



HAL
open science

Comparative study of the various methods of preparation of silicate solution and its effect on the geopolymerization reaction

N. Essaidi, L. Laou, S. Yotte, L. Ulmet, S. Rossignol

► To cite this version:

N. Essaidi, L. Laou, S. Yotte, L. Ulmet, S. Rossignol. Comparative study of the various methods of preparation of silicate solution and its effect on the geopolymerization reaction. *Results in Physics*, 2016, 6, pp.280-287. 10.1016/j.rinp.2016.05.006 . hal-01874586

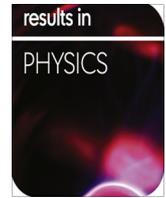
HAL Id: hal-01874586

<https://unilim.hal.science/hal-01874586>

Submitted on 14 Sep 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Comparative study of the various methods of preparation of silicate solution and its effect on the geopolymerization reaction



N. Essaidi ^a, L. Laou ^{a,b}, S. Yotte ^b, L. Ulmet ^b, S. Rossignol ^{a,*}

^a Univ Limoges, CNRS, ENSCI, SPCTS, UMR7315, F-87000 Limoges, France

^b Univ Limoges, (GEMH-GCD), Boulevard Jacques Derche, 19300 Egletons, France

ARTICLE INFO

Article history:

Received 18 May 2016

Accepted 20 May 2016

Available online 26 May 2016

Keywords:

Silicate powder

Bricks

Alkaline solution

Binders

Depolymerization

Metakaolin reactivity

ABSTRACT

This paper is based on the characterization of synthesized geopolymer binders based on either powder or solution silicate, and the amount of water contained in synthesized binders is determined to evaluate their possibility to coat a brick. The structural evolution of the formed geopolymers was investigated using FTIR spectroscopy. The mechanical properties were evaluated using compression tests. The structural evolution ensured that the solutions prepared from silicate powder or liquid had different degrees of polymerization, which modified the polycondensation reaction of the mixture. Nevertheless, the use of aluminosilicate solutions based on powder or liquid display similar behavior in a polycondensation reaction. The obtained materials show good mechanical properties, and it is possible to deposit this binder on the brick depending on the water content.

© 2016 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Introduction

The building and construction sectors have been identified among the major contributors to a global environmental impact owing to their high energy consumption [1,2]. This sector accounts for approximately 40% of total energy consumption and 38% of CO₂ emissions. Hence, it is necessary to adopt a global approach in this industry for material and building lifecycles and create this approach with a sustainable development perspective. Thus, the development of new composite materials called eco-materials that are composed of earth bricks, wooden frames and geopolymer binders can be considered as a constructive solution [3]. The idea of assembly with wood and earth bricks is used in many existing structures for construction systems owing to their good mechanical properties and the light weight of wood. Earth bricks also provide thermal inertia and stored moisture despite the cracks that may appear at the interface [4]. To inhibit crack formation, an inorganic mineral mortar, such as a geopolymer binder, can also be used because of its ecological properties [5] with respect to this type of structure. Indeed, a preliminary study on a porous geopolymer binder developed in the laboratory showed the ability of the binder to adhere to both wood and earth [6].

This new class of material called geopolymer binder features ill-organized, three-dimensional materials that result from the

activation of an aluminosilicate source using an alkaline solution. Many investigations have used common clays [7,8] and industrial waste as raw materials [9,10]. Among these materials, metakaolin is the most commonly used because it is the cheapest aluminosilicate with a good degree of purity and high reactivity [11]. The existing literature [12] has proved that through the dehydroxylation process, the effect of impurities is considered an indicator of metakaolin reactivity. Further, the activating solution is a critical parameter because it governs the reaction kinetics and the working properties of the final materials. In fact, it was demonstrated that the initial Si/M molar ratio of the silicate solution controls the nature and the quantity of the siliceous species; when the Si/M ratio decreases, the solution contains more depolymerized silicate species such as Q⁰ and Q¹ with the presence of a higher number of non-bridging oxygen atoms [13], inducing different reactivities. There are different methods to synthesize these silicate solutions. Autef et al. [14] prepared their solutions in laboratory by dissolution of amorphous silica in an alkali solution. Gharzouni et al. [15] used commercial solutions with different initial Si/K molar ratios. They demonstrated that the differences in terms of siliceous species and the degree of depolymerization between silicate solutions will induce different reactivities. However, great attention is given to the Na-geopolymers because they present different properties depending on the aluminosilicate source and the used solution [16]. The difference in the behavior between geopolymers based on K or Na can be related to the characteristics of the alkali solution. Thus, some works have related the use of Na and K as

* Corresponding author. Tel.: +33 5 87 50 25 64.

E-mail address: sylvie.rossignol@unilim.fr (S. Rossignol).

alkaline solutions [17]. In fact, some publications have addressed the comparison between sodium and potassium solutions. A molecular dynamics study [18] of the interaction of oxygen molecules and oxygen diffusivity in NaOH and KOH at different temperatures and concentrations highlighted that the diffusion coefficients for hydroxide Na^+ and K^+ decrease with increasing solute concentration. However, it is important to remember that the diffusion coefficient of oxygen in NaOH solutions is smaller than that in the corresponding KOH solutions at all concentrations. The common point in all of these works is that they use silicate in solution form, and few formulations with silicate powder are made. However, the use of liquid solutions requires drastic storage conditions [5]. As an alternative, the use of mixtures based on powders with only the addition of water will be considered. In this context, the use of powder-based mixtures seems to be easier to carry out in the samples. The use of silicate powder is rare despite the advantages of powder silicates, including its low price and ease of utilization [19]. Thus, it would be very interesting to conduct a work involving powder or liquid to understand the mobility of species in solution and control the Si/Na molar ratio.

Various reports have demonstrated that the solution preparation method has an impact on silicate species [20]. The authors [12,21] have shown that for the same Si/M ratio, a commercial silicate solution in which KOH pellets were dissolved and a laboratory solution result in the same silicate species in different amounts. For example, the decomposition of Raman spectra [22] of laboratory and commercial solutions with a Si/M ratio of 0.7 result in the same contributions but a different intensity. Brykov et al. [23] showed that the preparation of the solution has little influence on the connectivity of the silicon atoms compared with the solutions provided by dissolving a colloidal silica or a glass. It is suggested that commercial silicate solutions and laboratory-made solutions present differences in reactivity. A study based on various solutions with different cations and Si/M ratios by spectroscopy investigations (FTIR, Raman and NMR) has been conducted by Vidal et al. [24]. This work has demonstrated that the manufacturing process causes a slight variation in the amounts of the different silicate species responsible for the reactivity of the solution. In the same way, it has shown [25] that the nature of the silica introduced and its reactivity have an influence on the viscosity of formed binder. Consequently, the nature of the solution plays a significant role in the final material.

The aim of this study is to synthesize geopolymer materials based on powdered silicate from two different metakaolins and compare them with those synthesized based on commercial silicates. These formulations were analyzed by FTIR spectroscopy and a compressive mechanical test to investigate their later use as deposits on earth bricks.

Experimental part

Raw materials and sample preparation

Before preparing the geo-materials, the alkaline solution is synthesized from a mixture of silicate (powder (P) or liquid (L)), NaOH pellets (97% purity) and water to obtain a solution with a Si/M ratio equal to 0.7. The characteristics of the formed solutions are reported in Table 1. The metakaolins M1 ($\text{SiO}_2 = 55\%$, $\text{Al}_2\text{O}_3 = 40\%$) and M2 ($\text{SiO}_2 = 55\%$, $\text{Al}_2\text{O}_3 = 39\%$) are then added as described in Fig. 1. These two metakaolins are prepared differently: M2 is flash-calcined, whereas M1 is calcined in rotary furnace. The difference in the calcination method of these kaolins induces varying reactivity in the geopolymer reactions [26]. After stirring for 15 min at 700 rpm, the reactive mixture was placed in a sealed polystyrene mold at ambient temperature for 24 h to complete

Table 1
Characteristic of different solutions.

Samples	Chemical compositions			pH values
	% SiO_2	% H_2O	% Na_2O	
$\text{P}_{0.7}^{1.70}$	27.5	64.2	8.3	14
$\text{L}_{0.7}^{1.70}$	27.5	64.2	8.3	14
$\text{L}_{0.7}^{1.29}$	31.8	55.5	12.7	14

the polycondensation reaction. The samples were then stored for 7 days and then demolded. Owing to the high reactivity of M2, some water must be added to the mixtures [24]. Throughout the entire study, synthesized geopolymers will be denoted according to the MxW_z^y nomenclature; Mx represents the type of used metakaolin (M1 or M2), W is the type of alkaline silicate (P: powder, L: liquid), and z and y represent the initial and final Si/Na ratios, respectively. For example, $\text{M1 L}_{0.7}^{1.7}$ was synthesized based on M1 metakaolin and a silicate/sodium solution ratio Si/Na = 1.7. Different compositions with varying Si/Na values are summarized in Table 2.

Technical characterization

Fourier transform infrared (FTIR) spectroscopy in ATR mode was used to investigate the structural evolution of the geopolymer mixtures. The FTIR spectra were obtained using a Thermo Fisher Scientific 380 infrared spectrometer (Nicolet). A drop of the geopolymer reactant mixture was deposited onto the instrument's diamond crystal and protected with a small bell from any environmental pollution during the spectrum acquisition process, which was performed regularly until the end of the geopolymerization process. The IR spectra were gathered over a wavenumber range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . The atmospheric CO_2 contribution was removed with a straight line between 2400 and 2280 cm^{-1} . To follow the evolution of the involved bonds within the sample in time, a macro was used to acquire a spectrum every 10 min for 7 h, producing 64 scans in total. To allow comparisons of the various spectra, the spectra were baseline-corrected and then normalized.

The pH values were measured with using a Schott Instruments Lab860 pH-meter at $25\text{ }^\circ\text{C}$ for 2500 min. The samples in pellet form were placed in tubes (O : 35 mm and H: 70 mm) and covered with water to maintain the ratio of geopolymer weight to water weight equal to 0.08 ($m_{\text{geo}}/m_{\text{water}} = 0.08$) for each measurement. At the

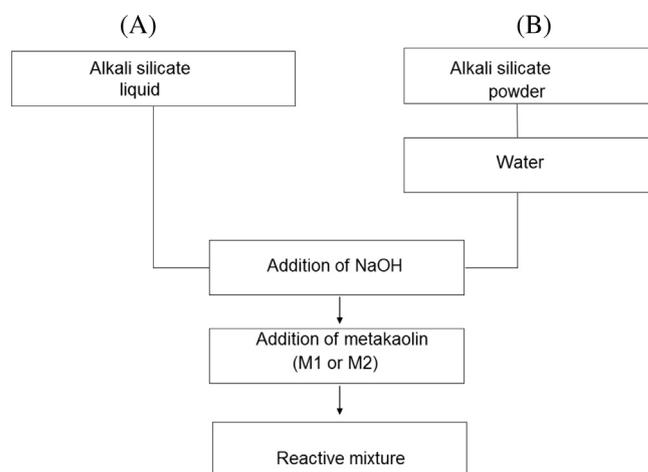


Fig. 1. Synthesis protocol of geo-materials (A) liquid and (B) powder silicate.

Table 2
Nomenclature and composition of different formulations.

Precursors			Samples	
Metakaolin M1 or M2 (g)	Silicate solution (g)	NaOH (g)		
12	L _{0.7} ^{1.29}	15.00 (L)	2.01	M1 L _{0.7} ^{1.70}
	L _{0.7} ^{1.29}			M1 L _{0.7} ^{1.29}
12	P _{0.7} ^{1.70}	5.37 (P)	2.37	M1 P _{0.7} ^{1.70}
	L _{0.7} ^{1.70} + 9 H ₂ O			M2 L _{0.7} ^{1.70}
	L _{0.7} ^{1.29} + 11 H ₂ O	M2 L _{0.7} ^{1.29}		
	P _{0.7} ^{1.70} + 9 H ₂ O	M2 P _{0.7} ^{1.70}		

beginning of the test, the pH measurements were taken at intervals of 1 h.

The compressive strengths were tested using a LLOYD EZ20 type universal testing machine with a crosshead speed of 0.1 mm/min. The compressive tests were performed on five samples for every composition. The compressive strength values represent the average of the five obtained values and are expressed in MPa. The test tubes used for the compression tests were cylindrical ($\Phi = 15$ mm; $h = 30$ mm) and aged for 7 days in a closed mold at room temperature.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on an SDT Q600 apparatus from TA instruments in a following dry-air atmosphere (100 mL/min) in platinum crucibles. The signals were measured with Pt/Pt-10% Rh thermocouples. The samples were heated to 1400 °C at 10 °C min⁻¹ in dry airflow.

Results and discussion

Characterization of starting alkaline solutions

The characteristics of the different synthesized alkali solutions (P_{0.7}^{1.70}, L_{0.7}^{1.70} and L_{0.7}^{1.29}) are presented in Table 1. These solutions are obtained by mixing sodium silicate solution and sodium hydroxide to obtain a final Si/Na ratio equal to 0.7. The powder P1.7 and the liquid L1.7 contain the same percentages of SiO₂, H₂O and Na₂O to compare the difference between silicate powder and liquid as a precursor. Their pH values are similar (14), demonstrating their basicity.

To determine the role and the reactivity of different alkali compounds used in the formulation of the geopolymer binder, infrared spectroscopy was performed to investigate the structure species of each solution. The infrared spectra of solutions without or with the addition of water recorded in the 700–1300 cm⁻¹ range are presented in Fig. 2. The addition of water was introduced during the preparation of geopolymer-based M2. All spectra exhibited similar contributions. The band located at 864 cm⁻¹ is attributed to the C–O bond of carbonates, and the broad bands centered at approximately 1003 cm⁻¹ (Q²) and 976 cm⁻¹ (Q¹) are ascribed to asymmetric stretching vibrations characteristic of Si–O–Si (Q²) and Si–O–Si (Q¹), respectively, as introduced by Engelhard et al. [27]. The shoulder observed at 1100 cm⁻¹ was attributed to Q³ species. The Q¹/Q² ratio gives qualitative information about the degree of polymerization of solution [24]. The calculated ratio and silicon concentration (0.81, 5.94), (0.84, 4.7) and (0.73, 8.02) for L_{0.7}^{1.70}, P_{0.7}^{1.70} and L_{0.7}^{1.29}, respectively, are plotted in Fig. 3. A higher Q¹/Q² ratio implies a higher amount of depolymerized species depending on the silicon content in the solution [26]. To exacerbate this phenomenon, the NBO values [28] determined from ²⁹Si NMR investigation on these solutions are plotted as a function of the [M⁺] concentration. In effect, the alkaline cation induces the formation of non-bridging oxygen atom as a function of the Si/M ratio, the nature of the alkaline and the preparation mode [21]. The variation

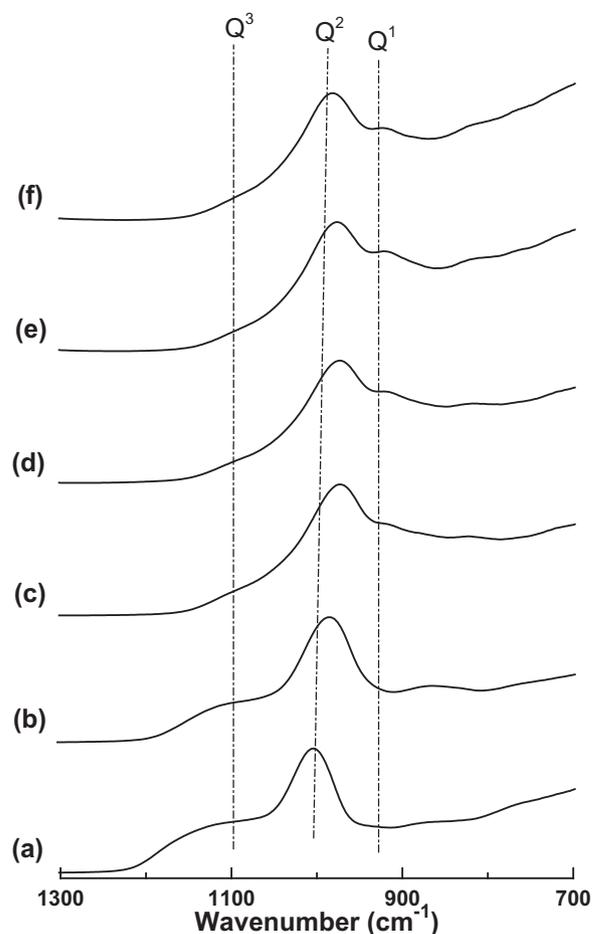


Fig. 2. In situ infrared spectra of solutions (a) L_{0.7}^{1.70}, (b) L_{0.7}^{1.70} + 9% H₂O, (c) L_{0.7}^{1.29}, (d) L_{0.7}^{1.29} + 11% H₂O, (e) P_{0.7}^{1.70} and (f) P_{0.7}^{1.70} + 9% H₂O.

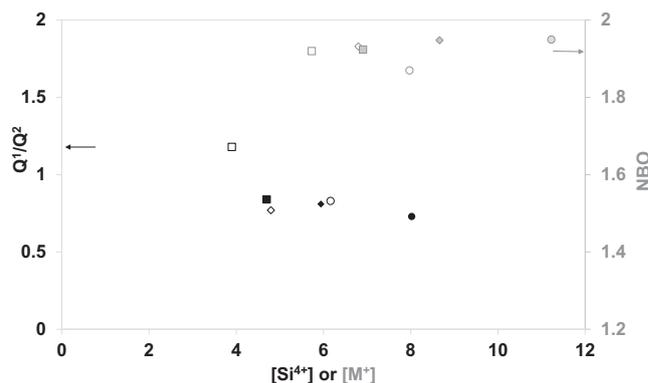


Fig. 3. Evolution of [Si⁴⁺] versus Q¹/Q² ratio and [M⁺] versus NBO for different solutions (◆) L_{0.7}^{1.70}, (◇) L_{0.7}^{1.70} + 9% H₂O, (●) L_{0.7}^{1.29}, (○) L_{0.7}^{1.29} + 11% H₂O, (■) P_{0.7}^{1.70} and (□) P_{0.7}^{1.70} + 9% H₂O.

reveals that the solution based on P_{0.7}^{1.70} displays the lowest NBO owing to the presence of cyclic species in relation of the dissolution of the silicate powder. The NBOs of the other solutions are also in agreement with the work of Gharzouni et al. [29]. Consequently, for the same initial Si/M molar ratio, the P_{0.7}^{1.70} solution contains more cyclic or chain species, and the two liquid solutions (L_{0.7}^{1.70}, L_{0.7}^{1.29}) appear to be more depolymerized [23]. It seems that the L_{0.7}^{1.70} solution is less depolymerized than L_{0.7}^{1.29} because it was shown by Vidal et al. [26] in a previous study that the decrease in initial

Si/M implies the depolymerization of the silicate species in the solution. This phenomenon is linked to the formation of cyclic species. The effect of water addition on the alkaline silicate solutions was studied owing to the geopolymer binder formulation, notably in the presence of M2 metakaolin. Regardless of the alkaline solution, the addition of water induced a modification of the NBO value and the Q^1/Q^2 ratio. This effect is in agreement with the speciation equilibrium [30]. The addition of water leads to a slight polymerization of the solutions with the presence of more cyclic or chain species. The weak modification in the case of $P_{0.7}^{1.7}$ can be correlated to the presence of certain cyclic entities, minimizing the polymerization effect.

When the percentage of water contained in the solution increases, the Q^1/Q^2 ratio decreases and the NBO value increases, which demonstrates that the addition of water induces the polymerization of the solutions. In effect, previous studies have shown that the presence of various species in silicate solutions depends on several parameters such as the Si/M molar ratio, the dilution rate and the alkaline cation [31,32]. These parameters determine the presence of the silicate species responsible for the silicate solution specification. The silicon and alkaline concentrations control the silicate species in the silicate solutions.

Binder composition

In situ FTIR spectroscopy

The spectra presented in Fig. 4 were recorded for the consolidated materials synthesized from different studied solutions of

Si/Na = 0.7 in the presence of M1. The M2 binders are not given because they present the same data. Only their interpretations are provided. The spectra of only M1 $P_{0.7}^{1.7}$ and M1 $L_{0.7}^{1.7}$ are presented. In the presence of metakaolin M1, for all recorded spectra, at $t = 0$ min, the bands on the spectra at 3300 cm^{-1} and 1620 cm^{-1} are attributed to the Si—O—H bond and the water, respectively [33]. Their intensities gradually diminished with time, owing to the water consumption during polycondensation reactions. The bands located in the $1100\text{--}950\text{ cm}^{-1}$ range are generally attributed to Si—O—R⁺ present in the aluminosilicate compounds (with R⁺ = Si, Al, K) [34]. The decrease in the OH band intensity with increasing curing time and the displacement of the Si—O—R⁺ band are characteristic of the formation of consolidated materials. The bands located at 1420 cm^{-1} were attributed to the C—O bond owing to the presence of some carbonates. The formed carbonates can be explained by the low reactivity of M1 in the alkaline solution. The two mixtures M1 $P_{0.7}^{1.7}$ and M1 $L_{0.7}^{1.7}$ exhibited the same contributions (Si—O—H, C—O and Si—O—M⁺). A displacement in the position of silicate species to a lower wavenumber was observed, owing to the reaction between the siliceous and aluminous species. These data reveal that the reactivity of the alkaline solution has a crucial role to promote polycondensation reactions. This will be verified later by different characterizations of formulations.

Fig. 5 shows the Si—O—M (980 cm^{-1}) shift as a function of time for different mixtures, indicating the substitution of Si—O—Si by Si—O—Al bonds, reflecting the reorganization of the network. In addition, the slope of the curve at the beginning of the reaction is characteristic of the kinetics of this substitution. The

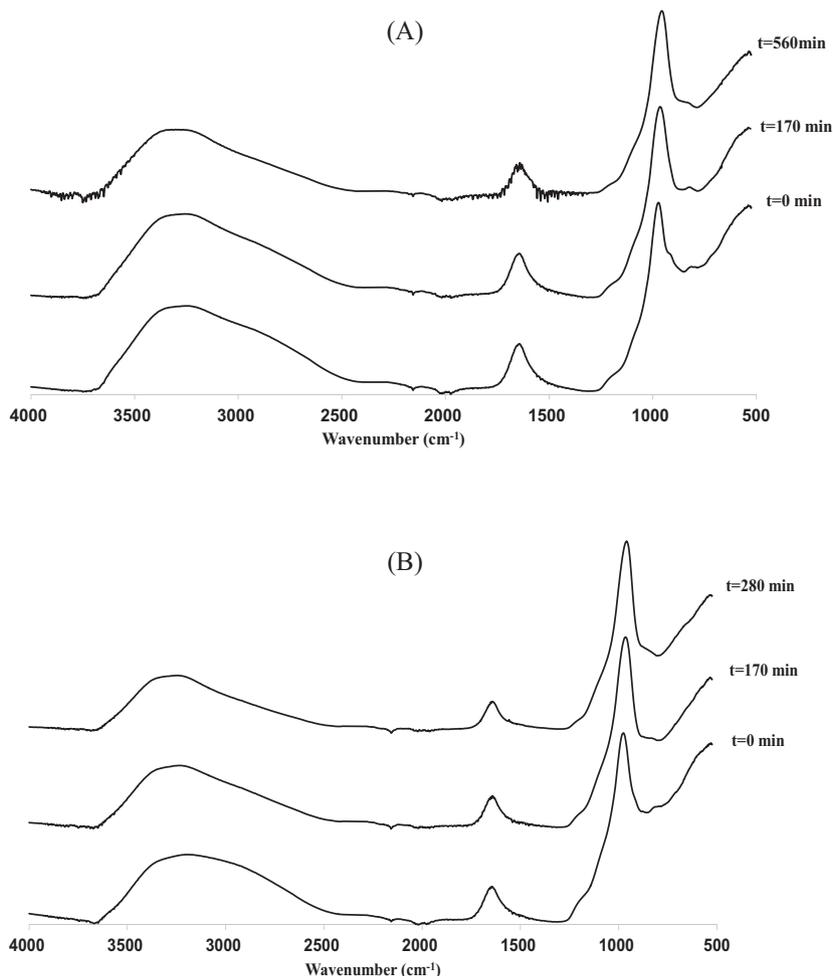


Fig. 4. In situ infrared spectra of compositions (A) M1 $L_{0.7}^{1.7}$ and (B) MP $L_{0.7}^{1.7}$ samples.

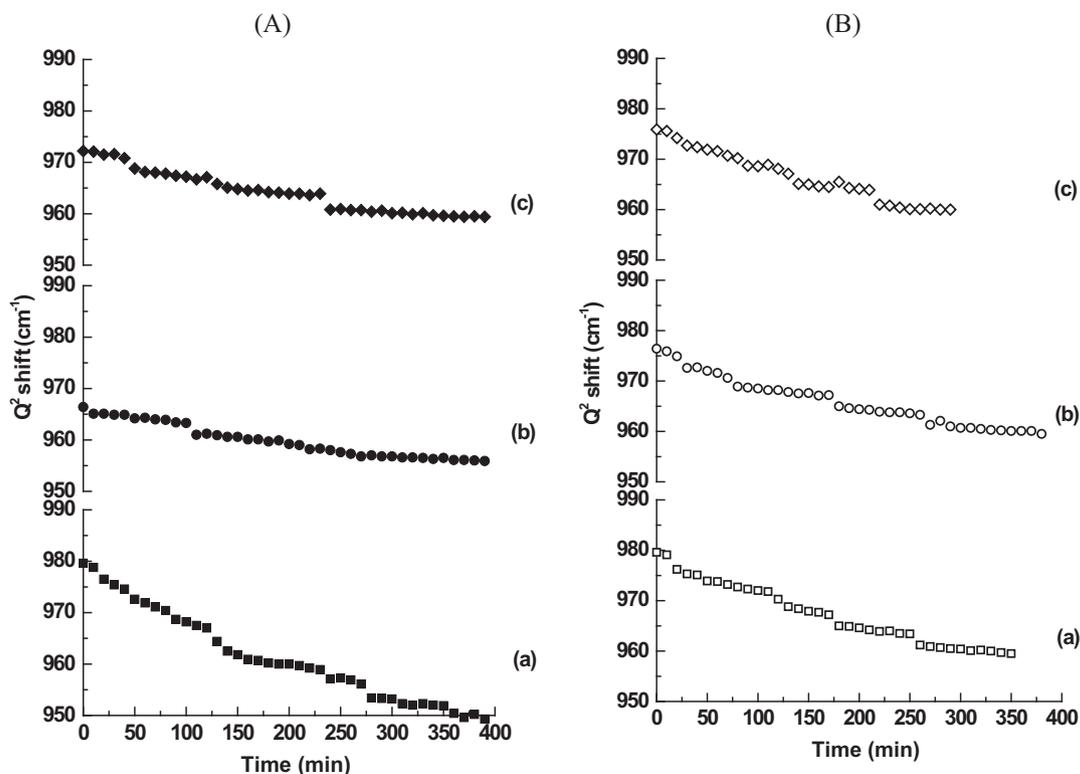


Fig. 5. Evolution of the band Si—O—R⁺ as function of the time during polycondensation reaction for (A) (a) ■ M1P L_{0.7}^{1.7}, (b) ● M1 L_{0.7}^{1.29}, (c) ◆ M1L_{0.7}^{1.7} and (B) (a) □ M2P L_{0.7}^{1.7}, (b) ○ M2 L_{0.7}^{1.29}, (c) ◇ M2L_{0.7}^{1.7} compositions.

displacement of the sample M1 P_{0.7}^{1.7} (Fig. 5 (a)) is approximately 30 cm⁻¹, which is considered higher than the other samples. Its initial peak position of the band Si—O—M is located at 980 cm⁻¹, which agrees with the basicity of the solution, thus leading to a lower value of Si—O—M owing to the presence of various cyclic species inducing the formation of several networks as evidenced by Autef et al. [35]. The M1 L_{0.7}^{1.29} sample was characterized by an initial position of the Si—O—M band at 966 cm⁻¹ owing to the Si/Na = 1.29 ratio of the initial solution. This ratio induces a reaction medium rich in non-bridging oxygen atoms (NBO ≈ 1.8), promoting depolymerization of the species in solution and consequently the formation of Si—O—M bonds during metakaolin addition [36], leading in this case to few local networks [37]. Furthermore, the displacement value of the samples M1 L_{0.7}^{1.7} and M1 L_{0.7}^{1.29} (Fig. 5 (b)) are similar (17 cm⁻¹). This similarity in displacement values can be linked to the different initial ratio Si/M = 0.7. The position of this band is directly correlated to the number of bridging oxygen atoms [29].

Given these data, the identical NBO value is responsible for this effect, in agreement with the control by the alkaline solution in this range of reactivity. The same behavior is observed in the presence of the M2 metakaolin for both solutions M2 L_{0.7}^{1.7} and M1 L_{0.7}^{1.29}. Nevertheless, a slight increase in the shift seems to appear in the presence of M2. In the presence of sodium solution, the metakaolin M1 reacts more rapidly than the M2 metakaolin. In effect, in this case, the sodium cation with a strong hydration sphere induces the polycondensation reaction with M1, owing to this low reactivity. Meanwhile, with the high M2 reactivity, it is difficult to favor one local network rather than several. This effect is not observed in the presence of the P1.7 solution because the solution contains more cyclic species, limiting the previous effect. The effect of the reactivity of metakaolin governs in this case. Moreover, in the presence of M2, the behavior is different because the value of displacement is close, owing to the reactivity of the aluminosilicate source,

which governs the reaction [31]. In this case, the use of the powder or solution has no effect.

The degree of polymerization plays a significant role in determining the structure and properties of the formed geopolymer. Consequently, the evolution of the slope obtained from the FTIR spectra as a function of the Na⁺ concentration is presented in Fig. 6. From these data, the slope values can be deduced. They are (-0.03, -0.07, -0.04, -0.08, -0.1 and -0.09 cm⁻¹/min) for (M1 L_{0.7}^{1.29}, M2 L_{0.7}^{1.29}, M1 L_{0.7}^{1.7}, M2 L_{0.7}^{1.7}, M1 P_{0.7}^{1.7} and M2 P_{0.7}^{1.7}), respectively. The synthesized P1.7 samples exhibited the lowest slope values that can be correlated to the presence of various species in this solution. The slope exhibits a linear trend versus [Na⁺], suggesting that the concentration of alkali cations influences the kinetics of the reaction. Provis et al. [14] demonstrated that the Na geopolymers exhibited an important kinetics dissolution rate.

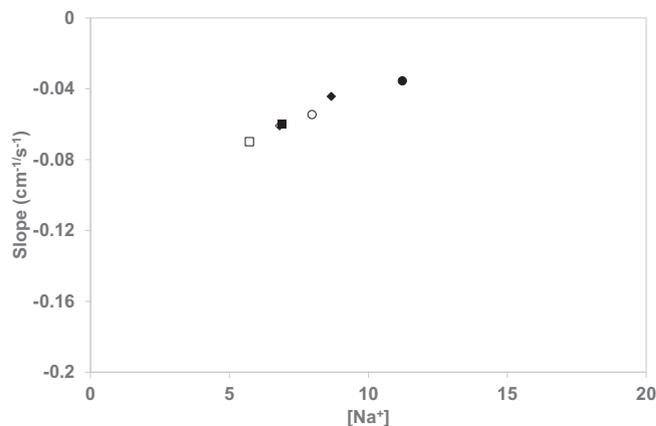


Fig. 6. Evolution of the slope value in function of the [Na⁺] for ◆ M1L_{0.7}^{1.7}, ■ M1P L_{0.7}^{1.7}, ● M1 L_{0.7}^{1.29}, ◇ M2 L_{0.7}^{1.7}, □ M2 P L_{0.7}^{1.7} and ○ M2 L_{0.7}^{1.29} compositions.

Diffusion of the Na⁺ ions ensures the formation of more reactive entities that can be combined with aluminosilicates differently for the two metakaolins. For the samples synthesized based on M1, the slope values are characteristic of the various exchanges between aluminosilicate species, whereas the kinetic reaction for samples based on M2 induces different networks. From these results, it can be concluded that they have similar behavior. Moreover, P1.7 and L1.7 display the same slope value.

Mechanical properties

To understand the influence of metakaolin reactivity on the working properties of formed materials, the values of the compressive strength corrected by the S/L ratio as a function of the $n_{Si}/(n_{Na} + n_{H_2O})$ ratio are shown in Fig. 7. A comparison between the two metakaolins shows that the compressive strength value corrected by the S/L ratio varied linearly versus the molar number ratio. As evidenced by FTIR data, the samples based on M2 display the quasi-same values, whereas with M1, the data are dispersed. This fact is certainly due to the effect of either the solution or the metakaolin. For M1 samples, S/L increases from 0.7 to 0.8 in the following order: M1 L_{0.7}^{1.29} < M1 P_{0.7}^{1.7} < M1 L_{0.7}^{1.7}. For the M2 samples, S/L seems to be constant (1.1), which corroborates the FTIR data [38,39]. The sample M1 L_{0.7}^{1.7} has the highest compressive strength value of approximately 72 ± 2 MPa. For M2 L_{0.7}^{1.7}, the compressive strength value decreases to 42 ± 2 MPa. Previous reports [40] demonstrated that M2 is more reactive than M1 in solution. However, in this case, the water added to achieve M2 modifies the mixture. As previously indicated in the characterization of starting alkaline solutions (Fig. 3), the addition of water involves the polymerization of the solution, inducing the loss of strength. Indeed, it has been shown by Wang et al. [41] that the compressive strength values increase with increasing NaOH concentration from 4 to 12 mol. L⁻¹. In our case, the [M] value is located in this range of concentration, supporting this behavior.

For the two other samples, M1 L_{0.7}^{1.29} and M2 L_{0.7}^{1.29}, the compressive strength values are approximately 36 ± 2 and 39 ± 2 MPa, respectively, which are considered similar and lower than those synthesized based on L_{0.7}^{1.7}. For these formulations, the alkaline solution governs the reaction contrary to samples based on L_{0.7}^{1.7}. This can be explained by the oligomer cycles contained in the L_{0.7}^{1.29} solution. The samples M1 P_{0.7}^{1.7} and M2 P_{0.7}^{1.7} exhibited compressive strength values of approximately 50 and 34 ± 2 MPa, respectively, which can be related to the solution reactivity, as previously

suggested for L_{0.7}^{1.7}. In this case, this property is directly linked to the behavior of the metakaolin in the presence of elemental sodium. As observed for the L_{0.7}^{1.7} solution, the P_{0.7}^{1.7} was also polymerized with or without the water addition, which involves weak reactivity in the presence of M2.

These data underline a novelty in this study, which is that a solution based on powder with a given molar ratio of Si/M is able to yield a material with behavior similar to that of the liquid solution.

Preliminary test

To understand the behavior of these binders in the presence of various supports, TGA analysis (Fig. 8) was conducted to calculate the amount of water contained in these samples. Representative TGA results for a geopolymer sample increases sharply to ~35% at 150 °C, owing to loss of free water, and then only gradually to ~37% at 600 °C owing to the loss of interstitial water, in general agreement with the observations of Perera et al. [41]. The total water contents of the samples were estimated using the data for mass loss at 600 °C. The values of water loss contained in these compositions deduced from TGA curves are presented in Table 3. The samples M1 L_{0.7}^{1.7}, M1 L_{0.7}^{1.29} and M1 P_{0.7}^{1.7} synthesized based on M1 exhibited lower weight loss (18%) than those synthesized based on M2. Their weight loss values are (24% for M2 L_{0.7}^{1.7}, 23% for M2 L_{0.7}^{1.29} and 20% for M2 P_{0.7}^{1.7}). These differences in the amount of water released can induce various distributions of the binder in the brick [42] and subsequently different interfaces. In effect, previous work in the laboratory based on the use of geopolymer binder or mortar interacting with bricks and wood demonstrate that the availability and amount of siliceous species from a mixture is a preponderant parameter influencing the nature of networks formed after consolidation [23]. Moreover, it was also suggested that increasing the amount of water released by the samples increases the internal tensions in the brick. Preliminary tests of adherence between the brick and the binder were conducted. Pictures of different binders based on M1 and M2 deposits on bricks are presented in Table 3 at the time of deposit and after 24 h. The binders based on M2 (M2 L_{0.7}^{1.7}, M2 L_{0.7}^{1.29} and M2 P_{0.7}^{1.7}) showed the presence of cracks after 24 h, whereas the other binders synthesized based on M1 (M1 L_{0.7}^{1.7}, M1 L_{0.7}^{1.29}, M1 P_{0.7}^{1.7}) exhibited adherence with the bricks. The presence of cracks may be related to interactions between the bricks and binder based on M2 owing to a delay in the polycondensation reaction that causes disruption in the setting of the binder. In this case, the use of metakaolin M1

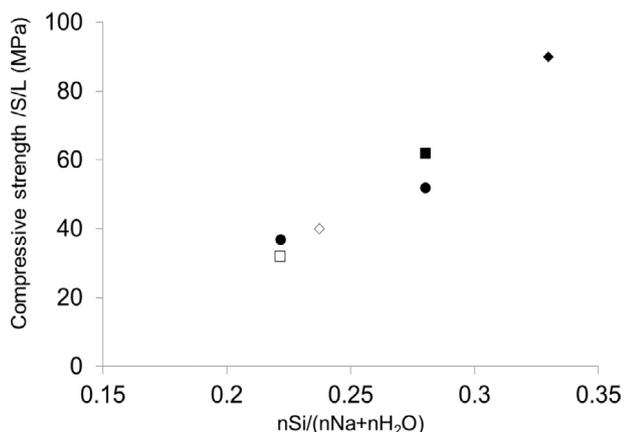


Fig. 7. Evolution of the compressive strength values corrected by the S/L ratio versus $n_{Si}/(n_{Na} + n_{H_2O})$ for ◆ M1 L_{0.7}^{1.7}, ■ M1 P_{0.7}^{1.7}, ● M2 L_{0.7}^{1.29}, ◇ M2 L_{0.7}^{1.7}, □ M2 P_{0.7}^{1.7} and ○ M2 L_{0.7}^{1.29} compositions.

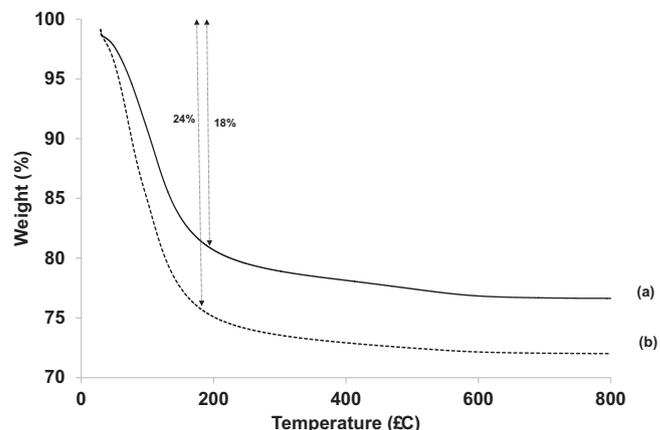
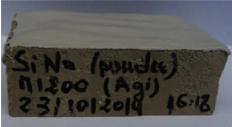
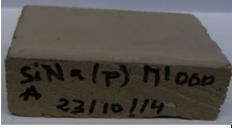


Fig. 8. TGA curves of (a) M1 L_{0.7}^{1.7} and (b) M2 L_{0.7}^{1.7}.

Table 3Deposits pictures of different geopolymer binder on brick (A) M1L_{0.7}^{1.70}, (B) M2L_{0.7}^{1.70}, (C) M1L_{0.7}^{1.29}, (D) M2L_{0.7}^{1.29}, (E) M1P_{0.7}^{1.70} and (F) M2P_{0.7}^{1.70}.

Composition	$t = 0$	$t = 24h$	Weight loss (DTA) (%)
(A)			18
(B)			24
(C)			17
(D)			23
(E)			17
(F)			20

with low reactivity must be the choice to favor the diffusion of each species between binder and brick.

According to these results, the silicate solution and powder again have almost the same behavior regardless of the metakaolin used.

Conclusion

This paper focuses on the effect of the use of powdered or silicate solution in the synthesis of geopolymer binders by studying the reactivity of two different metakaolins in the presence of these solutions. The result shows the possibility of geopolymer synthesis based on powder silicates. From the investigation of the FTIR and NMR results, in the presence of a metakaolin that is relatively less reactive (M1), the alkaline solution and the metakaolin act together, whereas in the presence of M2, which is more reactive, the aluminosilicate source governs the reaction. It was demonstrated that regardless of the MK that is utilized, the materials based on P_{0.7}^{1.7} and L_{0.7}^{1.7} solutions provide similar mechanical properties. The preliminary test of adherence binders on bricks shows that for adhesion, slowing the kinetics of polycondensation reactions will induce the creation of the interface between the binder and brick, whereas when the kinetics are fast, the binder will diffuse into the brick and subsequently result in cracks in the brick.

References

- [1] Junnila S, Horvath A. Life-cycle environmental effects of an office building. *J Infrastruct Syst* 2003;157:9–14.
- [2] Zabalza Brihan I, Uson AA, Scarpellini S. Life cycle assessment in buildings: state-of-the-art and simplified LCA methodology as a complement for building certification. *Build Environ* 2009;44:2510–20.
- [3] Gouny F. Nouveau système constructif multi matériaux bois/liant géopolymérique/brique de terre crue: formulation, caractérisation et transfert d'échelle. Thèse de l'université de Limoges; 2013.
- [4] Cagnon H, Aubert J, Coutand M, Magniont C. Hygrothermal properties of earth bricks. *Energy Build* 2014;80.
- [5] Guillaume H, Claudiane O-P. Recent update on the environmental impact of geopolymers. *RILEM Tech Lett* 2016;1:17–23.
- [6] Fouchal F, Gouny F, Maillard P, Ulmet L, Rossignol S. Experimental evaluation of hydric performances of masonry walls made of earth bricks, geopolymer and wooden frame. *Build Environ* 2015;87:234–43.
- [7] Buchwald A, Hohmann M, Kaps C. The suitability of different clay resources in respect to form geopolymeric binders. Third conference on alkali-activated materials, Prag. p. 137–48.
- [8] Essaidi N, Samet B, Baklouti S, Rossignol S. Feasibility of producing geopolymers from two different Tunisian clays before and after calcination at various temperatures. *Appl Clay Sci* 2014:221.
- [9] Cheng TW, Chiu JP. Fire-resistant geopolymer produced by granulated blast furnace slag. *Min Eng* 2003;16:205–10.
- [10] Ye N, Yang J, Ke X, Zhu J, Li Y, Xiang C, Wang H, Li L, Xiao B. Synthesis and characterization of geopolymer from Bayer red mud with thermal pretreatment. *J Am Ceram Soc* 2014;97:1652–60.
- [11] Soleimani MA, Naghizadeh R, Mirhabibi AR, Golestanifard F. Effect of calcination temperature of the kaolin and molar Na₂O/SiO₂ activator ratio on physical and microstructural properties of metakaolin based geopolymers. *Iran J Mater Sci Eng* 2012.
- [12] Autef A, Joussein E, Gasgnier G, Rossignol S. Importance of metakaolin impurities for geopolymer based synthesis. *Ceram Eng Sci Proc* 2014;34:3–12.
- [13] Gharzoui A, Joussein E, Samet B, Baklouti S, Rossignol S. Effect of the reactivity of alkaline solution and metakaolin on geopolymer formation. *J Non-Cryst Solids* 2015;410:127–34.
- [14] Autef A, Joussein E, Gasgnier G, Rossignol S. Role of the silica source on the geopolymerization rate: a thermal analysis study. *Ceram Eng Sci Proc* 2013;33:13–24.
- [15] Gharzoui A, Joussein E, Samet B, Baklouti S, Pronier S, Sobrados I, Sanz J, Rossignol S. The effect of an activation solution with siliceous species on the chemical reactivity and mechanical properties of geopolymers. *J Sol-Gel Sci Technol* 2015;73:250–9.

- [16] Irfan Khan M, Khairun A, Suriati S, Zakaria M. Sodium silicate-free geopolymers as coating materials: effects of Na/Al and water/solid ratios on adhesion strength. *Ceram Int* 2015;41(2):2794–805.
- [17] Provis JL. Modelling the formation of geopolymers. Department of Chemical and Biomolecular Engineering. The University of Melbourne; 2006.
- [18] Ye-Qing L, Shi-Li Z, Shao-Na W, Hao D, Yi Z. Structure and diffusivity of oxygen in concentrated alkali-metal hydroxide solutions: a molecular dynamics simulation study. *Acta Phys-Chim Sin* 2015:1045–53.
- [19] Rees C, Lukey GC, Van Deventer JSJ. The microstructural characterization of geopolymers derived from fly ash and solid silicates. International symposium of research student on material science and engineering Chennai, India. p. 1–13.
- [20] Svensson IL, Sjöberg S, Öhman L-O. Polysilicate equilibria in concentrated sodium silicate solutions. *J Chem Soc Faraday Trans* 1986;182:3635–46.
- [21] Prud'homme E, Autef A, Essaidi N, Michaud P, Samet B, Joussein E, Rossignol S. Defining existence domains in geopolymers through their physicochemical properties. *Appl Clay Sci* 2013;73:26–34.
- [22] Vidal L, Joussein E, Colas M, Absi J, Rossignol S. Identification of chains and rings in alkaline silicate solutions by Raman Spectroscopy. Submitted.
- [23] Brykov AS, Danilov V, Yu V, Aleshunina E. State of silicon in silicate and silica-containing solutions and their binding properties. *Inorganic synthesis and industrial inorganic chemistry*. *Russ J Appl Chem* October 2008;81(10):1717–21.
- [24] Vidal L, Joussein E, Colas M, Cornette J, Sanz J, Sobrados I, Gelet JL, Absi J, Rossignol S. Controlling the reactivity of silicate solutions: an FTIR, Raman and NMR study. *Colloid Surf A* 2016. <http://dx.doi.org/10.1016/j.colsurfa.2016.05.039>.
- [25] Gouny F, Fouchal F, Maillard P, Rossignol S. Study of the effect of siliceous species in the formation of a geopolymer binder: understanding the reaction mechanisms among the binder, wood and earth brick. *Ind Eng Chem Res* 2014;53:3359–569.
- [26] Autef A, Joussein E, Gasgnier G, Pronier S, Sobrados I, Sanz J, Rossignol S. Role of metakaolin dehydroxylation in geopolymer synthesis. *Powder Technol* 2013;250:33. Elsevier.
- [27] Engelhard G, Zeigan D, Janke H, Hoebbel D, Weiker Z. High resolution ^{29}Si NMR of silicates and zeolites. *Anorg Allg Chem* 1975;418:17–28.
- [28] Malfait WJ, Halter WE, Morizet Y, Meier BH, Verel R. Structural control on bulk melt properties: single and double quantum ^{29}Si NMR spectroscopy on alkali-silicate glasses. *Geochim Cosmochim Acta* 2007;71:6002–18.
- [29] Gharzouni A, Joussein E, Samet B, Baklouti S, Rossignol S. Effect of the reactivity of alkaline solution and metakaolin on geopolymer formation. *Non Cryst Sol* 2014;73:250–9.
- [30] Svensson IL, Sjöberg S, Öhman L-O. Polysilicate equilibria in concentrated sodium silicate solutions. *J Chem Soc Faraday Trans* 1986;1(82):3635–46.
- [31] Bourlon A. Physico-chimie et rhéologie des géopolymères frais pour la cimentation des puits pétroliers [Ph. D. thesis]. University of Pierre et Marie Curie; 2010.
- [32] Steins P. Influence des paramètres de formulation sur la texturation et la structuration des géopolymères [Ph. D. thesis]. Université de Limoges; 2014.
- [33] Innocenzi P. Infrared spectroscopy of sol-gel derived silica based films: a spectra microstructure overview. *J Non Cryst Solids* 2003;316:309–19.
- [34] Prud'homme E, Michaud P, Joussein E, Peyratout C, Smith A, Arrii-Clacens S, Rossignol S. Silica fume as porogen agent in geo-materials at low temperature. *J Eur Ceram Soc* 2010;30:1641–8.
- [35] Autef A. Formulation géopolymère: influence des rapports molaires Si/K et Si/Al sur les réactions de polycondensation au sein de gels aluminosilicatés. Thèse de l'université de Limoges; 2013.
- [36] Bunker BC, Tallant DR, Headley TJ, Turner GL, Kirkpatrick R. Structure of leached sodium borosilicate glass. *Phys Chem Glasses* 1988;29:106.
- [37] Autef A. Formulation géopolymère: influence des rapports molaires Si/K et Si/Al sur les réactions de polycondensation au sein de gels aluminosilicatés. Thèse de l'université de Limoges; 2013.
- [38] Heah CY, Kamarudin H, Mustafa Al Bakri AM, Bnhussain M, Luqman M, Khairul Nizar I. Study on solids-to liquid and alkaline activator ratios on kaolin-based geopolymers. *Constr Build Mater* 2012;35:912–22.
- [39] Kang G, Kae-Long L, Deying W, Chao-Lung H, Hau-Shing S, Yu-Ming C, Ta-Wui C. Effects $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio on mechanical properties and the microstructure of nano- SiO_2 metakaolin based geopolymers. *Constr Build Mater* 2014;53:503–10.
- [40] Autef A, Joussein E, Gasgnier G, Pronier S, Sobrados I, Sanze J, Rossignol S. Role of metakaolin dehydroxylation in geopolymer synthesis. *Powder Technol* 2013;250:33–9.
- [41] Wang H, Li H, Yan F. Synthesis and mechanical properties of metakaolinite-based geopolymer. *Colloids Surf A* 2005;268:1–6.
- [42] Liu J. Etude expérimentale de la perméabilité relative des matériaux cimentaires et simulation numérique du transfert d'eau dans le béton. Ecole centrale de Lille; 2001. thèse de doctorat.