



## Synthesis of porous hierarchical geopolymer monoliths by ice-templating



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### ABSTRACT

Hierarchical geopolymers with mesoporous matrices and lamellar macro-porosities were produced for the first time by ice-templating (freeze-casting) technique in a water-based sol–gel system.

Starting from an aqueous solution of metakaolin and potassium silicate, geopolymerization was triggered through a maturation step without reaching complete consolidation. Different amounts of water (20, 50, 70 vol.%) were then mixed with the geopolymer paste to induce lamellar ice growth by unidirectional freezing. The consolidation was completed during freeze-casting and drying.

Ice-templated hierarchical geopolymers had 53–83% total porosity and N<sub>2</sub> BET specific surface area values from 4 to 46 m<sup>2</sup> g<sup>-1</sup>, depending on the amount of water added. A broad mesopore Barret Joyner Halenda distribution was detected between 4 and 100 nm with maxima from 5 to 7 nm, while macropores in the 1-to-100 μm range were identified by Hg intrusion porosimetry. Lamellar monoliths (height 25 mm) were produced with a selected composition (50 vol.% of additional water) in order to assess the reproducibility of the ice-templating technique combined with geopolymerization.

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### 1. Introduction

Geopolymers are alkali-bonded ceramics [1], constituting a family of materials with properties varying among those characteristic of ceramics, cements, zeolites, or refractories, depending on their formulation. Geopolymers were produced by reacting alumino-silicate powders (metakaolins, blast furnace slags, fly ashes, pozzolana, etc.) with an aqueous alkali hydroxide and/or alkali silicate solution [2].

At the atomic scale, the geopolymer amorphous network is made by SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra connected by oxygen corners [2]. Recent results indicate that the tetrahedra form Si–O–Al–O rings of various sizes in the network and endow the geopolymer matrix with ion exchange properties [3]. From some standpoints, geopolymers can be regarded as either the amorphous counterpart or the precursor of crystalline zeolites.

The microstructure of a metakaolin-based geopolymer consists of nano-particulates separated by micro- and mesopores [4,5]. Since geopolymers are intrinsically mesoporous, a hierarchical pore system can be constructed by combining mesopores with macro-porosity. Geopolymers could be used to develop porous materials covering pore sizes ranging from a few tenths of nanometers to a few millimeters, as well as a total pore volume from 30% up to 90% [5]. Because of the high accessibility of pores, porous ceramics with three-dimensionally interconnected and distributed open pores (3D structures) are useful as catalysts, catalyst supports, filters, scaffolds, and adsorbents [6,7].

For all the above-mentioned applications, it is absolutely necessary to control the pore size dimension and distribution, as well as the pore amount and structure (shape, morphology, orientation, and surface properties). The required pore dimensions for catalysts and supports range from 1 nm to few tenths of microns, for filtering and purification systems from a few nanometers to a few millimeters, and for dust collecting from a few micrometers to a few millimeters [6].

The geopolymer production process in an aqueous medium makes it possible to obtain a custom-tailored porosity. Different

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techniques were used in order to meet porosity requirements for various purposes. Water contents in the starting mixtures affected the intrinsic mesoporosity of the geopolymer matrix, since water acted as a pore former during the polycondensation stage [5]. Moreover, ultra-macro-porosity was obtained by direct foaming, using hydrogen peroxide as a blowing agent [8], or exploiting the redox reaction of metallic Al [9] or Si powders [5,10] in an alkaline solution to induce porosity through H<sub>2</sub> evolution.

The water-based freeze-casting (i.e. ice-templating) is a useful technique for fabricating porous materials with main unidirectionally oriented pores and a high open porosity, where the final component results in a lamellar or laminate-like structure. This technique is particularly interesting for the peculiar structures and properties shown by porous freeze-cast ceramics, thus opening new opportunities in the field of cellular ceramics [11]. For example, unidirectional porous ceramics have a higher permeability than conventional porous ceramics, and are potentially good thermal insulators [6].

The ice-templating technique consists of freezing an aqueous suspension, followed by ice sublimation under reduced pressure. The resulting green body is generally sintered to consolidate the overall architecture as well as to obtain the desired mechanical and functional properties, while maintaining a high level of porosity. The unidirectional channel-like (lamellar) porosity is obtained in the case of unidirectional freezing, where pores are the replica of ice crystals [11–13].

The template can be easily removed through simple thawing and drying; this is a unique and beneficial feature of this method, overcoming the problems inherent in other templating techniques requiring the use of expensive templates removed through either high temperature or extremely high or low pH conditions [14]. The process is environmentally friendly, since it uses water as a removable template, highly versatile, and the resulting structures are highly tunable by changing process conditions. In detail, the final porosity content can be tuned by varying the particle content within the slurry, and the size of the pores is affected by freezing kinetics. Furthermore, since the solidification is often directional, a very anisotropic morphology of pores can be seen in the solidification plane, where porous channels run from the bottom to the top of samples [13].

Ice-templating has been applied to a large variety of materials such as alumina [15,16], hydroxyapatite [17,18], polymeric materials [19], zirconium diborides ultra-high temperature ceramics [20], zeolite monolith [21], and so on.

While literature reports ice-templating of colloidal inert ceramic suspensions, the aim of the present study is to apply this technique to a water-based sol–gel system capable of producing alkali-bonded ceramics, i.e. metakaolin-based geopolymers. To the author's best knowledge, this is the first time ice-templating has been applied to geopolymers.

Again, it is important to point out that the systems generally used for freeze-casting [13] are colloidal suspensions of inert ceramic particles with the addition of organic dispersants and binders with the aim of fostering ice-lamellar growth [22], and final samples are usually consolidated by sintering. Conversely, geopolymer slurries are based on a sol/gel reactive system with no addition of any organic dispersant or binder, while the consolidation is of a chemical type, thus avoiding any high-temperature thermal treatment.

The aim of the present work is to promote the simultaneous formation of geopolymer intrinsic mesoporosity and lamellar macroporosity by unidirectional ice growth, together with a final chemical consolidation.

Starting from a geopolymer mixture of metakaolin and potassium silicate aqueous solution, geopolymerization was triggered through a maturation step, but without reaching a complete consolidation.

Different amounts of water were then mixed with the geopolymer paste for ice templating. Chemical consolidation proceeded during freeze-casting and drying to avoid a sintering step. The ice-template metakaolin-based geopolymers were fully characterized in terms of macro- and micro-structure, intrinsic and induced porosity size distribution, and specific surface area. The most promising geopolymer composition was selected to produce lamellar monoliths.

## 2. Experimental

### 2.1. Sample preparation

Metakaolin grade M1200S was purchased from AGS Minéraux. The composition of the metakaolin has been reported elsewhere [23].

The activating alkali aqueous solutions were potassium di-silicate solutions with molar ratio SiO<sub>2</sub>:K<sub>2</sub>O = 2 and H<sub>2</sub>O:K<sub>2</sub>O = 13.5. Solutions were prepared by dissolving KOH pellets (purity >85% from Sigma–Aldrich) in distilled water and adding fumed silica powder (99.8% from Sigma–Aldrich) under magnetic stirring as described in a previous work [5].

The slurry, with a theoretical Si/Al molar ratio equal to 2, was prepared by the mechanical mixing of metakaolin and the potassium di-silicate solution for 20 min at 100 r.p.m. A reference geopolymer, coded G13 (Table 1), was prepared by casting the slurry into a plastic cylindrical mold and curing for 24 h at room temperature and 24 h at 80 °C in a heater. These process conditions made it possible to obtain a 97% geopolymerized material [5].

The production process of freeze-cast geopolymers is schematically reported in Fig. 1, while compositions and codes can be found in Table 1. The water addition is reported as vol.% over the theoretical volume of the geopolymer solid matrix plus the added water. Solid loadings refer to the wt% of the starting metakaolin in slurries.

After the preparation, the G13 slurry underwent a maturation phase of 4 h at room temperature, which was set by a trial-and-error approach in order to avoid the consolidation of the slurry. After maturation, distilled water was added to the slurry (20, 50 or 70 vol.%) and mechanically mixed for 8 min. The mixture was cast in cylindrical rubber molds, and pre-cooled on the freeze dryer shaft, set at –40 °C, to produce monoliths reaching a height of 10 or 25 mm.

Cast slurries were frozen at –40 °C and the solidified phase was sublimated at P = 10 Pa in 24 h (Edwards Mod. MFD01, Crawley, UK). After demolding, samples were rinsed in deionized water to remove any residues of unreacted potassium silicate and then dried in a heater at 100 °C for 5 h. At least five samples for each formulation were produced for the reproducibility assessment of the ice-templating process.

### 2.2. Characterization and analytical techniques

The morphological and microstructural features of freeze-cast geopolymers were examined by environmental Scanning Electron Microscopy (E-SEM FEI Quanta 200, FEI Company).

**Table 1**  
Freeze-cast and reference geopolymer compositions.

Sample code	K Silicate dilution, H <sub>2</sub> O/K <sub>2</sub> O	Additional H <sub>2</sub> O for freeze casting (vol %)	Solid loading wt%	Maturation step
G13	13.5	–	63	24 h RT + 24 h 80 °C
G13-20	13.5	20	53	4 h RT
G13-50	13.5	50	36	4 h RT
G13-70	13.5	70	23	4 h RT

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