

Preconditioning of Specimens - Drying Influence on Alkali-Activated and Geopolymer Mortar

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Abstract. *Alkali-activated materials (AAM) are now seriously considered by the cement industry as an economical alternative to Portland cement, especially for its low CO₂ footprint. However, their durability still remain to be assessed in more details. The aim of this study is to focus on the sample preconditioning conditions required for testing, especially the drying stage involved in most of the current tests. Four alkali-activated binders were studied: a geopolymer (Na-silicate activated metakaolin), a Na-carbonate activated slag (GGBS), a Na-silicate activated slag and a Na-silicate activated mixture of 50% metakaolin with 50% GGBS. After an endogenous cure of 28 days at 20°C, mortar specimens were dried at different temperatures (from 20°C to 125°C) until mass stabilization. Drying kinetics and released water contents were evaluated, as well as physical, mechanical and mineralogical analyses at the end of drying. Optimal drying temperature for each alkali-activated binder was determined by coupling mechanical strength measurements and mercury intrusion porosimetry. This study revealed that an inappropriate drying temperature could modify the porosity of some classes of AAM, and reduced the compressive strength by up to 30 to 40%. Antagonistic behaviors were observed in the four alkali-activated materials studied, therefore one should be careful about selecting preconditioning protocols for assessing the properties and the durability of these binders.*

Keywords: *Alkali-Activated Binder, Geopolymer, GGBS, Drying Conditions, Durability.*

1 Introduction

Alkali-activated binders are produced from a source of aluminosilicates (precursor) mixed with a highly alkaline solution (*e.g.* sodium (Na) or potassium (K) silicate solutions) called the activating solution (Davidovits, 1991; Provis and Van Deventer, 2009). There are two main types of alkali-activated binders, based on the calcium content of the precursors. They differ from the chemical mechanism that takes place and from the reaction products. For those rich in calcium, such as ground granulated blast-furnace slag (GGBS), chemical reactions are based on dissolution/precipitation steps. The main reaction products are C-A-S-H type phases (CaO-Al₂O₃-SiO₂-H₂O) (Pacheco-Torgal *et al.*, 2015). For precursors with low calcium content, such as metakaolins and type F fly ashes, the term geopolymer is used (Davidovits, 1991). This time, the chemical reactions consist in a dissolution/polycondensation steps, leading to a 3D-aluminosilicate network. In this network, silicon and aluminium are IV-fold coordinated and the alkali cation plays the role of a charge-balancing ion (Rowles *et al.* 2007).

An abundant literature is available regarding the alkali-activated materials (AAM) formulation, but only few studies deals with durability (Luukkonen *et al.*, 2018). Accelerated procedures for durability testing of Portland cements mixtures are often applied to AAM

without any modification, although the raw material used and physico-chemical reactions are different. These tests usually require a preconditioning of the specimens at temperatures ranging from 45°C (*e.g.* accelerated carbonation XP-P-18-458_2008), 80°C (*e.g.* permeability XP-P-18-463_2011), or even at 105°C (*e.g.* porosity NF-EN-18-459_2010). Alkali-activated binders contain gels and hydrates that can be affected and even destroyed at these temperatures (*e.g.* Zhang *et al.*, 2019). Thus, the effects of the preconditioning conditions on AAM need to be assessed, in order to avoid a deterioration of the specimens that could lead to misleading interpretations of durability tests.

2 Material and Methods

2.1 Samples Preparation

The raw materials used are Argicem metakaolin from the ARGECO Company; GGBS from ECOCEM; Betol 47T Na-silicate solution from Woellner ($\text{SiO}_2/\text{Na}_2\text{O} = 1.7$), Na-carbonate powder (Na_2CO_3) from Solvay, tap water from Toulouse city and standardized sand (NF EN 196-1_2016 and ISO 679_2009). Metakaolin and GGBS properties are available elsewhere in literature (*e.g.* Sabir *et al.*, 2001; Pouhet and Cyr, 2015; Pouhet and Cyr, 2016a; Samson *et al.*, 2017a).

Four alkali-activated mortars with a water/binder ratio of 0.4 were studied (see Table 1). The first formula is a metakaolin-based geopolymer developed by Pouhet *et al.* and which has been the subject of several publications (Pouhet and Cyr, 2014; 2015; 2016a; 2016b; Cyr and Pouhet, 2015a; 2015b; Pouhet *et al.*, 2019). Two formula of activated GGBS were prepared, with either a Na-Carbonate or a Na-silicate activating solution (GGBS-carbonates and GGBS-silicates). Finally, a mixture of 50% metakaolin with 50% GGBS activated by silicates is proposed in this study (Mk-GGBS-silicates) to test the coupling of the two hardening systems (based on Ca or Na). This formula has been previously tested on paste (Samson *et al.*, 2017a).

Table 1. Mix design, masses in grams.

	Metakaolin	GGBS	Na-silicate	Na-carbonate	Tap water	Sand
Geopolymer	450		354.9		46.2	1350
GGBS-silicates		450	101.3		141.8	1350
GGBS-carbonates		450		45	198	1350
Mk-GGBS-silicates	225	225	228.1		94	1350

Mortar specimens $4 \times 4 \times 16 \text{ cm}^3$ were made according to the standard protocol NF EN 196-1_2016. Most of samples were demolded 24 hours after pouring, except the GGBS-carbonates formula which was demolded at 48 hours because of its low mechanical properties at early age. The specimens were then endogenously cured (wrapped in plastic film and sealed in humidified plastic bags) for 28 days at 20°C. After this cure, some samples were kept in endogenous conditions, other were dried in different environments (20°C-95% RH, 20°C-50% RH, 20°C under vacuum, 40°C, 60°C, 80°C, 105°C and 125°C). Depending on the drying rate, the mortar specimens were analyzed at different times (the drying time varies from 12 to 49 days) and most of them at 60 days, and then compared to the mortar specimens kept in endogenous conditions for each due date. As regards the geopolymer specimens

placed in the vacuum desiccator, the pump operated only during laboratory's office hours (8 hours a day, otherwise the vacuum was maintained over the test period).

2.2 Characterizations

Several analyses were carried out in order to assess the effect of drying on the four alkali-activated materials:

- Mass monitoring was performed until mass stabilization, *i.e.* until the mass loss is less than 0.01 % between 7 consecutive days (except with 20°C-50%RH conditions which would take months to dry).
- Compressive strengths were determined using a standardized 3R press (NF EN 196-1_2016). Three measurements per mortar prism were made using a ramp of 5 kN / second. Measurements were carried out on the dry specimens as well as on control ones stored under endogenous conditions over the same period. In order to evaluate the dispersion of data, three specimens by drying condition were analyzed for each formula.
- Mercury intrusion porosimetry was performed using an AutoPore IV 9500 Porosimeter from Micromeritics according to the ISO 15901-1_2005 standard. Unlike what is recommended in the standard, samples did not undergo pretreatment for mercury intrusion analysis (*i.e.* 110°C heating in a vacuum oven at 3 Pa for 4 h). Endogenous samples containing water are therefore not dried, but dehydrated during evacuation step in the porosimeter. In order to be consistent for all samples, the test did not start until the exhaust pressure was $\leq 50 \mu\text{mHg}$ assuming complete removal of pore water.

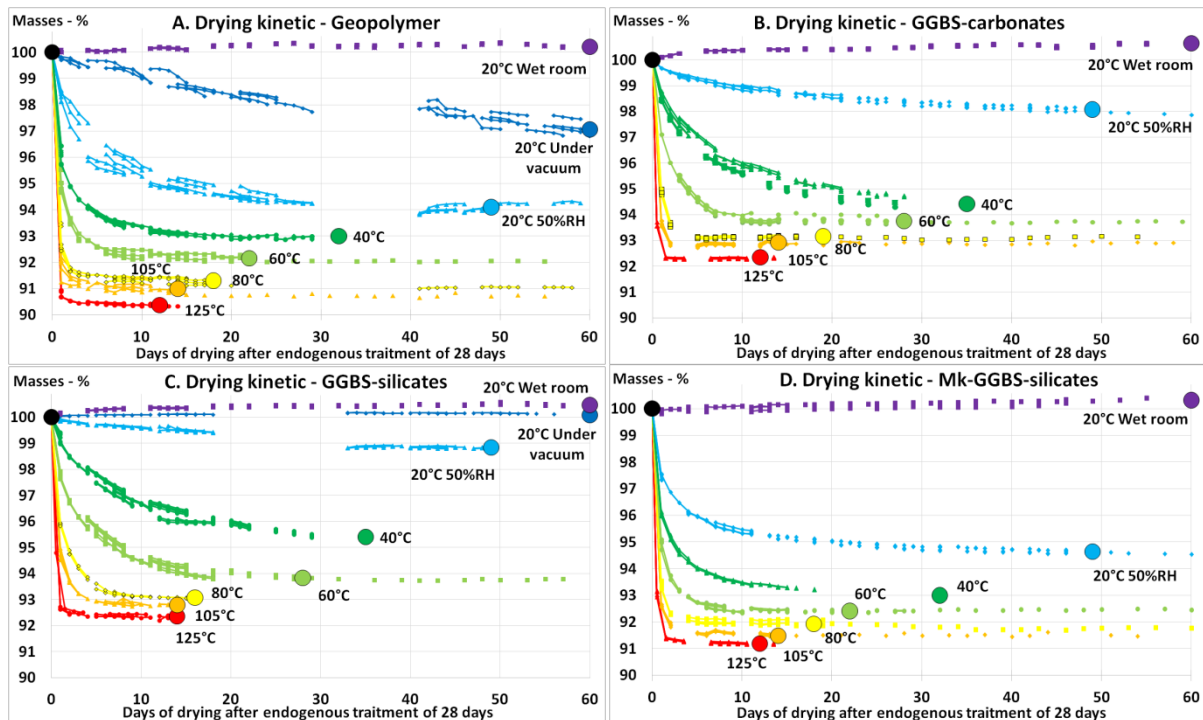


Figure 1. Mass evolution during drying at different temperatures of Geopolymer (A), GGBS-silicates (B), GGBS-carbonates (C) and Mk-GGBS-silicates (D). The circles represent the mass stabilization point.

3 Results and Discussion

3.1 Mass Monitoring

The mass variations recorded during the different drying processes show that the higher the temperature, the faster and more important the drying process (Figure 1). The comparison between the four materials shows different drying kinetics and different water content trapped in the structure of the material depending on the type of AAM. The drying rate is quicker when metakaolin is used as a precursor (Figures 1A and 1D), especially at lower temperatures, *i.e.* 20°C, 40°C and 60°C. Besides, almost all the mixing water has been evaporated in geopolymers at 105°C while almost 8% is remaining in GGBS-silicates (results not shown here). This can be explained because in geopolymers, all the water initially introduced is located in the porosity of the materials or in the alkali hydration sphere in the structural cavities of the Si-Al network (Rowles *et al.*, 2007), while in GGBS systems part of the water is bound in reaction products (C-A-S-H).

3.2 Mechanical Compressive Strengths

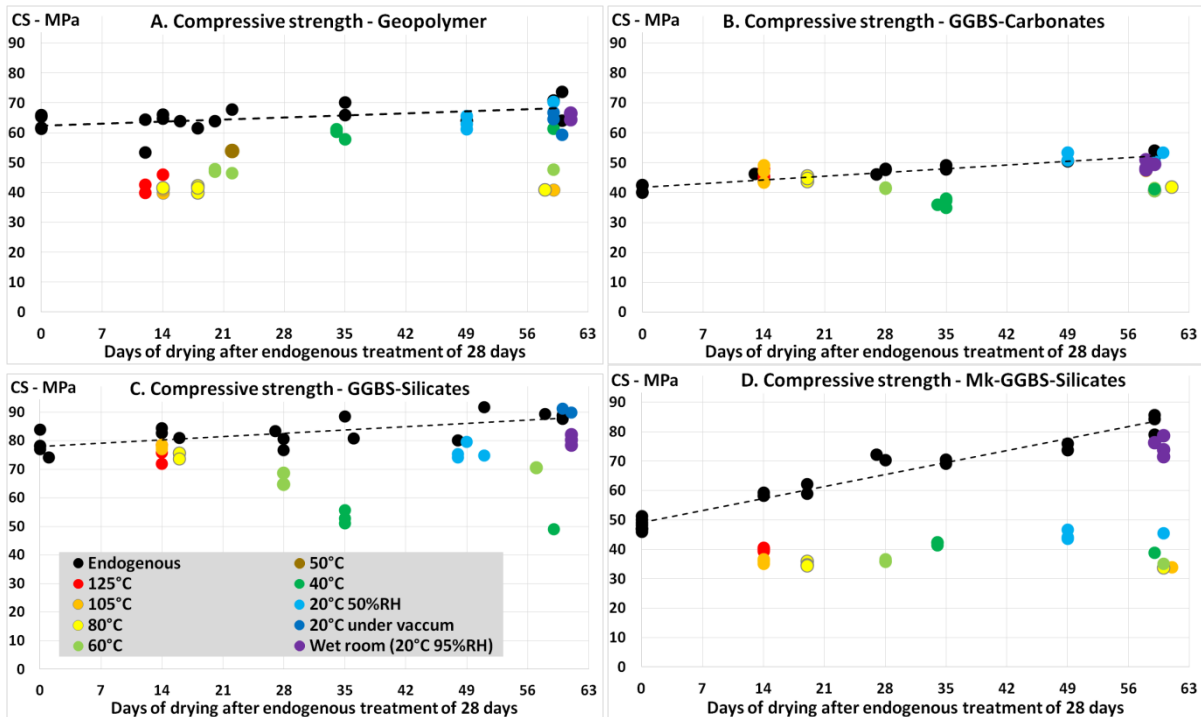


Figure 2. Compressive strengths (CS) of mortars cured in endogenous conditions (black spots) or dried at different temperatures (after endogenous treatment of 28 days). Geopolymer (A), GGBS-carbonates (B), GGBS-silicates (C) and Mk-GGBS-silicates (D). The legend inserted in C is valid for all figures.

In endogenous conditions, geopolymer samples show a slow increase of mechanical compressive strengths (CS) from 61 ± 6 MPa at 28 days to 70 ± 5 MPa at 88 days (Figure 2A). This increase seems to be stabilized after three months, as confirmed by six-months sample analyses. For GGBS-carbonates and GGBS-silicates, CS start from 41 ± 2 MPa and

77 ± 6 MPa at 28 days, respectively, then reach 54 ± 2 MPa and 89 ± 4 MPa two months later (Figure 2B-C). The CS increase is greater than for the geopolymer, and seems stabilized beyond 6 months. CS of the Mk-GGBS-silicates formulation increase from 49 ± 1 MPa at 28 days to 75 ± 4 MPa at 77 days (Figure 2D). To conclude, all four formulations show a progressive CS increase during the first months in endogenous conditions, probably linked to the pursue of chemical processes with time.

When the mortar specimens are dried (after endogenous curing for 28 days), the mechanical strength depends on both formula and drying conditions. For a drying temperature $\geq 50^\circ\text{C}$, geopolymer shows an important CS loss (up to - 36 %), even if the temperature conditions are extended for several weeks (Figure 2A). On the other hand, at drying temperature $\leq 40^\circ\text{C}$, CS were similar to endogenous ones. For GGBS-carbonates and GGBS-silicates, drying with temperature $\geq 80^\circ\text{C}$ or at 20°C (with several humidities) does not decrease the CS, which are similar to those of samples stored under endogenous conditions (Figure 2B-C). However, drying at 60°C or more significantly at 40°C decreases the CS up to -24% and -29% for GGBS-carbonates and GGBS-silicates, respectively. As for geopolymer, when the drying is maintained for a longer period than required, CS do not evolve anymore whereas in endogenous conditions the CS slightly increases, probably due to the wet storage that enable the further reaction of the materials. Finally, drying of the Mk-GGBS-silicates formulation considerably reduce CS (from - 30% to - 50%) whatever the temperature used (Figure 2D). Only samples cured in wet room (20°C 95% RH) retain similar mechanical strengths before and after curing.

3.3 Hg Porosity

In endogenous conditions, the total porosity of the four formulas does not change significantly between 28 and 88 days. Also, only the average value has been reported in Figures 3 and 4. Mean porosity is closed to 18 % for geopolymer, 15 % for GGBS-carbonates, 12.5% for GGBS-silicates and 15.5 % for Mk-GGBS-silicates. GGBS blends therefore have a lower porosity due to the formation of hydrates, when in geopolymers the water expelled during condensations reactions is responsible for more porosity.

In drying conditions, the total porosity evolves differently for each system, as it seems to increase with the temperature level for the geopolymer (Figure 3A, 3B and 4A), to be quite stable for GGBS-carbonate (Figure 4B), having a maximum value for a drying temperature of 40°C as regards of GGBS-silicates (Figure 4D) and to be higher but stable for Mk-GGBS-silicates (Figure 4D).

Concerning the pore size distribution, geopolymer kept in endogenous conditions has half of the porosity attributed to pores < 10 nm, a quarter to 10-100 nm and the last quarter to > 100 nm (Figure 4A). However, this does not mean that half of the porosity is < 10 nm, but that the access to half of the porosity is possible by a diameter lower than 10 nm (according to inkbottle effect, *e.g.* Benavent *et al.*, 2016; Muller and Scrivener, 2017). Except desiccation under vacuum which is not an efficient drying, even a smooth drying at 20°C has the effect of replacing all the porosity < 10 nm by the category 10-100 nm. A strong drying replaces half of the 10-100 nm by the 0.1-1 μm and there is an increase of the 1-10 μm pore size. In summary, for the geopolymer, the more intense the drying, the greater the pore size (or at least the size of the necks).

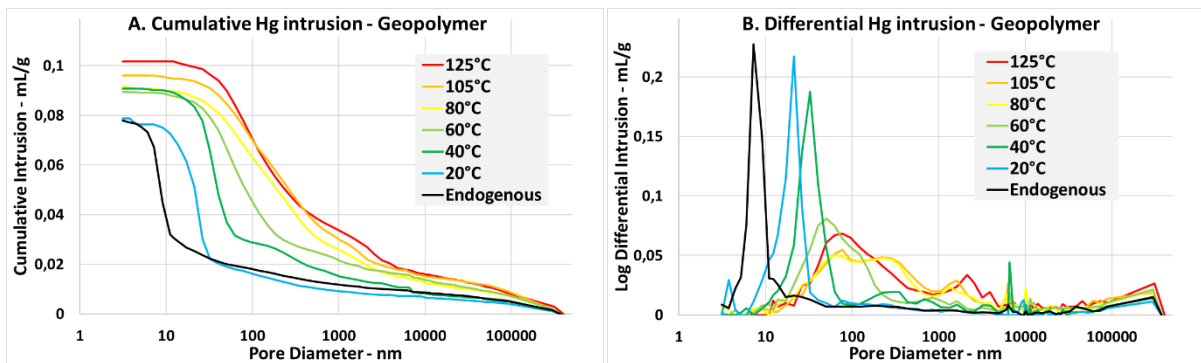


Figure 3. Geopolymer mortars mercury porosimetry as a function of drying: cumulative intrusion vs. pore diameter (A); differential intrusion vs. pore diameter (B).

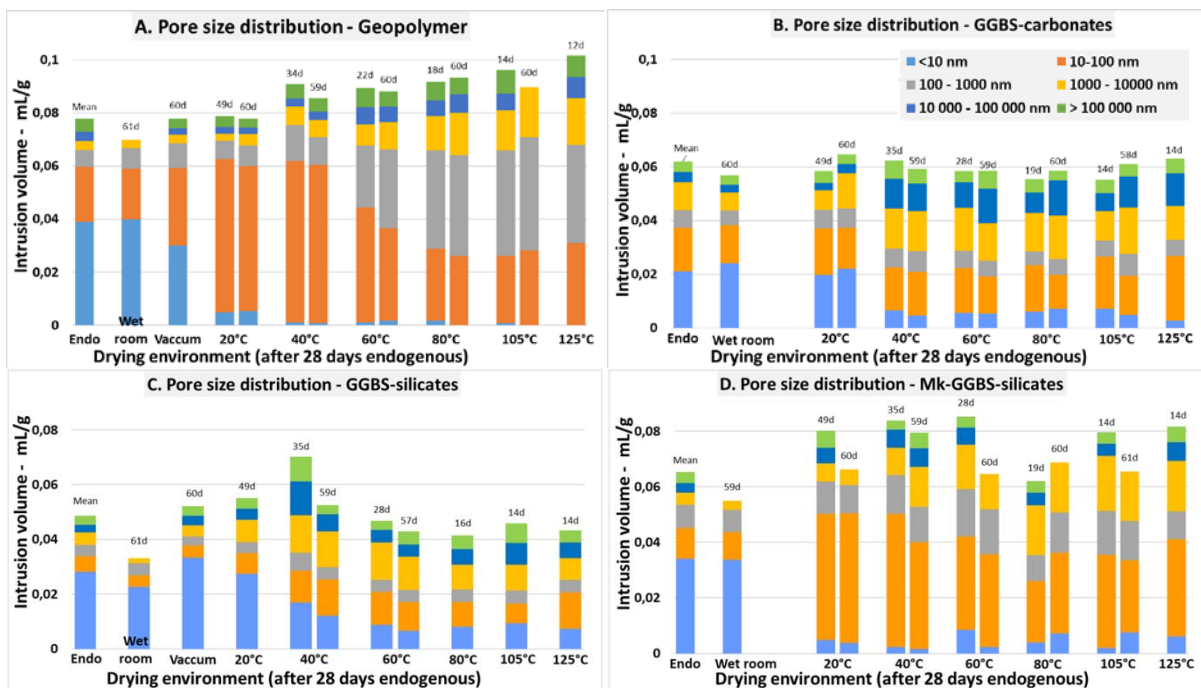


Figure 4. Pore size distribution for mortars of geopolymer (A), GGBS-carbonates (B), GGBS-silicates (C) and Mk-GGBS-silicates (D). Endo column represents the average of the samples conserved under endogenous conditions, analyzed at different ages (28 to 88 days), and showing similar properties. 50% RH for 20°C column. Up to 10 μm porosities are sometime missing due to porosimetry low vacuum problem.

Globally the same pore size distribution trend was observed for the other three formula, *i.e.* a pore size augmentation linked with drying temperature strength. However, pore size distribution modes slightly differ from one formula to another, for example with a < 10 nm pore contents varying from one third to half of the total porosity in endogenous conditions. Furthermore, the change in pore size family towards bigger sizes occurs starting from 20°C for the metakaolin materials, and from 40°C for the GGBS ones (Figure 4). Both geopolymer and Mk-GGBS-silicates show an evolution of the porosity with the increase of temperature from 20°C up to 125°C, while this evolution is limited to the range 20-60°C for GGBS materials (the pore size distribution remains constant for temperatures ranging from 60°C to

125°C). It should be noted, however, that the GGBS-silicates has a sharp increase in porosity for a drying temperature of 40°C, possibly related to micro-cracking induced by mineralogical transformations as suggested on GGBS alkali-activated concrete (Azar *et al.*, 2020).

Preconditioning recommendations must be a compromise between the drying efficiency and the impact on both the porous structure and the mechanical resistances. However, in the absence of mineralogical and microstructural data, results presented in this study should be interpreted with caution. As it has been demonstrated on Portland cements, capillary stress, the loss of physically or chemically bonded water from gels or hydrates, the potential micro-cracking as well as mineralogical changes within the material can lead to misestimating pore volumes (Gallé, 2000).

4 Conclusions on Preconditioning Drying

The effect of drying 4x4x16 cm samples at different temperatures has been assessed on four alkali-activated materials, in order to give recommendation for durability test preconditioning. The drying rate and level depend not only on the nature of the binder, in particular if chemically bonded water is present or not, but also on the porous arrangement. The results showed AAM mortars are sensitive to drying, with modifications of porosity and mechanical strengths. From mercury intrusion measurements, the pore diameter access increases starting from a drying at 20°C for the formula containing metakaolin as a precursor, and from 40°C for formula containing GGBS only.

Geopolymer drying at a temperature above 60°C is fast, but increases the measured pore size, and affects the compressive strength by 40% as a consequence. It is likely that this will affect the permeability of the material. Using a temperature below 20°C takes a lot of time, is not efficient, but does not affect the CS and the pore size. Between 20°C and 60°C there may be a drying optimum to find. A drying temperature of 40°C may be more appropriate for geopolymer, as it has less impact on the mechanical strength. Drying ramps could be tested to see if the fall of strength is due to the kinetics of drying or to the temperature itself.

As regards to GGBS-carbonates and GGBS-silicates, drying at $T \geq 80^\circ \text{C}$ is fast, does not affect CS and slightly increases the measured pore size. In contrast, this study highlights that the material should not be dried at temperature closed to 40°C, otherwise it could lead to significant loss of mechanical strengths.

Finally, the Mk-GGBS mixture activated with silicates seems to cumulate the drawbacks of both alkali-activated systems. Whatever the temperature used, a high degree of damage to the mechanical strengths is observed, correlated with an increase of the porosity. For such mixtures, a drying by solvent exchange or by freeze-drying might be interesting, but this type of drying can only be performed on small samples.

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