



## Predictive tools to control the structure and the properties of metakaolin based geopolymer materials



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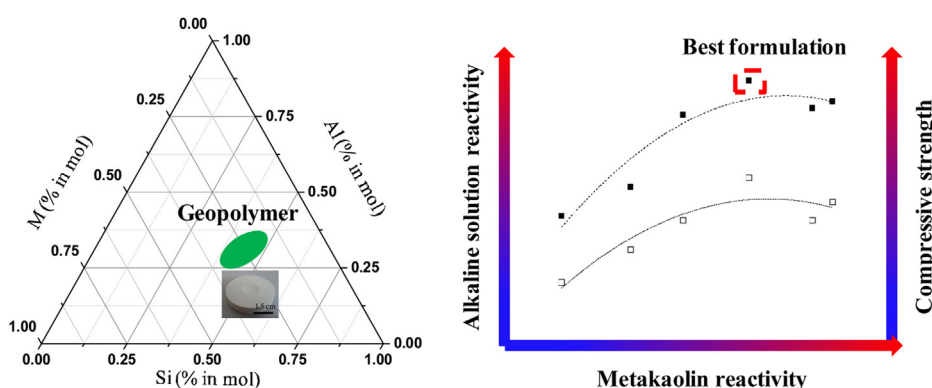
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### HIGHLIGHTS

- Metakaolin reactivity depends on its physical, chemical and structural properties.
- Geopolymer existence domains in Si–Al–M/O ternary diagram were identified.
- The pores distribution and size are influenced by raw materials reactivity.
- Higher reactive precursors favor the formation of geopolymer network.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Geopolymers are innovative mineral binders. These materials are still under research development in order to better understand the formation mechanism, the local structure and the final working properties. The aim of this study is to provide predictive tools permitting to control the geopolymerisation reaction. At first, it is important to determine the parameters responsible of raw materials reactivity. For alkaline solutions, the siliceous species distribution and connectivity control the reactivity. Concerning metakaolins, the Si/Al molar ratio, the wettability value, the amorphous phase content and the amount of reactive tetrahedral aluminum are responsible of metakaolin reactivity. Moreover, the reactivity of raw materials was proven to determine the geopolymer existence domains in the Si–Al–M/O ternary diagram. Thermal analysis during and after curing give informations about the amount of water consumed during the reaction and trapped in the final structure as well as the energy required for oligomer formation which seem to be directly related to raw materials reactivity. The pores distribution and size are also influenced by raw materials reactivity. Reactive precursors, especially reactive alkaline solutions, induce higher densification rate and, therefore, lower porosity and larger pore size. Furthermore, reactive precursors favor the formation of geopolymer network. This fact was evident by <sup>29</sup>Si NMR. As a consequence, the increase of geopolymer phase in the structure improves the mechanical strength while the competition of different networks is source of weakness.

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## 1. Introduction

Geopolymers are amorphous binders synthesized by the activation of an aluminosilicate source by an alkaline solution at atmospheric pressure and a temperature below than 100 °C [1]. The term “geopolymer” was introduced in 1978 by the French chemist Joseph Davidovits to designate their inorganic character and their structure similar to polymers. Geopolymers are formed by a three-dimensional network of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra. The alkali cation M<sup>+</sup> compensates the deficit of charge created by the substitution of Si<sup>4+</sup> by Al<sup>3+</sup>. There is a wide range of potential and existing applications for geopolymers. Nevertheless, deeper fundamental research on the parameters governing the mechanism of formation and the working properties are still required.

The role played by silicium, aluminum and alkali cation on geopolymer formation and properties was extensively discussed. Recently, Gao et al., [2] have examined the influence of the Si, Al and K contents from a metakaolin and two potassium silicate solutions (commercial and laboratory made) on geopolymer existing domains in Si–Al–K/O ternary diagram. Four types of materials were obtained including geopolymers, gel, sedimented and hardened materials. Moreover, the effect of Si/Al ratio was extensively studied. It was demonstrated that the Si/Al ratio influences the dissolution of the aluminosilicate source and therefore the availability of silicium and aluminum. Weng et al., [3] have focused on the mechanisms of Al speciation and the distribution of [Al(OH)<sub>4</sub>]<sup>−</sup> ions depending on the metakaolin properties. They have highlighted the effect of aluminates not only on geopolymer formation by promoting polycondensation reaction but also on improving mechanical properties of strengthened materials. Duxon et al., [4] have shown that samples with a Si/Al molar ratio > 1.65 exhibit higher compressive strength and Young's modulus. Above this value, the mechanical properties decrease due to higher amount of non reacted species.

In addition to that, the alkaline solution is also a crucial parameter in geopolymer formation. Taking into account the differences in size and hydration properties [5], the alkali cations may engender variations on the reaction rate and the final properties of consolidated materials. In fact, sodium cation is known to facilitate aluminosilicate source dissolution. However, potassium cation has the advantage of ensuring higher condensation rate and more disordered structure [6,7]. As a result, potassium-based geopolymers have shown better compressive strength than sodium-based one. Moreover, it was also demonstrated that the compressive strengths increase with increasing concentration of the NaOH solution from 4 to 12 mol L<sup>−1</sup> [8].

Water also influences the geopolymer formation. It was evident that water facilitates the dissolution of the aluminosilicate source, favors the ion transfer and enhances the polycondensation reaction. However, it was shown that low solid to liquid ratio, that means high water content, accelerates the dissolution but perturbs the polycondensation reaction. The impact of water on the mechanical properties was also studied. In final geopolymer materials, water was found to be, predominantly, free water (about 60%) and the rest is interstitial and structural bounded water [9,10]. Zuhua et al., [11] have demonstrated that higher water content induces higher pore volume and low mechanical strength. However, lower water content lead to denser structure with higher mechanical strength.

The existing literature emphasis the dependence of geopolymer materials of used raw materials. However, there is a strong requirement to identify tools to control the formation, the structure and the working properties of these materials. This is a why a deeper comprehension of raw materials is necessary.

In this topic, the main objectives of the present work are (i) to identify the parameters governing raw materials reactivity, (ii) to establish predictive tools to determine the nature of obtained

**Table 1**

Nomenclature and characteristics of the various studied solutions.

Nomenclature	Cation	Si/M	% water	density
S <sub>K</sub> 1	K	1.7	79	1.18
S <sub>K</sub> 3		0.7	59	1.51
S <sub>Na</sub>	Na	1.7	64	1.36

materials from the chemical composition of the mixture and finally (iii) to exacerbate the influence of raw materials reactivity on local structure and mechanical properties of obtained geopolymers. To achieve these objectives, different metakaolins and alkaline solutions were studied and their reactivity rates were evaluated by physical, chemical and structural characterization. Then, numerous formulations were tested in order to identify the geopolymer existing domains in the Si–Al–M/O ternary diagram. The influence of raw materials on the local structure was determined by differential thermal analysis and thermogravimetric analysis (DTA–TGA), mercury intrusion porosimetry (MIP) and nuclear magnetic resonance (<sup>29</sup>Si NMR). The impact on the mechanical properties of the strengthened materials was evaluated by compression tests.

## 2. Material and methods

### 2.1. Raw materials and sample preparation

Geopolymer samples were synthesized using six metakaolins (named M1 through M6) (Table 1) and three commercial silicate solutions provided by woellner (i) Two potassium silicate solutions named S<sub>K</sub>1, S<sub>K</sub>3 with different Si/K molar ratio (1.7 and 0.7, respectively) and (ii) a sodium silicate solution named S<sub>Na</sub> with Si/Na molar ratio of 1.7. Potassium and sodium hydroxide pellets (VWR, 85.2% and 97.0% pure) were dissolved into the starting silicate solutions to maintain the Si/M (with M=K or Na) molar ratio at 0.5 and 0.7 for potassium and sodium silicate solutions respectively. Then, metakaolins were added. The obtained mixtures were placed in a closed sealable polystyrene mold at room temperature (25 °C).

### 2.2. Sample characterization

X-ray diffraction patterns were acquired via X-ray diffraction (XRD) experiments on a Bruker–AXS D 5005 powder diffractometer using CuKα radiation (λKα = 0.154186 nm). The analytical range is between 5° and 55° (2θ), with a step of 0.04° and an acquisition time of 2 s for raw metakaolins powder. JCPDS (Joint Committee Powder Diffraction Standard) files were used for phase identification. The amorphous phase for each metakaolin was determined using the Rietveld method [12].

The wettability value (μL/g) corresponds to the volume of water that can be adsorbed by one gram of powder before saturation.

High-resolution NMR experiments were performed on alkaline solutions, metakaolins and consolidated geopolymers at room temperature using a Bruker AVANCE-400 spectrometer, operating at 104.26 MHz for <sup>27</sup>Al signal and 79.49 MHz for <sup>29</sup>Si signal. The <sup>29</sup>Si (I = 1/2) NMR spectra were recorded after a π/2-pulse irradiation (4 μs) using a 500 kHz filter to improve the signal/noise ratio. In each case, 400 scans were collected. The time between acquisitions was set to 10 s to minimize saturation effects. Powder samples were spun at 10 KHz.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on an SDT Q600 apparatus from TA Instruments in an atmosphere of flowing dry air (100 mL/min) in platinum crucibles. The signals were measured with Pt/Pt–10%Rh thermocouples. Thermal analysis was conducted during the formation of the consolidated materials using the thermal cycle

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