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Porous geopolymers: processing routes and properties

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Abstract. Cellular ceramics constitute a specific class of materials containing a high level of porosity, greater than 60 vol%, which are characterized by the presence of three-dimensionally arranged open and/or closed cells. Because of their structure, cellular ceramics exhibit a unique combination of properties such as low density, low thermal conductivity, low thermal mass, high permeability, high thermal shock resistance and high specific surface area, making them essential for various engineering application. Nowadays, porous geopolymers have been the focus of promising research in the field of porous inorganic materials because of their unique combination of good thermal stability and excellent mechanical properties. An interesting technological feature is that their solidification kinetics is easily adjustable and thanks to ceramic-like structure they have significant structural stability at elevated temperatures. The processing methods used for the fabrication of porous geopolymers can be divided into various approaches. Many methods have been explored to synthesize reproducible porous sponges or foams from geopolymer systems, such as gaseous method, rapid solidification, foaming, freeze-casting and/or combination of them. Concerning the macro/micro-structure of cells, the processing can be strongly influenced by various characteristics as a chemical composition, rheological behaviour of the slurries, kinetics of pore formation and hardening behaviour. This study presents methods of processing and manufacturing approaches with respect to types of porous materials and experimental results in this field.

1. Introduction

Porous inorganic materials have been attracting significant attention in widespread application fields such as catalysis supports, electrolyte carriers, membranes for separation and purification, insulators, filters, sensor carriers and biomedical scaffolds. Mainly, for these applications ceramic materials are suitable due to their exceptional combination of properties such as excellent chemical resistance, high melting point and thermal conductivity, thermal shock resistance, low thermal expansion coefficient, controlled permeability, high surface area, low density and high specific mechanical strength [1].

Extensive research efforts have been directed in development of porous ceramics because of possessing pivotal microstructural properties such as stable and uniform porous structure, high surface area, tunable pore size and well-defined surface properties. The role of porous structure in ceramic materials for different application is not identical and porous ceramics have several main types of structure, which mostly depend on the pore-formation method. Porous materials are classified into three classes depending on the pore diameter, d: macroporous ($d > 50$ nm), mesoporous ($50 \text{ nm} > d > 2$ nm), and microporous ($d < 2$ nm), according to the nomenclature of IUPAC (International Union of Pure and Applied Chemistry). Moreover, porous materials can be described through pore type, morphology and orientation. Besides the classification to open (interconnected) and closed (isolated) porosity the shape of the pores can be design as honey-comb, lotus-type, reticulated or bubble-like foamed materials and/or combination of these [2, 3].

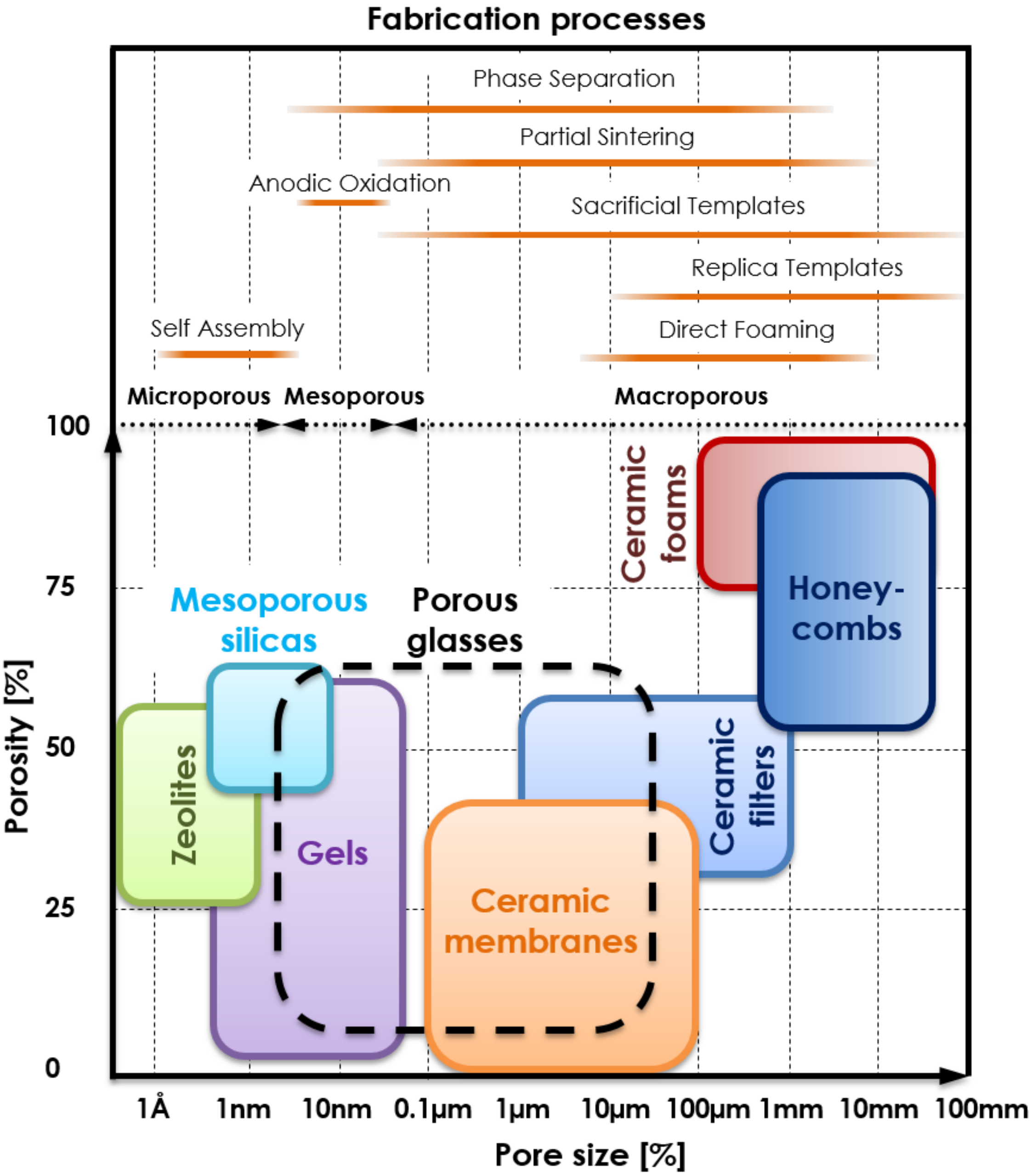

Figure 1. Pore size and porosity of typical porous materials and fabrication processes.

There are numerous pore-formation methods, which differ in principle: a) impregnation of a polymer cellular matrix with a ceramic suspension; b) templating of natural porous materials; c) introduction of foam-forming additives producing pores into an initial mixture; d) mechanical incorporation of air (gases) into ceramic suspension; e) swelling of the ceramic mixtures; f) introduction of filler grains with their own porosity into the ceramic mixture; g) mechanical pultrusion/injection or additive manufacturing of ceramic slurries; h) electrochemical treatment/deposition and varied modifications of these. Subsequently, many manufacturing techniques are applied to obtain preferred porous structure of ceramic mixtures such a freezing, drying, evaporation, dissolution and thermal treatment [4, 5].

Figure 1 shows schematic illustration of typical porous ceramic/ceramic-like materials depending on porosity and pore size, supplemented by fabrication processes. Micro-macro porous ceramics of vast chemical compositions have been prepared using these fabrication routes, based on Al_2O_3, SiO_2, ZrO_2, TiO_2, MgO, Cr_2O_3, Fe_2O_3 and their binary/ternary compounds or more complex compositions. Besides, carbides, nitrides, borides, silicides and combination of these were intensively studied. Also, natural clays and minerals, phosphate-based compounds or compositions with exotic elements were extensively prepared and tested [6].

Comparing to traditional ceramic materials, geopolymers are a relatively new group of materials that have been extensively studied for over three decades [7]. In general, geopolymers can be prepared by dissolution of natural or synthetic aluminosilicate raw materials (clays, slags, fly ashes, glasses) under strong alkaline conditions. The alkalination has the effect of depolymerization of silicates/aluminates. The structural reorganization results in polycondensation followed by formation of rigid aluminosilicate framework [8]. Over the past years, the geopolymers showed a variety of interesting properties and characteristics, such as excellent thermal stability, mechanical strength, acid resistance, low shrinkage, low thermal conductivity, adjustable setting at relatively low production costs. Their physical properties make them a viable alternative for many conventional binders and their synthesis at low temperature is an important benefit in industrial scale. Also, the chemical composition allows transformation of predominantly amorphous structure into various crystalline forms due to the applied heat treatment [9-12].

In recent years, porous geopolymers have gained a lot of attention because of unique properties associated with thermal and chemical resistance. Moreover, significant material and technological advantages are ceramic-like structure with high melting point and easy control of solidification kinetics [13]. Many methods have been explored to synthesize reproducible porous geopolymer sponges, foams, graded and/or hollow structures. In general, processing techniques can be divided into several methods such as: a) Direct foaming, b) Sacrificial template, c) Emulsion templating, d) Additive manufacturing, e) Replica templating and combination of these. Detailed processing features of each approach have been provided by excellent review article published elsewhere [14].

2. Processing techniques

2.1. Direct foaming

In the direct foaming technique, fresh geopolymer foam is produced by incorporating of air or gas products into a wet geopolymer slurry which is subsequently cured and solidified under slightly increase temperature (40-80°C). Gaseous products are usually formed by the dissolution of chemical additives (blowing agents) under alkaline conditions of geopolymer slurries. Examples of these additives may be aluminum or silicon metal powders or silicon-containing compounds [15-17]. Also, the most commonly used solution-based additive is hydrogen peroxide or other compounds based on hypochlorites and perborates [18,19]. It should be noted that blowing agents generate porosity through gas bubbles (mostly O_2 and H_2) under unstable conditions (high surface tension, coalescence, drainage). For these reasons, the resultant porous structure is formed by heterogeneous pores of varying size and distribution. In order to prevent or reduce such a structural phenomenon a number of stabilizing agents can be added to the suspension (surfactants, particles, fibers). **Figure 2** shows schematic fabrication route of direct foaming incl. applied additives and key properties. A wide variety of material and processing properties (chemistry, blowing agents, surfactants, rheology, solidification conditions) leads to the formation of porosity which is ranging from closed inhomogeneous cell size distribution to cellular morphology with open-cell structure and interconnected pores [20]. In summary, the experimental results reveal that using of direct foaming technique in geopolymer mixtures generates both open and closed-cell structures with a wide range of pore size (5 – 3000 μm) and total porosity (30 – 85 vol%).

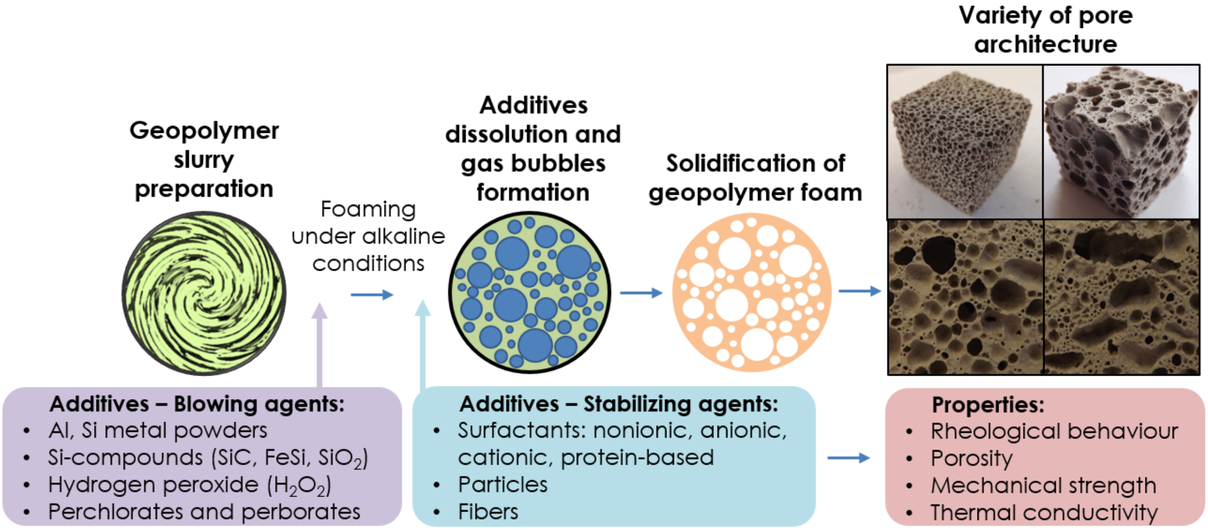

Figure 2. Schematic fabrication route of direct foaming method.

2.2. *Sacrificial template*

The sacrificial template method is one of the fabrication techniques where porous geopolymer is formed by mixing appropriate amounts of sacrificial template as a pore forming additive with a geopolymer slurry. This method leads to formation of porous material displaying a negative replica of the original sacrificial template. The porosity can be generated by extraction of template from the biphasic material through thermal decomposition by applying of thermal treatment and/or melting, dissolution and sublimation. The way that the sacrificial template is extracted from the biphasic material depends primarily on the type of pore former (e.g. natural/synthetic organics, liquids, salts).

The experimental results reveal successful synthesis of lamellar macro-porous potassium-based geopolymer by ice-templating via freeze-casting procedure. Ice-templated hierarchical structure had 53–83% total porosity. A broad mesopore distribution was detected between 4 and 100 nm with maxima from 5 to 7 nm, while macropores in the range from 1 to 100 µm [21]. Different amounts of water (20, 50, 70 vol%) were mixed with the geopolymer slurry to induce lamellar ice growth by unidirectional freezing. A lower water content (30%) and curing at 80°C after maturation at room temperature was conducive to a narrow lamellar pore width distribution in the range from 30 to 130 µm [22]. **Figure 3** shows schematic fabrication route of sacrificial template method with an example of polymer filler and water/ice-based templating.

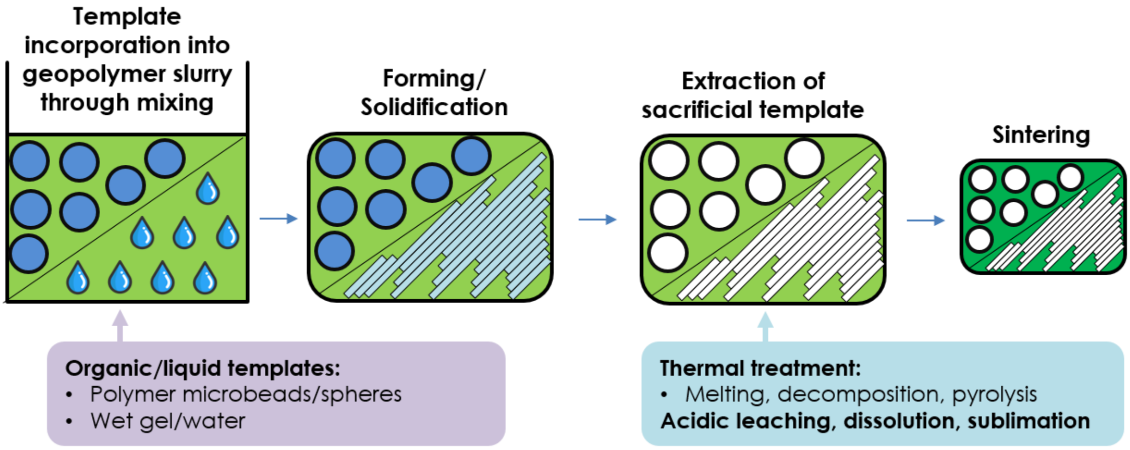

Figure 3. Schematic fabrication route of sacrificial template method.

2.3. Additive manufacturing

In the past few years, additive manufacturing (3D printing) has received considerable attention from a number of grounded reasons. This technology brings benefits to the creation of materials with a complex geometry and high precision, maximum material savings and flexibility in design. A wide range of material are currently used in 3D printing include metals, polymers, ceramics and inorganic pastes.

Recently, highly porous ceramic lattices (porosity up to ~ 71 vol%) were fabricated with ~ 0.8 mm struts based on metakaolin and sodium silicate solution geopolymer mixtures. Rheological properties of geopolymer pastes were optimized to possess Bingham shear thinning behavior and graded lattice with increasing spacing between subsequent struts was designed [23].

Also, innovative methodology of powder-based 3D printing process was developed to fabrication of slag-based geopolymer. Cubic and plate structures with complex geometries were manufactured by depositing binder liquid selectively into to powder bed. The cubic structure revealed apparent porosity ~ 57% and uniaxial compressive strength ~ 0.9 MPa. A post-processing method (1-day alkaline solution immersion) reduced the anisotropy of the printed material and increased the strengths up to ~ 10 MPa [24].

Moreover, additive manufacturing of geopolymer based on fly ash, granulated blast-furnace slag, silica fume and potassium hydroxide/silicate solution was introduced. Comparing to casted, printed sample exhibited similar or higher compressive strength when load was applied in a plane perpendicular to the layers ranging from 30 to 40 MPa after 28 days [25].

Besides, extrusion based 3D printing graphene oxide/geopolymer nanocomposite was reported. The nano-graphene oxide in the Na-based geopolymer system resulted in proper rheological properties for extrusion, the higher compressive strength of about 30 MPa and increased electrical conductivity [26].

2.4. Replica templating

In the replica technique, a highly porous polymeric sponge is initially soaked into a ceramic suspension until the internal pores are filled in with ceramic material. During the next stage, the suspension has to be sufficiently fluid to be partially removed by applied pressure but viscous enough to avoid dripping. Hence, ceramic suspensions exhibiting shear-thinning behavior are needed to efficiently coat the polymeric template. The ceramic-coated polymeric template is subsequently dried and heat treated to allow the gradual decomposition and diffusion of the polymeric material. Densification by sintering at desired temperature by specific heat treatment regime usually follows.

This procedure has been successfully applied for synthesis of leucite-based ceramic foam derived from potassium-based geopolymer precursor. Compared with traditional ceramics, the fabrication process has been greatly time reduced by accelerating the solidification kinetics of geopolymer mixture through heat treatment at 60 °C for 30 min in a closed container. Compressive strength reached ~ 0.85 MPa after sintering at 1300 °C, with an open porosity of ~ 79 vol%. The entire structural grid is presented by interconnected network with cellular structure where pore size ranges from 1 to 2 mm. It was demonstrated that the predominantly amorphous geopolymer matrix can be effectively reinforced by fine ceramic filler for the applied heat treatment [27]. Also, different types of ceramic fillers (alumina, cordierite) were tested and demonstrated a positive influence on the thermal resistance of the geopolymer composite during the heat treatment [28].

Figure 4 shows schematic fabrication route of replica template method for geopolymer mixtures with an important processing parametres in the sense of step by step process.

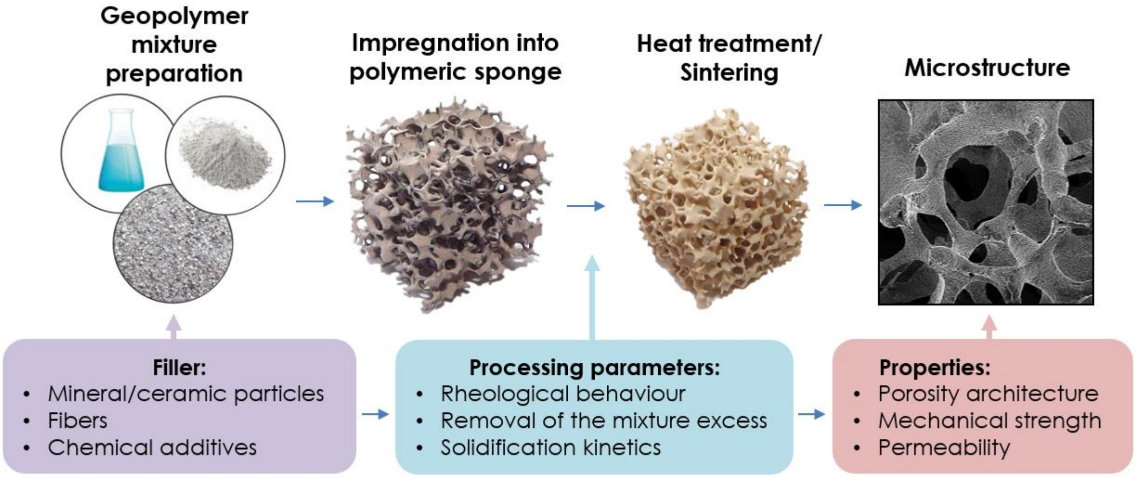

Figure 4. Schematic fabrication route of replica template method for geopolymer mixtures.

3. Conclusion

Various processing routes using direct foaming, replica, sacrificial template or additive manufacturing methods are nowadays available for the production of meso/macroporous ceramics. The use of this knowledge has led to the successful application of these techniques in the preparation of many types of porous geopolymers. The combination of these techniques or the modification of the manufacturing process may lead to the preparation of non-traditional porous materials with unique properties. The diversity of the chemical composition of geopolymer materials, including the conditions of preparation, implies the need for innovative processes. The resultant porous structures can therefore be an improved alternative to traditional ceramic materials in certain applications.

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