

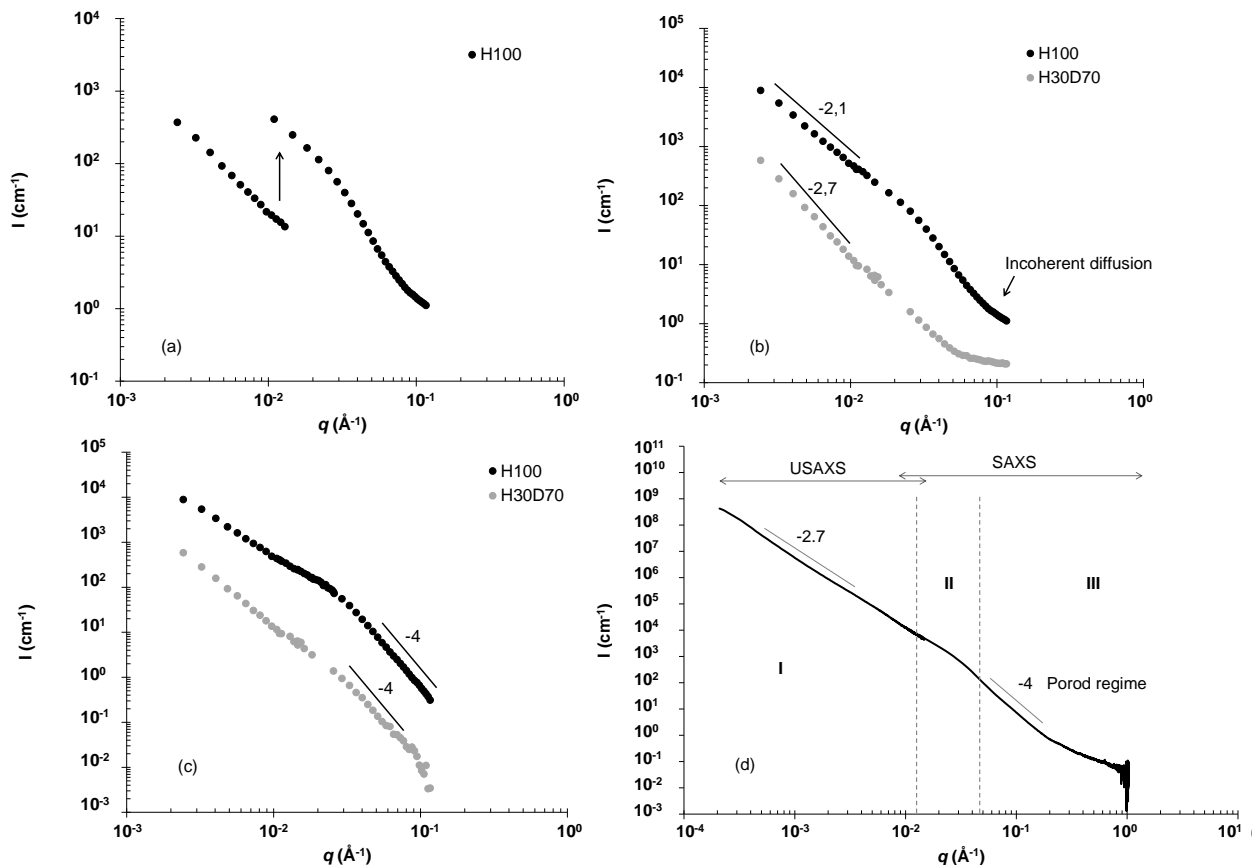
Supporting information

Effect of composition and aging on the porous structure of metakaolin-based geopolymers

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SI.1. Small-angle neutron scattering data treatment.

Data treatment in small-angle neutron scattering (SANS) is detailed in this section. After the experiment, the measured intensity I_m is corrected for the sample transmission and thickness, the contribution of the empty cell is subtracted and the signal is normalized by the water scattering signal in order to correct for the inhomogeneity of the detector response. After these basic corrections, we get the scattering profiles presented in figure FigSI.1a for the geopolymer paste Na-3.6-11.5 in the low- q configuration (wavelength $\lambda = 17 \text{ \AA}$ and sample-detector distance $d = 4.7 \text{ m}$) and in high- q configuration (wavelength $\lambda = 6 \text{ \AA}$ and sample-detector distance $d = 3 \text{ m}$).



FigSI. 1 – Small-angle neutron scattering data treatment on the geopolymer paste Na-3.6-11.5: (a) rescaling of the low- q data, (b) analysis of slope values, (c) correction of the incoherent diffusion of water, (d) ultra and small-angle X-ray scattering data. For SANS experiments, H100 represents a geopolymer saturated with 100% of light water and H30D70 a geopolymer saturated by a mixture of 30% of light water and 70% of heavy water.

Rescaling of the data have to be done between the low- q configuration and the high- q configuration in order to obtain the global scattering spectra, as shown in FigureSI.1a.

After this first step, the shape of the scattering profile in FigureSI.1b needs corrections because of low transmission at low- q , incoherent scattering of water and certainly multiple scattering.

- Low- q scattering pattern:

For this particular sample (Na-3.6-11.5 **H100**), the transmission in the low- q configuration was only equal to 7%, and in every case it was lower than 11%. Consequently, SAXS was performed as a complementary technique to get the correct shape (slope of the intensity at low- q range) of the scattering profile. Indeed, no problem of transmission or multiple scattering occurred during the SAXS experiment, leading to a high confidence in the shape of the curve. However, the saturation degree of porosity (relative humidity) has not been controlled during the SAXS experiments. Therefore, the intensity level is doubtful which can lead to quantitative errors in the data analysis in terms of pore volume and specific surface area. Moreover, it is difficult to carry out the contrast matching method with X-rays, while it is easy to use the strong interaction of neutrons with water and the big difference in scattering length densities between light and heavy water.

In FigureSI.1b, the slopes are different from that found with ultra-small-angle and small-angle X-ray scattering (USAXS and SAXS) shown in FigSI.1d. In USAXS, the slope was equal to -2.7. Here, they are equal to -2.1 and -2.7 for the geopolymer sample saturated with water (H100) and with the extinction mixture (H30D70), respectively. In this wave vector range, the slope corresponds to the mass fractal dimension of the solid network structure: there is no reason for the slopes to be different. The low transmission of the samples in SANS (at low q and for H100 samples) can explain that the first slope is incorrect. The strong interaction of neutrons with hydrogen may be responsible for the lack in intensity in this q -range: as a matter of fact, the same sample in the extinction mixture (Na-3.6-11.5 H30D70) had a transmission of 61% when the saturating solution was mainly composed of heavy water and the slope was then the same than in USAXS experiments.

Multiple scattering is also suspected to decrease the intensity value on the first points as observed by Maitland et al.¹. However, no correction on the slopes was applied to the scattering profile because it does not affect the data analysis in terms of pore volume and mean pore size, for which only the high- q data are required.

- High- q scattering pattern:

At high- q , incoherent scattering due to the solvent disrupts the signal. SAXS in FigSI.1d shows a Porod regime with a q^{-4} evolution of the scattered intensity. A correction was applied to the neutron data to get the same evolution as in SAXS experiments. This step is illustrated in FigSI.1c and the obtained scattering profiles are used for fitting.

SI.2. Micro-porosity calculations: *t*-plot method.

The method consists in comparing the specific area calculated from the BET theory a_{BET} with the external surface a_{ext} . The external surface is the area developed by a non-porous solid. In the case of a porous solid, the area developed by the pores can be counted in the external

surface, if the pores are large enough to allow the formation of a multimolecular layer. If the porous solid is mesoporous or macroporous, a_{BET} and a_{ext} are very close. However, if the adsorbent is a microporous solid, then:

$$a_{BET} - a_{ext} \neq 0$$

The difference between a_{BET} and a_{ext} is attributed to microporosity. The external surface a_{ext} is evaluated by comparing the thickness t of the adsorbed layer at a given equilibrium relative pressure between the studied adsorbent and a non-porous reference solid. The Harking-Jura equation has been chosen to calculate t :

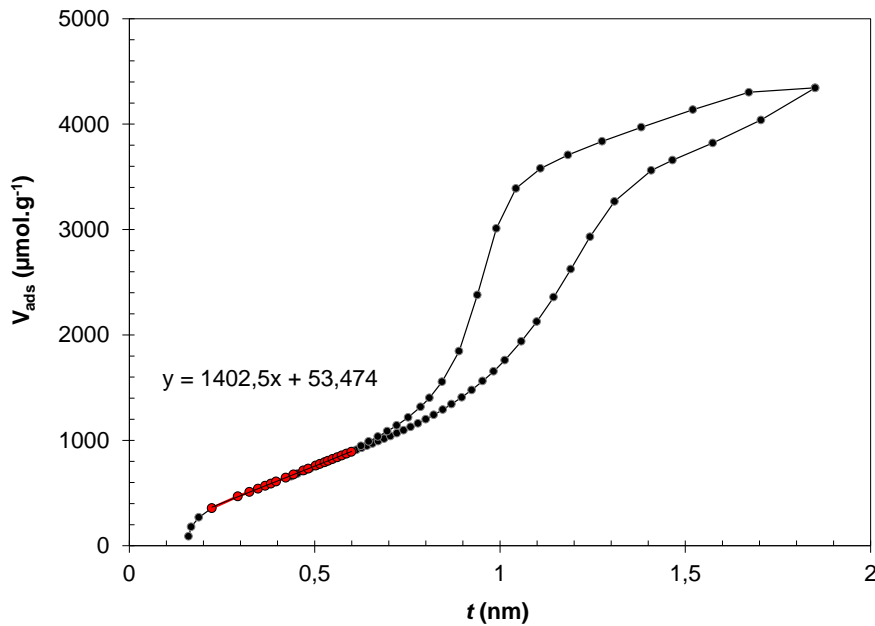
$$t \text{ (nm)} = \left(\frac{0.1399}{0.034 - \log \left(\frac{P}{P_0} \right)} \right)^{1/2}$$

The nitrogen adsorption-desorption isotherms were transformed into t-plot by plotting the nitrogen adsorbed volume V_{ads} ($\mu\text{mol}\cdot\text{g}^{-1}$) as a function of t :

$$V_{ads}(\mu\text{mol}\cdot\text{g}^{-1}) = \frac{V(\text{cm}^3\cdot\text{g}^{-1}STP)}{22.4 \times 10^3} \times 10^6$$

The external surface is then proportional to the slope $s(t)$ of the linear part of the curve as shown in FigSI.2 in red.

$$a_{ext}(t) = 0.0346s(t)$$



FigSI. 2 - t-plot calculation for the geopolymer paste Na-3.6-11.5

In TableSI.1 are reported the a_{BET} and a_{ext} values for all the geopolymer paste formulations. The estimated fraction of microporosity is always lower than 10%. These results are questionable because of the small difference between a_{ext} and a_{BET} . It seems that only a few $\text{m}^2\cdot\text{g}^{-1}$ can be attributed to microporosity. Thus, it was assumed that almost no microporosity exists in geopolymers.

TableSI. 1 – Specific area a_{BET} calculated with the BET theory, external area a_{ext} from the *t*-plot method for several geopolymer formulations and estimated fraction of microporosity.

Geopolymer formulation	a_{BET} ($m^2 \cdot g^{-1}$)	a_{ext} ($m^2 \cdot g^{-1}$)	%micro
Na-3.6-15	67	60	9
Na-3.6-13	58	53	9
Na-3.6-11.5	53	49	8
Na-3.6-10	46	43	7
Na-4-13	64	61	4
Na-4-11.5	57	53	7
Na-4-10	40	38	5
K-3.6-11.5	101	92	9

- (1) Maitland, C.F.; Buckley, C.E.; O'Connor, B.H.; Butler, P.D.; Hart, R.D. Characterization of the pore structure of metakaolin-derived geopolymers by neutron scattering and electron microscopy. *J. Appl. Crystallogr.*, *44*, 697-707.