their mechanical properties, probably due to the formation of microcracks or geometrical distortions that occurred during heating. The strength value of the K<sup>6</sup>M5 BC sample dropped from 47 MPa at room temperature to 27 MPa after treatment, while the mechanical strengths of untreated and treated K<sup>5</sup>M5 BC were 46 MPa to 44 MPa, respectively. After heat treatment, the mechanical properties decreased by an average of 15%, showing 47 and 50 MPa for (SB)/(CD) and (S/B)CD, respectively, which were still greater than those of the previous samples. At high temperature (> 800 °C), the carbonates, both calcite and dolomite, present in the geopolymer formulations decompose, releasing Ca<sup>2+</sup> and Mg<sup>2+</sup> ions. These species can combine with the amorphous phase of the geopolymer to form wollastonite (CaSiO<sub>3</sub>), as discussed in section 3.4, which enhances thermal stability [19,20,21]. The differences between the K<sup>6</sup>M5- and K<sup>5</sup>M5-based samples after heat treatment are associated with the potassium concentrations of the samples. Higher concentrations indicate lower thermal stabilities, probably due to the crystallization of metastable phases, confirmed by the following diffraction data. A slight positive trend in the overall compressive strength, measured both at room temperature and after heating, is noticeable, meaning that first changing the potassium concentration of the solution from 6 to 5 mol/l and then adding more carbonates to the mixture from 15 to 21.5% wt., is a good approach for improving mechanical properties. The evolutions of geopolymer densities after heating are presented in Figure 2 (c). It can be seen that the ratios between densities measured after ( $\rho$ ) and before ( $\rho_0$ ) heat treatment of all samples are approximately 1, which indicates that there are no noticeable density differences between samples. The differences between K<sup>6</sup>- and K<sup>5</sup>-based geopolymers

can be explained by the content of potassium, which can lead to different consolidation mechanisms, as discussed in the viscosity section, and consequently different physical properties.

Figure 3 shows a comparison of the different environments, relative humidities and total times, of exposure of the K<sup>5</sup>M5 (S/B)CD samples, with  $\sigma_{HT}/\sigma_{RT}$  ratio values. The mechanical properties seem to not differ from those of the K<sup>5</sup>M5 (S/B)CD geopolymer obtained by the standard method. All samples, regardless of their exposure to different conditions, present similar compression stress values before and after heating, with the exception of samples cured for 7 days in air at room conditions, of which the mechanical properties increase by approximately 16% after heating at 1000 °C, from 49 MPa at room temperature to 57 MPa; but considering the errors, this is negligible. Changing filler ratios could mean changing the granular skeleton, which can lead to different mechanical properties regardless of post-curing conditions.

### 3.4 Structural data

X-ray investigation is carried out for the 10 K<sup>6</sup>M5-, K<sup>5</sup>M5-based geopolymers and for the four K<sup>5</sup>M5 (S/B)CD samples exposed to different conditions at room temperature and after heat treatment to underline the structural variations resulting from the temperature treatment and the different phases presented. The XRD pattern of the K<sup>6</sup>M5 SBCD geopolymer before heat treatment (Figure 4 (a)) shows a typical amorphous structure, visible from 20 to 40° 2 $\theta$ , of geopolymers. Some of the crystalline phases of the fillers and impurities in the raw materials can be recognized, such as quartz, rutile, orthoclase, calcite and dolomite. After treatment at 1000 °C (Figure 4 (a')), quartz is still present as a majority component, and wollastonite, leucite and kalsilite can be noted as new phases. Calcite and dolomite are no longer observed because their decomposition occurs between 500 and 800 °C [20]. The availability of calcium ions, which react with the silica present in the amorphous phase, leads

to the formation of wollastonite ( $\text{CaSiO}_3$ ), as highlighted by previous works [19,20]. The formation of leucite ( $\text{KAlSi}_2\text{O}_6$ ) and kalsilite ( $\text{KAlSiO}_4$ ) at high temperature in the silica-rich K-based geopolymers was previously evidenced [10]. The change in the concentration of the potassium solution with similar fillers induces the same behavior (Figure 4 (b)). Nevertheless, in  $\text{K}^5\text{M5}$  SBCD after heat treatment (Figure 4 (b')), the kalsilite phase disappears. For all samples, this same behavior was evidenced. In the same way, the diffractograms of  $\text{K}^5\text{M5}$  (S/B)CD samples exposed to different conditions showed the formation of the same phases (leucite) (see supplementary file).

To understand the difference between the two geopolymers, viscosity data are observed. In fact, different behaviors can be deduced:  $\text{K}^6\text{M5}$  formulations show quicker reactions and the presence of kalsilite, which corresponds to a kinetic behavior, and  $\text{K}^5\text{M5}$  ones show slower reactions, which suggests a thermodynamic behavior. As already stated by Z. Yi [36], leucite is a more thermodynamically stable crystalline phase than kalsilite, which could explain the lower mechanical properties after heat treatment for  $\text{K}^6\text{M5}$  geopolymers compared to  $\text{K}^5\text{M5}$  geopolymers. This phenomenon can be linked to some differences in the local geopolymeric network. The investigation and understanding of different behaviors and reactions between the geopolymers analyzed in this study will be investigated in future work.

#### **4. Conclusion**

This work aims to investigate the possibility of producing a geopolymer with enhanced fire-resistant properties. The optimization of its formulation was carried out with the use of additives of different natures, sands and carbonates. For this purpose, 10 mixtures, 4 based on  $\text{K}^6$  solution and 6 on  $\text{K}^5$  solution, were chosen out of the initial formulations as the most thermally stable. The characterization of these geopolymers by viscosity analysis, mechanical tests and XRD underlined two different behaviors. More specifically:

- i. Samples based on a high potassium concentration ( $K^6$ ,  $[K] = 6 \text{ mol/l}$ ) show quicker reactions and the presence of kalsilite after heat treatment, which can be explained by the kinetic behavior of geopolymerization, leading to poor mechanical properties.
- ii. Mixtures with lower potassium concentrations ( $K^5$ ,  $[K] = 5 \text{ mol/l}$ ) exhibit slower reactions, which implies thermodynamic behavior during geopolymerization. Moreover, the absence of kalsilite in the heated samples prevents distortions of the local geopolymeric network, giving greater overall mechanical characteristics.

Moreover, it was possible to understand the influences of additives and their combinations. In particular, the addition of a combination of all of the experimental fillers increased the consolidation time, enhancing the mechanical properties before and after heat treatment.

The different reaction behaviors of the two geopolymer binders will be further analyzed in future works focused on in situ thermal and infrared techniques.

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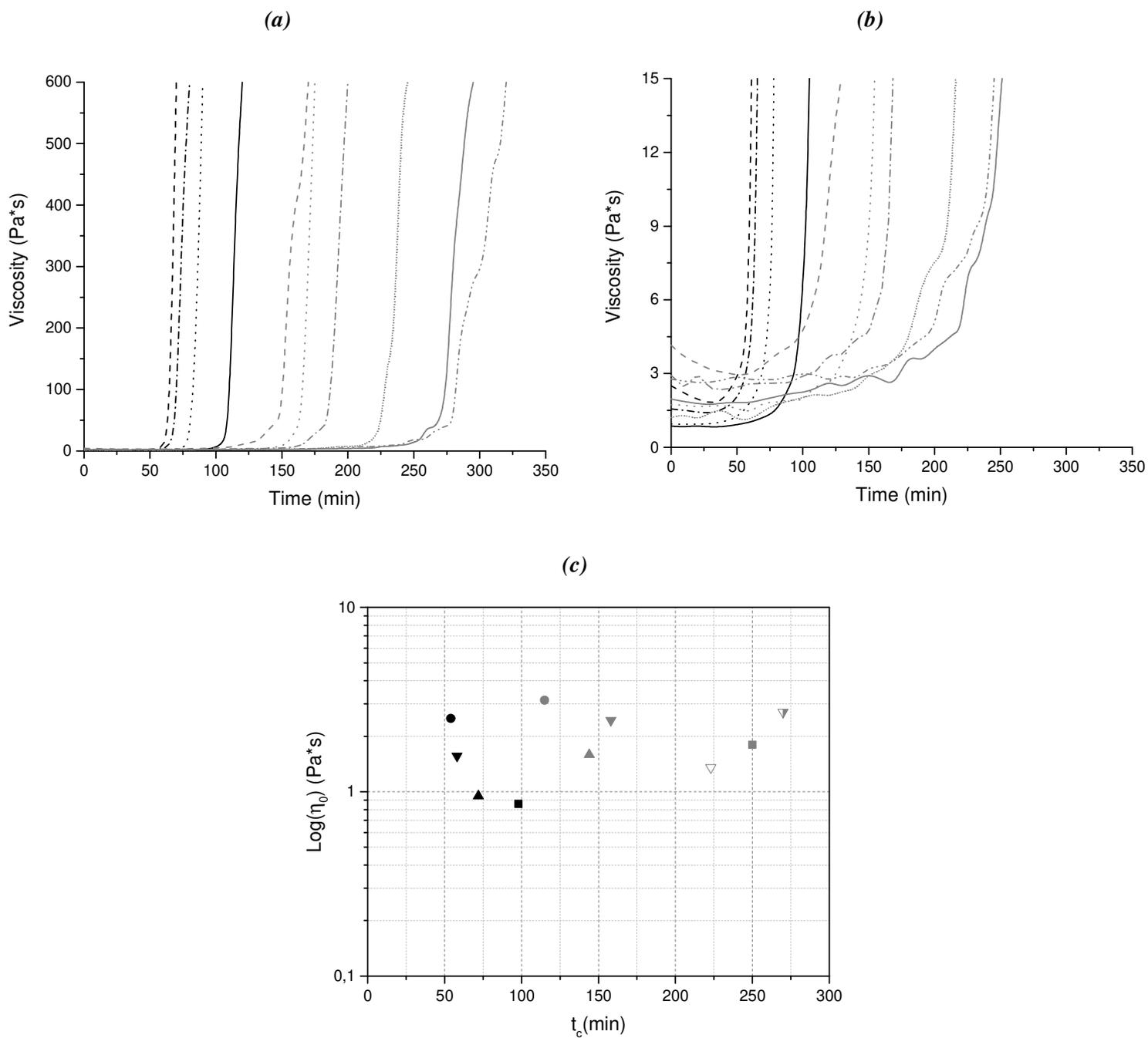
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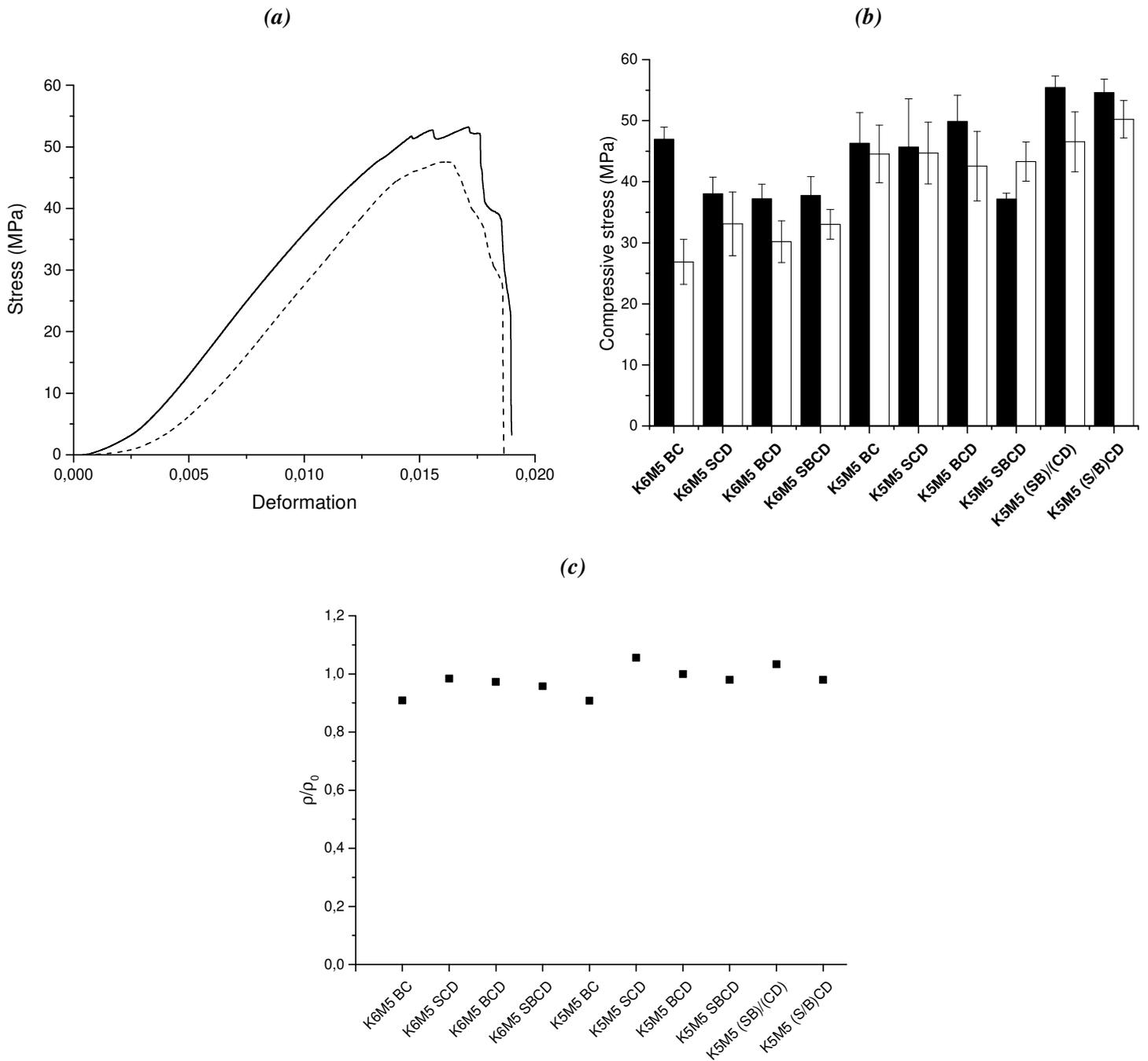
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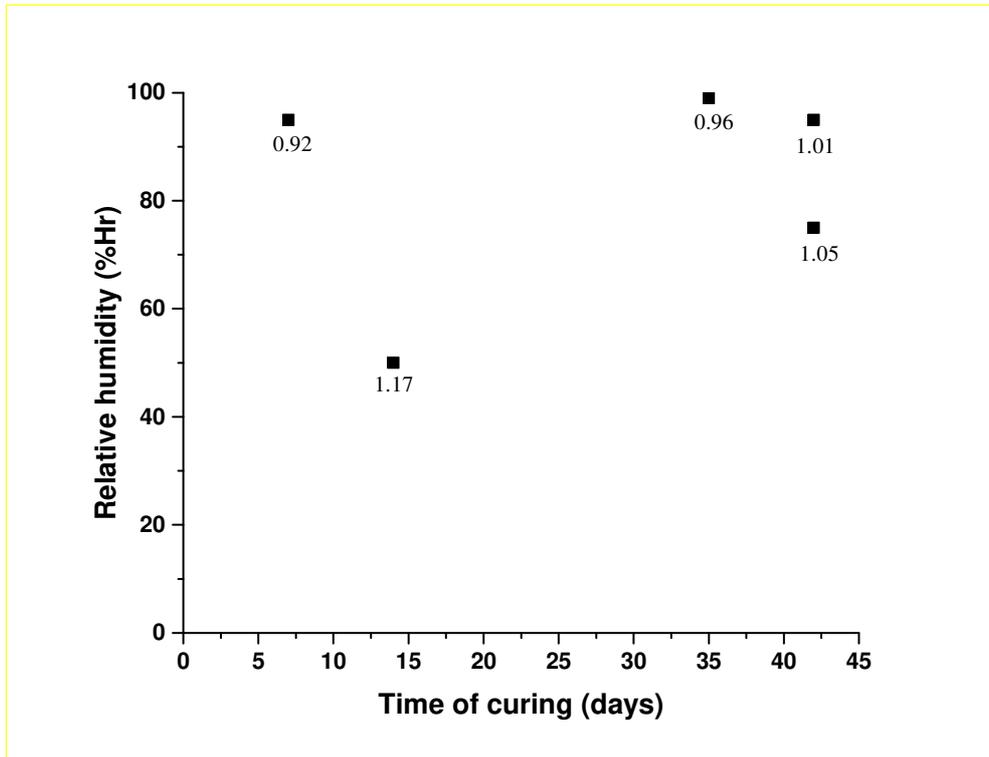
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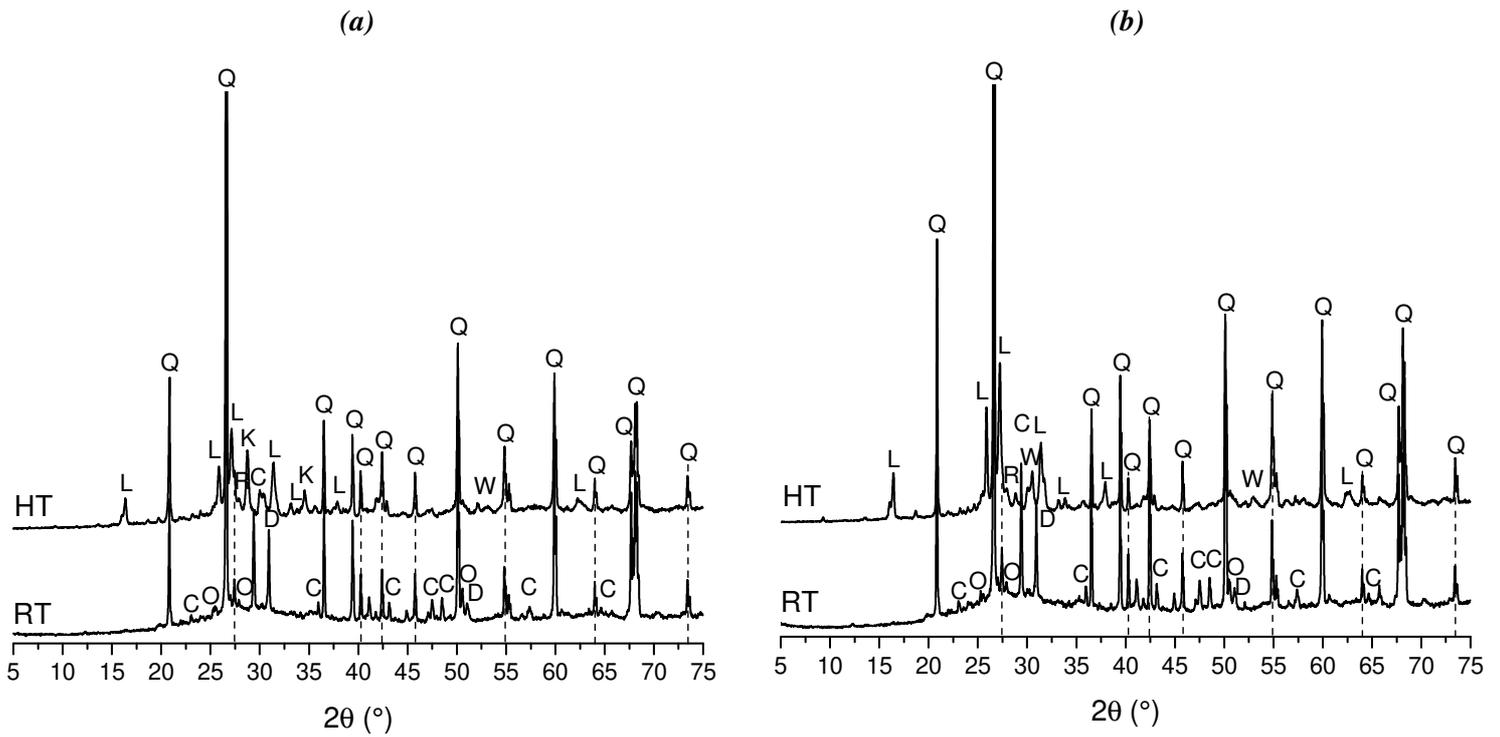
**Figure 1:** (a) viscosity evolution over time, (b) reaction enlargement and (c) initial viscosity ( $\eta_0$ ) and starting consolidation time ( $t_c$ ) in black K<sup>6</sup>M5, in grey K<sup>5</sup>M5 mixtures: (■,—) BC, (●, - - -) SCD, (▲, . . .) BCD, (▼, -.-) SBCD, (▽, -.-) (SB)/(CD), (▽, ...) (S/B)CD.



**Figure 2:** (a) loading profile of the  $K^5M5 (S/B)CD$  sample before (—) and after (---) heat treatment; (b) maximum compressive stress for the 10 mixtures after 7 days at room temperature (■) and after heat treatment (□) and (c) values of density ratio for the 10 mixtures before ( $\rho_0$ ) and after ( $\rho$ ) heat treatment.



**Figure 3:** relative humidity as function of total time of curing, numbers represent ratios between maximum compressing stress before and after heat treatment ( $\sigma_{HT}/\sigma_{RT}$ ) for K<sup>5</sup>M5 (S/B)CD samples cured in different conditions.



**Figure 4:** XRD patterns before (RT) and after firing at 1000°C (HT) of (a) K<sup>6</sup>M<sup>5</sup> SBCD and (b) K<sup>5</sup>M<sup>5</sup> SBCD samples: Q (quartz PDF 01-070-3755), R (rutile PDF 04-003-0648), O (orthoclase PDF 01-075-1592), C (calcite PDF 01-086-2334), D (dolomite PDF 00-036-0426) W (wollastonite PDF 00-043-1460), L (leucite PDF 04-013-2099) and K (kalsilite PDF 04-013-2099).

**Table 1:** weight percentages referred to the mass of M5 metakaolin of fillers used in the 10 geopolymer formulations.

| <i>Sample</i>                    | <b>Feldspar<br/>% wt. M5</b> | <b>Sablon<br/>% wt. M5</b> | <b>Blansil<br/>% wt. M5</b> | <b>Calcite<br/>% wt. M5</b> | <b>Dolomite<br/>% wt. M5</b> |
|----------------------------------|------------------------------|----------------------------|-----------------------------|-----------------------------|------------------------------|
| <i>K<sup>6</sup>M5 BC</i>        | 10                           | 0                          | 35                          | 15                          | 0                            |
| <i>K<sup>6</sup>M5 SCD</i>       | 10                           | 35                         | 0                           | 7.5                         | 7.5                          |
| <i>K<sup>6</sup>M5 BCD</i>       | 10                           | 0                          | 35                          | 7.5                         | 7.5                          |
| <i>K<sup>6</sup>M5 SBCD</i>      | 10                           | 17.5                       | 17.5                        | 7.5                         | 7.5                          |
| <i>K<sup>5</sup>M5 BC</i>        | 10                           | 0                          | 35                          | 15                          | 0                            |
| <i>K<sup>5</sup>M5 SCD</i>       | 10                           | 35                         | 0                           | 7.5                         | 7.5                          |
| <i>K<sup>5</sup>M5 BCD</i>       | 10                           | 0                          | 35                          | 7.5                         | 7.5                          |
| <i>K<sup>5</sup>M5 SBCD</i>      | 10                           | 17.5                       | 17.5                        | 7.5                         | 7.5                          |
| <i>K<sup>5</sup>M5 (SB)/(CD)</i> | 10                           | 14.25                      | 14.25                       | 10.75                       | 10.75                        |
| <i>K<sup>5</sup>M5 (S/B)CD</i>   | 10                           | 8.75                       | 26.25                       | 7.5                         | 7.5                          |

**Table 2:** picture of samples ( $\varnothing= 28.50$  mm) of the selected mixtures before and after heating.

|                  | <b>K<sup>6</sup>M5</b>  |   | <b>K<sup>5</sup>M5</b>   |   |
|------------------|---|---|--|---|
|                  | <b>RT</b>   | <b>HT</b>   | <b>RT</b>  | <b>HT</b>   |
| <b>BC</b>        |  |  |    |    |
| <b>SCD</b>       |  |  |    |    |
| <b>BCD</b>       |  |  |    |    |
| <b>SBCD</b>      |  |  |    |    |
| <b>(SB)/(CD)</b> | -   | -   |    |    |
| <b>(S/B)CD</b>   | -   | -   |  |  |

