

Space- and time-resolved SAXS study of capillary rise in nanoporous solids : Early report

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March 31, 2023

Abstract

The report first summarizes the proposal A26-2-941, highlighting the purpose of the experiments and their methodology, and presents afterwards some results and conclusions based on the data processed so far.

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1 Introduction

The purpose of the experiments is to understand the wetting of porous materials at the nanometer scale. To achieve this objective, space- and time-dependent SAXS experiments were conducted on nanoporous materials during capillary rise of water. These experiments were planned on different porous materials. Among these samples, three of them have a different mesopore sizes, and subsequently underwent treatments aiming at modifying their microporous volume. For more information, please refer to the related proposal. In this early report, only the results of the time-resolved experiments are presented.

2 Materials investigated

Three xerogels were synthesized according to a well-established protocol through the polycondensation of resorcinol and formaldehyde in water with sodium carbonate as catalyst [1, 2, 3], and shaped as cylinders.

Some of the so-obtained mesoporous xerogels underwent a pyrolysis process under nitrogen atmosphere at 800 °C [4]. This resulted in carbon xerogels with micropores in addition to the mesopores (see Fig.1). Subsequently, a fraction of the materials were activated under a CO₂ atmosphere at 900 °C to increase the microporous volume.

In this report, we focus on four samples which are representative of all others. These samples are named CX17_{P/A} and CX29_{P/A}, with CX standing for “carbon xerogel”, the numeral being the approximate mesopores size in nanometers, and the subsequent letters referring to the post-treatment, namely 'P' for pyrolysed and 'A' for activated.

In addition to the scattering experiments, all samples were characterized by state-of-the-art porosimetry : nitrogen physisorption and mercury intrusion (see Table 1).

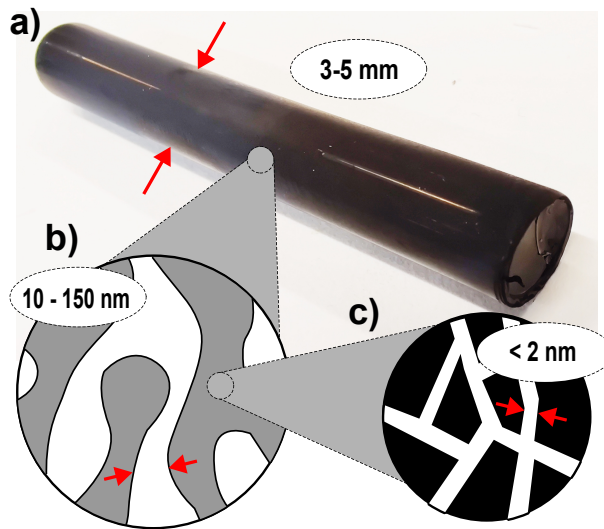


Figure 1: (a) Carbon xerogel sample macroscopically shaped like a rod, with hierarchical porosity displaying both (b) mesopores and (c) micropores.

3 Methods

Carbon xerogels detailed in the previous section (see Fig.2(a)) are held in place by a 3D-printed support (see Fig.2(b)) made so as not to interfere with the beam. An aluminium foil is added to avoid water evaporation during the capillary-rise measurements

Table 1: Textural properties of the carbon xerogels. V_{Hg} and d_{HG} : pore volume and pore size obtained by mercury porosimetry; V_{N_2} : pore volume obtained by nitrogen adsorption; S_{BET} : BET surface area; V_{μ} and S_m : micropore volume and meso/macroporous surface area obtained by a t-plot.

Sample	V_{Hg} (cm^3/g)	d_{HG} (nm)	V_{N_2} (cm^3/g)	S_{BET} (m^2/g)	V_{μ} (cm^3/g)	S_m (m^2/g)
CX17 _P	0.81 ^a	17	1	701	0.17	272
CX17 _A	0.87 ^a	17	1.22	1011	0.28	316
CX29 _P	1.17 ^a	29	1.1	756	0.19	262
CX29 _A	1.34 ^a	29	1.12	943	0.27	273

^a underestimates the pore volume;

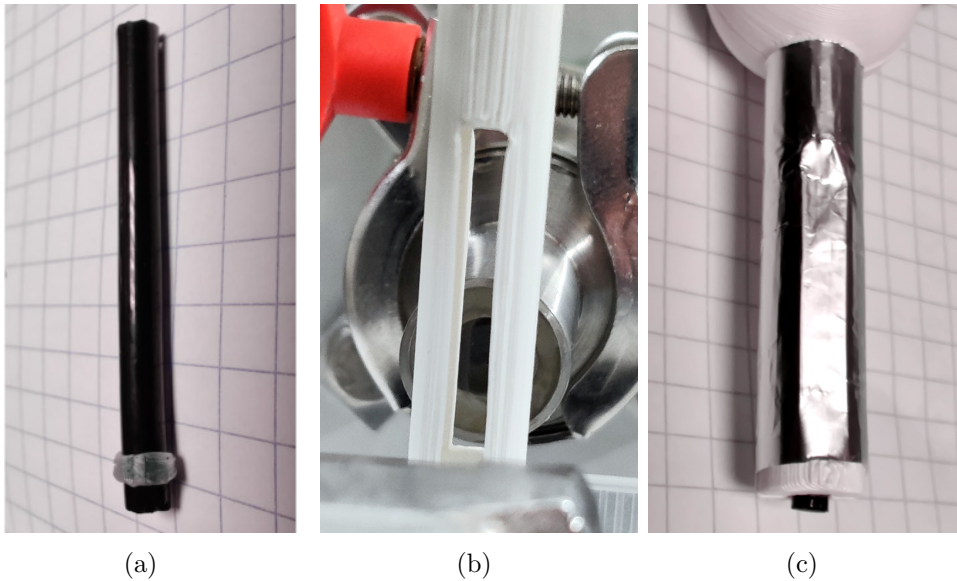


Figure 2: (a) Carbon xerogel sample macroscopically shaped like a rod with a small piece of Parafilm to hold it in place. (b) 3D printed support made so as not to interfere with the beam. (c) Combination of (a) and (b) with an aluminum foil to avoid the evaporation of water during the capillary rise experiment.

(see Fig.2(c)). The entire setup is held in place with a lab stand; the contact with water (initiating the capillary rise) is done by raising a water reservoir placed on a lab lift.

During the capillary-rise experiments, the entire setup (including the sample holder and the water reservoir) was moved back and forth vertically over approximately 30 mm, so as to perform a space- and time-resolved SAXS study (see Fig. 3). Measurements are taken at each height, starting from $z = 0$ where the water comes in contact with the porous carbon, and ending at $z = 30$ mm, with intervals of 0.5 mm. A vertical scan takes less than 5 min whereas the capillary rise of water takes several hours.

Prior to each capillary rise experiment, *i.e.* before contacting the porous sample with water, a scan is performed on the dry sample to be used as a blank.

4 Results

The following results are divided into two categories. First, the intensity drop of the X-ray beam through the sample gives us information about the quantity of water inside the sample. Then, SAXS intensity profiles provide additional information.

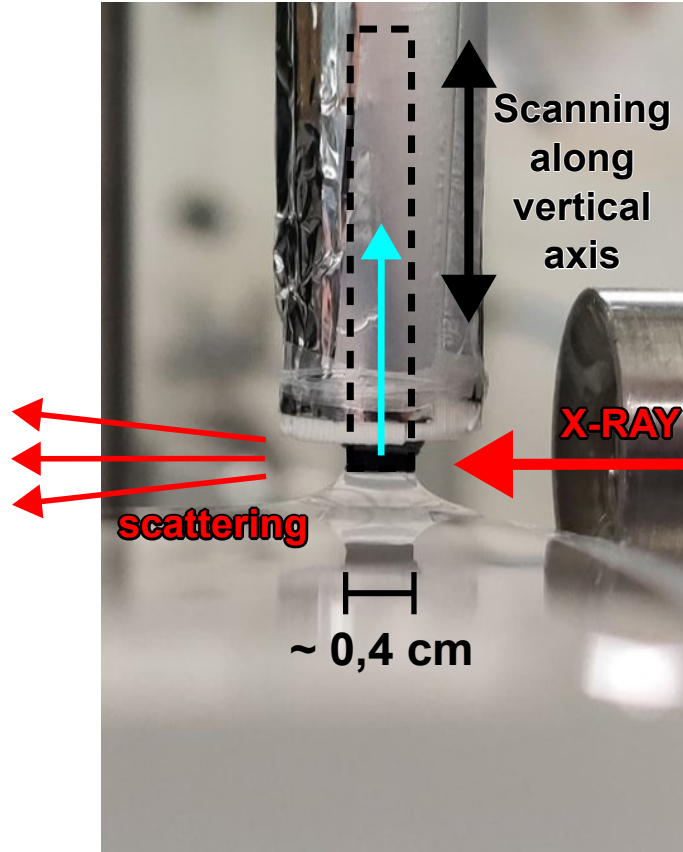


Figure 3: Setup of the sample during SAXS measurements. The platform including water reservoir and sample holder move along the vertical axis between each measurements.

4.1 X-ray absorption

At each height z , the beam of intensity I_0 crosses the sample composed of carbon 'c' and water 'w', and emerges with an intensity $I(z)$. The intensity drop obeys the Beer-Lambert law :

$$I(z) = I_0 \exp(-\mu_c l_c) \exp(-\mu_w l_w) \quad (1)$$

where μ is the linear attenuation coefficient and l is the attenuation distance related to the material in the total thickness. The value of μ_w is fixed at 3.01 cm^{-1} according to the NIST table of attenuation coefficient [5] at 12 keV. The result obtained at each height on the dry sample is given by

$$I(z) = I_0 \exp(-\mu_s l_s(z)) = I_{dry}(z). \quad (2)$$

In the following, $I_{dry}(z)$ is used as reference for the analysis of the data obtained during the capillary rise experiment. At each height, the amount of carbon xerogel is constant, allowing us to calculate the distance travelled by the beam through water using the equation

$$-\frac{\ln\left(\frac{I(z)}{I_{dry}(z)}\right)}{\mu_w} = l_w(z). \quad (3)$$

It should be noted that the incident intensity I_0 is not constant over time. These fluctuations are corrected by assuming that the top end of the cylinder remains dry throughout the entire capillary rise experiment. If the assumption is correct, the scattered intensity only varies with the incident intensity.

From Fig. 4(a) to Fig. 4(c) we see the data evolution due to the corrections apply to the data. As shown in Fig. 4(c), the water thickness increases sharply up to 98% at the

bottom of the sample before slightly decreasing to 91%. Additionally, the water thickness above $Z=20$ varies between -1% and 1% ($\pm 18 \mu\text{m}$ of water) indicating the potential error in the results. It is important to note that nothing has been calibrated to obtain 100% at most in the sample. Values are obtained solely from the linear attenuation coefficient of water, the measured intensity, and the sample characteristics.

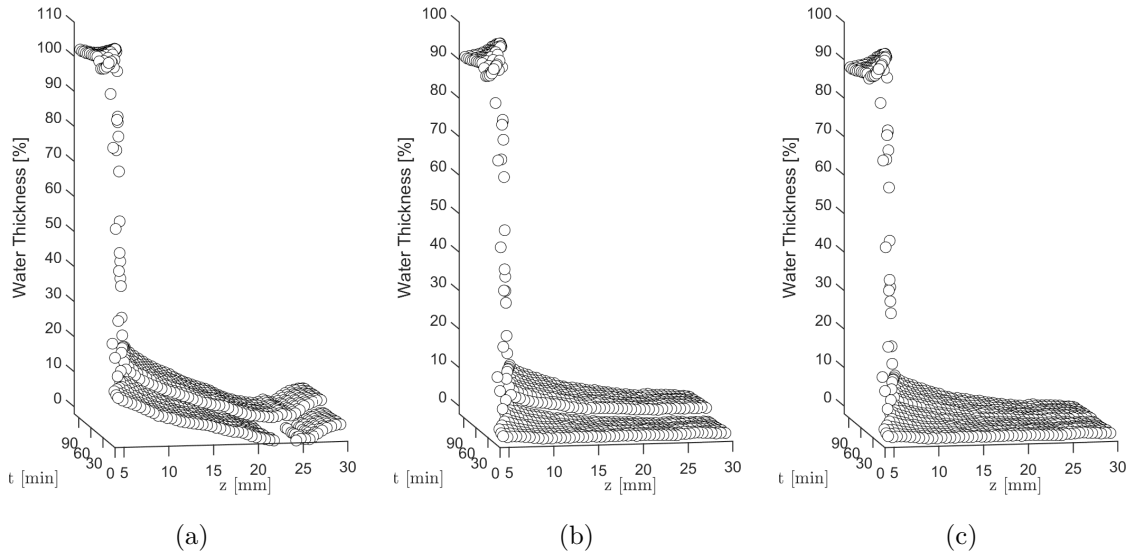


Figure 4: CX17_P : Space and time evolution of the water thickness inside the porous media obtained by the Beer-Lambert law on the absorption of the X-ray beam. The only parameter used is the linear attenuation coefficient of water. 100% corresponds to 1.8 mm of water. (a) The reference I_{dry} is taken arbitrarily at $z=27$ from the dry sample. (b) The reference is taken from the dry sample at the height of each measurement. (c) Same as (b) but with the additional consideration of the evolution of I_0 over time.

The first observation to be made is the two-step process of the capillary rise of water inside the porous material. As shown in Fig. 4(c), a small and progressive front of water precedes an abrupt second front of water that corresponds to the filling of almost 100% of the porous volume. It is important to note that the liquid can advance up to 1 cm in advance of the second front and its quantity is not negligible, corresponding up to 10% of the total porous volume.

4.2 SAXS intensity profiles

We have access to the SAXS intensity profile at each point represented in the space and time evolution of the water thickness. These data allow us to study the wetting process in more detail. As seen in Fig. 5(a), the intensity profiles decrease sharply at all q -values when the liquid invades almost all of the porous volume. This decrease can be easily understood as the water replaces the air inside the porous volume and thus decreases the scattering contrast between the solid and the pores. It is also observed that the water ahead of the steep front tends to decrease the intensity at high q -values (lower than $2\pi/q \approx 2 \text{ nm}$) and slightly increase the intensity at low q -values. This change can be interpreted as the filling of the microporous volume by the liquid, as shown in Fig. 5(b). The water inside the micropores decreases the scattering contrast between the solid and the microporous volume and increases the scattering contrast between the microporous carbon and the empty mesopores.

This precursor of impregnation only appears in the presence of microporosity. The Fig. 4.2 shows all the data obtained with CX17 and CX29. As depicted in Fig. 6(a)

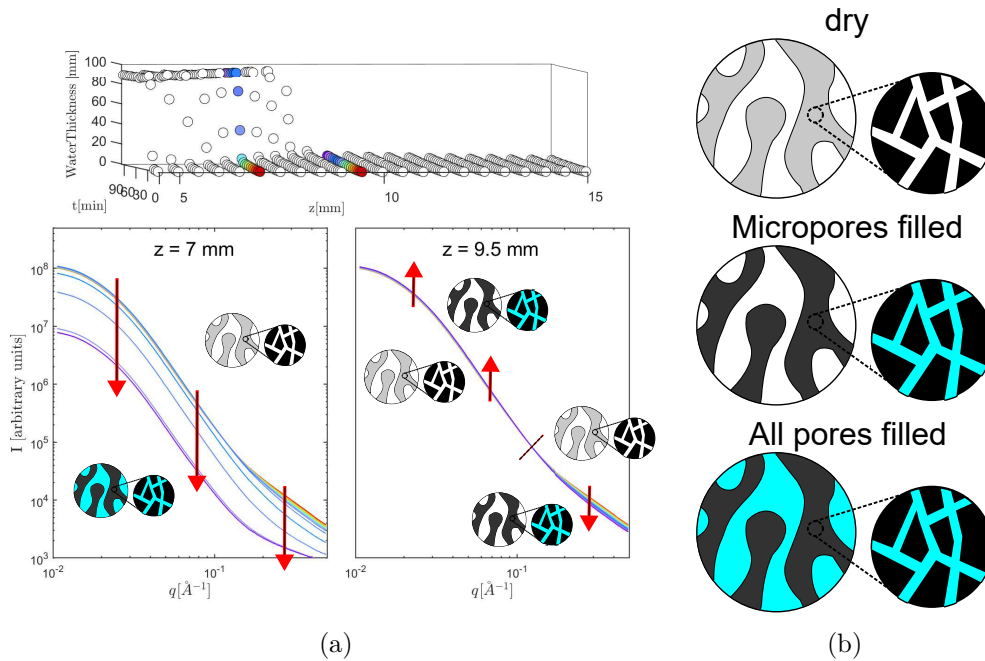


Figure 5: (a) Evolution of the SAXS intensity profiles at two different height located in color in the 3D space and time evolution. The intensity at all q -values decrease when all the pores are filled with water. The intensity slightly increase at small q and decrease at high q when only the micropores are filled with water. (b) Sketch where the evolution of the scattering contrast is represented by the color contrast.

and Fig. 6(b), xerogels before the pyrolysis step, i.e. without microporosity, do not exhibit any precursors of impregnation unlike the others. Additionally, the increase in microporous volume from Fig. 6(c) and Fig. 6(d) to Fig. 6(e) and Fig. 6(f) highlights this phenomenon.

5 Conclusion

During the capillary rise of water inside the porous material, a precursor of impregnation is found to precede up to 1 cm ahead of the water front and to fill up to 50% of the microporous volume at its edge. However, it is unclear how the water is propagating inside this microporous volume. A more advanced SAXS intensity analysis is currently being developed to investigate this question. In addition, more data than those presented in this report have been collected, and WAXS has been collected for every measurement. The observations contained in this report are already interesting enough to warrant a future publication.

References

- [1] R. W. Pekala. Organic aerogels from the polycondensation of resorcinol with formaldehyde. *Journal of Materials Science*, 24(9):3221–3227, 1989.
- [2] S. A. Al-Muhtaseb and J. A. Ritter. Preparation and properties of resorcinol-formaldehyde organic and carbon gels. *Advanced Materials*, 15(2):101–114, 2003.
- [3] N. Job, A. Théry, R. Pirard, J. Marien, L. Kocon, J. Rouzaud, F. Béguein, and J. P. Pirard. Carbon aerogels, cryogels and xerogels: Influence of the drying method on the textural properties of porous carbon materials. *Carbon*, 43(12):2481–2494, 2005.

- [4] M. L. C. Piedboeuf, A. F. Léonard, K. Traina, and N. Job. Influence of the textural parameters of resorcinol-formaldehyde dry polymers and carbon xerogels on particle sizes upon mechanical milling. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 471:124–132, 2015.
- [5] C.T. Chantler, K. Olsen, R.A. Dragoset, J. Chang, A.R. Kishore, S.A. Kotochigova, and D.S. Zucker. X-ray form factor, attenuation and scattering tables (version 2.1) [online] available: <http://physics.nist.gov/ffast> [2023, march 29]. *National Institute of Standards and Technology, Gaithersburg, MD.*, 2005.

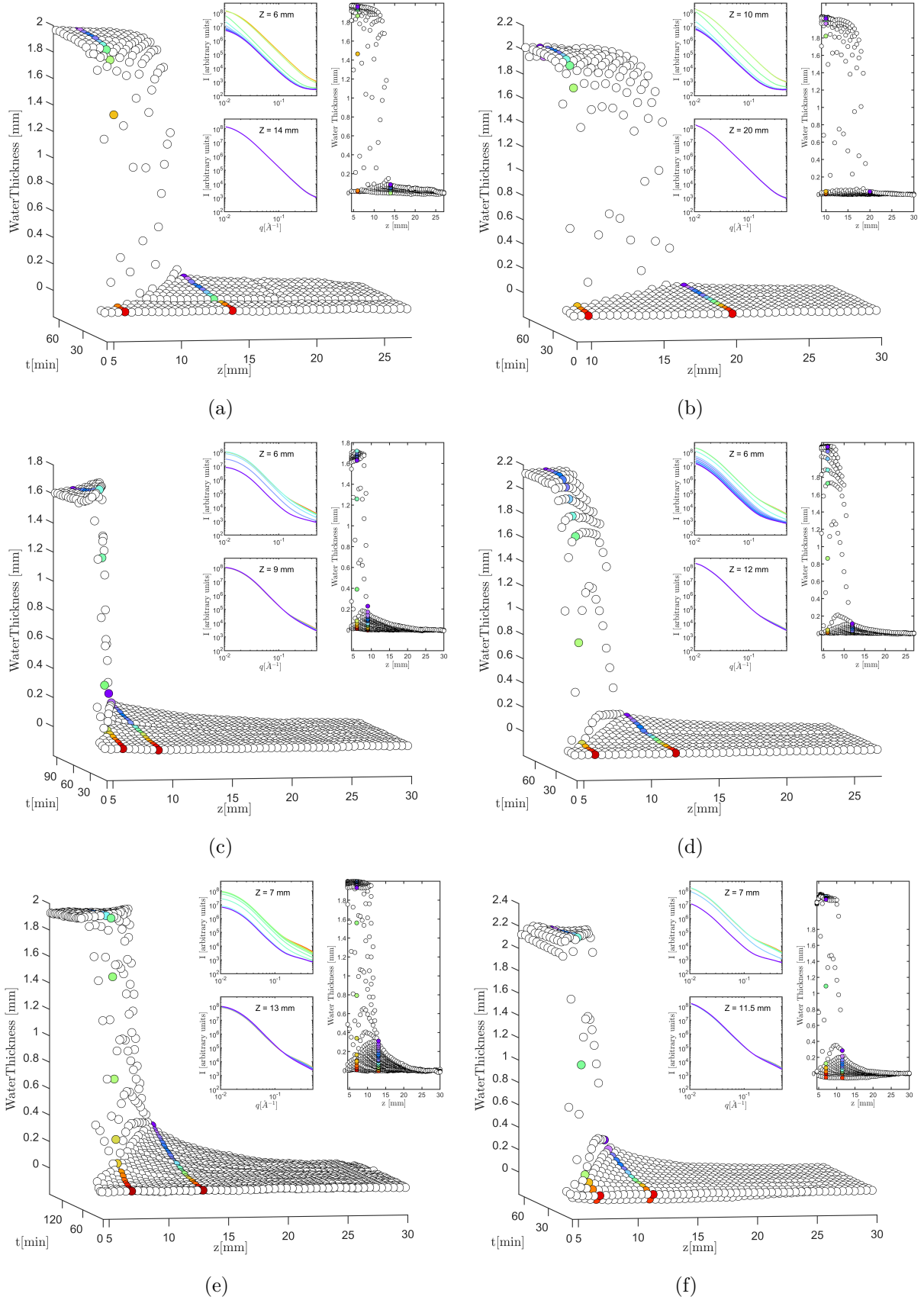


Figure 6: Space and time evolution of the water thickness during the capillary rise experiment for various porous materials. (a) CX17 and (b) CX29 without microporosity. (c) CX17P and (d) CX29P with microporosity exhibit a precursors of impregnation. (e) CX17A and (f) CX29A with a higher microporous volume.