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RAPID COMMUNICATION**Journal**
of the American Ceramic Society**Highly porous mullite ceramics from engineered alkali activated suspensions****Acacio Rincón Romero¹**  | **Hamada Elsayed^{1,2}**  | **Enrico Bernardo¹** ¹Dipartimento di Ingegneria Industriale, Università degli Studi di Padova, Padova, Italy²Ceramics Department, National Research Centre, Cairo, Egypt**Correspondence**Enrico Bernardo, Dipartimento di Ingegneria Industriale, Università degli Studi di Padova, Padova, Italy.
Email: enrico.bernardo@unipd.it**Funding information**

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Abstract

Air may be easily incorporated by vigorous mechanical stirring, with the help of surfactants, of activated geopolymer-yielding suspensions. The cellular structure is stabilized by the viscosity increase caused by curing reactions, configuring an “inorganic gel casting”. The present paper is aimed at extending this approach to mullite foams, obtained by the thermal treatment of engineered alkali activated suspensions. “Green” foams were first obtained by gel casting of a suspension for Na-geopolymer enriched with reactive γ -Al₂O₃ powders. Sodium was later extracted by ionic exchange with ammonium salts. In particular, the removal of Na⁺ ions was achieved by immersion in ammonium nitrate solution overnight, with retention of the cellular structure. Finally, the ion-exchanged foams were successfully converted into pure mullite foams by application of a firing treatment at 1300°C, for 1 hour. Preliminary results concerning the extension of the concept to mullite three-dimensional scaffolds are presented as well.

KEYWORDS

ceramic foam, geopolymer, mullite

1 | INTRODUCTION

Geopolymers, i.e., products of the condensation of hydrated alumino-silicate oligomers (in turn provided by alkaline dissolution of alumino-silicate raw materials) are receiving a growing interest in many industrial fields, particularly for the replacement of traditional cementitious materials as well as of traditional ceramics. In fact, besides being formed at low temperature, geopolymer components can be used up to medium-high temperature (typically below 1200°C).¹⁻⁴

The present paper is essentially aimed at merging concepts, corresponding to two different emerging research directions in the field of geopolymers, represented by the obtainment of highly porous foams by frothing of geopolymer-yielding suspensions,⁵ and the conversion of geopolymers into advanced ceramics by controlled heat treatment.⁶⁻⁸

The foaming of geopolymers, by frothing, relies on the significant increase of viscosity caused by the progressive curing of oligomers, dispersed in aqueous suspensions, in turn due to alkali activation. More precisely, alkali activated suspensions exhibit a marked pseudoplastic behavior, so that air bubbles, incorporated by intensive mechanical stirring (with the help of surfactants), at high shear rates and low viscosity, are effectively “frozen” when stirring stops, at low shear rate and high viscosity.^{5,9,10} Since this behavior does not depend on the introduction of any organic gelling additive (typically adopted for gel casting of ceramic and glass-ceramic foams^{11,12}), we can define the process as “inorganic gel casting”. The zeolitic gel from silicate oligomers can actually be replaced by other gels, caused by alkali dissolution and subsequent condensation of corrosion products, like C-S-H gels from the use of glass powders as starting materials.^{13,14}

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The conversion of geopolymers into advanced ceramics generally corresponds to the transformation of hydrated zeolite-like gels (i.e., aluminosilicate network structures, consisting of cross-linked AlO_4^- and SiO_4 tetrahedra), incorporating alkali ions, such as Na^+ , K^+ , and Cs^+ (providing the charge balance), into anhydrous alkali aluminosilicates, in the form of feldspathoids, at temperatures from 800°C to 1400°C .⁶⁻⁸ The chemical and thermal stability of the developed phases depend on the alkali ion: Cs-based geopolymers, as an example, are known to yield more refractory phases, such as pollucite ($\text{Cs}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$),⁸ featuring also a low thermal expansion coefficient.¹⁵

The molecular balance between alkali oxides, Al_2O_3 and SiO_2 , in the final ceramic, obviously depends on the formulation of the geopolymer. Chemical treatments on the geopolymer, however, may determine significant changes, especially for the removal of alkali. In fact, the alkali containing charge-balancing sites of aluminosilicate networks can be replaced with a range of other cations, not only for enhancing the functional properties of geopolymers (e.g., as antimicrobial agents or photocatalysts)^{16,17} but also for modifying the thermal transformation products. In particular, alkali-free ceramics are fundamentally achievable by ion exchange of alkali ions with ammonium ions, before firing.^{16,18,19} Mullite containing ceramics are thus feasible, although the low $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in geopolymers does not allow for the obtainment of this relatively alumina-rich phase ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) as the only phase (the silica excess forming a vitreous matrix).^{16,18}

In this investigation, the ceramic residue of the transformation of geopolymers, after dealkalinization, is corrected in order to have nearly phase pure mullite, by introduction of a reactive alumina filler in the starting suspensions. A valuable inspiration came from previous experiences concerning geopolymers embedding a reactive carbon filler,^{19,20} allowing for carbothermal reduction and nitridation of ion-exchanged geopolymers, with the obtainment of SiAlONs,¹⁸ in the form of powders. A similar approach is known to lead to SiC nanoparticles.²¹ In our case, the introduction of the filler, consisting of γ -phase Al_2O_3 (already known to yield mullite by interaction with silicone resins, pyrolyzed in air, as silica precursors²²), did not compromise the shaping into highly porous foams, by frothing. The approach was later extended to the fabrication of three-dimensional scaffolds, by direct ink writing of suspensions undergoing progressive gelification (by analogy to what was previously done with conventional geopolymers¹⁰).

2 | EXPERIMENTAL PROCEDURE

Metakaolin (Argical 1200s, AGS Mineraux) and commercial γ - Al_2O_3 (Puralox TH 100/150, of mean particle size

$<35\ \mu\text{m}$, SASOL, Hamburg, Germany) were dissolved in an aqueous solution of 2.5 mol/L NaOH (reagent grade, Sigma–Aldrich, Gillingham, UK), in order to achieve an overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 0.67 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2/3$, typical of mullite); the total solids content of the suspension was 28 wt%. The mixture was kept under mechanical stirring (500 rpm) at room temperature for 2 hour in order to achieve the dissolution of the metakaolin and the dispersion of the alumina filler in the slurry. The mixture was cast in closed polystyrene (PS) cylindrical molds and underwent a precuring step of 2 hour at 75°C . The suspension was later added with Triton X-100 (polyoxyethylene octyl phenyl ether— $\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$, $n = 9-10$, Sigma–Aldrich, Gillingham, UK) surfactant, for a total amount of 4 wt%, and subsequently subjected to intensive mechanical stirring (2000 rpm, for 10 minute), in PS molds. After curing at 40°C for 48 hour, foamed samples could be demolded and subjected to ion exchange, consisting of immersion for 24 hour in a 0.1 mol/L NH_4NO_3 solution (following the approach of Bortnovsky et al¹⁸), for a solid/liquid ratio of 1/100. Finally, ion-exchanged samples were subjected to thermal treatment at 1300°C for 1 hour ($10^\circ\text{C}/\text{min}$ heating rate).

The partially gelified suspension, after the precuring step, could be used also for direct ink writing experiments. It was transferred into plastic syringes (having a volume of approx. $30\ \text{mm}^3$), which served as a cartridge for extrusion by means of a Delta printer (Delta Wasp 2040 Turbo, Wasproject, Massa Lombarda, Italy) equipped with a pressurized vessel. The syringe base system mounted conical nozzles (Nordson Italia S.p.a., Segrate, IT) with a diameter of $400\ \mu\text{m}$, while the printer operated at a layer resolution of $50\ \mu\text{m}$. Printed pastes were subjected to curing, ion exchange and firing in the same conditions as adopted for the foams.

Geopolymer composite samples, before and after firing, were subjected to microstructural characterization, by means of X-ray diffraction (Bruker D8 Advance, Karlsruhe, Germany— CuK_α radiation, $0.15418\ \text{nm}$), pycnometry, optical, and electron microscopy (AxioCam ERc 5 second Microscope Camera, Carl Zeiss Microscopy, Thornwood, NY; FEI Quanta 200 ESEM, Eindhoven, The Netherlands). The phase identification, from diffraction patterns, was performed by means of the Match![®] program package (Crystal Impact GbR, Bonn, Germany), supported by data from the PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA). Selected samples were subjected to compression tests by using an Instron 1121 UTS (Instron, Danvers, MA) machine, with a crosshead speed of $0.5\ \text{mm}/\text{min}$. The tests involved foam samples of about $10\ \text{mm} \times 10\ \text{mm} \times 10\ \text{mm}$, cut from larger specimens, as well scaffold samples of about $10\ \text{mm} \times 10\ \text{mm} \times 6\ \text{mm}$. Each data point corresponded to 5-6 samples.

3 | RESULTS AND DISCUSSION

Figure 1 represents the evolution of samples, from the “after foaming” condition to the “dealkalinized” and “fired” states. We can note that despite the significant filler loading, the inorganic gel casting approach led to a quite homogeneous cellular structure (Figure 1A), not degraded by the ion-exchange process; in fact, no cracks were visible in the transformed foam (Figure 1B). The homogeneity and the absence of cracks were confirmed after firing at 1300°C (Figure 1C).

Figure 2 confirms the nature of the adopted filler, effectively consisting of γ - Al_2O_3 (PDF#49-0134). This phase remains clearly detectable in the geopolymer composite, after curing, along with minor traces of quartz (PDF#87-2096), attributed to impurities in the metakaolin, and paragonite ($\text{NaAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, PDF#87-0091). The latter phase is known to form upon curing of Na-based synthetic aluminosilicate binders.²³ The broad amorphous hump, in the 2θ range of 18° – 40° , is actually not consistent with amorphous stoichiometric geopolymers, typically exhibiting a bump from 24° to

34° .^{24,25} Owing to the formation of paragonite (including significant amounts of Na and Al), the developed gel probably did not possess the zeolite-like structure found in true geopolymers.²⁶ The assessment of the real nature of the gel (e.g., by TEM) will be object of future studies.

The thermal treatment was clearly sensitive to the ion exchange. Fragments of geopolymer foam not subjected to ion exchange led to a glass matrix composite, with strong peaks of α - Al_2O_3 (PDF#75-1862) emerging from the typical “halo” of amorphous phase. A minor peak could be ascribed to nepheline (PDF#79-0992), in analogy with the firing of Na-based geopolymers, as previously mentioned.⁷ In other words, with sodium still incorporated in the matrix, the same matrix and the filler had a substantially independent evolution. On the contrary, the two phases reacted significantly, after ion exchange, with mullite (PDF#83-1881) being clearly recognized.

The flat background revealed the practical absence of glass phase, while only minor peaks could not be ascribed to mullite. The best matching with experimental data was

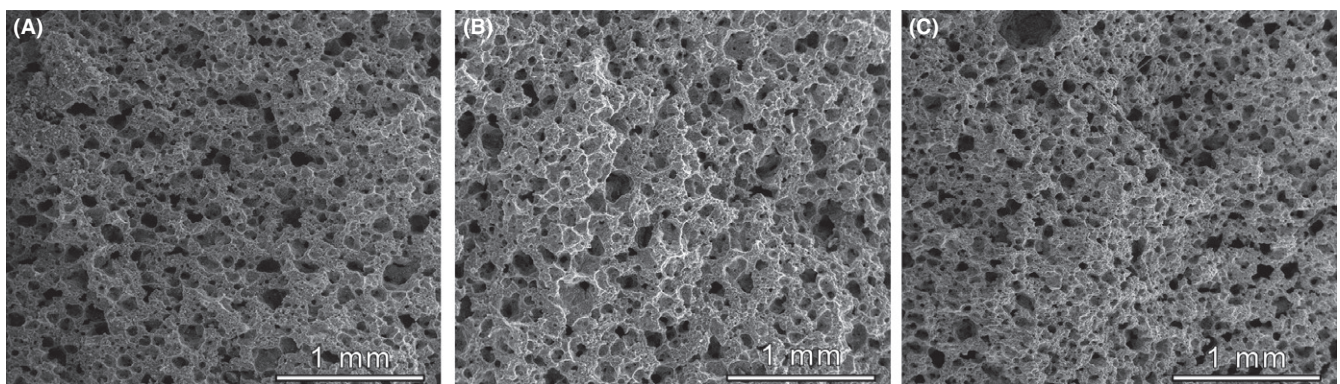


FIGURE 1 Morphology of geopolymer composites at various processing steps: (A) after low temperature curing; (B) after ion exchange; (C) after firing at 1300°C

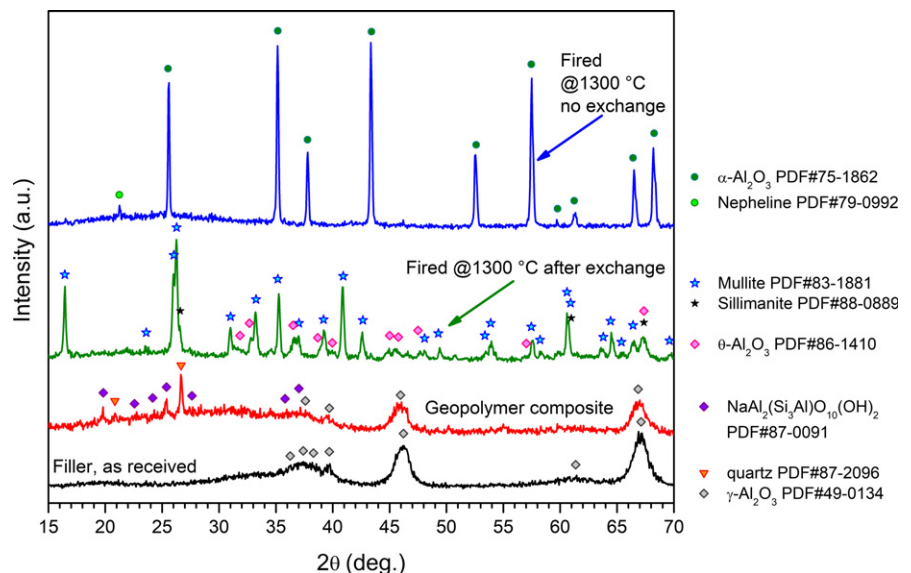


FIGURE 2 Mineralogical evolution of geopolymer composites at various processing steps

provided by sillimanite (PDF#88-0889), i.e., a silica-rich alumino-silicate ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) and $\theta\text{-Al}_2\text{O}_3$ (PDF#86-1410), both attributable, in our opinion, to incomplete reaction between the constituents. $\theta\text{-Al}_2\text{O}_3$ can be seen as the result

of the thermal transformation of the γ -phase, with progressive dehydration (transition aluminas are known to transform into corundum, by progressive heating, in the sequence $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ ^{27,28}), but its presence was quite

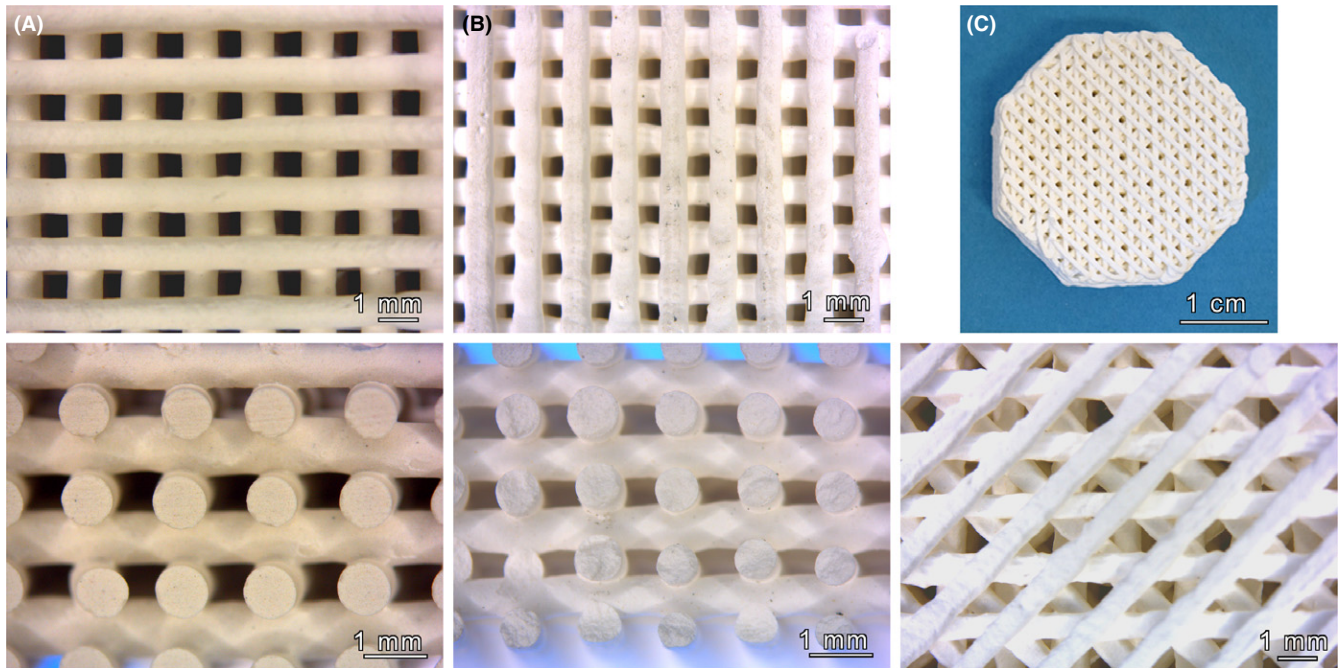


FIGURE 3 Morphology of geopolymer composites: (A) typical scaffold geometry after curing and ion exchange (up, top view; down, cross section); (B) scaffold geometry after firing (up, top view; down, cross section); (C) alternative scaffold design

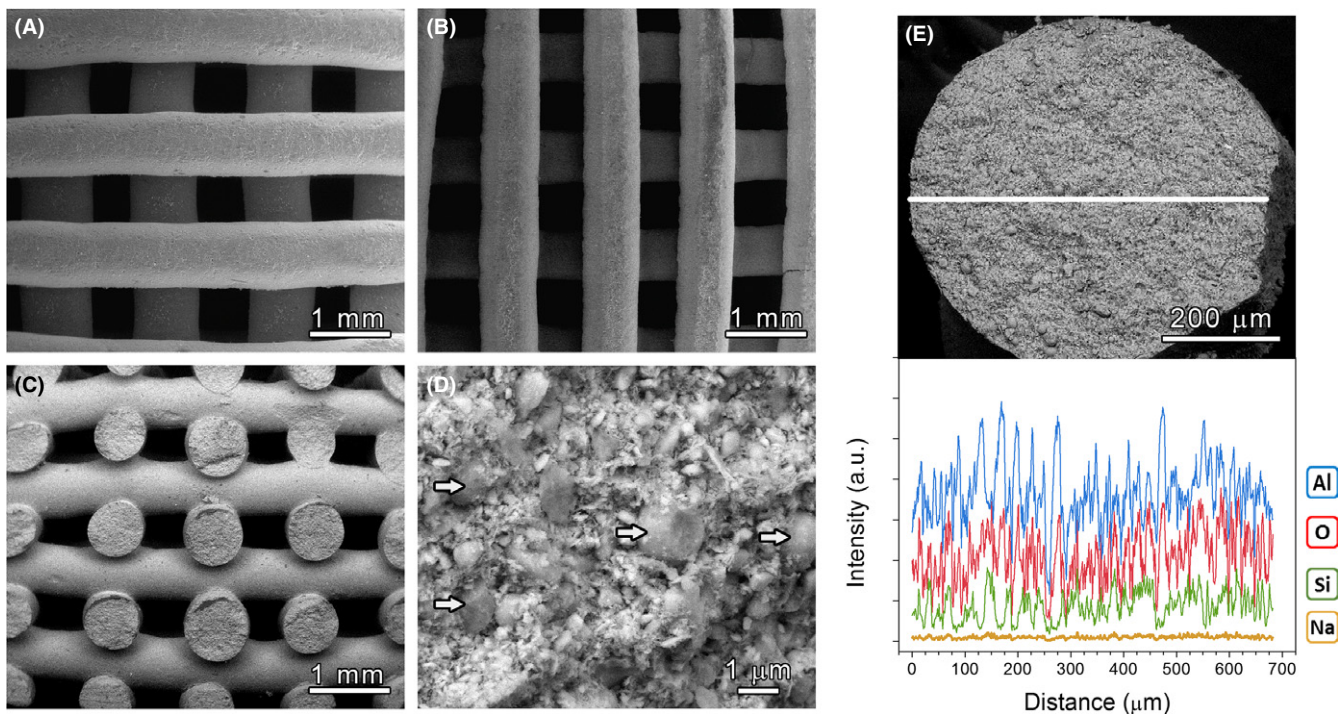


FIGURE 4 Microstructural details of geopolymer-derived mullite scaffolds: (A) after curing; (B) after firing (C) interpenetration of overlapping filaments; (D) high magnification of a strut (Al-rich granules marked by arrows); (E) X-ray fluorescence signals through the filament diameter

surprising, being found after a treatment well above its stability range (1100°C).²⁸ In our opinion this could be due to a reaction between the hydroxyl groups of alumina and a silicon-containing precursor (in this case represented by the geopolymer matrix), already known to stabilize the γ -phase.²⁹ Longer treatments at 1300°C would probably determine a complete reaction, and will be the object of further investigations.

The high filler loading also favored a secondary shaping option. As shown by Figure 3A, direct ink writing of pastes available after the precuring step led to reticulated scaffolds with no evidence of viscous collapse. The overlapping filaments remained parallel after curing, keeping wide pores in the z direction (Figure 3B).

The ion exchange and the firing did not determine any degradation. From Figure 4A, B and C we can observe that the transformations did not cause any microcracking, even for larger filament spacings (the absence of sagging, even for large voids, again indicated the marked pseudoplasticity of the pastes). The practical absence of Na⁺ was demonstrated along a whole filament, in Figure 4E, showing the elemental distribution through the diameter (obtained by collection of X-ray fluorescence signals): the Na-related signal is flat and close to zero. The inherent micro- and meso-porosity of geopolymers evidently favoured an in-depth ion exchange. The fluctuations in the Al and Si distributions, along the diameter, were consistent with the X-ray analysis. Some Al-rich granules (marked by arrows in Figure 4D), in fact, could be ascribed to θ -Al₂O₃.

The absence of cracks in both foams and scaffolds is the reason for good strength-to-density ratios. With a porosity of 73% \pm 3%, almost completely open (pycnometry analysis yielded an open porosity of 65% \pm 2%) the foams reached a compressive strength of 11 \pm 1 MPa, in good agreement with the values for commercial foams, typically used for thermal protection and metal filtration.³⁰ Scaffolds (for a close filament spacing, like that in Figure 4A) achieved a compressive strength 5 \pm 2 MPa, with a density of 0.84 \pm 0.04 g/cm³ (73% \pm 5% total porosity).

Given the application of time-consuming processes, such as ion exchange, the proposed approach might be found hardly sustainable against the processes already applied for commercial mullite foams; however, the flexibility in the shaping is believed to provide a valid compensation. As an example, the refinements in the processing of geopolymer foams by gel casting (leading to significant enhancement of both overall porosity and specific surface, owing to the overlapping of contributions of surfactants and gas release, e.g., from decomposition of H₂O₂^{31,32}) can be reasonably transferred to geopolymer composites. Additional opportunities may be provided by the control of free water segregation, e.g., by addition of acrylate-functional silane coupling agents.³³ Direct ink writing, on the other hand, may be

applied to a number of alternative shapes (an example is shown in Figure 3C). Finally, the proposed technology has some potential even beyond mullite: treatments in alternative atmospheres (e.g., N₂) are currently under investigation with the aim of testing the formation of oxynitride phases (SiAlONs), in analogy with what done for ion-exchanged C-filled geopolymer powders.^{19,20}

4 | CONCLUSIONS

One may conclude that:

1. Gel casting of alkali activated metakaolin suspensions can be exploited for the development of highly porous geopolymer composite foams as well as reticulated scaffolds, by frothing and direct ink writing, respectively;
2. Both types of cellular geopolymer composites were successfully subjected to dealkalinization, by means of ion exchange in aqueous solution of ammonium nitrate, with no degradation of the microstructure;
3. Owing to dealkalinization, the geopolymer matrix could react easily with the γ -Al₂O₃ secondary phase, leading to the development of nearly phase pure mullite; again, the transformation did not cause any significant microstructural degradation;
4. Geopolymers with the support of engineered fillers and dealkalinization treatments have a large potential for the obtainment of advanced ceramics, with a distinctive coupling of synthesis and shaping.

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ORCID

Acacio Rincón Romero  <http://orcid.org/0000-0003-0350-8304>

Hamada Elsayed  <http://orcid.org/0000-0002-9818-4498>

Enrico Bernardo  <http://orcid.org/0000-0003-4934-4405>

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