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# Influence of the initial water content in flash calcined metakaolin-based geopolymer

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**Keywords:** Geopolymer, Metakaolin, water content, compressive strength, porous network, transfer properties.

## Abstract.

This study assesses the influence of the initial amount of water in metakaolin-based geopolymer on some of its properties in the hardened state. Results suggest a linearly decreasing influence of the amount of water on the mechanical performance of the geopolymer and showed that the majority of this water was not bonded to the structure. Moreover, it was found that whatever the amount of water initially introduced, all the samples contained the same amount of water after a drying period. The study of the porous network showed a large pore volume of 50% of the total volume which corresponds to the volume of water initially introduced. Finally, the observation of numerous macropore helped to explain the high transfer coefficients measured on the geopolymer.



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# 1. Introduction

The evolution of knowledge on alkali activated materials (AAM) and, more specifically, on geopolymers (GP), tends to show that they could provide an efficient alternative to ordinary Portland cement (OPC) (Shi et al., 2006; Provis et al., 2009a; Bligh et al., 2013; Pacheco-Torgal et al., 2014; Palomo et al., 2014). Geopolymers are aluminosilicate materials formed by the activation of an aluminosilicate source, such as metakaolin, by a strongly basic alkaline solution. This results in the formation of amorphous materials at room temperature (Duxson et al., 2007a), showing compressive strength comparable to that of a traditional hydraulic binder (Pouhet and Cyr, 2016a). For the geopolymer the Water/Cement mass ratio is not much used in the literature, as it could be for OPC. However, without necessarily anticipating the consequences that it can have on the hardened state of the material, it is easy to see that the amount of water introduced can be very important. The purpose of this study is to anticipate the performance of a metakaolin-based geopolymer by studying the influence of the proportion of water initially introduced into the mixture.

The silica, aluminium, alkali and water brought to the geopolymer mixture by the raw materials are mentioned in the literature in the form of three molar ratios, which fix the total formulation of a geopolymer: $SiO_2/Al_2O_3$, $Na_2O/Al_2O_3$ and $H_2O/Na_2O$. The main issue with the use of these ratios is that the variation of any one of them induces a variation of the total quantity of water in the mixture. Thus it is often difficult to distinguish the influence of just the initial amount of water on the parameters studied. Some authors use special molar ratios to define the total amount of water in the formulation: $H_2O/(SiO_2+Al_2O_3)$, $H_2O/R$ (some use $H_2O/R_2O$, R=Na or K) or $H_2O/Al_2O_3$ (Lizcano et al., 2012; Perera et al., 2005; and Okada et al., 2009, respectively) but that implies that the other molar ratios have already been set. Other authors use a “Liquid-to-solid” or Water-to-solid” mass ratio (Álvarez-Ayuso et al., 2008; Provis et al., 2009b; Zuhua et al, 2009; Zang et al., 2010; Park and Pour-Ghaz, 2018). However, this is not always defined in the same way due to the fact that the activation solution is liquid but contains sodium and silica. Sometimes the ratio corresponds to the mass of activating solution over the aluminosilicate mass (Álvarez-Ayuso et al., 2008; Provis et al., 2009a), sometimes it is the total mass of water over the sum of all the solid components introduced into the mix (Pouhet and Cyr, 2016a), and sometimes it is used without being defined (Zang et al., 2010; Zuhua et al., 2009).

The impact of the molar ratios on the hardened state of metakaolin-based geopolymer is now widely referenced in the literature regarding their mechanical performances (Kamalloo et al., 2010; Rowles et al., 2003; Duxson et al., 2007b), microstructures (Duxson et al., 2005; Barbosa, 2000), and porous networks (Duxson, 2005; Steins et al., 2013) but very few studies discuss the influence of the initial amount of water introduced into the mixture on the hardened state of geopolymer, independently of the other components (Zuhua et al., 2009; Okada et al., 2009; Lizcano et al., 2012). Among these authors, Lizcano et al. assessed the effects of chemistry, and curing and ageing conditions on water loss kinetics, porosity, and the structure of metakaolin-based geopolymers (Lizcano et al.; 2012). Their results showed that the initial amount of water was the dominant factor affecting the density and the open porosity of geopolymers after curing and extended ageing. This study also showed that whatever the amount of water introduced initially, after 21 days in open moulds at 20 °C and around 74 % R.H., all specimens had a final water content of around 15% to 20% (for geopolymer activated by sodium). Finally, the authors demonstrated a strong correlation between the initial water content and the open porosity of the geopolymer. Okada et al. (Okada et al., 2009) obtained similar results on metakaolin-based geopolymer, showing that the increase in the initial water content increased both the size and the volume of the porous network. Perera et al. (Perera et al, 2005) showed that water was present in the geopolymer in three forms: 1- "free water" (or intergranular water), which is removed between room temperature and 150 °C; 2- water removed between 150 °C and 300 °C, which would correspond to the "interstitial water"; and 3- water related to $OH^-$ groups bound into the structure of new-formed products, representing only very small amount of water measured between 300 °C and 700 °C (Perera et al., 2005). White et al. (White et al, 2010) used neutron pair distribution function (PDF) to improve their understanding of the local atomic structural characteristics of geopolymer binders derived from metakaolin, specifically the nature and amount of the water associated with these materials. Their findings were consistent with those of previous studies, showing that only small amounts of water (<5% for geopolymer activated by potassium) may exist in small pores and as terminal hydroxyl groups in the Si–Al framework structure. Most of the water is lost below 200 °C, indicating that it is mainly found in large pores or hydrating the charge-balancing cations associated with the Si–Al framework.

The above mentioned studies provide some important information about the organization of the water in the hardened metakaolin-based geopolymer, but none of them addresses the consequences of this presence of water. This study therefore proposes an investigation into the influence that the initial water content in metakaolin-based geopolymer has on the hardened state, in the aim of being able to anticipate the final behaviour of the material in terms of mechanical performance and transfer properties.

# 2. Materials and methods

## 2.1. Geopolymer raw materials and synthesis

The source of aluminosilicate was a metakaolin obtained by flash calcination, produced in the south west of France by ARGECO Développement. The term "flash calcination" refers to the combustion process where the particles of kaolinite are transformed into metakaolin by passing near a flame for a few tenths of a second (temperature around 700 °C) (San Nicolas, 2013). Table 1 presents the mass content of oxides in the flash metakaolin, obtained by ICP-OES, using an Optima™ 7000 DV ICP-OES (PerkinElmer) equipped with a CCD sensor. These results show very large silica content, mainly due to the presence of quartz in the raw kaolin, confirmed by XRD analyses. However, after quantification, only the amorphous part of this silica (around 29% of the metakaolin mass) was taken into account in the formulation of the geopolymer. The specific surface area of the flash metakaolin was 13 m²/g (BET). The activating solution used was an industrial sodium silicate solution (Bétol 49T, Woellner) containing 8 % $Na_2O$ by mass and having an $SiO_2/Na_2O$ ratio of 3.3 (Table 1). In order to adjust the sodium content, pure-grade NaOH was added to this commercial solution 24 h before the geopolymer preparation. This initial solution had a high water content (65.6 wt%,

Table 1), so a moderate evaporation of a certain amount of water, performed at low temperature 24 h before the preparation, was necessary for some geopolymers.

**Table 1.** Mass composition of raw materials.

| | $SiO_2$ | $Al_2O_3$ | CaO | MgO | $Fe_2O_3$ | $K_2O$ | $Na_2O$ | $TiO_2$ | $SO_3$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **Flash metakaolin** | 68.10 | 24.10 | 0.91 | 0.22 | 3.73 | 0.35 | 0.08 | 1.14 | 0.03 | - |
| **Waterglass solution** | 26.5 | - | - | - | - | - | 8.0 | - | - | 65.6 |

The geopolymer was prepared in two steps. First, pure NaOH and water were added to the industrial waterglass solution to obtain the desired $SiO_2/Na_2O$ and $H_2O/Na_2O$ molar ratios. After total dissolution of the sodium hydroxide, the solution was cooled to 20 °C for 24 h and then mixed with the metakaolin until the mixture was homogeneous.

The geopolymer mortars were mixed and made according to French standard EN 196-1 in a 5 L mixer (Automix, Controls®), using the activation solution instead of the mixing water. The formulations are presented in Table 2. Standard sand (EN 196-1 and ISO 679: 2009 standards) composed of well crystallized quartz and having a controlled particle size between 0 and 2 mm was used. The mortar specimens were cast in 4 x 4 x 16 cm moulds using a shock table, and pastes were cast in 7 x 4.3 x 2.2 cm plastic prisms. All specimens were cured at 20 °C in sealed bags for the first 24 hours and then demoulded and stored at 20 °C and 95 % R.H. until testing.

**Table 2.** Mass composition of geopolymer (solid molar composition: $3.6SiO_2{\bullet}1Al_2O_3{\bullet}0.9Na_2O$)

| Sample ID | Mk (g) | Silicate (g) | NaOH (g) | $H_2O$ (g) | Sand (g) | Water in GP (wt.%) | Water/ solid |
|---|---|---|---|---|---|---|---|
| **GP0.38** | 450 | 372 | 37.8 | -12.1* | 1350 | 27% | 0.38 |
| **GP0.4** | 450 | 372 | 37.8 | 5 | 1350 | 29% | 0.40 |
| **GP0.5** | 450 | 372 | 37.8 | 65.1 | 1350 | 33% | 0.50 |
| **GP0.6** | 450 | 372 | 37.8 | 125.1 | 1350 | 37% | 0.60 |
| **GP0.7** | 450 | 372 | 37.8 | 185.1 | 1350 | 41% | 0.70 |

* negative value corresponding to the mass of water evaporated from the alkali silicate solution.

## 2.2. Test methods

The mechanical tests in flexion and compression were performed on 3 prismatic mortar specimens of dimensions 4 x 4 x 16 cm, according to EN 196-1 (Automatic mortar press, Class A - 3R® RP30/200FP). The mineralogical study was carried out by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer, with Bragg-Brentano configuration and copper radiation (Cu Kα, λ = 1,5406Å). The acquisitions were made on powder having a maximum particle size of 80 µm, between 5° and 70° 2θ, with a step size of 0.02° and an acquisition time of 1.075 seconds per step. The total pore volume was determined in this study by measuring the porosity accessible to water via the French standard NF P18-459 (2010). Tests were carried out on at least three 7 x 4.3 x 2.2 cm prisms of geopolymer paste. The balance accuracy for the mass measurements was 0.001g. Mercury intrusion porosimetry measurements (MIP) were performed with a Pascal 140 porosimeter coupled with a Pascal 240 (Fusion Instrument) and the samples analysed were pieces of paste of around 1 g obtained by fresh fracture at 7 days. Gas absorption/desorption analyses were performed using a Tristar 3020 apparatus (Micromeritics), with a degassing temperature of 100 °C, on a geopolymer paste piece prepared in the same way as those studied by mercury porosimetry. X-ray microtomography images were obtained with a Nanotom 180 from Phoenix / GE. The acquisition parameters used were a voltage of 80 kV and an intensity of 100 µA. The resolution obtained for this type of sample was a 5.4 micron voxel. The volumes were rebuilt using the Datos X software (Phoenix) and VG Studio Max (Volume Graphic) to obtain an image of the porosity of the material. Finally, cross-sections of 100 day old geopolymer were observed by scanning electron microscopy (SEM) after application of a focused ion beam (FIB) apparatus (FEI Helios NanoLab 600i). FIB uses $Ga^{+}$ ions to remove material with a very high spatial precision. In this way, cross-sections of a representative sampling area were obtained at a specific location after surface observation. For this operation, the sample was positioned in the SEM chamber, tilted at 52° and a 2 micron thick layer of platinum (Pt) was laid down for surface protection. FIB milling was then applied to etch the sample.

# 3. Results and discussion

## 3.1. Influence of water content on mechanical performance

Using three molar ratios (*$SiO_2/Al_2O_3$*, *$Na_2O/Al_2O_3$* and *$H_2O/Na_2O$*) to formulate the geopolymer led to a systematic variation of the water content, as illustrated in Figure 1. Increasing the $SiO_2/Al_2O_3$ ratio decreased the amount of water in the formulation. Conversely increasing the $Na_2O/Al_2O_3$ or the $H_2O/Na_2O$ ratios increased the total water content.

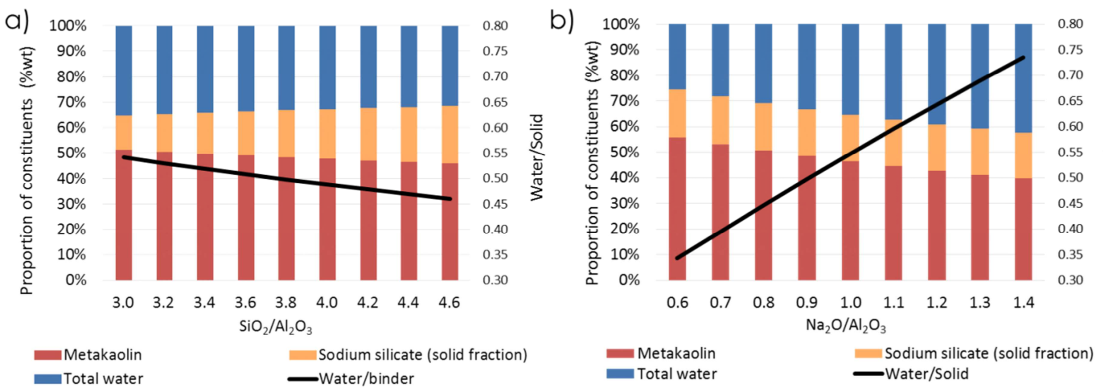


***Figure 1.*** *Examples of evolution of the proportions of the geopolymer constituents (MK + sodium silicate (solid fraction) + total water) and the Water/Solid mass ratio depending on a) $SiO_2/Al_2O_3$ and b) $Na_2O/Al_2O_3$ molar ratios, the other two molar ratios being keep constant (including $H_2O/Na_2O$).*

In this study, we chose to work around these ratios and clearly dissociate the solid from the liquid. Thus only two parameters had to be fixed:

- The geopolymer molar formulation, corresponding to the solid part initially introduced and written in the form $xSiO_2$• $yAl_2O_3$• $zNa_2O$.
- The amount of water introduced, written in the form of the water content (mass percentage) or the Water/Solid mass ratio.

The formulation of the metakaolin-based geopolymer was the subject of an earlier study, which highlighted an optimal proportion regarding the mechanical performances corresponding to the initial composition: $3.6SiO_2$•$1Al_2O_3$•$0.9Na_2O$ (Pouhet, 2015).

To assess the influence of the water content on the mechanical performance, five geopolymer mortars with increasing amounts of water were tested in flexural and compressive strength. The corresponding formulations are listed in Table 2. Given that the waterglass solution provided large quantities of water in addition to silica and sodium, one formulation, GP0.38, required an additional step during its preparation. The significant water contribution of the activation solution (65.5%) made it impossible to obtain formulations having a Water/Solid mass ratio lower than 0.4. Excess water was therefore removed from the waterglass solution by evaporation 24 h before the mortar preparation, by heating at 50 °C under agitation until a loss of mass equal to the required amount of water was achieved. No visual modification was observed on the remaining solution. The results of the mechanical tests (performed in compression and in bending) on the five mortars of Table 2 are presented in Figure 2.

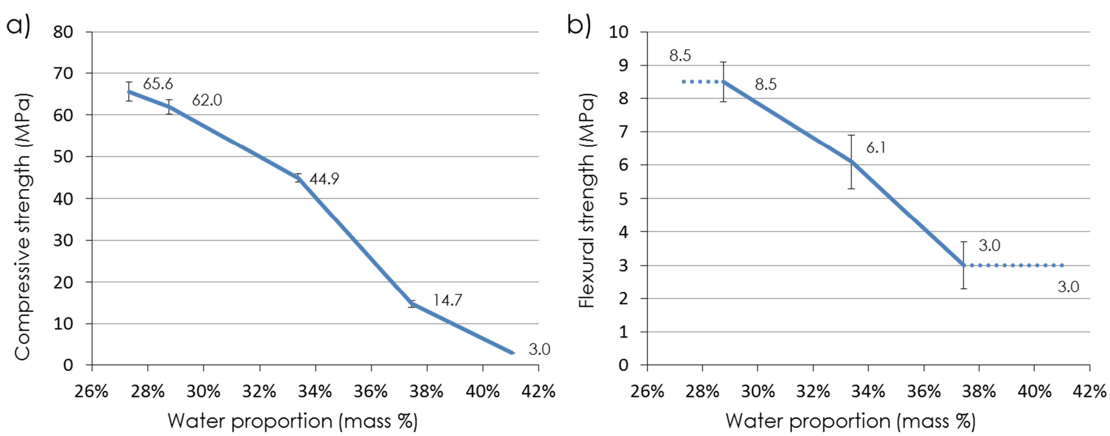


***Figure 2.*** *a) Compressive and b) Flexural strengths of geopolymer mortars at 7 days depending on the water proportion introduced in the initial mixture (Solid formulation: 3.6 $SiO_2$ • 1 $Al_2O_3$ • 0.9 $Na_2O$)*

Plotting the measured strengths as a function of the proportion of water in the mixture showed the same trends in flexion and compression. It was observed that, between water proportions of 28% and 37%, increasing the amount of water decreased the mechanical performance (only between 29% and 37% in the case of the flexural strength). In view of these figures, it would seem that the mechanical performance of the geopolymers would follow a linear trend with a decrease in mechanical strength proportional to the initial amount of water, at least in the W/S domain studied.  This result therefore demonstrates a different behaviour that observed for cement witch shows a non-linear decrease in performance with the addition of water (e.g.

Bolomey). Furthermore , this observation is in agreement with the literature, which postulates that the introduced water is not used for the formation of hydrate as in Portland cement (Perera et al., 2005, White et al., 2010), and therefore does not participate in the structuration of the material. Thus the addition of water in a geopolymer formulation systematically entails a weakening of the material, probably by increasing the porosity.

## 3.2. Investigation on the bound water

The literature shows that, in the hardened geopolymer, the water does not appear to be bound in the network in hydrate form as it is in cement matrix (Barbosa et al., 2000; Lizcano et al., 2012; White et al., 2010; Perera et al., 2005). Thus, determining the fate of the water in the hardened geopolymer paste is indispensable for a better understanding of its influence. It was therefore decided to study the amount of water that could be removed by drying the specimens at relatively moderate temperature, in order to observe the influence on the mechanical performances. Three water contents were chosen, corresponding to W/S ratios of 0.40, 0.47 and 0.56, with three drying temperatures of 50 °C, 80 °C and 105 °C. After stabilization of the mass loss for each drying temperature, the amount of water remaining in the geopolymer was calculated.

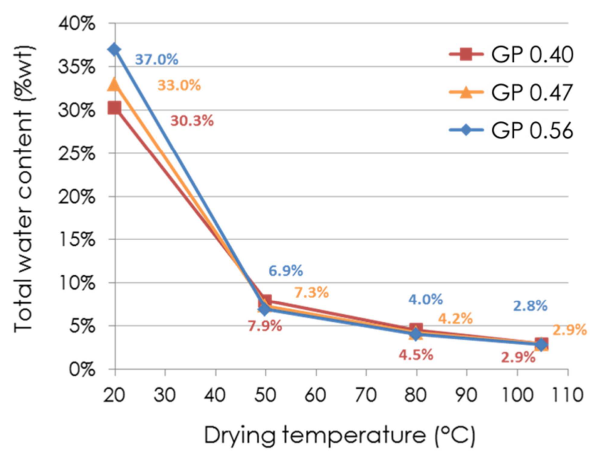


***Figure 3.*** *Evolution of the total amount of water in GP0.40, GP0.47 and GP0.56 depending on the drying temperature.*

Total water contents of the geopolymers for the three W/S ratios according to the drying temperature are presented in Figure 3. The figure clearly shows that, whatever the initial water content in the geopolymer paste, this content was reduced to about 3% for all the formulations after drying at 105 °C, which corresponds to a relative loss of 90-92% of the initial water mass. The evolution of the water content in geopolymer versus the drying temperature tended to an asymptotic value above 105 °C, suggesting a slower evolution for the loss of the 10% remaining water.

In order to visualize the temperature at which the remaining water evaporates, TGA analysis was carried out on the GP0.40, coupled with mass spectroscopy. The results obtained are presented in Figure 4. According to the TGA result, evaporation of the remaining water would be a long process, as traces of water were still measured at 700 °C. This could indicate that a small proportion of the water initially introduced remained in small pores or as terminal hydroxyl groups in the structure and that this quantity of water would be the same regardless of the initial amount of water introduced, as described in the literature (Perera et al., 2005; White et al., 2010). At the end, the total molar formulation calculated by considering the water “fixed” to the structure (therefore not evaporated at 105 °C) was nearly the same for the three formulations and corresponded to 3.6 $SiO_2$ • 1 $Al_2O_3$ • 0.9 $Na_2O$ • 1.3 $H_2O$. The presence of carbon dioxide in the mass spectroscopy spectrum means that carbonation took place during the seven days of curing, which is consistent with results obtained in a previous study (Pouhet and Cyr. 2016b).

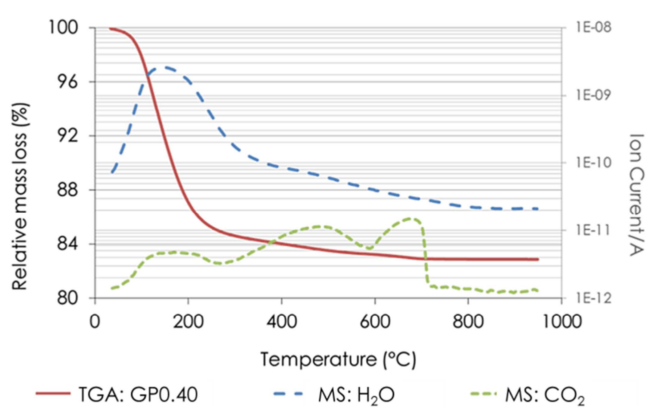


***Figure 4.*** *Thermogravimetric analysis of geopolymer GP0.40 at 7 days performed at 20.0 °C/min up to 950 °C with $H_2O$ and $CO_2$ mass spectroscopy spectrum.*

In order to confirm that the departure of this "free water" was not detrimental to the geopolymer structure, the same drying protocol was applied to GP0.40, GP0.47 and GP0.56

geopolymer mortars, which were then tested in compression. As previously, the geopolymers were kept without external exchanges for seven days and then placed in a climatic chamber until stabilization of the mass loss. Figure 5 presents the compressive strengths measured according to the drying temperature for the three W/S ratios studied. Two behaviours can be observed:

- The formulation having the least water, GP0.40, showed a loss of strength that was moderate but increased with increasing drying temperature.
- The GP0.47 and GP0.56 formulations showed similar behaviour, with very close compressive strength values regardless of the applied temperature.

Some hypotheses can be advanced to explain the behaviours observed. It was measured that about 90% of the introduced water was evaporated between 20 °C and 105 °C. The fact that the mechanical performances of the GP0.47 and GP0.56 formulations did not change between these two temperatures could validate the assumption that it was indeed "free water" and therefore not related to the structure and its stiffness. In view of the above results, it is highly probable that this was also the case for the GP0.40 formulation despite the loss of strength. However, for this formulation having the lowest water content, the loss of strength observed could have been due to a difference in the organization of the porous network containing this "free water". In this case, the porosity could have been finer or arranged differently, so that the evaporation of the "free water" would lead to damage in the material and therefore to a decrease in mechanical performance.

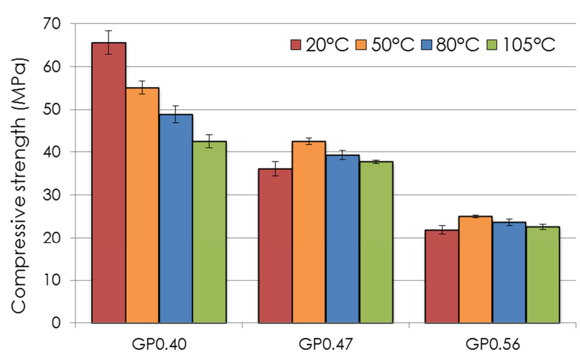


***Figure 5.*** *Compressive strength of geopolymer mortars at 7 days performed after mass loss stabilization depending on the drying temperatures for three different Water/Solid mass ratios.*

### 3.3 Influence of the water content on the volume and organization of the porous network of geopolymers

In this study the intention was to characterize all of the water in the geopolymer. So it was firstly necessary to evaluate the size and organization of the water present in the air bubbles trapped during preparation. GP0.40 geopolymer paste prepared without any shocks or vibration was analysed by X-ray tomography to visualise the air occlusions, assess their size distributions and quantify their cumulative volume. A 3D section of the sample, having dimensions 2 x 2 x 5 mm was isolated and analysed. Figure 6a presents the 3D section, showing the overall sample and the air occlusions, which were easily identified by their dark coloration. Using this strong contrast between the air and the matrix allowed the software to isolate this volume and to represent it separately. Figure 6b, which isolates the entrapped air fraction, shows significant numbers of spheres with diameters ranging from 40 µm up to nearly 300 µm. It was calculated that this cumulative volume represented 2% of the sample. The distribution of the sphere sizes is illustrated by different colours: the blue corresponds to diameters smaller than 200 µm, with decreasing diameters shown in darker shades of blue, while all other colours correspond to diameters ranging from 200 µm to 300 µm. Figure 6b shows a homogeneous distribution of the bubbles in the sample with no privileged organization. However, the result does not show if there is an interconnectivity of the porosity, which would be too fine for the resolution of the device.

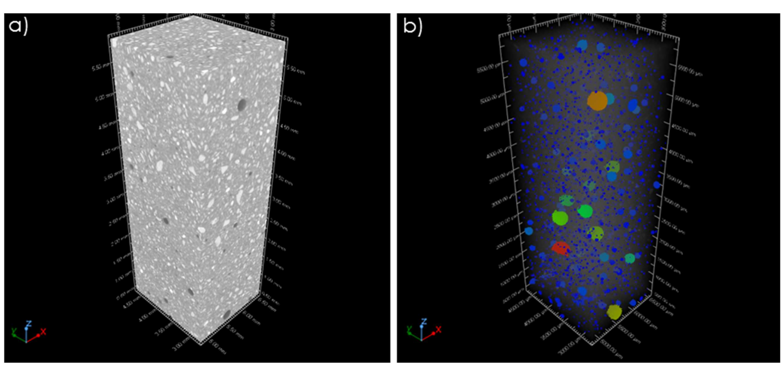


***Figure 6.*** *X-ray tomography visualization of G0.40 paste showing: a) 3D section of the sample and b) the same 3D section presenting only the air occlusions.*

To define the porosity of the geopolymer and the influence of the initial water content, the total porosity accessible to water was measured (NF P18-459) and mercury intrusion porosimetry (MIP) was performed on geopolymer specimens having three different W/S mass ratios. Figure 7a shows the porosity accessible to water measured using the same three drying temperatures as those used for the study of the bonded water.

The information obtained as described in the previous two paragraphs showed that, for the GP0.47 and GP0.56 formulations, the temperature of 105 °C caused no loss of strength and led to final water contents close to 3%. Thus, the total porosity values measured for these formulations with a drying temperature of 105 °C was very probably close to the total porosity values of the materials, i.e. 53.0% and 56.4% respectively. Since the drying behaviour of the three formulations was similar (Figure 7a), it seems reasonable to conclude that, despite the loss of mechanical strength, the total porosity of the GP0.40 formulation can be measured by drying at 105 °C and so would be 49%. This value is in agreement with values found in the literature for similar formulations (Boher, 2014).

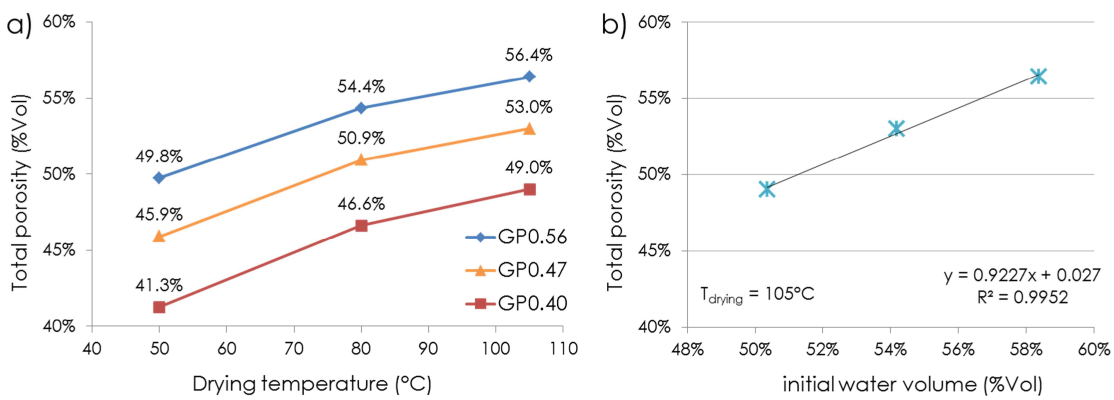


***Figure 7.*** *Total porosity accessible to water a) versus the drying temperature used and b) versus the volume of water introduced in the initial geopolymer mixture, for a drying temperature of 105 °C*

For the three W/S mass ratios, the initial water volume introduced into the mixture was calculated, then compared to the total pore value (obtained at $T_{drying}$ of 105 °C). These results, presented in Figure 7b, show a very good correlation, illustrating a direct proportionality between the volume of water introduced and the final porosity of the geopolymer. So, in addition to confirming that the water in the geopolymer appears to be present mostly as "free water", these results show that the total porosity of a geopolymer can be chosen and fixed before its preparation. Since a linear relationship was also made between the initial amount of water and the mechanical performance (Figure 2 a), it is possible to say that there is a direct correlation between total porosity and mechanical strength. Furthermore , knowing that the porosity has a direct influence on the transfer properties and thus on the durability of the materials, the possibility of choosing its value in advance could be a clear advantage for the development of geopolymer.

MIP analysis was performed on GP0.40, GP0.47 and GP 0.56 to evaluate the influence of the water content on the geopolymer porous network microstructure. The relative mercury volume introduced versus the pore access diameter is presented in Figure 8a along with the curve of the relative pore volume versus diameter (Figure 8b). For the geopolymer having a W/S mass ratio of 0.40 it was calculated that 95% of the mercury was introduced for pore diameters of 7 to 20 nm (with 83% between 10 and 20 nm), which shows a homogeneous distribution of the pore access diameter. Thus, when the curve of the relative pore volume versus diameter is observed (Figure 8b), the geopolymer has a single population of pore access centred on a diameter of 13 nm. These results confirm the monomodal nature of the porous network of the geopolymer observed in the literature (Rovnaník 2010, Boher 2014).

These figures also show that all three formulations led to monomodal porous networks, whatever the amount of water initially introduced. The cumulative pore volume representation confirmed the increase in total volume measured with water intrusion when the initial water amount increased and its derivative revealed that the pore access diameter also increased.

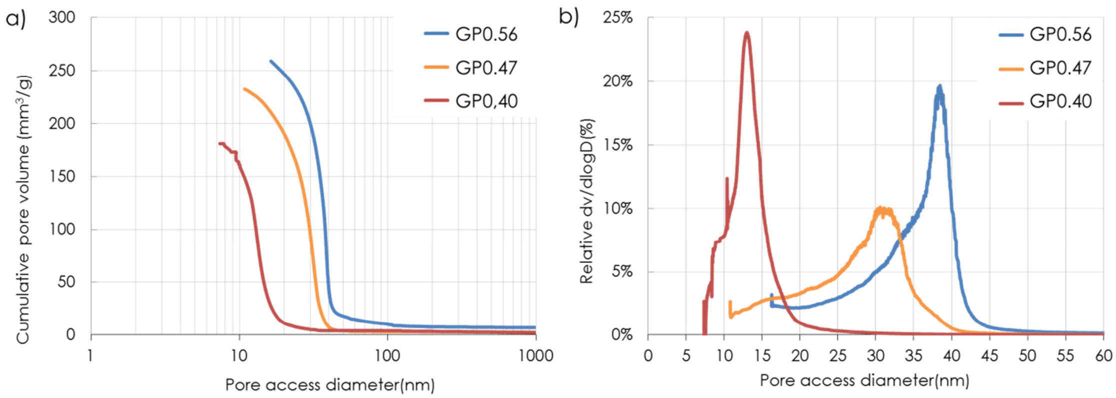


***Figure 8.*** *Relative mercury volume introduced and relative pore volume versus pore access diameter for geopolymer pastes G0.40, GP0.47 and GP0.56.*

The median pore access diameter therefore increased from 13 nm for GP0.40 to 29 nm for GP0.47 and, finally, 36 nm for GP0.56. When the median diameter increased, the spread of the value also increased, as 90% of the mercury was introduced between 7 and 18 nm for GP0.40, between 11 and 35 nm for GP0.47, and between 16 and 42 nm for GP0.56. The notable difference in pore access diameter between the formulation having the least water and the other two could support the hypothesis made previously on the fact that GP0.40 had such a fine porosity that the evaporation of the "free water" during drying damaged the structure.

A study of nitrogen adsorption–desorption isotherms also made on geopolymer GP0.40 provided additional information. The adsorption and desorption isotherms of Figure 9a show a distinct hysteresis loop for relative partial pressure ($P/P_0$) between 0.8 and 1.0. The passage of the desorption curve below the absorption curve (until $P/P_0$ of 0.75) was associated with degassing problems during the analysis (degassing temperature of 100 °C). Nevertheless, the closeness of the hysteresis loop at $P/P_0 > 0.40$ and a type IV sorption behaviour with a hysteresis loop of type 1 on a loop of type 2, which have already been identified on metakaolin geopolymer samples by Steins et al. (2013), indicate the absence of micropores and the formation of a well-defined mesoporous texture having interconnected pores with narrow necks and wide voids, called ‘ink-bottle pores’. The BJH pore-size distribution (Figure 9b) confirms the monomodal nature of the porous network centred on 15 nm.

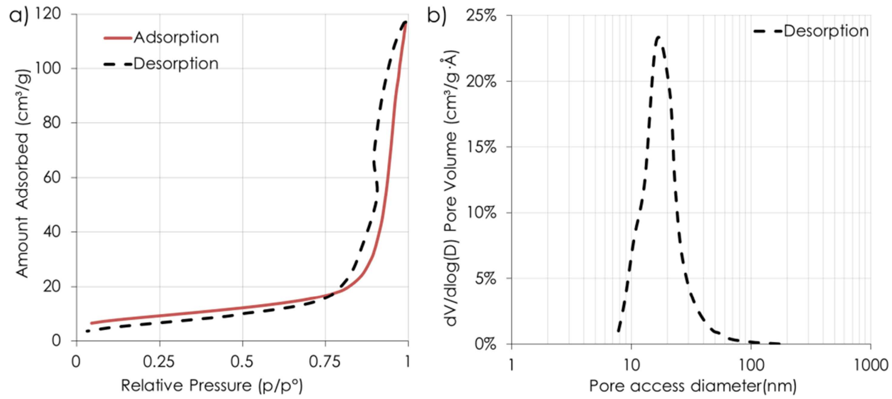


***Figure 9.*** *a) Nitrogen adsorption–desorption isotherms and b) BJH pore-size distribution for the GP0.40 geopolymer paste.*

Finally, in order to be able to observe the porosity of a hardened geopolymer clearly, SEM observations were made on a 100 day old GP0.40 section obtained by cutting with the focused ion beam technique. With this cutting of nanometric precision, it is possible to see inside the material without degrading the porous network, as can be seen in Figure 10. It should be noted that the black streaks observed on the SEM images are due to the ion beams used to cut the materials, and the lighter layer at the top of the cross-section corresponds to the platinum depot made to protect the cut out.

Valuable information can be obtained from these images:

- Heterogeneity is clearly observed within the geopolymer in Figure 10a and b as, in addition to the quartz grains recognisable by their well-defined shapes and their grey colour, many cavities are also observed.
- A larger zoom (Figure 10 b) and c)) reveals that these cavities seem to be formed by multiple layers contained within the matrix. The shape, orientation and size of these layers and cavities recall the structure of kaolinite or metakaolinite layers (San Nicolas, 2011). This shows that some of the introduced metakaolin was not fully dissolved by the activating solution during the geopolymerization.
- In addition to this large layered porosity, the largest zoom (Figure 10d) clearly shows the monomodal mesoporosity of the geopolymer observed during MIP. The many black holes visible in Figure 10d all measure around 10-30 nm and were found in very

large quantities in the section observed. The presence of these two forms of porosity confirms the presence of the "ink bottle" effect observed by analysis of the results of absorption/desorption of gas.

- The observation of this monomodal mesoporosity on this scale, resembling that of a sponge, also confirms the interconnectivity of geopolymer porosity.

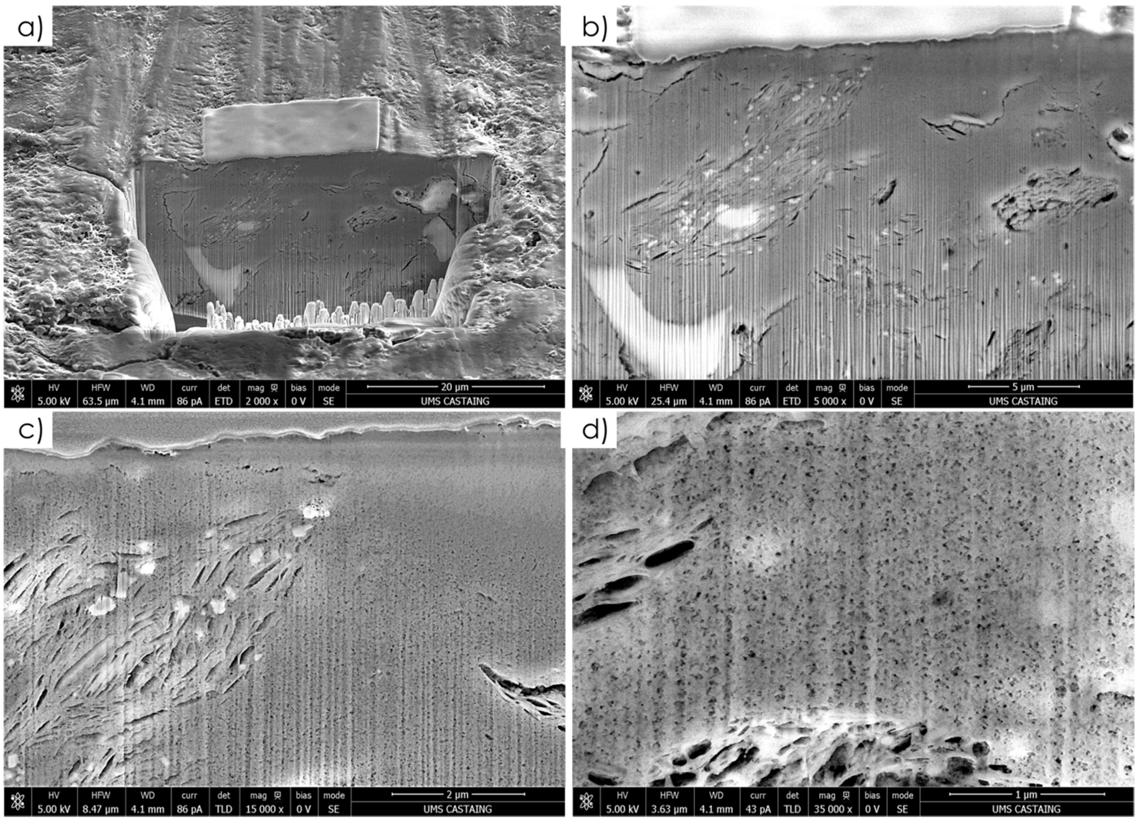


***Figure 10.*** *Electronic scanning microscope images of a cross section of 100 day old geopolymer obtained by focused ion bean a) x2000, b) x5000, c) x10000 and d) x35000*

## 3.4 Consequences regarding the durability

To go further, it is interesting to discuss the direct consequences of these results for the development of geopolymers as construction materials. In the science of building materials, porosity is sometimes considered as a direct indicator of the durability of materials (Baroghel-Bouny, V; 2004). In fact, the porosity is related to the transfer properties of the material, which are responsible for the more or less rapid intrusion of compounds that are harmful to the structure, such as carbon dioxide or chlorides. In view of the large interconnected porosity of metakaolin-based geopolymers, the transfer properties had to be considered. Intrinsic air permeability measurements were performed on geopolymer mortars using the Cembureau apparatus. A very high permeability of $8456.10^{-18}$ m² was measured after drying at 105 °C. Tests of chloride ion diffusion by migration were also carried out on three geopolymer concrete samples, according to standard NT Build 492. Generally, for cementitious materials, the depth of penetration of chloride ions corresponds to about half of the sample at the end of the test. On geopolymer samples, the chloride ions had completely passed through the test piece at the end of the test (i.e. after 24 h at 10 V) making it impossible to calculate a chloride diffusion coefficient. Thus it seems that the diffusion of chlorides through metakaolin-based geopolymer is much faster than through known materials based on Portland cement and the transfer properties of this geopolymer appear to be unfavourable compared with those of Portland cement. The SEM images obtained (Figure 10) confirm these data by showing a large volume of void in the structure, allowing the transport of air or water. However, comparison with a cement matrix is difficult in view of the great differences in chemical composition between these two materials. A carbonation study previously performed on the same geopolymer material concluded that, although carbonation of the pore solution was extremely rapid in geopolymer, the risks related to the durability of the structure would be limited (Pouhet and Cyr, 2016b). The amount of water initially introduced into the formulation of geopolymers necessarily has a direct influence on the transfer properties of the material and must be taken into account. However, it would be hasty to draw conclusions regarding the consequences on the durability of the structure without further investigations.

# 4. Conclusion

This study has proposed an evaluation of the influence that the amount of water initially introduced has on the hardened properties a geopolymer mixture with a fixed formulation. The conclusions drawn and the consequences that can be expected regarding the development and the durability of geopolymer are listed below.

Increasing the amount of initial water in the mixture significantly reduces the mechanical performance measured at 7 days. It seems that this decrease follows a linear trend, which implies that the final performance can be anticipated as soon as the water content is known. However, this also implies that great caution must be taken during the fabrication of geopolymer, especially in large quantities, as a small error in the mass of water introduced may result in a significant variation in the final mechanical performance. That being said, a very wide range of applications seem possible for geopolymers, particularly in the field of construction, as they develop significant mechanical performance in just seven days with a range of water content traditionally used in construction materials.

The investigation of the bonded water during geopolymerization led to the conclusion that more than 90% of the water introduced would be "free water", which is easily removable, and therefore would not contribute to the stiffness of the material. The water present in the hardened geopolymer porosity would thus have no influence regarding the mechanical performance of the material. This water could be largely withdrawn, which could be useful for certain applications such as refractory materials. However, it should be noted that the departure of this pore water can in some cases be detrimental to the structure and lead to a decrease in strength.

The porosity studies reported here show a pore volume for the geopolymer paste that is large but in agreement with the literature. It appears that the total volume of the geopolymer pores is proportional to the volume of water initially introduced in the mixture, which is consistent with the conclusion of the bonded water study presented in this paper. The quantity of water introduced thus makes it possible to fix the final pore volume, and also the mean diameter of the mesoporosity. The transfer properties measured in this study are in agreement with the large porosity observed for the geopolymer, but further investigations on the durability must be carried out before drawing conclusions on the long term behaviour of these materials.

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