



# Influence of various metakaolin raw materials on the water and fire resistance of geopolymers prepared in phosphoric acid

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## ABSTRACT

Different formulations of geopolymers were synthesized in acidic media (phosphoric acid) starting from three different raw metakaolin materials to identify compositions of interest. Four different property groups were highlighted based on the most favorable thermal and water resistance properties (while maintaining acceptable mechanical properties). The groups were related to the chemical composition, setting time and setting temperature of the synthesized geopolymers. Indeed, mechanical strength was determined by chemical composition, such as the aluminum content and the amount of water in each sample. The results showed that the sample with  $\text{Si/Al} \geq 1$  and  $\text{Al/P} = 1$  exhibited compressive stress to rupture values ranging between 66 and 120 MPa and was thermal resistant. Water resistance with a mechanical strength of 50 MPa was obtained for the samples with  $\text{Al/P} = 1$  or 4 and  $\text{Si/Al} \leq 1$ . This work highlights the possibility of selecting a specific property associated with the mechanical performance for an acidic geopolymer.

## 1. Introduction

During the last several decades, a new class of materials called “geopolymers” belonging to the family of cements and concrete products has emerged. It was first reported in 1978 by Professor J. Davidovits [1], who has been recognized as a pioneer of such aluminosilicate-based materials. Geopolymers are very attractive materials because they can be used to manufacture precast structures, concrete pavement, and concrete products and to immobilize toxic waste that is resistant to heat and aggressive environments [2]. The synthesis of these geopolymers is based on the alkaline activation of aluminosilicates, which induces the formation of free  $\text{Si}[\text{OH}]_4$  and  $\text{Al}[\text{OH}]_4^-$  oligomers [3,4].

Many authors have investigated the parameters related to the formation, structure and physical properties of geopolymers [3,5,6]. Key factors for controlling the geopolymerization reaction in basic media, such as the roles of the aluminosilicate source and the alkaline solution, have been recently identified. This control requires perfect knowledge of the raw material characteristics and structure, including the reactivity. For example, for a metakaolin source, accurate quantification of surface reactivity is of interest: a high reactivity requires (i) a low molar ratio of  $\text{Si/Al}$ , (ii) a high wettability value, (iii) a large amount of amorphous phase, and finally, (iv) a great proportion of reactive tetrahedral aluminum ( $\leq 1.2$ ,  $\geq 760 \mu\text{L/g}$ ,  $\geq 63 \text{ wt\%}$ , and  $\geq 19\%$ ,

respectively) [7]. These data have been plotted to determine the location of geopolymers in the ternary diagram of  $\text{Si-Al-M/O}$  [8]. The relationship between the feasibility of the geopolymer preparation and the reactivity of the introduced raw materials has been highlighted. The existing domain of geopolymers is even more reduced when the reactivity of the raw materials is weak. Moreover, the concentrations of alkali and aluminum cations strongly affect the feasibility of these materials [9].

Another possible processing method consists in favoring the reaction of metakaolin in an acidic medium to produce an acidic geopolymer. In the preparation of an acidic geopolymer, the geopolymerization process begins with the dissolution of the aluminosilicate source, leading to the release of  $\text{Al}^{3+}$ . These aluminum ions react with phosphoric acid, leading to the formation of  $\text{AlPO}_4$ . The presence of  $\text{AlPO}_4$  within the geopolymer has been observed by several authors [10,11], supporting this proposed mechanism of geopolymer formation. The aluminosilicate source whose aluminum has been dissolved also reacts with phosphoric acid, leading to the formation of a three-dimensional network of  $[\text{Si-O-P}]$ . Thus, the formed geopolymer consists of a three-dimensional network of  $[\text{Si-O-P}]$  and  $\text{AlPO}_4$ . The amount of acid affects the geopolymerization process as well as the structure and final properties of the geopolymer. Thus, if the  $\text{Si/P}$  ratio is decreased (i.e., the amount of acid is increased), a more amorphous geopolymer structure is formed due to improved dissolution [12]. The reactivity of

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the aluminosilicate source [11] also affects the geopolymerization process. The synthesis of acid-based geopolymers produces geopolymers with enhanced mechanical performances, as demonstrated by D.S. Perrera [13], where the geopolymers prepared in an acidic medium exhibited a two-fold higher resistance to compression (146 MPa) than the geopolymers synthesized in a basic medium (72 MPa). According to Perrera, this improvement in the properties can be related to a decrease in the pore volume fraction and/or to the presence of stronger bonds in the acidic geopolymer. Similarly, H.K. Tchakouté [10] observed an improvement in the mechanical properties of an acid-reacted geopolymer, typically exhibiting a compressive stress to rupture value near 93 MPa.

Materials exhibiting flame-retardant characteristics can be combined with other materials, such as polymers, to form a composite with improved fire-resistant properties [14]. According to Chiou [15], in the case of aluminum matrix composites, the presence of aluminum metaphosphate ( $\text{Al}(\text{PO}_3)_3$ ) favors a high thermal resistance of up to at least 1000 °C. Moreover, Jiang [16] showed that the presence of silicon is beneficial for improving these properties, where a layer of silica that forms on the surface after heat treatment protects the material. In that study, silicon also reacted with phosphorous to form silicon pyrophosphate ( $\text{SiP}_2\text{O}_7$ ,  $\text{Si}_3(\text{PO}_4)_4$  and  $\text{Si}_3\text{P}_6\text{O}_{25}$ ), which is known to improve the flame retardancy. Moreover, the use of a polymer matrix leads to the generation of smoke during heat treatment. Yan [17] demonstrated that the addition of nanosilica reduced the amount of smoke generated and enhanced the flame resistance. Thermal resistance is also observed in alkali-activated materials and was improved by the addition of fillers [18,19,20], such as refractory aluminosilicate particles and fibers. According to Bernal et al. [21], additives such as calcium powder can also improve the densification of materials during heat treatment.

The resistance of materials containing aluminum, silicon and phosphorous to water is seldom reported in the literature [22,23]. In the case of glasses, the properties of iron phosphate and borosilicate glasses have been compared [24], and iron phosphate glasses exhibited better chemical durability in water at 90 °C than borosilicate glasses. The substitution of phosphorous with iron in the P–O–P bonds can explain this better resistance to hydration. However, these glasses are very sensitive to water because the P–O–P bonds hydrolyze easily. Thus, incorporation of water in the form of –OH groups must be considered as a network modification [25]. Few references on the water resistance of geopolymers are available. However, Ilkentar et al. [26] noted that in the case of an alkali-activated fly ash geopolymer, the water absorption of the material tended to increase with the setting temperature. However, the samples immersed in water leached alkali ions, which do not react [27].

The objective of this work was to identify the most favorable experimental conditions for processing geopolymers in an acidic medium (phosphoric acid), which are closely linked to the structures formed from several metakaolin raw materials that are already commonly used in basic media [7]. As few scientific studies have focused on the water and thermal resistances of acidic geopolymers, thermal and water resistance tests completed by thermal and structural analyses were performed to determine the most effective formulation.

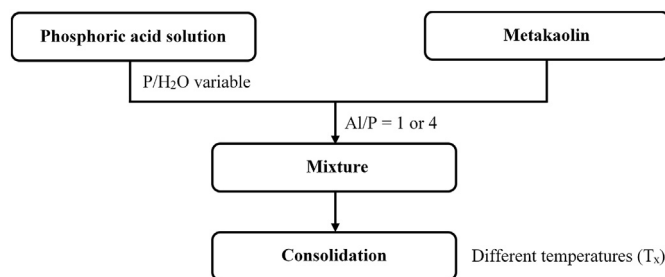
## 2. Experimental details

### 2.1. Raw materials

Three types of aluminosilicate sources supplied by Imerys were used in this study (Table 1). Denoted M1, M3 and M4, the sources have been characterized by Gharzouni et al. [7]. M1 and M4 had already been heat-treated by the supplier, whereas M3 was obtained from the transformation of initially supplied kaolin in metakaolin after thermal treatment at 750 °C for 4 h (heating rate of 5 °C/min). The phosphoric acid used in the study was an 85 wt% phosphoric acid solution supplied by VWR with a concentration of 14.7 mol.L<sup>-1</sup>. Consolidated materials

**Table 1**  
Physical and chemical properties of the raw metakaolins. [1]

Metakaolin	Si/Al	d50 (μm)	BET value (m <sup>2</sup> /g)	Wettability (μL/g)	Amorphous phase (%) [1]	Heating process
M1	1.17	10.0	17	760	63	Rotary
M3	1.00	8.0	8	1010	98	Oven
M4	0.98	6.0	17	1186	98	Flash



**Fig. 1.** Synthesis protocol of samples.

were synthesized (experimental procedure illustrated in Fig. 1) by mixing the metakaolin materials with diluted phosphoric acid solutions to obtain different Al/P molar ratios (Al/P = 1 and 4) and concentrations of phosphoric acid to prepare consolidated materials. The different Al/P, Al/H<sub>2</sub>O and Al/Si ratios used are reported in Table 2. The obtained mixtures were placed in a sealable polystyrene mold at different temperatures (20 °C, 40 °C and 70 °C). Samples with typical dimensions of 15 mm in diameter and 30 mm in height are denoted x-My-T, where x represents the Al/P ratio, My represents the metakaolin source, and T represents the consolidation temperature of the samples. All samples names are compiled in Table 3.

### 2.2. Sample characterization

The setting time is defined as the moment when the geopolymer can sustain manipulation without any deformation [28]. Consolidation was checked every hour the first day after preparation and then every 12 h each following day.

Consolidated samples were immersed in water after 7 days at an liquid/solid ratio equal to 1. The external visual aspect of the samples was observed after 7 days of static immersion in water: if coarse cracks or disaggregations could be observed on a specimen, the specimen was

**Table 2:**  
Al/P, Al/H<sub>2</sub>O and Al/Si ratios used for different compositions.

Samples	Al/P	Al/H <sub>2</sub> O	Al/Si
1-M1-20	1	0.62	0.85
1-M1-40	1	0.62	0.85
1-M1-70	1	0.62	0.85
1-M3-20	1	0.41	1.00
1-M3-40	1	0.41	1.00
1-M3-70	1	0.41	1.00
1-M4-20	1	0.27	1.02
1-M4-40	1	0.27	1.02
1-M4-70	1	0.27	1.02
4-M1-20	4	0.23	0.85
4-M1-40	4	0.23	0.85
4-M1-70	4	0.23	0.85
4-M3-20	4	0.19	1.00
4-M3-40	4	0.19	1.00
4-M3-70	4	0.19	1.00
4-M4-20	4	0.15	1.02
4-M4-40	4	0.15	1.02
4-M4-70	4	0.15	1.02

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