Curing process and pore structure of metakaolin-based geopolymers: Liquid-state $^1$H NMR investigation

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A B S T R A C T

Geopolymers are emerging construction materials with lower carbon dioxide emissions compared to the conventional cementitious materials. The knowledge of the curing process and the related pore structures are important for optimizing the properties of these materials for different applications. The curing process and final pore structure are sensitive to the amount of used water, however the specifics are unclear. The curing process and pore structures of metakaolin-based geopolymers with a narrow water-to-solid (w/s) ratio (0.59-0.66) were monitored by nuclear magnetic resonance (NMR) relaxometry and cryoporometry. The 14-day curing process was investigated by monitoring the change of $T_2$ and $T_1$ relaxation times and water signal intensity. After the curing, the pore structures were characterized by 2D $T_1$-$T_2$ correlation and $T_2$-$T_2$ exchange measurements of absorbed water. The pore size distributions (PSDs) were measured with NMR cryoporometry and compared to nitrogen physisorption and mercury intrusion porosimetry (MIP) results. We found that the relaxation times decreased as the pore structure of the geopolymers matured during the curing while the dissolution and the condensation periods of the curing were distinguished by the changes in signal amplitude reflecting the proton density. After the curing, three distinct pore sizes and connectivity between pores were identified from $T_2$-$T_2$ spectra. Their PSDs were measured, and they were found to correspond to two different pore sizes originating from the arrangement of clusters and defective pores. In the narrow w/s ratio (0.59-0.66), the curing times were the same for all samples when cured at 24 °C while the pore sizes were observed to increase as a function of the w/s ratio.

1. Introduction

Geopolymers are eco-friendly alternatives to conventional cementitious materials, such as ordinary Portland cement (OPC) [1,2]. They are synthesized through alkaline activation of aluminosilicate precursors, such as metakaolin [3] and fly ash [4], with alkali activators. In addition to lower carbon dioxide emissions [1], the use of geopolymers in construction applications is motivated by other desirable properties such as high compressive strength [5,6], fire resistance [7] and acid resistance [8–10].

In order to use the geopolymers in commercial applications, it is critical to understand the curing process and characterize the pore structure of geopolymers. Pore structure and pore network characteristics including pore size, pore connectivity, porosity, pore volume and specific surface area, have a defining role on the durability of inorganic binders and are therefore of vital importance [11–14]. As a result, they have been thoroughly characterized in cementitious systems, but not as thoroughly in the case of geopolymers which are a more recent innovation.

Gas adsorption-desorption [15–18] and mercury intrusion porosimetry (MIP) [19–22] are the most common conventional methods to investigate the pore structures during and after the curing process of cement-based materials and geopolymers. However, these measurements have several drawbacks that render them not optimal for observing cementitious materials. Both of them are destructive and measurements have several drawbacks that render them not optimal for observing cementitious materials. Both of them are destructive and potentially alter the structure they intend to measure as they require drying the material and introducing probe molecules at a high pressure. As a result, neither method is suitable for longitudinal studies as the...
sample is destroyed in the course of the measurement. Additionally, further error is introduced during data interpretation as a structural model is required for interpretation.

By contrast, nuclear magnetic resonance (NMR) enables in situ observation of elements of interest, yielding precise information without altering the sample. NMR relaxation measurements reveal the rates of recovery of the initially perturbed magnetization to the thermal equilibrium mainly due to the random rotational motion of molecules. Previously, it has been shown that one-dimensional $^1$H NMR $T_2$ and $T_1$ relaxation measurements are sensitive to curing [23–26], drying [27–29], and aging [30,31] in various cement systems. In these NMR measurements, the water molecules in hydrated cement paste are observed and their change of state is monitored as they transition from free liquid through dissolution and condensation to finally being confined in the pore network. To study the pore environment in cement systems, 2D $T_1$-$T_2$ correlation and $T_2$-$T_2$ exchange experiments of water saturated cement samples have been utilized. $T_1$-$T_2$ correlations improve the resolution of water in pore spaces as compared to 1D $T_1$ or $T_2$ measurements [32]. $T_2$-$T_2$ exchange enables the measurement of water exchange between pore environments [33].

NMR cryoporometry [34,35] is based on the fact that the melting point of the liquid confined in a small pore is inversely proportional to pore size. As $T_2$ relaxation time of frozen liquid is much shorter than that of unfrozen liquid, the amount of unfrozen liquid as a function of temperature can be readily measured by using a spin echo $T_2$ filter and the data can be converted into a pore size distribution (PSD). NMR cryoporometry is suitable for the measurement of micropores and mesopores. NMR cryoporometry has been used to measure the PSD of the hydrated pore structure in both wet cement pastes and the dried state [33,36–39].

So far $^1$H NMR relaxometry studies of geopolymers have been scarce, and they have limited to one-dimensional measurements; 1D $T_1$ measurements were used to observe the initial curing stages (0–20 h) of metakaolin-based geopolymers [40]. Furthermore, to the best of our knowledge, there are no scientific articles about the use of NMR cryoporometry on the characterization of pore structure of geopolymers in the literature. Hence, NMR relaxometry and cryoporometry techniques have a lot to offer in increasing our understanding of the curing process and pore structure development of aluminosilicate geopolymers.

Therefore, we carried out a 1D and 2D $^1$H NMR relaxometry as well as NMR cryoporometry characterization of aluminosilicate geopolymers with three water/solid ratios ($w/s$), defined as $H_2O/\text{(SiO}_2 + \text{Al}_2\text{O}_3 + \text{Na}_2\text{O})$, to gain a more nuanced understanding of the curing process and pore structure as well as the effect of dilution. Longitudinal $T_2$ and $T_1$ measurements of water within the paste were used to detect the duration of the curing process and to study the effect of the $w/s$ ratio on curing process. 2D $T_1$-$T_2$ correlation and $T_2$-$T_2$ exchange measurements as well as NMR cryoporometry analysis of water saturated cement samples were utilized to investigate the pore structures of the three geopolymers after 14 days of curing. For the comparison, the PSDs were also measured using $N_2$ physisorption and MIP. The novelty of this study is that it utilizes the knowledge about how to interpret 1D and 2D NMR relaxometry measurements and cryoporometry PSDs gained from studying cement systems to gain greater insight into the curing process and pore structure development of aluminosilicate geopolymers.

2. Materials and methods

2.1. Sample preparation

Three alkaline activators with different water contents were mixed (Fig. 1). The solutions included 7 g NaOH (VWR), 10.6 g fumed SiO$_2$ (SIGMA) and 25, 23.5 or 22 g H$_2$O. The solutions were then mixed with 20 g metakaolin (MetaMax, BASF). Three of each sample were loaded into 5 mm NMR tubes and then placed into curing chamber set to 24 °C and 100% humidity. They were used for NMR measurements on Magritek Spinsolve 43 MHz spectrometer. Another group of three samples with 6 mm diameter and 8 cm height were prepared using TeBon moulds in same curing chamber and they were for performing NMR cryoporometry experiments on Bruker Avance III 500 MHz spectrometer. The $w/s$ ratios of three geopolymers were 0.66, 0.63 and 0.59 and they were named G0.66, G0.63 and G0.59, respectively. The oxide molar ratios were: SiO$_2$:Al$_2$O$_3$:Na$_2$O:H$_2$O = 4:1:1:X, where $X = 17$, 16 and 15 for G0.66, G0.63 and G0.59, respectively.

2.2. NMR experiments

The $T_2$, $T_1$, $T_1$-$T_2$, and $T_2$-$T_2$ experiments were performed on Magritek Spinsolve 43 MHz spectrometer with the 5 mm diameter geopolymers (Fig. 1). Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [41] was used to measure $T_2$ data. $T_1$ data was acquired with a Saturation-Recovery (SR) pulse sequence [42,43]. The three samples were scanned during curing at the following time points: 1 h, 5 h, 16 h, 28 h, 2 days, 3 days, 5 days, 8 days, 11 days and 14 days. The spin-echo time $\tau$ in the spectrally resolved CPMG experiments was 160 μs. The echoes were detected collected from 1 to 120 echoes with 120 linearly spaced steps. The maximum CPMG encoding time was 19.2 ms. The repetition time was 1 s, number of scans was 4 and the experiment time was 8 min. In the SR experiments, a recovery time of 1 ms to 2 s with 64 logarithmically spaced steps was used. The repetition time was 2 s. The

![Fig. 1. The scheme of the experimental procedures. Three metakaolin-based geopolymers (G0.66, G0.63 and G0.59) with different w/s ratios were synthesized by mixing metakaolin with alkaline activators. The mixtures were loaded into 5 mm NMR tubes and put into curing chamber. At 1 h, 5 h, 16 h, 28 h, 2 days, 3 days, 5 days, 8 days, 11 days and 14 days of curing, the (a) $T_2$ and $T_1$ were measured for curing monitoring. After 14 days of curing, geopolymers were submerged in water for 9 days to saturate, after which the (b) $T_1$-$T_2$ and $T_2$-$T_2$ spectra and (c) NMR cryoporometry were acquired for pore structure observation.](image-url)
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number of scans was 4 and the experiment time was about 13 min.

After 14 days of curing, water was added to cover three geopolymers in 5 mm NMR tubes. After 8 days of saturation, the 2D $T_1$-$T_2$ [44,45] and $T_2$-$T_2$ [46] experiments were conducted. For the $T_1$-$T_2$ experiments, the spin echo time was 150 μs and 1000 echoes were collected in a single scan. The $T_1$ recovery time was 1 ms to 5 s with 64 logarithmically spaced points. The direct dimension of $T_2$-$T_2$ experiment had an echo time of 150 μs and 1000 echoes. The indirect $T_2$ dimension utilized 64 logarithmically spaced points from 2 echoes to 100 echoes, and the echo time was 150 μs. The mixing time was 1 ms. The number of scans was 128 and relaxation delay was 5 s for both $T_1$-$T_2$ and $T_2$-$T_2$ experiments. The experiment time was about 11 h for $T_1$-$T_2$ and about 14 h for $T_2$-$T_2$.

NMR cryoporometry experiments [36] were conducted on Bruker Avance III 500 MHz spectrometer with a 10 mm broadband probe. Before performing the NMR cryoporometry experiments, three 6 mm samples were submerged into water for 8 days after 14 days curing. The water-saturated samples were then loaded into 10 mm diameter NMR tubes whose inner diameter was 8 mm (Fig. 1). A smaller diameter of samples compared to the tube inner diameter was used because we found that, if the samples were directly prepared in NMR tubes (like how 5 mm diameter samples were made), the tubes crushed after freezing at around 250 K. The volume expansion with the transformation from water inside geopolymers to ice at low temperature should be responsible for the breaking glass. Experiments were performed over a temperature range of 167 K to 277 K with temperature steps of 1.3 K for a total of 78 points. CPMG experiments were performed at every temperature point. The spin-echo time $T_{2,1}$ was 140 μs and 400 echoes were collected in a single scan. The number of scans was 64. The CPMG acquisition time was 28 ms and the relaxation delay was 5 s. The experiment time for CPMG was 5.5 min. In the temperature increase, after arriving the target temperature of 167 K, 6.5 min was used for temperature stabilization between steps, and the average heating rate of the sample was low, about 5 min/K, ensuring the thermal equilibrium. The total NMR cryoporometry experiment time for one sample was about 18 h.

2.3. NMR data analysis

2D $T_1$-$T_2$ and $T_2$-$T_2$ data was analysed by the 2D Laplace inversion [41] using MATLAB (MATLAB, R2017b, Mathworks). 1D $T_2$ and $T_1$ data were analysed with a mono-exponential fit. The Laplace inversion analysis of the $T_1$ and $T_2$ data is available in the Supporting material (Fig. S1).

The function for the 1D $T_2$ CPMG signal data fitting is

$$S(t) = \exp \left( -1/T_2 \right) S_0,$$  

where $t$ is the time, and $S_0$ is the signal at $t = 0$. The function for the 1D $T_1$ SR signal data fitting is

$$S(t) = \left[ 1 - \exp \left( -1/T_1 \right) \right] S_0.$$  

Error in the fit was estimated by using Curve Fitting Tool embedded in MATLAB (MATLAB 2017b, Mathworks). Using the mean and standard deviation of the fit, a gaussian curve was generated to display the results as a probability distribution [47].

The NMR cryoporometry PSDs were calculated using the following equation:

$$\frac{dV}{da} = \frac{k}{(a_0 - 2a_0)} \frac{dS}{d\Delta T_m}.$$  

Here, $a_0$ is the pore diameter, $a_0$ is the thickness of non-freezing layer of water on the surface of the pore, $k$ is a constant characteristic of each probe liquid, $\Delta T_m = T_0 - T_{pore}$ is the melting point depression ($T_0$ is the melting point of bulk liquid and $T_{pore}$ is the melting point of liquid confined to the pore), and $S$ is the NMR signal of the unfrozen liquid. The detailed method about how to analyse the cryoporometry data was shown in Valckenborg’s work [36]. For the geopolymer system, $k = 89$ K nm [36] and $a_0 = 0.4$ nm [48] were used.

2.4. $N_2$ physisorption experiments

After 14 days of curing, the six samples were ground to powder by using vibrating disc mill Resch RS200. 700 rpm and 1 min were used for grinding. The physisorption measurements were done using physisorption of nitrogen at −196 °C with Micromeritics ASAP 2020, US. PSDs were obtained using the Barret-Joyner–Halenda (BJH) method [49]. Prior to adsorption, the samples were degassed under vacuum at 100 °C for 120 min.

2.5. MIP experiments

The PSDs of the paste samples were determined through mercury intrusion porosimetry (Micromeritics AutoPore IV 9500, US). For this purpose, the hydrated samples after 14 days of curing were cut to dimensions of about (1 x 1 x 1) cm$^3$. The measurements were performed in the pressure range between 0.034 atm and 2041 atm. One measurement per sample type was performed.

3. Results and discussion

3.1. Curing process monitoring by one-dimensional $^1$H NMR relaxometry

Curing of geopolymers is a multistage process, which is defined as storing the material in a controlled temperature and moisture environment so that the geopolymers develops the desired properties, such as final pore structure and mechanical properties of the material [50]. Adequate curing is essential to both durable concrete and geopolymer, and therefore it is important to characterize the curing kinetics. In this work, 1D $T_2$ and $T_1$ measurements are utilized to study the curing process of geopolymers as the function of w/s ratio.

The measured $T_2$ and $T_1$ of water in pores are related to the surface area-to-volume ratio ($S/V$) and surface relaxivity according to [51]:

$$\frac{1}{T_2^{\text{measured}}} = \frac{1}{T_2^{\text{bulk}}} + \frac{S}{\rho_{\text{surf}}}.$$  

where $T_2^{\text{measured}}$ is the measured $T_2$ or $T_1$ value, $T_2^{\text{bulk}}$ is the $T_2$ or $T_1$ value of bulk water, $\frac{S}{\rho_{\text{surf}}}$ is the surface area-to-volume -ratio, and $\rho_{\text{surf}}$ is the surface relaxivity. If the surface relaxivity is not changing significantly during the curing procedure, a decrease in the measured $T_2$ or $T_1$ values indicates an increase in the surface area-to-volume ratio.

The curing process of the samples was studied by measuring the $T_2$ decay from hour 1 to day 14 (Fig. 2). $T_2$ values are higher when the sample contains more water. The signal decays fit well with a mono-exponential decay (Fig. 2a–c) and significant deviation is seen only after 99% of signal decay (which is close to the noise level).

Observing the trends over time, $T_2$ decreases for all the three geopolymers until 8 days (Fig. 2g) and remains constant after that. The decrease in $T_2$ indicates an increase in $\frac{S}{\rho_{\text{surf}}}$, which can be interpreted to be caused by the reaction products filling in larger pores, therefore leading to decrease in the pore sizes [21]. Following the structural reorganization and condensation, which lasts for 8 days, structural stability is reached by day 8 in all samples as indicated by the relaxation rates and stable signal intensity (Fig. 2g-h).

There are earlier studies, in which the changes in $T_2$ and $T_1$ were exploited to monitor the curing process in cement-based materials [26,51-53] and metakaolin-based geopolymers [46]. Based on $T_1$ measurements, curing was monitored [23,24] in cement materials for 24 h and metakaolin-geopolymers for 20 h [40]. The curing time of cement was found to be less than 20 h and that of geopolymers with a
The molar oxide ratio of SiO$_2$:Al$_2$O$_3$:N$_2$O:SiO$_2$:H$_2$O = 3.07:1:0.68:5.9 and w/s ratio of 0.32 was found to be 6 h. In our study, we monitored the curing process for much longer time 14 days, for samples with a w/s ratio of 0.59–0.66, using both $T_2$ and $T_1$ contrast. The same decreasing trends of $T_2$ and $T_1$ were found. However, significantly longer curing times were observed for our three samples than in the previous geopolymer study (8 days vs. 6 h).

The large difference in curing times is assumed to be related to the difference in water contents. The lower water content has been found to shorten the curing process for both geopolymers and cement-based systems alike [23,54]. In this study, different w/s ratios did not lead to significant differences in curing kinetics. This may be a consequence of the relatively small range of w/s ratios. The hypothesis is that the curing process is dependent on w/s ratio but is stable over the range of w/s ratios studied here.

In addition to $T_2$, $T_1$ relaxation was also used to study the curing process (Fig. 3). The same trend is observed as in the case of $T_2$, $T_1$ is decreasing until day 8. In geopolymers, the curing process is hypothesized to include two processes: the dissolution of precursor and a condensation period. The condensation period includes four stages: the speciation equilibrium, the gelation, the reorganization and the polymerization [55]. However, the $T_2$ and $T_1$ relaxation times do not show such distinct changes in the rate of change of $T_2$ as a measure of the stages as was seen in cements [24]. Therefore, this data suggests that the stages in hydration process of geopolymers are continuous and overlapping without a delay between stages. This overlapping was also found with a broad exothermic peak by using isothermal calorimetry measurement [56].

It has been proved that the water inside frameworks can be used as an indicator of the curing process for both concrete [57] and fly ash-based geopolymer [58]. Hence, apart from the $T_2$ and $T_1$ monitoring, $S_0$, which is proportional to the proton density, was also derived from both CPMG and SR experiments to monitor the curing process (Figs. 2h–i and 3h–i). The $S_0$ represents the amount of detectable water during this period. The evaporable water is mobile in the pore structure and is detectable using relaxation methods while the strongly-bound water, i.e. hydration water is not detectable due to its short $T_2$ (about 10 μs) [59]. Therefore, $S_0$ is interpreted to represent the amount of mobile water. In the CPMG experiments (Fig. 2h–i), $S_0$ increased from 1 h to 5 h. The comparatively low initial signal intensity is a reflection of the fact that there is a large amount of immobile adsorbed water when the metakaolin dissolves during the first hour (Fig. 7) [55]. After the dissolution period, the condensation starts. Some adsorbed water is released and the signal intensity increase from 1 h to 5 h. After 5 to 16 h, $S_0$ starts to decrease as the mobile water transitions to bonded water. In previous works, the immobilization of the water molecule on the solid matrix was found by using $^{29}$Si, $^{27}$Al and $^1$H solid-state NMR spectra [60–62]. These dynamics are captured in Fig. 7, which depicts the origin of the changes in the mobile water content. In terms of w/s ratio, detectable water increases as the w/s ratio increases as expected.
3.2. Pore structure study with 2D T₁-T₂ and T₂-T₂ measurements

The 1D T₂ and T₁ spectra shown above provide information about the curing process, but they do not give detailed information about the pore structure. In order to detect the pore structures of mature samples, the samples were saturated for 8 days and the pore water was studied. The pore water is used as a probe molecule in this experiment. The samples were submerged in water for 8 days to saturate them. 2D T₁-T₂ correlation and T₂-T₂ exchange spectra were measured. 2D T₁-T₂ and T₂-T₂ measurements have previously been shown to resolve water in gel and capillary pores and provide information of pore structures in cement-based systems [32]. They have higher specificity than 1D relaxation measurements in pore detection and the T₂-T₂ experiment is also able to provide information on pore-to-pore exchange of water [63], which can be related to tortuosity of the material.

In the T₁-T₂ plot, bulk liquid can be seen on the T₁ = T₂ line whereas liquid confined in a pore has a T₁ > T₂. The peaks along the line of T₁ = XT₂ (X > 1) represent water in pores with different sizes. According to Eq. (4), for a sample with homogeneous surfaces, 1/ρsurf is fixed and, therefore, the T₂ and T₁ of water in pores are only dependent on X. Hence, larger pores are associated with longer T₁ and T₂ relaxation times. McDonald and co-workers [32] found several discrete peaks along T₁ = 4 T₂ when studying hydrated white cement, indicating that the relaxation is dominated by surface interactions. Similar offset from T₁ = T₂ from the surface interactions has been observed in many other porous structures as well [64].

In the T₁-T₂ spectra of the three geopolymer samples (Fig. 4a–c), there are three peaks, which are visible in every spectra. The top of the dominant peak (peak II) falls on the line T₁ = 3.7 T₂, indicating that it arises from water in pores. Its T₂ is 20 ms. Two other peaks also lie close to the T₁ = 3.7 T₂ line. Peak I is a small peak with a short T₁ (about 2 ms). Peaks I is associated with smaller pore structures in the geopolymer. The small peak (peak III) with a long T₁ (about 220 ms) is interpreted to arise from a little amount of free water on the surface of the geopolymers. Apart from the three abovementioned peaks, a cross-peak is also seen above the line of T₁ = 3.7 T₂ between peaks I and II. Such a cross peak is expected to appear between two pores when there is exchange of water molecules between them within the timescale of the measurement [11,32]. Two further observations for G0.63 and G0.59 peaks can be made. First, no separated Peak I is observed for G0.63, but it is probably overlapping with the exchange peak. Secondly, the G0.59 map is distinct from the other two samples with a wide and not clearly resolved distribution of T₁-T₂ peaks.

In the T₂-T₂ spectra, two peaks are seen along the diagonal line T₂, direct = T₂, indirect and a single cross-peak is observed below this line for all three geopolymer samples (Fig. 4d–f). Peak I (shown in the lower left corner of T₁-T₂ maps) is missing here because it is filtered by the storage time (1 ms). The peak with a T₂ of about 5.5 ms on the line T₂, direct = T₂, indirect corresponds to peak II shown in T₁-T₂ spectra. The small peak on the diagonal line T₂, direct = T₂, indirect with a T₂ of about 59 ms corresponds to peak III in the T₁-T₂ spectra. A notable peak below the diagonal line is observed with a T₂, direct of 0.5 ms and T₂, indirect of 5.5 ms.
This peak is attributed to the exchange between the peaks I and II, and similar exchange peak has been reported by previous T$_2$-T$_2$ exchange studies of white cement paste [32].

3.3. PSDs study with cryoporometry, N$_2$ physisorption and MIP

To further characterize the pores detected in the 2D relaxation spectra, PSDs were measured with NMR cryoporometry and the results were compared to N$_2$ physisorption and MIP findings. N$_2$ physisorption and MIP are the two conventional methods for measuring PSDs, especially for mesoporous materials (i.e. pore sizes between 2 and 50 nm).

To probe the relationship between pore size information and T$_2$ relaxation, NMR cryoporometry PSDs with varying T$_2$ weighting were processed (see Fig. 5). The PSDs include three partially overlapping peaks: there is a narrow peak around 2.5 nm corresponding to the smallest pores (pore A), another peak around 9 nm (pore B) and a broad peak of the largest pores (pore C) around 30 nm. The pore size values of the maxima of the peaks are shown in Table 1. At the shortest overall echo time (140 μs), the integral of the largest pores (pore C) is about 70% of the total integral (see Table 2), so the largest pores have the biggest overall volume. As the echo time increases, intensities of the smaller pores A and B decrease significantly due to T$_2$ filtering effect, while the largest pore C does not change so much. Therefore, it is evident that pores A and B have shorter T$_2$ relaxation time than pore C. We interpret that pore A corresponds to shortest T$_2$ peak I in the T$_1$-T$_2$ and T$_2$-T$_2$ spectra, while pores B and C correspond to the largest amplitude peak II. T$_2$ of peak II is much longer than the echo times in the NMR cryoporometry PSDs, and therefore signal of pore C is much less T$_2$ weighted. All three samples show peaks corresponding to the three different pore sizes. The biggest pores increase their pore size with increasing w/s ratio. The measured temperature dependence of signal intensity at three echo times and the T$_2$ values correlated to the pore size distribution are provided in Supporting material (Figs. S2–3).

To determine the accuracy of the NMR cryoporometry, the PSDs of the three samples measured by using NMR cryoporometry are compared to N$_2$ physisorption and MIP in Fig. 6. The exact pore size values are displayed in Table 1. The methods are in agreement on the order of magnitude for pore sizes but differ in exact values. Cryoporometry shows pore A at about 2.5 nm and two broad and partially overlapping peaks (pores B and C) at about 9 and 30 nm, while N$_2$ physisorption shows two pores at about 3.5 nm and 14 nm. The MIP shows only a single peak corresponding to pore size of about 9 nm. Here, NMR cryoporometry was the only method measuring pores below 3 nm. All the techniques detect the pores around 10 nm pores (pore B). MIP does not detect the largest pores. Previously, it has been shown that MIP measures smaller pore sizes in shale materials than N$_2$ adsorption because

![Fig. 4. (a–c) 2D T$_1$-T$_2$ spectra and (d–f) T$_2$-T$_2$ correlation spectra of G0.66, G0.63 and G0.59 samples. In T$_1$-T$_2$ spectra (a–c), the grey dash and solid lines are T$_1$ = T$_2$ and T$_1$ = 3.7 T$_2$, respectively. In T$_2$-T$_2$ spectra, the dashed line indicates T$_2$ direct = T$_2$ indirect. The mixing time in the T$_2$-T$_2$ measurements was 1 ms. The spectra were measured after 8 days of water saturation.](image-url)
the MIP quantifies the sizes of the pore throats instead of pore bodies [65]. This implies that the largest pores are not accessible without through the intermediate size pores and/or maybe the smallest pores. The largest pores are detected both by NMR cryoporometry and N₂ physisorption. While each method has its limitations, such as water expansion during freezing in cryoporometry or the use of high pressure in N₂ physisorption, the fact that the methods are in agreement with one another indicates that these pore sizes are likely correct.

3.4. Pore structure of geopolymers with different w/s ratios

The pore structure of geopolymer is fundamentally different when compared to that of cement-based systems (such as OPC). The cement hydration product consists of 2-dimensional chains [66]. Geopolymers, on the other hand, are more likely to be the amorphous analogue of zeolite, which has a 3-dimensional pore structure [67]. Geopolymers and zeolites have the same unit cells in the short range but for the long range, the unit cells are disordered in geopolymer systems without a long-range order. It has been found that there are X-ray amorphous faujasite (zeolite Y) structures in metakaolin-based geopolymer [68]. Here, three types of pores are detected in the pore analysis. Pore A has the smallest integral in the NMR cryoporometry PSDs. Its pore size is 2.5 nm and its proportion is independent of the w/s ratio. This pore size in N₂ physisorption, the fact that the methods are in agreement with one another indicates that these pore sizes are likely correct.

Fig. 5. (a–c) The pore size distributions (PSDs) of geopolymers measured by NMR cryoporometry with an overall CPMG echo time of 140 µs, 420 µs and 700 µs. Largest pores (pore C) at about 30 nm are always dominating the distribution. When the echo time increases, the pore A and pore B is decreasing due to T₂ filtering effect and the pore C increase their distribution. (d–f) Comparison of the PSDs of different samples. The pore size of biggest pore C increases as the w/s ratio increases. The volume of each pore is almost identical with the change of w/s ratio.

Table 1
Pore diameters of G0.66, G0.63 and G0.59 measured by NMR cryoporometry (with 140 µs echo time), N₂ physisorption and MIP. The locations of the maxima of the peaks are shown.

<table>
<thead>
<tr>
<th>Pore diameter (nm)</th>
<th>Cryoporometry</th>
<th>N₂ physisorption</th>
<th>MIP</th>
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<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
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<tr>
<td>G0.66</td>
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<td>9.9</td>
<td>35</td>
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<td>9.9</td>
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</table>

Table 2
Integral percentages of three pores of G0.66, G0.63 and G0.59 measured by NMR cryoporometry with echo times of 140 µs, 420 µs, 700 µs and N₂ physisorption.

<table>
<thead>
<tr>
<th>Integral percentage (%)</th>
<th>G0.66</th>
<th>G0.63</th>
<th>G0.59</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Cryoporometry (140 µs)</td>
<td>8.1</td>
<td>25</td>
<td>67</td>
</tr>
<tr>
<td>Cryoporometry (420 µs)</td>
<td>1.8</td>
<td>20</td>
<td>78</td>
</tr>
<tr>
<td>Cryoporometry (700 µs)</td>
<td>0.88</td>
<td>16</td>
<td>84</td>
</tr>
<tr>
<td>N₂ physisorption</td>
<td>0.33</td>
<td>41</td>
<td>58</td>
</tr>
</tbody>
</table>
consistent with the unit cell size of zeolite Y (Fig. 7), 2.4 nm [69] and the measured pore structure seems to be consistent with a structure consisting of a missing zeolite Y unit cell. However, the exact pore size in NMR cryoporometry depends on many factors, such as the value of the calibrated constant for the relation between the melting point depression and pore size in the Gibbs-Thompson equation, and therefore pore A may correspond to supercage (1–1.2 nm) [70] as well. Hence, in either case, pore A is dubbed ‘zeolite-analogous pore’. The fixation of the unit cells also explains why pore A size is independent of water content.

Pore B has a pore size of about 9 nm. It is assumed to be the disordered arrangement of the unit cells. It is unavoidable that there are larger pores than the zeolite-analogous pores due to the disordered arrangement. Also, there are about 20% of these pores.

The size of pore C is the largest and it is in the range of 17 nm to 35 nm. These pores are much larger than the zeolite-analogous pores (2.5 nm). Interestingly, their size and quantity are found to depend on the w/s ratio unlike the smaller pores; G0.66 has larger pore C size than G0.63 and G0.59. Pore C is assumed to stem from defective sites, consisting of a large cluster of defects. The defective sites are related to the presence of the terminal hydroxyls, instead of the unreacted metakaolin. Unreacted metakaolin or other precursors are often seen to lead to the defective sites for geopolymers, but the defects from unreacted metakaolin are orders of magnitude larger, on the order of tens of microns as seen in SEM micrographs [55,71]. The defective sites due to the presence of the terminal hydroxyl are common for the zeolite. The sites with the dealumination have a terminal hydroxyl (Si-O-H) and are called the defective sites. The pore size of the dealuminated zeolite Y is commonly 20 nm [72]. Here, the pore C is much smaller than voids originating from unreacted metakaolin. It is reasonable to hypothesize that the pore C is the defective site like shown in zeolites. This is also supported by the 27Al solid-state NMR spectra (Fig. S4). As shown on the 27Al solid-state NMR spectra, there is the main peak at around 56 ppm and a barely discernible peak at 0 ppm. The peak at 56 ppm is the signal from the tetragonal Al from the structure of geopolymer and the peak at 0 ppm is ascribed as the octahedral Al of the unreacted metakaolin [73]. Judging from the size of the 0 ppm peak height, metakaolin has fully dissolved and reacted regardless of the water amount. The extra water used in the synthesis lowers the pH during reaction. However, this did not affect the reaction kinetics within the narrow water window studied here. In the final structure, the extra water used in synthesis leads to increased pore size as expected, but not across the board: pores between 2 and 10 nm remain unaffected, while there is a distinct increase in the amount of 17–35 nm pores. One explanation is related to the competition between space filling tendency of the precipitating nano-zeolites and the energy penalty caused by the non-ideal stretching and bending of the covalent bonds that takes place at the crystal boundaries between the nano-zeolites: the more water used in the synthesis, the more space there is available for the precipitates, and therefore there is a decreased tendency for the crystal boundaries to connect due to the energy penalty. Here, we see evidence that this tendency manifests itself as the slight increase in 30 nm mesopores, but evidently not in increase of smaller pore structures. Therefore, it seems that the large mesopore sizes are somewhat controllable by changing the w/s ratio, which maybe a valuable property of the geopolymer in some applications.

Regarding pore connectivity, two different kinds of pore interconnections are confirmed with the 2D relaxation maps (Fig. 4) and the MIP data (Fig. 6). Firstly, there is an apparent connectivity between geopolymer pores (pore B) and the zeolite-analogous pores (pore A), as evidenced by water exchange peak in the 2D relaxation maps (Fig. 4). Secondly, the geopolymer pores (pore B) and the defective site pores (pore C) can indirectly be seen to be connected. As previously stated, the MIP shows a smaller geopolymer pore size value than other two methods and the defective site pores are not be able to be measured by MIP (Fig. 6). This is most like because the probe mercury molecules cannot pass through the geopolymer pores into the defective site pore. This can be thought to be indirect evidence of the water-passable interconnection between the geopolymer pores and the defective site pore. This is also consistent with the hypothetical formation process of the defective site pores.

3.5. Limitations

A few limitations of this work should be noticed. One limitation is that a narrow w/s ratio is used. Apart from the possibility that the curing is not dependent on the w/s ratio, the narrow w/s ratio would be another reason why no difference in the curing process was detected among the three samples. Another hypothesis is that the curing time more dependent on other parameters such as Si/Al ratio which has been shown to impact the skeleton formation in metakaolin-based geopolymers [11]. Further work with wider w/s ratio would give valuable information about the influence of water content on the curing. Another limitation is that the geometry of the geopolymers is derived only from the pore structure detection. To clarify more detailed and reliable morphology of geopolymers, a good combination with other chemical characterization methods, such as atomistic simulation [75,76] and X-ray powder diffraction will be performed as a part of the future work.

![Pore Size Distribution](image-url)
4. Conclusions

NMR relaxometry and cryoporometry were found to be effective tools to monitor the curing and characterize the pore structure of geopolymers. We found that geopolymers with a w/s ratio of 0.59–0.66 are fully cured after 8 days at 24 °C and the curing time does not depend on the w/s ratio in this narrow range. Furthermore, unlike in OPC systems, the different stages in hydration process of geopolymers are continuous and potentially overlapping as there are no detectable delays between stages. The pore structures of the geopolymer samples over this limited w/s ratio depend on water content in the 17–35 nm pore size range, but surprisingly remain constant between 2 and 10 nm. This dynamic was only visible in the NMR cryoporometry although in all the three methods used for PSD analysis, the w/s ratio is seen to affect the PSDs to some degree. The higher water content contributes to the larger pores while less considerable influence on the small pore size was detected. Of the compared PSD measurement methods, NMR cryoporometry has a widest detection limit and was the only method measuring pores below 3 nm. 2D NMR relaxation techniques are also suitable to provide information about pore connectivity. The intermediate size pores are seen to connect with small and large pores. So far, liquid-state NMR techniques have been underutilized in geopolymer characterization and hold untapped potential to shed light on other aspects of geopolymers as well, including aging, water ingress and drying.

CRediT authorship contribution statement

Jing Li: Investigation, Formal analysis, Writing - Original Draft.
Sarah Mailliott: Investigation, Methodology, Formal analysis, Writing - Review & Editing, Supervision.
Harisankar Sreenivasan: Investigation, Methodology, Writing - Review & Editing, Supervision.
Anu M. Kantola: Methodology, Writing - Review & Editing, Supervision.
Mirja Illikainen: Conceptualization, Resources, Writing - Review & Editing, Supervision.
Elijah Adesanya: Investigation, Methodology, Writing - Review & Editing.
Lubica Kriskova: Investigation, Writing - Review & Editing.
Ville-Veikko Telkki: Conceptualization, Resources, Writing - Review & Editing, Supervision, Funding acquisition.
Paivo Kinnunen: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


