



Development of membranes based on recycled geopolymer and zeolite through a cold sintering process

Valentina Medri^{*}, Maria Chiara Marchioni, Elena Landi, Elettra Papa^{*}

National Research Council - Institute of Science, Technology and Sustainability for Ceramics (CNR-ISSMC), Via Granarolo, 64, Faenza, RA 48018, Italy

ARTICLE INFO

Keywords:

Cold sintering process
Porosity
Geopolymer
Membrane
Recycling

ABSTRACT

The cold sintering process (CSP) was used to produce membranes and improve the densification of a geopolymer-zeolite matrix, fully recycling a waste geopolymer powder. The role of CSP parameters were studied varying temperature (25, 40 and 80°C), applied pressure (56 MPa and 168 MPa) and reactive solution (H₂O, KOH or NaOH 2, 4, 6, 8 M). CSP applied on the waste geopolymer powder (molar ratio Si/Al = 2.0 and K/Al = 1.0) resulted in relative densities ranging from about 50–77%, while modal pores varied from 0.006 μm to 0.017 μm in the mesopore range. Compressive strength was up to 45 MPa. The addition of 10 wt% of the waste geopolymer powder to a geopolymer-zeolite powder containing 81% of *in situ* synthesized NaA phase allowed a densification approaching 70% with mechanical strength up to 7.4 MPa.

1. Introduction

Nowadays, the reduction of environmental impact is an increasingly urgent issue and requires concrete actions that can allow to achieve the Green Deal of the European Commission [1]. To this end, one of the possible ways is to develop materials starting from waste and/or discarded raw materials in a circular economy model of materials loops [2]. Geopolymerization process is a well-known chemical process at low temperature for the production of synthetic alkali aluminosilicate materials. Wastes and by products [3–6] as well geopolymers [7,8] can be recycled by geopolymerization, mainly for building and construction application.

However, the field of application of geopolymers is much broader, being inorganic, intrinsically mesoporous and easy shaping (and “foaming”) materials [9–12]. The combination of these characteristics makes geopolymers appreciable both for structural use (thermal and acoustic insulation) as well as catalysts [13–15], oxygen carriers [16] and pH regulators [17]. Finally, geopolymers have possible uses as solid adsorbents for CO₂ [18–20] and water treatment [21,22], filters [23] and membranes [24–32] due to the different separation mechanisms (chemi- and physi-sorption, ion exchange) [33].

Recently Medri et al. [34] developed metakaolin K-based geopolymer granules suitable for the scale-up of ammonium recovery in a circular economy perspective. Beside the valuable adsorption properties, granules were also easy regenerable thanks to their stoichiometry

(molar ratio Si/Al = 2.0 and K/Al = 1.0) obtained through an optimized process able to synthesize a fully geopolymerized bulk material with a specific surface area of 77 m² g⁻¹ and a monomodal pore size distribution centred at about 0.01 μm. Granules were therefore obtained by grinding and sieving the bulk geopolymer thus leaving a fine portion of material unused. The possibility to recycle this “waste” fraction to reconstitute a highly stoichiometric and nearly mesoporous bulk geopolymer represents a challenge in view of a possible reuse as membrane, as in the case of selective adsorption of CO₂ [35] and/or filtration, such as ultrafiltration (range 0.01–0.1 μm) [36].

Gharzouni et al. [37] found that up to 20% of crushed geopolymer can be incorporated in substitution of metakaolin in the synthesis of metakaolin based geopolymers, while the use of a highly alkaline solution can promote polycondensation, increasing the mechanical properties. However, with the perspective of the 100% recycle, for geopolymer materials it is possible to use alternative production processes with lower environmental impact, such as those involving very low energy sintering (ULES - Ultra Low Energy Sintering) as the cold sintering process (CSP) [38]. In CSP the inorganic powder humidified with a transient liquid phase (in a fraction generally between 1% and 10% by volume [39]), is placed in a mould and then heated and simultaneously densified through the application of a uniaxial pressure [38]. The application of pressure (in a range between 100 and 500 MPa) and the presence of a reactive liquid are essential to achieve low-temperature sintering (from room temperature up to a maximum of 300°C). In fact,

^{*} Corresponding authors.

E-mail addresses: valentina.medri@issmc.cnr.it (V. Medri), elettra.papa@issmc.cnr.it (E. Papa).

<https://doi.org/10.1016/j.jeurceramsoc.2024.05.053>

Received 12 March 2024; Received in revised form 16 May 2024; Accepted 20 May 2024

Available online 23 May 2024

0955-2219/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

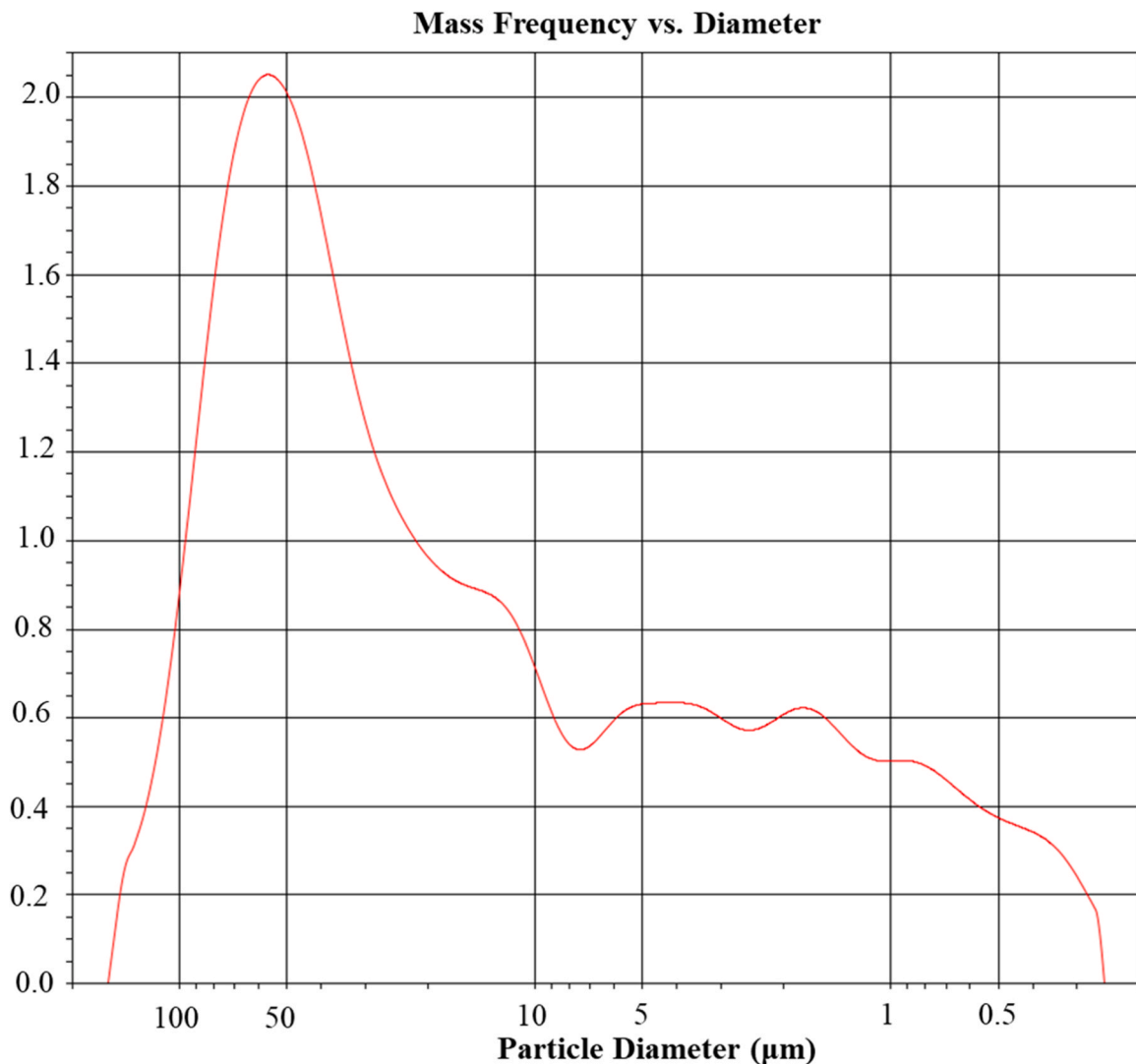


Fig. 1. The granulometric distribution of the K-G₂ powder.

the liquid phase must at least partially solubilize the inorganic powder (which must provide mobile ions), in order to allow the mass transport of the species that take part in the dissolution and precipitation processes, which are responsible for the densification of the material. The literature about CSP is rare and the aim is generally to increase the mechanical strength and reduce porosity. CSP protocols applied to geopolymers mainly focused on ‘reaction sintering’ of geopolymers, namely the geopolymer synthesis occurred during pressing [40] [41–44]. Filipponi et al. [40] investigated CSP on a mixture humidified with water of metakaolin and anhydrous sodium metasilicate. Pressure loads up to 20 MPa at 70 °C were used to achieve open porosities ranging from 30% to 65% with pores ranging from 1 to 20 µm to develop microfiltration membrane supports. Nishikawa et al. [41] used fly ash and sodium metasilicate hydrate as precursors obtaining almost zero porosity and a compressive strength of 425 MPa when using 100 MPa and 130 °C. Ranjbar et al. [42] hot-pressed a mixture of fly ash and alkali activator at 41.4 MPa and 350 °C achieving a compressive strength of 134 MPa with a porosity around 20%. On the contrary, Takeda et al. [45] proposed the “warm pressing” of an already reacted fly ash-based geopolymer powder at 70 °C–140 °C with a pressure of 200 MPa, indicating as a densification mechanism a secondary condensation of the unreacted geopolymer still containing –OH groups. At 130 °C the mechanical strength was 133 MPa with a porosity of 30%, while at 75 °C the mechanical strength was around 40 MPa. Concerning metakaolin-based

geopolymers, in view of producing geopolymer-based brake pads [46] CSP was applied at 20 MPa and 150 °C. The compressive strength which varied from around 12 MPa with a porosity of 50% up to over 200 MPa with a porosity of 10%, depended on the starting formulation as the highest strength values were achieved passing from a SiO₂/Al₂O₃ ratio around 4–5.

The present study aims to reconsolidate geopolymer powder and geopolymer-zeolite powder while maintaining a suitable porosity to produce membranes. For this purpose, CSP was used to fully recycle a waste geopolymer powder arising from the production of geopolymer granules previously used for the recovery of ammonium in a pilot plant [34]. CSP was tested on geopolymer-NaA zeolite powder, where crystalline NaA was *in situ* synthesized for CO₂ adsorption purposes [18], with the aim of increasing densification compared to the original matrix prepared through geopolymerization (i.e. the “slurry route”). The role of the CSP parameters on densification, textural and mechanical properties were studied varying temperature (25, 40 and 80 °C), applied pressure (56 MPa and 168 MPa) and reactive solution used to humidify the powders (H₂O, KOH or NaOH 2, 4, 6, 8 M).

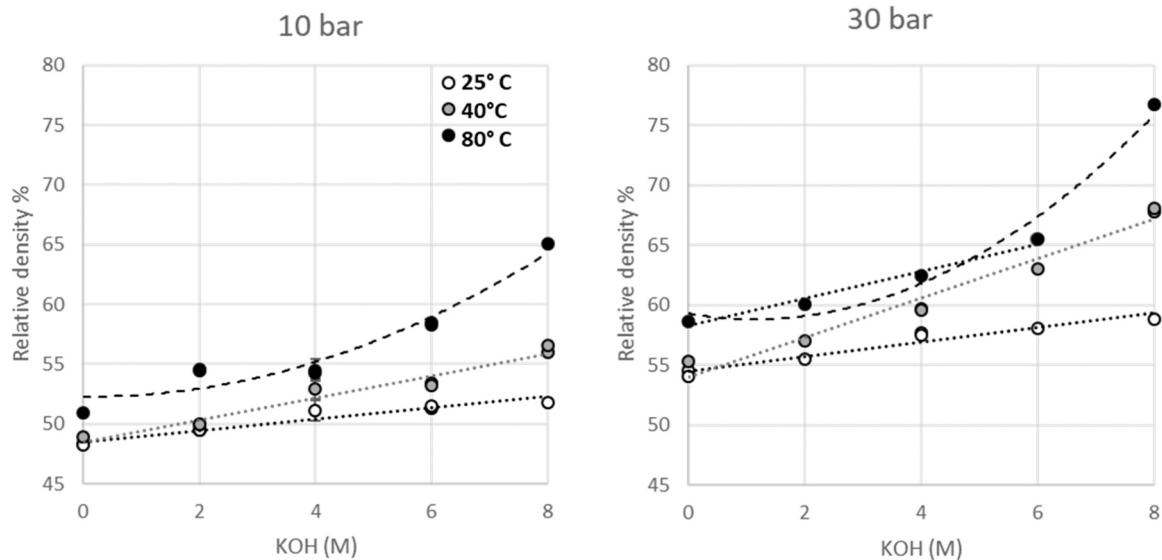


Fig. 2. Influence of the temperature on the densification of K-based samples at constant pressure and increasing molarity of the activator KOH. The nominal pressures of 10 and 30 bar correspond to 56 MPa and 168 MPa applied on the sample, respectively.

2. Materials and method

2.1. Sample preparation

The waste fraction generated during the production of geopolymer granules [34] was used as potassium-based geopolymer powder coded K-G₂. The K-G₂ bulk geopolymer, having a theoretical ratios Si/Al = 2.0 and K/Al = 1.0, was obtained using a “slurry route” from metakaolin and potassium disilicate solution. The sodium-based geopolymer (Na-G_{1,2}) was synthesized by adding a 12 M NaOH solution to the metakaolin. In the latter case, the presence of the Na⁺ cation and a Si/Al = 1.2 and Na/Al = 1.0 ratios allowed the *in situ* nucleation of the NaA zeolite, obtaining a geopolymer-zeolite material with 81% of crystalline NaA phase, as reported in [18].

After curing in silicone molds at 80°C, the consolidated materials were subsequently ground and sieved: K-G₂ and Na-G_{1,2} powders were the fractions with a particle size less than 200 μm. The granulometric distribution of the K-G₂ powder is reported in Fig. 1. The most frequent size value is 56 μm. (by X-ray Sedimentation, Sedigraph 5100, Micromeritics).

Then, an aqueous activator was added to the powders then consolidated using the Cold Sintering Process to obtain samples with a diameter of approximately 8 mm and a height of approximately 6 mm. For K-G₂ 0.3 ml of activator (KOH or H₂O) were added to 0.5 g of powder. In the case of the Na-G_{1,2}, a fraction of K-G₂ powder was added. From preliminary tests, in fact, it was not possible to obtain pellets based only on the Na-G_{1,2} matrix. For this purpose, maintaining a total quantity of powder equal to 0.5 g, CSP was carried out by adding 10 wt% of K-G₂, that was the minimum quantity to obtain materials that did not break during extraction from the mold. In this way, the K-based powder was used as a binder for the Na-G_{1,2} powder. Then, 0.3 ml of NaOH or H₂O were added as activator.

The wet powder was placed in a thermostated mold as reported in Medri et al. [47], where constant pressure was applied for a total time of 45 minutes (15 minutes with the thermostated system in operation and 30 minutes in the cooling phase of the mold). CSP was carried out by varying the following parameters: mold temperature (25, 40 and 80°C), nominal pressure of the press (10 and 30 bar corresponding respectively to 56 MPa and 168 MPa applied on the 0.8 cm diameter sample [47]) and activator (H₂O, KOH or NaOH 2, 4, 6, 8 M). After CSP, pellets were dried in heater at 80°C. All samples were then subjected to a conditioning treatment by washing. Specifically, the samples were left in

distilled water for 24 hours to remove any residues of alkaline solution, then in acetone for 1 hour, to remove residues of piston lubricant.

Samples by CSP were coded indicating the starting powders followed by pressure, temperature and activator. In detail, “G” is for the K-G₂ powder, while GZ refers Na-G_{1,2} powder mixed with a 10 wt% of K-G₂ powder. The letter “P” (for pressure) is followed by the value of nominal pressure of the press, while “T” (for temperature) is followed by the mould temperature. Finally, the letter “K” or “N” followed by a number indicates the alkaline solution of KOH or NaOH and respective molarity, while “W” indicates the use of water. As an example, the code G-P30-T25-W refers to a CSP sample obtained using K-G₂ powder, a nominal pressure of 30 bar, a temperature of 25°C and using water as activating solution.

2.2. Characterization

The densification of the samples after CSP was related to the relative density, calculated as reported in Eq. 1:

$$\text{Relative density \%} = \frac{\rho_{\text{bulk}}}{\rho_{\text{real Na-G}_{1,2}} \cdot x_{\text{Na-G}_{1,2}} + \rho_{\text{real K-G}_2} \cdot x_{\text{K-G}_2}} \cdot 100 \quad (1)$$

where:

- ρ_{bulk} is the bulk geometric density calculated by weight-to-volume ratio;
- ρ_{real} is the real density from a helium pycnometer (Multivolume pycnometer 1305, Micromeritics), namely $\rho_{\text{real K-G}_2} = 2.27 \text{ g cm}^{-3}$ and $\rho_{\text{real Na-G}_{1,2}} = 2.12 \text{ g cm}^{-3}$;
- x is the mass fraction of K-G₂ or Na-G_{1,2} in the powder mixture.

The microstructural characterization was performed by a field emission gun-scanning electron microscope (FE-SEM, ΣIGMA: Zeiss, Germany). The samples were coated with a thin layer of gold using a turbo-pumped sputter coater (Quorum Q150T ES).

Porosimetric characterization was performed by Mercury Intrusion Porosimetry (MIP) in the range 0.0058–100 μm using a Thermo Finningam Pascal 140 and Thermo Finningam Pascal 240, Thermo Fisher Scientific, Waltham, MA, USA.

Compressive strength tests were carried out on at least 3 specimens for each type of CSP samples, (diameter = 0.8 cm, height = 0.5–0.8 cm depending on relative density), with CSP net-shaped base faces using a testing machine (Zwick Z050, GmbH, Ulm, Germany) and a cross-head speed of 1 mm min⁻¹.

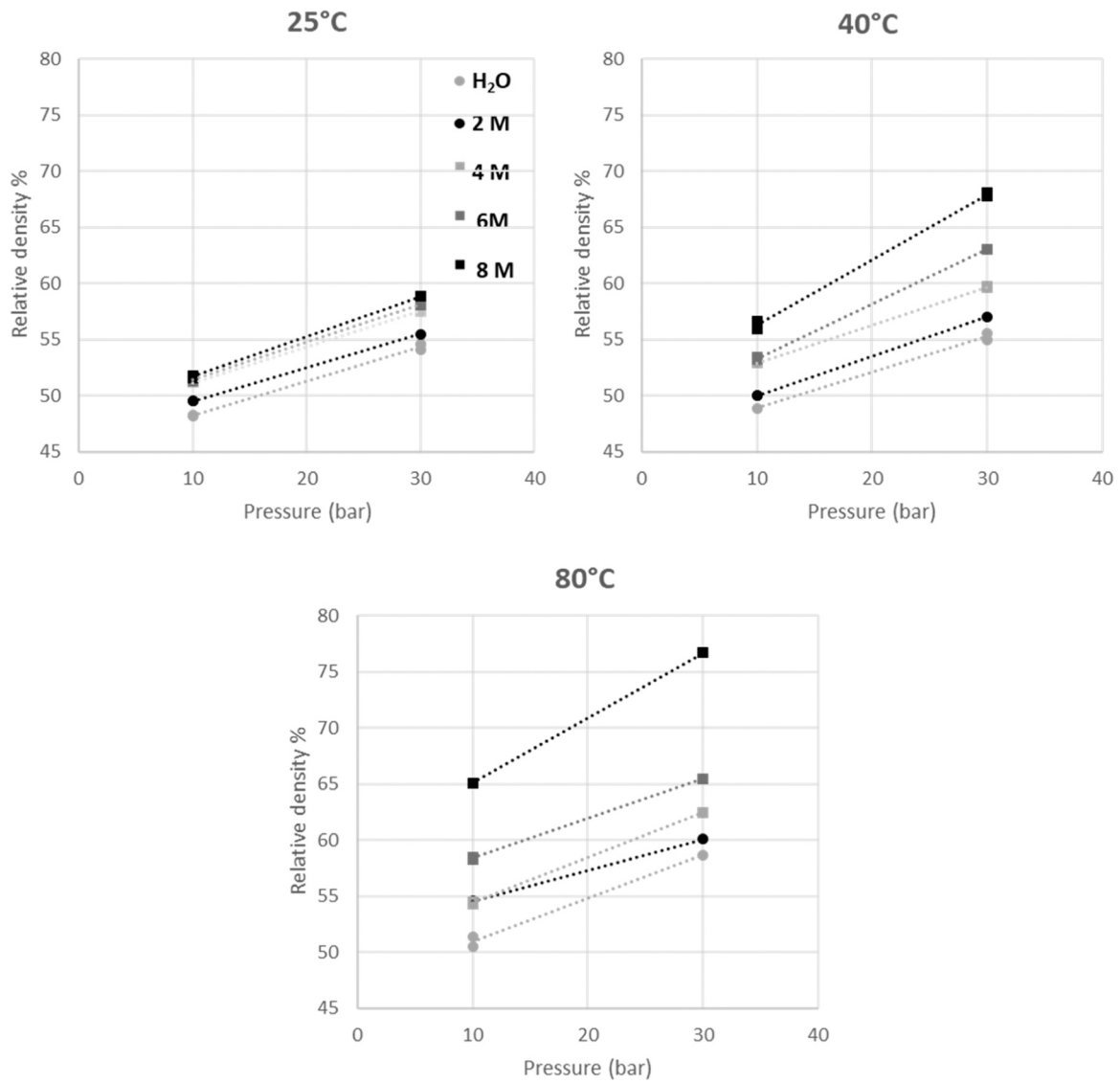


Fig. 3. Influence of the pressure on the densification of K-based samples at constant temperature and increasing molarity of the activator KOH. The nominal pressures of 10 and 30 bar correspond to 56 MPa and 168 MPa applied on the sample, respectively.

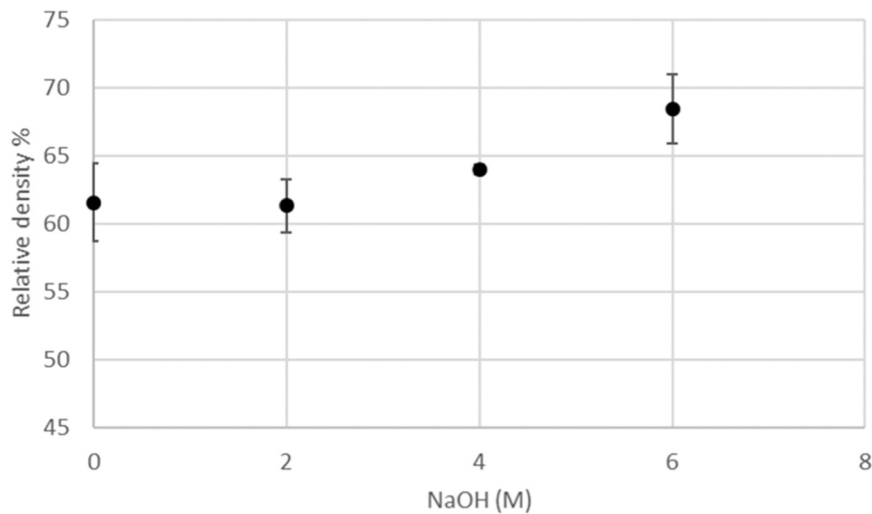


Fig. 4. Relative density of Na-based samples at increasing molarity of the activator NaOH and constant pressure (10 bar) and temperature (40°C). The nominal pressures of 10 bar correspond to 56 MPa applied on the sample.

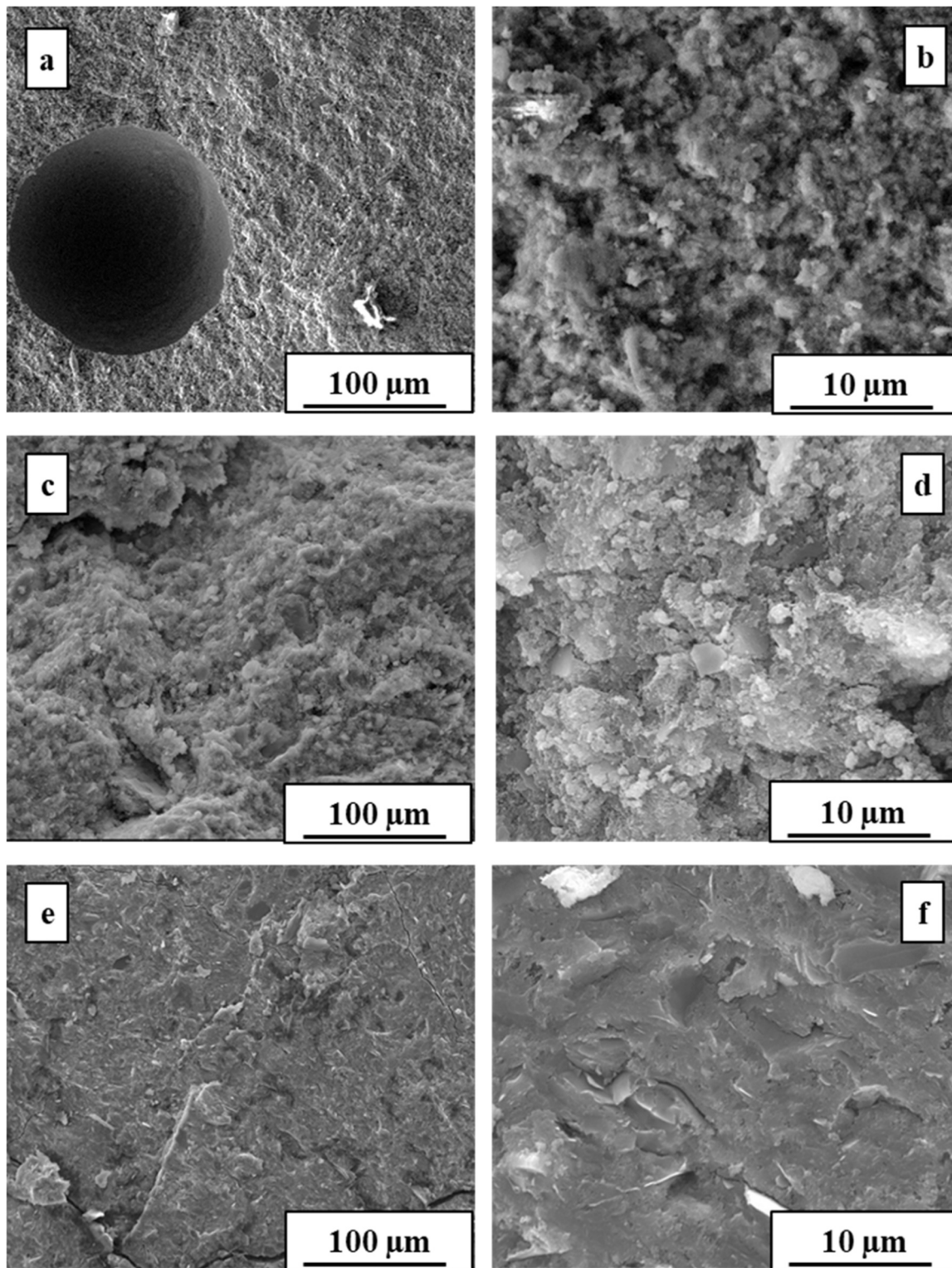


Fig. 5. SEM micrographs of the fracture surfaces of K-G₂ (a, b), G-P30-T25-W (c, d) and G-P30-T80-K8 (e, f).

3. Results and discussion

3.1. Effects of CSP parameters on densification

The geometric density of K-G₂ was 1.17 g cm⁻³, namely the relative density was 52% by slurry route. Fig. 2 shows the influence on the densification of the CSP temperature as the concentration of the activator varied, keeping the pressures constant. Densification of K-based

samples increased linearly at 25°C and 40°C while at 80°C the trend was almost linear up to a concentration of 6 M followed by a marked increase at 8 M.

Fig. 3 as well examines the role of concentration of the activator at constant temperature and increasing pressure. From Figs. 2 and 3 at 30 bar (i.e. 168 MPa) a relative density close or over 55% was achieved at every temperature and concentration. In details, 60% of relative density was reached at mild CSP conditions such as 40°C and KOH 4 M

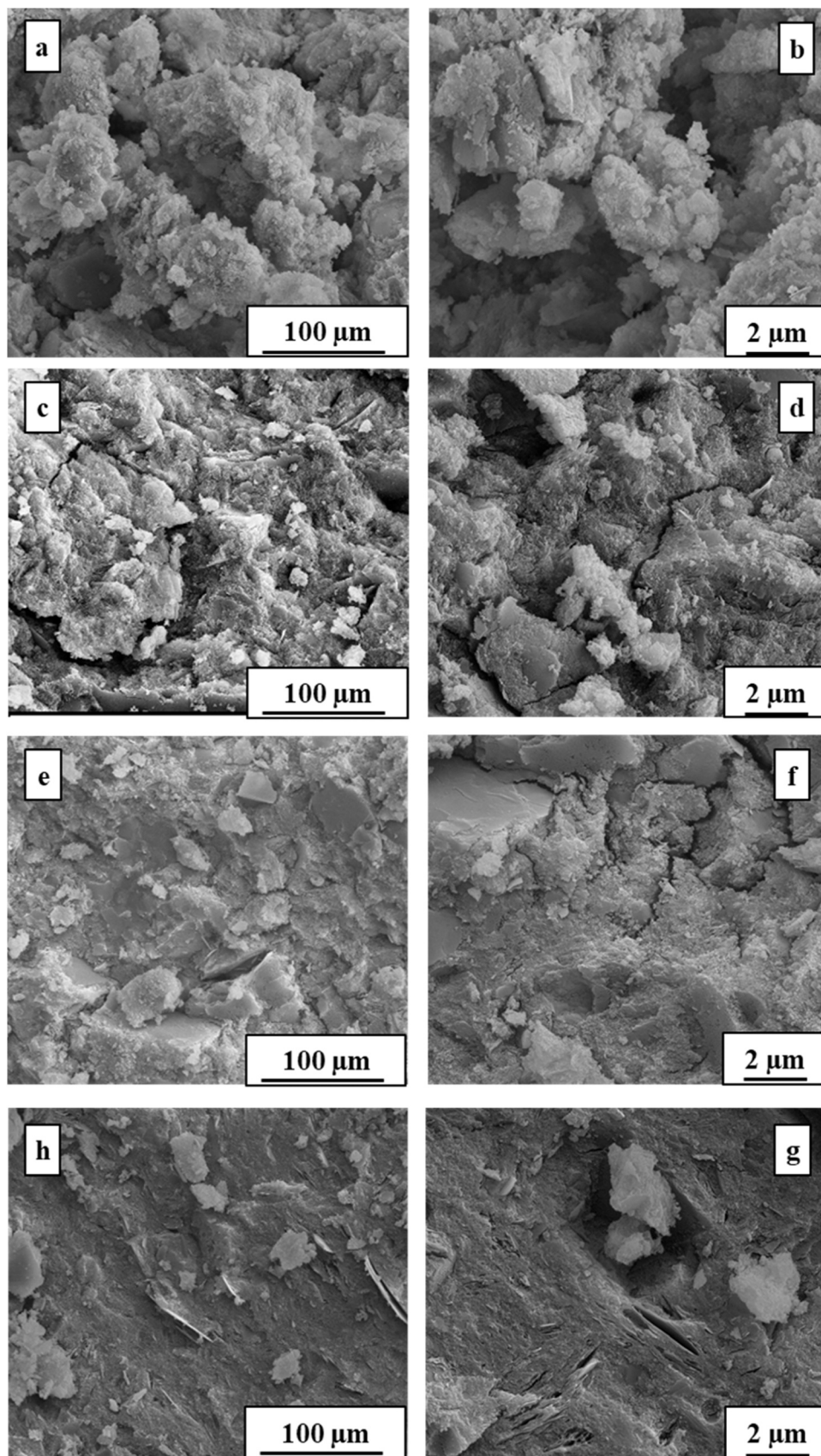


Fig. 6. SEM micrographs of the fracture surfaces of G-P30-T40-W (a, b), G-P30-T40-K2 (c, d), G-P30-T40-K4 (e, f), G-P30-T40-K6 (g, h).