# How to control the geopolymer setting time with the alkaline silicate solution

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## ARTICLE INFO

## ABSTRACT

Geopolymers are new binders resulting from the activation of an aluminosilicate source by an alkaline solution. It is well-established that the precursors that are used affect geopolymer formation. This study focuses on how to control the geopolymer setting time with an alkaline silicate solution. To conduct this investigation, various geopolymer mixtures based on different alkaline silicate solutions were characterized in terms of viscosity and setting time. To understand the link between geopolymer formation and the properties of the solution, the ionic conductivity and the viscosity of the solutions were measured. The solutions were also characterized by Raman spectroscopy. The characterization of the geopolymer mixture shows that the properties of the alkaline silicate solution highly depend on the viscosity and setting time of the geopolymer. Therefore, the alkali molar concentration ($3 < [M] < 10 \, mol \cdot L^{-1}$) influenced the properties of the solution (silicate species, ionic conductivity, and viscosity). A relationship among the chemical composition, the silicate species of the solution and the geopolymer setting time is highlighted depending on the $\frac{n(si)}{n(Al)+n(M)}$ ratio. For example, a ratio of $\frac{n(si)}{n(Al)+n(M)} > 1.1$ permits a slower geopolymerization reaction, and the setting time of the geopolymer mixture is higher.

## 1. Introduction

Geopolymer materials are three dimensional, amorphous materials that are interesting for various potential applications. These materials, prepared at room temperature via alkaline activation by aluminosilicate sources [1], exhibit high thermal resistance [2] and mechanical properties. The geopolymer properties are strongly affected by the raw materials that are used. Geopolymer materials are formed by geopolymerization reactions; the final structure of the material depends on the nature of the oligomers formed during polycondensation reactions. Several authors noted that the properties of the precursors, i.e., the metakaolin and the alkaline solution, influence the structure of the final materials. Numerous studies investigated the influence of metakaolin reactivity on reaction kinetics, network formation, and therefore properties of the consolidated materials [3]. For example, the metakaolin Si/Al ratio influences the dissolution of the aluminosilicate source and therefore the availability of silicium and aluminum species.

Different studies have demonstrated the effect of the alkaline source on geopolymer properties [4–6]; alkaline silicate solutions play an efficient role in the various reactions since the amount of each species (i.e., the monomers or oligomers) leads to different behaviors. In fact,

depending on the cation, the structure formed can be different. The existing literature has highlighted the influence of the alkaline silicate solution (water content, nature of the cation) on geopolymer materials. However, it is necessary to identify the tools that can be used to control the geopolymer setting time by manipulating the characteristics of the alkaline solutions that are used.

Raman spectroscopy has been used in several studies on silicate solutions [7–9] to investigate the effects of different parameters such as the contributions of monomers and oligomers [9,10]. This characterization provides information on the entities such as the vibrations of 3-, 4- or 5-membered rings [10]. Previous studies have demonstrated the impact of the Si/M molar ratio, the dilution level, and the alkaline cation on the silicate species in the solution [11]. Mysen et al. [12] have demonstrated that an increase in the Si/M molar ratio causes the polymerization of the silicate solution. Moreover, it was shown that increasing the number of alkali cations increases the number of three-membered rings and monomers and reduces the number of four-membered rings and oligomers [9,13]. The nature of the cation in the silicate solution modifies the Raman spectra and therefore the silicate species of the solution [14]. Le Losq et al. [15] demonstrated that the intensity of the peak located at $450 \, cm^{-1}$, attributed to the vibration of

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the Si−O−Si bonds in five-, six-, or higher-membered rings, decreases when the potassium is replaced by a sodium cation. This could be due to the M−O distance (where M is the alkali cation), which is larger for K−O (2.81 Å) than Na−O (2.43 Å).

In the geopolymer field, the roles of the different parameters that impact geopolymerization were studied. Nevertheless, for a given metakaolin, few studies have focused on the effect of the silicate solution on the geopolymer mixture. The objective of this work is to determine how to control the geopolymer mixture properties by controlling the alkaline silicate solution. For this purpose, the characterization of the reactive mixture based on different silicate solutions (viscosity and setting time) was performed. Then, the silicate solution properties, such as ionic conductivity and viscosity, were measured. In parallel, the different sodium and potassium silicate solutions used were characterized by Raman spectroscopy.

## 2. Experimental part

### 2.1. Raw materials and sample preparation

Various sodium and potassium silicate solutions were studied and are referenced in Table. 1. The main parameters studied are the cation, the Si/M molar ratio, where M = K or Na (from 0.40 to 0.90), and the alkali molar concentration. The solutions ($S_{K1}$, $S_{K3}$ or $S_{Na}$) are supplied by Woellner. The Si/M molar ratio was adjusted by dissolving hydroxide pellets (KOH or NaOH) supplied by Sigma Aldrich into the solution.

Geopolymer samples were synthetized by mixing a metakaolin (named $M_1$), supplied by AGS, into the different silicate solutions. The reactive mixture was obtained using the procedure presented in Fig. 1. Solutions or reactive mixtures are denoted as $S_{X.Y}^Z(M_1)$, where x refers to the commercial silicate solution ($S_{K1}$, $S_{K3}$ or $S_{Na}$), Y represents the hydroxide pellets used to adjust the Si/M molar ratio, and z represents the Si/M molar ratio. In the case of a reactive mixture, $M_1$ is added to the nomenclature. For example, $S_{K1.K}^{0.40}$ refers to the solution obtained from the potassium silicate solution, $S_{K1}$, and the KOH hydroxide pellets used to adjust the Si/M molar ratio at 0.40, and $S_{K1.K}^{0.40}M_1$ refers to its geopolymer mixture.

### 2.2. Technical characterization

Raman spectroscopy was performed on the silicate solutions using a T64000 Horiba–Jobin–Yvon spectrophotometer with a 514-nm laser operating on the sample at a power of 30 mW. Scattered light was collected in backscattering mode using a long-working-distance objective (×50) with a triple-diffraction grating (1800 lines/mm). The spectral range was 100 to 1200 $cm^{-1}$, and the acquisition time was 60 s. The acquired spectra were corrected by subtracting the baseline, which was modeled by a 5° polynomial curve. Then, the spectra were decomposed using the Wire 4.0 software. An example of the Raman decomposition of the $S_{N.Na}^{0.58}$ solution is presented in Fig. 2. After
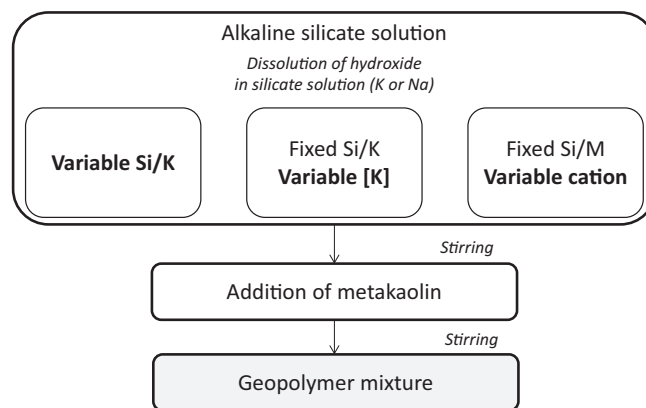


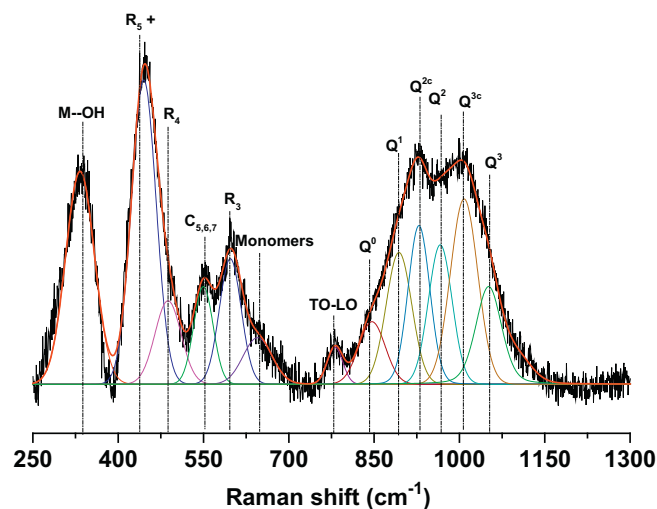**Fig. 1.** Synthesis protocol of geopolymer mixtures.



**Fig. 2.** Example of decomposition of Raman spectra obtained for $S_{N.Na}^{0.58}$.

baseline subtraction, the spectra were decomposed by various pseudo Voight functions arising from several contributions as described in the literature [16]. To compare the solutions after decomposition, the different contributions were normalized by the total area in the 250 to 1400 $cm^{-1}$ range. Based upon previous work [17], the contributions observed in the various spectra are presented in Table 2. Regardless of the solution used, the same contributions are observed in the Raman spectra. The contribution located near 325 $cm^{-1}$ is attributed to the M−O− bonds [18]. The bands observed near 440, 550, 600, 500 and 645 $cm^{-1}$ were assigned, to the ring breathing mode of a ring with 5 or more tetrahedral bonds (denoted $R_{5\ or\ more}$), $R_3$, $R_4$ [14,19,20,22], the stretching of the $\nu$(Si−O−Si) of the chains (C5,6,7) [21] and monomers

**Table 1**
Nomenclature and composition of the alkaline solutions.

| | Density (g·cm$^{-3}$ ± 0.02) | [M] (mol·L$^{-1}$) | [Si] (mol·L$^{-1}$) | Codes |
|---|---|---|---|---|
| $S_{K1.K}^{0.40}$ | 1.35 | 6.87 | 10.82 | ■ (red) |
| $S_{K1.K}^{0.58}$ | 1.34 | 5.22 | 11.97 | ■ |
| $S_{K1.K}^{0.70}$ | 1.32 | 4.41 | 12.34 | ■ (green) |
| $S_{K1.K}^{0.90}$ | 1.27 | 3.07 | 12.89 | ■ (blue) |
| $S_{K1.Na}^{0.58}$ | 1.35 | 5.61 | 12.82 | ⊠ |
| $S_{N.Na}^{0.58}$ | 1.51 | 9.88 | 16.08 | ◆ |
| $S_{N.K}^{0.58}$ | 1.54 | 8.95 | 14.96 | ◈ |
| $S_{K1(0.75)}S_{K3(0.25).K}^{0.58}$ | 1.40 | 5.85 | 12.99 | ○ |
| $S_{K1(0.50)}S_{K3(0.50).K}^{0.58}$ | 1.42 | 6.39 | 13.79 | ○ (light gray) |
| $S_{K1(0.25)}S_{K3(0.75).K}^{0.58}$ | 1.48 | 7.11 | 14.97 | ● (gray) |
| $S_{K3.K}^{0.58}$ | 1.56 | 8.67 | 15.88 | ● |