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 curve presented in figure FigSI.1a for the geopolymer paste Na-3.6-11.5 in the low-q configuration (wavelength $\lambda = 17$ Å and sample-detector distance d = 4.7 m) and in high-q configuration (wavelength $\lambda = 6$ Å and sample-detector distance d = 3 m).
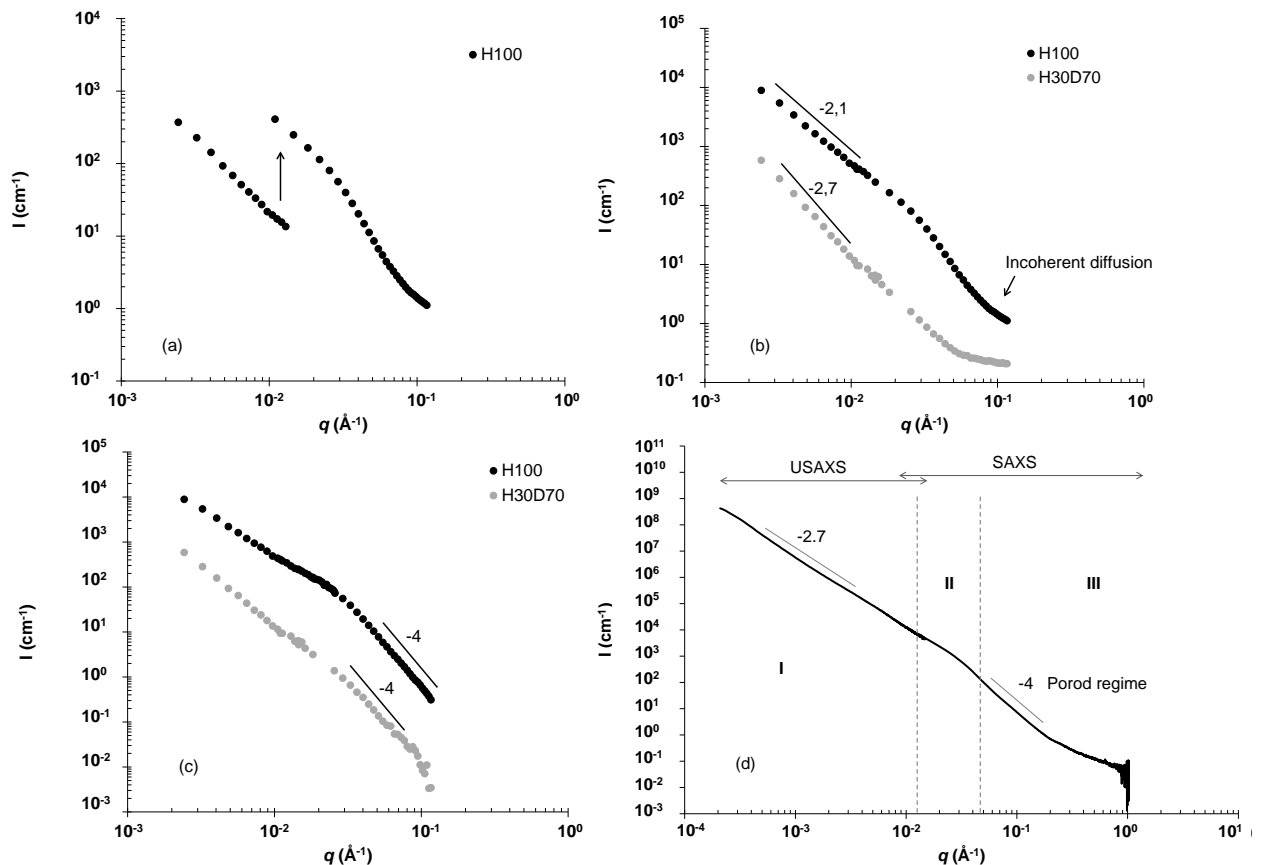
FigSI. 1 – Small-angle neutron scattering data treatment on the geopolymer paste Na-3.6-11.5: (a) rescaling of the low-q data, (b) analysis of slope values, (c) correction of the incoherent diffusion of water, (d) ultra and small-angle X-ray scattering data. For SANS experiments, H100 represents a geopolymer 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 spectrum 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 spectrum. 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 spectrum 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 spectra are used for fitting.

SI.2. SAXS and SANS: Multiple scattering at low-q.

Low-q data obtained at the LIONS and LLB suffer of multiple scattering which decreases low-q intensity and false the q-evolution. However, as shown by FigSI.2 high-q data are still valuable, allowing the determination of a characteristic size and specific area in the Porod region.
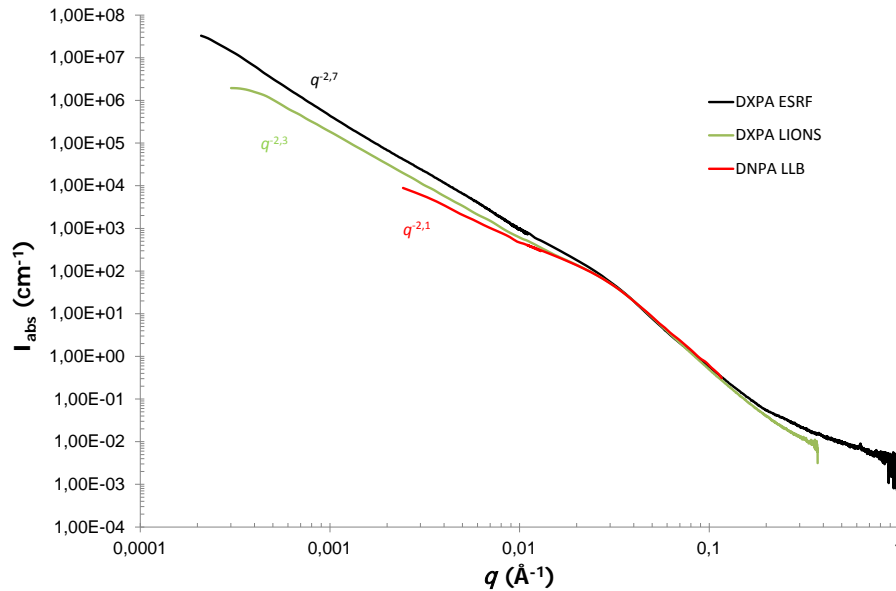
**FigSI. 2 – Evidence of multiple scattering on low-q SAXS and SANS data obtained at the LION and LLB.**

It was proven that no multiple scattering affect ESRF data by analyzing two discs with different thicknesses. Obtained spectra showed the same q-evolution. Small differences in intensity and characteristic mesoporous size are present, because of inhomogeneity of geopolymer sample. It was also checked that such differences are also present in the same sample, depending on the beam position on the geopolymer disc.
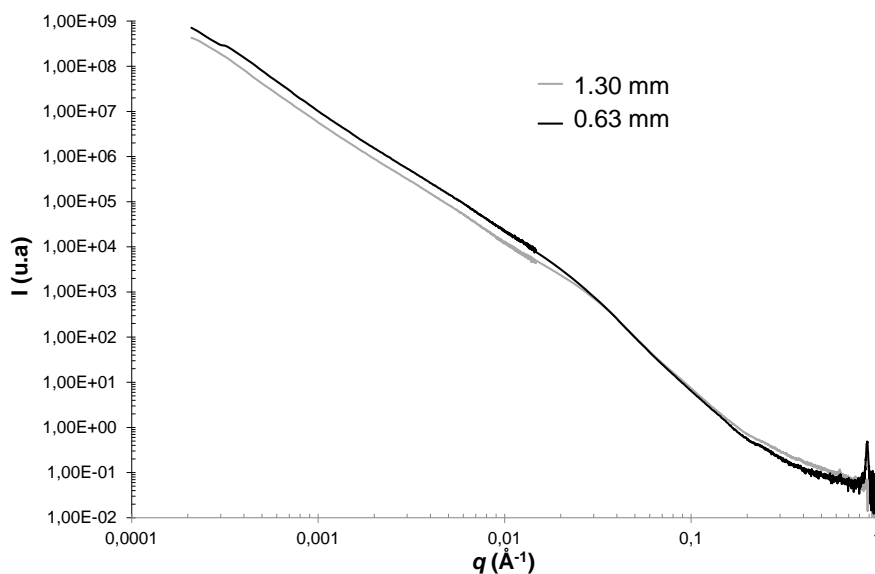
FigSI. 3 – SAXS data comparison on two Na-3.6-11.5 geopolymer discs of two different thicknesses.

**SI.3. Modelling SAXS data by a two or a three-level Beaucage model.**

The Kratky representation ($I \times q^2$) revealed three characteristic distances in geopolymer paste. The first one is attributed to a mesopore size, the second one to a macropore size at low-q, and in between there is a third contribution, which might correspond to a mesopore-mesopore correlation distance, without being able to be sure. Indeed, Fig SI. 4 shows that when the quantity of water increases, the third contribution disappears to the detriment of a structure factor in the high-q region. The increase of the initial water content seems to tend to a more homogeneous porous network. The modelling of the overall scattering data is then very complex and we decided to remain as simple as possible by using a two level Beaucage model even if a three-level Beaucage model (see below) gives a better fit or a more complex model would certainly give a good fit as well (Guinier-Porod for macropores + $S(q)_{fractal}*P(q)_{cyl}*$polydispersity for mesopores)
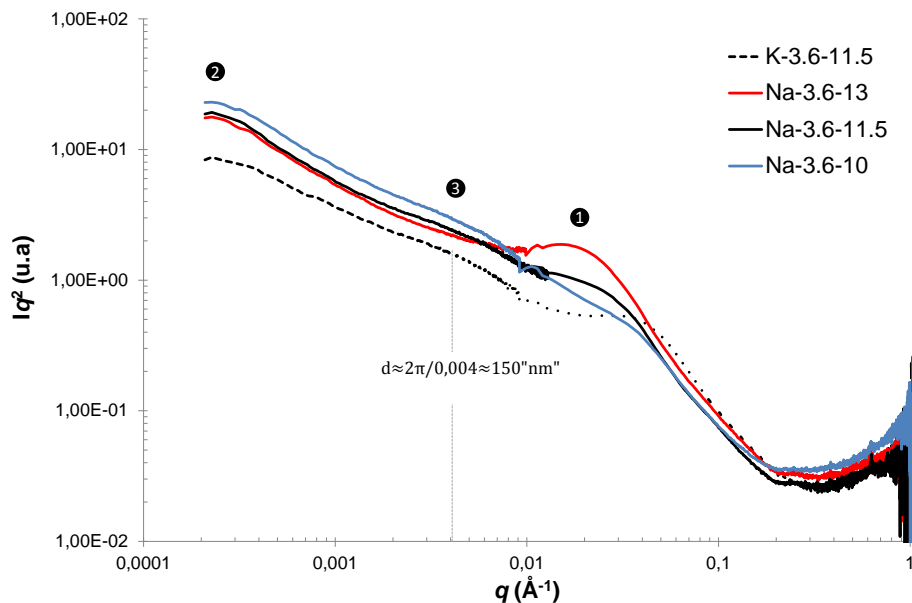
FigSI. 4 – Kratky representation of SAXS data.

Three-level Beaucage model:

Modelling SAXS spectra with a three-level Beaucage model gives a very good representation of the data. However, the position of the characteristic distance (3) is hard to fit exactly because it is large and undefined. Thus, the relevance of fitting parameters for level 3 is questionable. Fits are represented in FigSI.6 and fitting parameters are reported in Table 2.
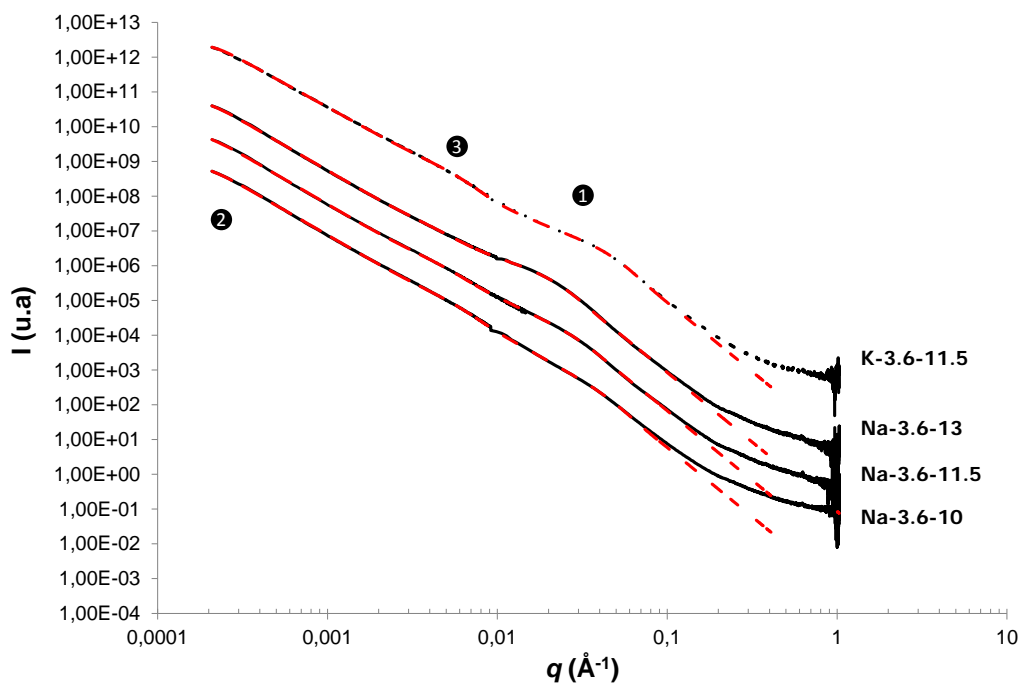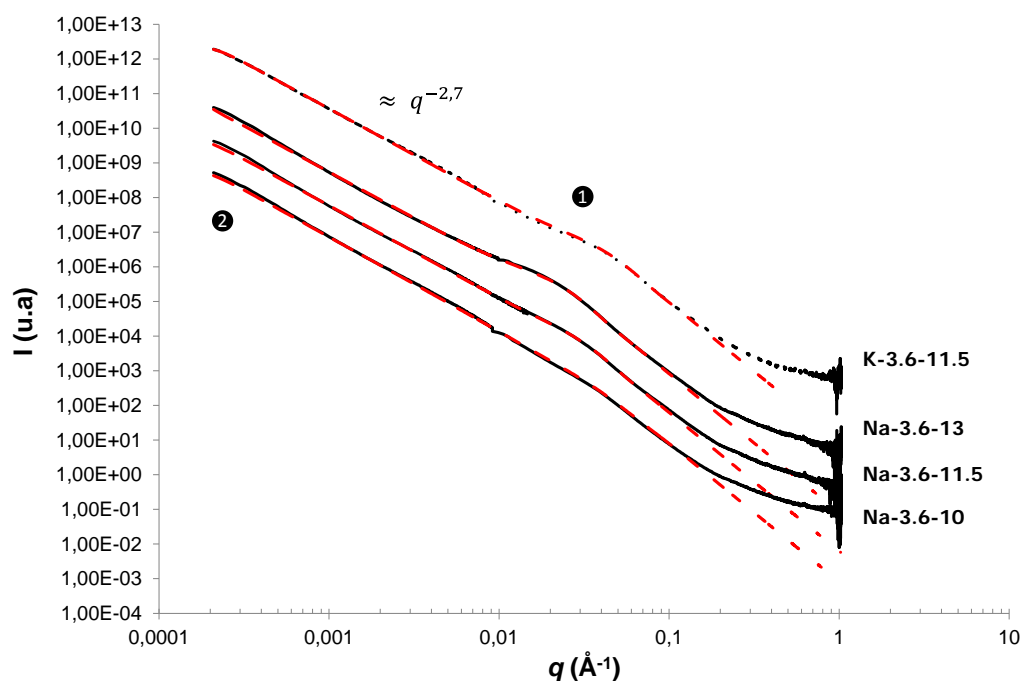
FigSI. 5 – Modelling SAXS data with a tree-level model.

Table 1 - Fitting parameters for the three-level Beaucage model.

	Na-3.6-10	Na-3.6-11.5	Na-3.6-13	K-3.6-11.5
$R_{g,1}$	52 Å	75 Å	100 Å	48 Å
D_1	4	4	4	4
G_1	$1.3.10^4$ u.a	$6.7.10^4$ u.a	$2.8.10^5$ u.a	$1.65.10^4$ u.a
B_1	0.012 u.a	0.015	0.017	0.018
$R_{g,2}$	$1.8.10^4$ Å	$1.8.10^4$ Å	$1.8.10^4$ Å	$1.8.10^4$ Å
D_2	2.805	2.83	2.817	2.685
G_2	8.10^{10} u.a	10^{11} u.a	10^{10} u.a	10^9 u.a
B_2	0.6 u.a	0.43 u.a	0.4 u.a	0.65 u.a
$R_{g,3}$	350 Å	410 Å	430 Å	350 Å
D_3	2.77	2.765	2.87	2.59
G_3	$3.8.10^6$ u.a	$5.2.10^6$ u.a	$4.3.10^6$ u.a	2.10^6 u.a
B_3	0.76 u.a	0.84 u.a	0.38 u.a	0.79 u.a

Two-level Beacauge model:

A two-level Beaucage model is a good representation of the two-level porous structure of geopolymer and decreases the number of fitting parameters. Fits are represented in FigSI.6 and fitting parameters are in Table 2.
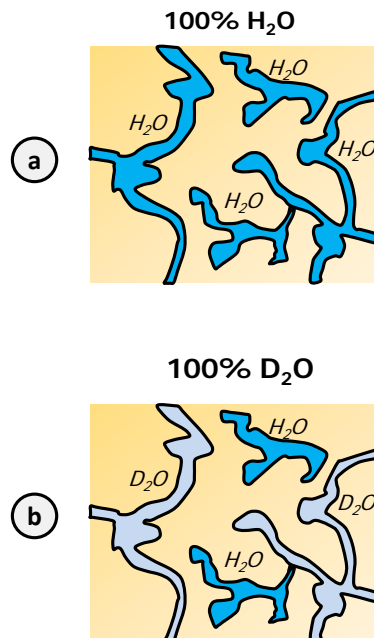

FigSI. 6 – Modelling SAXS data with a two-level model.

Table 2 - Fitting parameters for the three-level Beaucage model.

|	Na-3.6-10	Na-3.6-11.5	Na-3.6-13	K-3.6-11.5
$R_{g,1}$	53 Å	70 Å	90 Å	49 Å
D_1	4	4	4	4
G_1	$1.5.10^4$ u.a	5.10^4 u.a	$1.2.10^5$ u.a	3.10^4 u.a
B_1	0.018 u.a	0.013 u.a	0.01 u.a	0.032 u.a
$R_{g,2}$	$1.8.10^4$	$1.8.10^4$	$1.8.10^4$	$1.8.10^4$
D_2	2.71	2.67	2.66	2.67
G_2	9.10^{10} u.a	9.10^{10} u.a	10^{11} u.a	3.10^9 u.a
B_2	1.2 u.a	1.2 u.a	0.7 u.a	1.2 u.a

SI.4. Contrast variation: $H_2O \rightarrow D_2O$ exchange.

In order to check the presence of close porosity, the pore solution was exchanged by light water H_2O or heavy water D_2O for one week. The principle consists in realizing two experiments one geopolymer discs, schematized in FigSI.7.

100% H_2O

100% D_2O

FigSI. 7 – Modelling SAXS data with a two-level model.

In FigSI.7a, both open and closed porosity are filled with light water, and the resulting scattering curve is the result of the neutronic contrast between the solid phase of geopolymer and water inside the porosity. In FigSI.7b, if closed porosity exists in the sample, then it is inaccessible to D_2O and the resulting scattering curve is the result of two contributions: (i) the neutronic contrast between the solid phase of geopolymer and H_2O inside closed porosity, (ii) the neutronic contrast between the solid phase of geopolymer and D_2O inside open porosity. Because of strong differences in scattering length densities between hydrogen atoms and deuterium atoms, neutronic contrast are very different. Results in FigSI.8 show the scattered intensity normalized by respective neutronic contrasts do not superimposed (100% H2O and 100% D2O). This means the D2O exchanged was not complete, and that red curves are the result of two contributions as mentioned above. In conclusion, there is some closed porosity in geopolymer paste.

Another interesting results concern the fact that the normalized intensities are equal at low scattering vector (visible for the formulation Na-4-10 and Na-3.6-10 because the mean pore size is the lowest and then clearly detectable in the scattering vector window). If the normalized intensities are equal at low-q, it means that all the open porosity (part of mesopores and macropores) have been correctly exchanged.
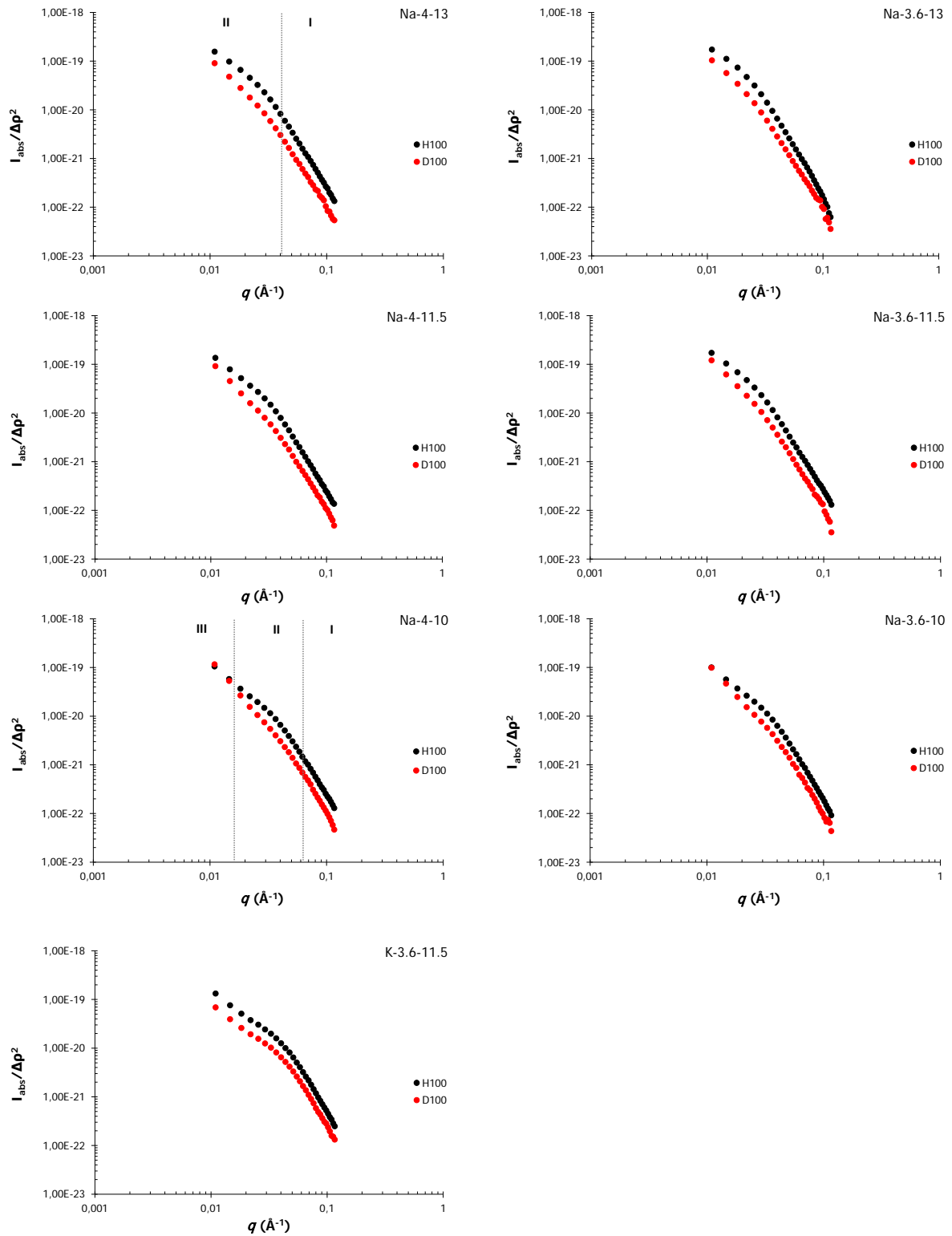
FigSI. 8 – Highlighting the presence of closed porosity in several geopolymer pastes by SANS. Red circles stand for the scattering spectrum of the geopolymer discs in D₂O and black circles stand for the scattering spectrum of the geopolymer discs in H₂O.

SI.5. 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:
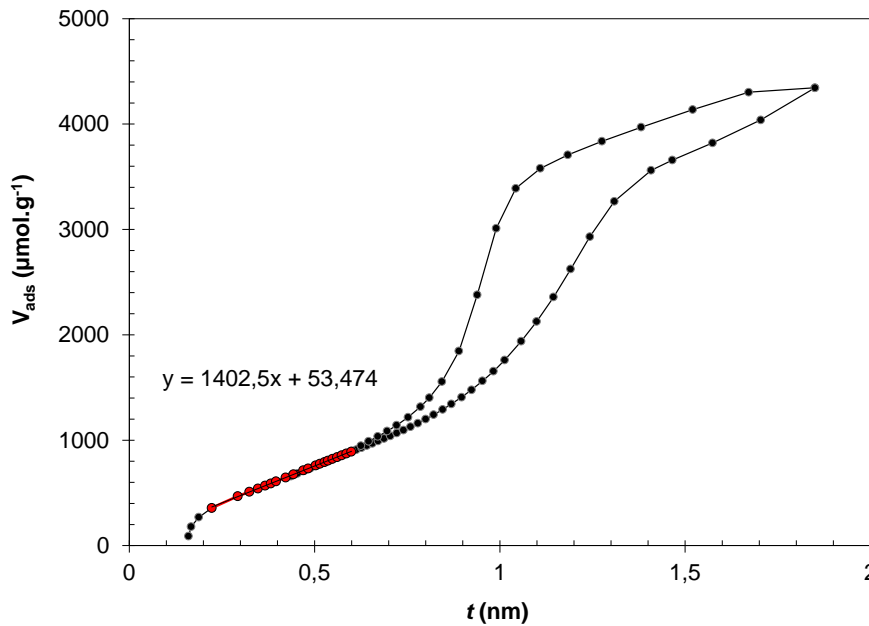
$$t\ (nm) = \left(\frac{0.1399}{0.034 - \log\left(\frac{P}{P^0}\right)} \right)^{1/2}$$

The nitrogen adsorption-desorption isotherms were transformed into t-plot by plotting the nitrogen adsorbed volume V_{ads} (µmol.g^{-1}) as a function of t:

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

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 m^2.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.g^{-1})	a_{ext} (m^2.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. **2011**, *44*, 697-707.