**New X-ray microtomography setups and optimal scan conditions to investigate
methane hydrate-bearing sand microstructure**

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29 **Abstract**

30 Methane hydrates, naturally formed at high pressure and low temperature in marine
31 and permafrost sediments, represent a great potential energy resource but also a
32 considerable geo-hazard and climate change source. Investigating the grain-scale
33 morphology of methane hydrate-bearing sandy sediments is crucial for the
34 interpretation of geophysical data and reservoir-scale simulations in the scope of
35 methane gas production as methane hydrate morphologies and distribution within the
36 porous space significantly impact their macroscopic physical/mechanical properties.
37 X-ray computed tomography (XRCT) and Synchrotron X-Ray computed tomography
38 (SXRCT) are commonly used to analyze the microstructure of geo-materials.
39 However, methane hydrates exist only at high pressure (up to several MPa) and low
40 temperature (a few °C). This article describes the development of three experimental
41 setups, which aim at creating methane hydrates in sandy sediment, adapted to XRCT
42 and SXRCT observations. The advantages and drawbacks of each setup are
43 discussed. The discussions focus on the effects of the choice of the system to control
44 temperature and pressure on the quality of images. The obtained results would be
45 useful for future works involving temperature and/or pressure control systems
46 adapted to XRCT and SXRCT observations of various geo-materials.

47 *Keywords:* Methane hydrate-bearing sand, X-ray computed tomography (XRCT),
48 synchrotron XRCT, experimental setups, scans conditions, high pressure, low
49 temperature.

50 **Introduction**

51 Methane hydrates (MHs), being solid ice-like compounds of methane gas and water,
52 are naturally formed at high pressure and low temperature in marine and permafrost
53 settings. They are being considered as an alternative energy resource but also a
54 source of geo-hazards and climate change (Collett et al. 2009). Depending on the
55 characteristic particle size and the effective stress, different morphologies and pore
56 distribution within natural sediments of methane hydrates, such as nodules/chunks,
57 lenses/veins or pore-filling have been identified (Boswell et al. 2011; Dai et al. 2012).
58 In the scope of methane gas production from methane hydrate-bearing sediments,
59 currently, due to technical feasibilities, only pore-filling MHs at high hydrate saturation
60 in sandy sediments are being considered. Most experimental works concern
61 laboratory tests on synthetic samples because of challenges to get cored-intact
62 methane hydrate-bearing sediment samples. In the objective of creating synthetic
63 pore-filling methane hydrates in sandy sediments (to mimic natural sediments),
64 different methods have been proposed such as the excess-gas, ice-seeding, or
65 excess-water methods (Clayton et al. 2005; Priest et al. 2009; Waite et al. 2004).
66 However, by using seismic wave velocities (Chand et al. 2004; Dvorkin et al. 2000;
67 Dvorkin and Lavoie 1999; Dvorkin and Nur 1996; Helgerud et al. 1999), MHs are
68 believed to exist in four idealized arrangements or “pore-habits”: cement, with grain-
69 grain contacts; cement, with mineral coating; load-bearing and pore-filling. Physical
70 and mechanical properties of sediments containing MHs depend considerably on
71 methane hydrate morphologies and distribution within the pore space, which are thus
72 of the essence for interpretation of geophysical data and reservoir-scale simulations
73 in the scope of methane gas production (Taleb et al. 2018; Le et al. 2019; Nguyen-Sy

et al. 2019; Alavoine et al. 2020; Taleb et al. 2020). Therefore, pore-scale observations of MH morphologies and pore-habits in sandy sediments are crucial.

Laboratory X-ray computed tomography (XRCT) and Synchrotron X-Ray Computed Tomography (SXRCT) have been extensively used to investigate the 3D microstructure of gas hydrate-bearing sediments (Chaouachi et al. 2014, Kerkar et al. 2009; Kerkar et al. 2014; Ta et al. 2015; Zhao et al. 2015). Studying synthetic methane hydrate-bearing sand (MHBS) with these techniques is really challenging due to not only the need of special experimental setups (i.e. high pressure and low temperature should be maintained) but also to the poor image contrast between methane hydrate and water, which depends mainly on the difference of material density and atomic number. To improve XRCT/SXRCT image contrast, other gas/fluid (Tetrahydrofuran-THF, Carbon dioxide-CO₂ or Xenon-Xe) and/or saline water solutions (Sodium chloride-NaCl, Barium chloride-BaCl₂, Potassium iodide-KI) have been used (Chaouachi et al. 2014, Kerkar et al. 2009; Kerkar et al. 2014; Ta et al. 2015; Chen and Espinoza, 2018). By using gas/fluid different from methane, experimental setups are less complicated. For instance, there is no need of pressure control for the THF hydrate (THF hydrate can be formed at atmospheric pressure) while lower pressure and/or higher temperature are needed for studies of CO₂ or Xe hydrates. Note that gas hydrate morphology depends on the type of gas/fluid used. Furthermore, the phase boundary of methane hydrate formation is shifted depending on salt concentration contained in water Sloan and Koh (2008) and salt exclusion during gas hydrate formation increases the salt concentration in the remaining water.

Concerning XRCT image, spatial resolution mainly depends on the distances between the source, the object and the detector. Complex experimental setups of MHBS studies usually limit the image spatial resolution to avoid the collision between the source, the experimental setup and the detector. Morphologies and pore habits of methane hydrate formed in sandy sediments following the excess-gas method (MHs are formed by injecting methane gas into an unsaturated sandy sediment) have been investigated previously by Yang et al. (2015) and Zhao et al. (2015). Within voxel size of 25 μm , it was impossible to directly observe MHs as the voxel size was in the same order of magnitude as the size of the largest MH crystals. By using a conventional segmentation method based on gray levels (which are, as a first approximation, proportional to material density), methane hydrates were found to be formed at gas-water interfaces, floating between sand grains without coating grain surfaces (a water layer was found to envelop grain surfaces). However, image noise and partial volume effect (gray levels of voxels at interfaces of different phases are intermediate between the gray levels of the different phases) did influence the segmentation and the attributed phases (morphologies and pore habits of methane hydrates).

Note that reported XRCT scans were usually performed at the end of the gas hydrate formation process in sandy sediments as the scanning time is long (several hours). Within the high temporal resolution of SXRCT (a few minutes), the formation and growth of gas hydrate in sandy sediments could be captured over time.

In the present study, three experimental setups have been developed in the objective of investigating pore-scale morphologies and pore habits of MHs in sandy sediments via XRCT and SXRCT. Their designs aim at improving the image contrast and the image spatial resolution. As CT images can hardly differentiate pure water from methane hydrate, saline water (i.e. KI solution) was used to better distinguish the liquid phase and methane hydrate when both coexist. Furthermore, efforts have been made to enhance the image spatial resolution in order to distinguish methane hydrate from the liquid phase (either tap or saline water) on the basis of their morphology (regular water menisci or more complex geometry of MH). In the following sections, the optimization of XRCT scan conditions for MHBS is first described. Afterwards, the three experimental setups and their corresponding advantages and drawbacks are discussed.

Optimization of scan conditions

Absorption XRCT and SXRCT consist in exposing an object to X-rays from multiple orientations (by rotating the sample in this study) and measuring the intensity decrease for all source-detector paths. Gray levels of the obtained radiographic images, after calibration, quantify the attenuation of the sample, *i.e.* reflect the proportion of X-rays absorbed/scattered as they pass through the object. More precisely, X-ray attenuation follows a Beer-Lambert type law (Swinehart 1962), which involves the linear attenuation coefficient (μ). Different phases in the object can be well distinguished if their attenuation coefficients are significantly different from each other. Indeed, μ is a function of the energy of X-rays. In a polychromatic setup (as for

XRCT), the gray levels of the image result from a complex average of μ , which is relative to the used energy range.

Lei et al. (2018) used potassium iodide solutions and in-line propagation-based phase-contrast CT analysis of X-ray attenuation and diffraction for pore-scale visualization of MHBS with XRCT. In the present study, theoretical ratios of μ of different phases (methane gas, pure water, methane hydrate, saline water, quartz) are first calculated in order to quantify the induced contrast between phases on the image gray scale (see Figure 1). For the considered materials, sand grains are the most absorbing objects while methane gas is the least absorbing. We thus plot the absorption of the other phases (water, MHs and saline water) in a normalized scale where 1 corresponds to grains and 0 corresponds to gaz. The XCOM program established by the National Institute of Standards and Technology (NIST XCOM) provides the mass attenuation coefficients (μ/ρ) of various compounds for various values of photon energy. These data allowed plotting the curves corresponding to water/quartz and methane hydrate/quartz shown in Figure 1. For the saline solutions (*i.e.* Potassium iodide KI), the value of the mass attenuation coefficient of the solution is obtained according to a simple addition:

$$\mu/\rho = \sum_i w_i (\mu/\rho)_i \quad (1)$$

where w_i is the mass proportion of the component i (water or salt) and ρ is the unit mass, being for water and Potassium iodide (KI) equal to 1 and 3.12 (Mg/m³), respectively. The results obtained for the KI solution of 2, 3.5 and 5 wt% are also plotted in Figure 1. Note that the adopted density of quartz, methane gas, methane hydrate and water is 2.65, 0.0007, 0.9 and 1 Mg/m³ respectively.

169 Figure 1 shows that, for the whole considered energy range (10-200 keV, which
170 corresponds to typical energies considered in a laboratory XRCT setup), there is
171 almost no difference between the ratio of pure water/quartz and that of methane
172 hydrate/quartz (red and black curves). The difference in gray level of these two
173 phases is in the order of image noise (which typically varies from 2 % to 10 % of gray
174 level range). That explains the difficulty in distinguishing methane hydrate from water
175 in a XRCT image. For the case of KI solutions (blue curves), their ratios are
176 significantly different from that of methane hydrate in the range of photon energy
177 higher than 33 keV where an absorption edge is observed. At a concentration of 5 %
178 for KI, the maximum ratio is close to 1 (*i.e.* saline solution absorbs almost as quartz)
179 while at 2 % of concentration, the increase in contrast (allowed by the KI solution) is
180 moderate. Therefore, saline water of 3.5 % of KI by weight was chosen in this study
181 so that saline water can be optimally distinguished from both methane hydrate and
182 sand grain. More precisely, for energies between 33 and 60 keV, the gray level of
183 saline solution would be at equal distance from quartz and MH, optimizing the image
184 contrast. Note that the laboratory XRCT source is a polychromatic source with a wide
185 energy spectrum with a maximal energy corresponding to the prescribed electron
186 beam acceleration voltage. However, its maximum intensity, due to the
187 Bremsstrahlung effect, is somewhat below that maximum. Furthermore, to avoid
188 beam hardening artifacts in XRCT images and more specifically to reduce X-rays
189 below 33 keV, a copper filter (Cu) was used to eliminate low energy X-rays. Relative
190 transmission of X-ray intensity $\exp(-\mu_{Cu} \times t_{Cu} - \mu_{Al} \times t_{Al})$ of two cases of copper
191 thickness (t_{Cu}), is also shown in Figure 1 (Aluminum tube thickness, t_{Al} is 2×0.89
192 mm). In the present study, a Cu filter with a thickness of 0.1 mm was used for the

scans to preserve a higher X-ray flux in the energy range of 30 – 100 keV where the linear attenuation coefficient ratio of the KI solution at 3.5 wt% is well separated from that of methane hydrate.

Preliminary scans at abovementioned optimized conditions (acceleration voltage of source was 80 or 100 keV; 0.1 mm thick Cu filter) were done. Typical close views of cross sections of 3D images obtained on mixtures of dry sand with either pure water or saline water compacted in an aluminum tube (exterior diameter, $d_{ext.} = 6.45$ mm; thickness, $t = 0.89$ mm) are shown in Figure 2. For the case of sand wetted with pure water, Figure 2a, the mean gray levels of each phase were determined from the gray level profiles along the yellow line in Figure 2a, plotted in Figure 3a: $G_a = 21100$ (for air, A); $G_q = 22700$ (for quartz, Q); $G_w = 21600$ (for pure water, W). Similarly, for the case of sand wetted with saline water (Figure 2b), Figure 3b shows: $G_a = 12400$; $G_q = 14150$; $G_{sw} = 13400$ (saline water, SW). The ratios of water, $R_{w/q}$ and of saline water, $R_{sw/q}$ were calculated as follows:

$$R_{w/q} = (G_w - G_a) / (G_q - G_a) \quad (2)$$

$$R_{sw/q} = (G_{sw} - G_a) / (G_q - G_a) \quad (3)$$

According to profiles shown in Figure 3, $R_{w/q}$ is equal 0.3 while $R_{sw/q}$ equal 0.6. Furthermore, it is expected that the ratio of methane hydrate/quartz is close to that of water/quartz. These scan conditions should be then appropriate for MHBS scans, with an optimal contrast between air, MH, saline water and quartz (relative gray levels equal 0, 0.3, 0.6, and 1, respectively).

Unlike conventional laboratory XRCT, the so-called “pink beam” SXRCT makes use of a narrower energy spectrum, which is more concentrated around a mean energy. Details of effective linear attenuation coefficient has been defined in the work of Lei et al. (2018). Preliminary SXRCT scans (typical cross sections shown in **Erreur ! Source du renvoi introuvable.**) were performed at the Psiche beamline at the French synchrotron SOLEIL (King et al. 2016) run in pink mode with a mean energy of 44 keV. $R_{w/q}$ and $R_{sw/q}$ are 0.25 and 0.6 respectively (Figure 5). These values are close to the theoretical estimations at 44 keV (see Figure 1). Note that the Paganin filter (Paganin et al. 2002), designed to account for and partly correct phase contrast artifacts, has been used during the image reconstruction. It can also be noticed from profiles in Figures 3 and 5 that noise levels are significantly lower in SXRCT images than in XRCT ones.

Experimental setup investigations

Materials and methodology

The sediment used in this study was Fontainebleau silica sand (NE34). Classified as SP according to the Unified Soil Classification System (USCS), it consists of quartz grains having a diameter ranging from 100 to 300 microns. Tap water and saline solution (KI with concentration of 3.5 %) were used for the test. Standard purity of the used methane gas was 99.995 %. The characteristics of tap water provided by the supplier are: total chlorine 0.48 mg(Cl₂)/L; pH 7.7; electrical conductivity (at 25 °C) 609 μ S/cm; total iron < 10 μ g/L; total aluminum 53 μ g/L. In the present work, we consider that the salinity and the total dissolved solids in the tap water are negligible.

Moist sand was first compacted by tamping in layers into an aluminum tube (exterior diameter, $d_{\text{ext}} = 6.45$ mm; thickness, $t = 0.89$ mm). Aluminum was chosen instead of beryllium as used in other studies (e.g. Lei et al. 2018) to facilitate the manipulation because of the toxicity of beryllium. The initial water content was fixed in the range between 10-15 % with an accuracy of $\pm 0.1\%$. In the present work, we consider that the initial water content does not influence the quality of the obtained images. The average porosity (volume of gas and liquid phases divided by total volume of the sample) was estimated at 0.40 by segmenting several 3D images obtained on the samples at various locations (see Le 2019, for more details about the segmentation technique). Both high pressure and low temperature (2-3 °C; 7 MPa) were maintained for the MH formation.

To maintain low temperature, cooled air was circulated around the aluminum tube. Compressed air was cooled down by using a combination of chilled water (controlled by a cryostat) and a heat exchanger. Cooled air temperature, as well as sample temperature, were controlled via the compressed air flow rate (by imposing a compressed air pressure). Note that air was chosen instead of liquids for the temperature control to avoid additional X-ray absorption. In addition, preliminary experiments with wet sand showed an identical temperature (measured by thermocouples) in the air, outside of the aluminum tube, and that in the wet sand, at the center of the aluminum tube, at the same height.

Methane gas was injected into the sample to maintain a high methane gas pressure. It is supposed that methane gas pressure is constant in a closed system once the

MH formation is finished (no need of additional methane gas for further MH formation). Therefore, at the end of the MH formation when the media are supposed to be stable, there is no need to control methane gas pressure during the XRCT scans. However, when the purpose is to follow the MH formation over time by SXRCT scans, methane gas pressure needs to be controlled and maintained constant during the whole process.

The above thermal and pressure conditions were maintained during the laboratory XRCT scans, which lasted about 12 hours each to avoid MH dissociation. A generic view of various experimental setups developed in this purpose is shown in Figure 6. The sample was fixed on a turntable for scans. An Ultratom micro-tomography setup, from RX Solutions, using either a Hamamatsu L10801 micro-focus reflection (230 keV) or a Hamamatsu L10712 nano-focus (160 keV) transmission X-ray source together with a Paxscan Varian 2520V flat-panel imager (1920x1560 pixels², pixel size of 127 μm), was used for the laboratory XRCT scans. At an optimized Source Detector Distance (SDD), governed by the divergence of the X-Ray cone-beam of the X-Ray source in use, a smaller Source Object Distance (SOD) would provide a higher spatial resolution (or a smaller voxel size).

Furthermore, SXRCT scans were performed at the Psiche beamline at the French synchrotron SOLEIL (King et al. 2016) with a mean energy of 44 keV. Voxel size was 0.9 μm and the scan time 12-15 minutes. Paganin filter was optimized to limit the phase contrast at the interfaces between constitutive phases so that gray level of each phase in the images remains almost homogenous (apart from noise).

288

289 In the present study, three setups have been developed. The details of each of them,
290 their advantages and drawbacks and the obtained results are presented in the
291 following sections.

292

293 **Experimental setup No. 1**

294

295 Figure 7 shows the first setup used for XRCT scans of MHBS. A poly-methyl-
296 methacrylate tube (PMMA tube; exterior diameter, $d_{ext} = 24$ mm; thickness, $t = 3.5$
297 mm) was fixed around the aluminum tube for the cooled-air circulation from its bottom
298 to its top. A manometer was fixed at the top of the aluminum tube to monitor methane
299 gas pressure in the tube. The aluminum tube height was chosen to avoid collision
300 between the manometer and the X-ray source during the scan (the distance from the
301 turntable to the top of the aluminum tube is 430 mm, see Figure 7). Note that both
302 XRCT sources available on the Ultratom setup can be used. A thermocouple was
303 installed between the aluminum tube and the PMMA one at the middle of its height.
304 Methane gas at 7 MPa was injected during the MH formation by a pressure
305 controller, which was connected to a gas flowmeter. These conditions were
306 maintained during two days for the MH formation. At the end of the MH formation,
307 pressure controller and gas flowmeter were removed, and all the valves were closed
308 prior to the transportation of the whole system to the XRCT room.

309

310 A cooling gel was wrapped around the PMMA tube during the cell transportation
311 (which lasted about five minutes during which the cooled-air circulation had to be cut

off) to avoid MH dissociation. The cooled-air circulation around the aluminum tube was reset as quickly as possible once the cell was installed inside the XRCT room. Sample pressure and temperature were verified before the scan. The Source Object Distance (SOD) was limited by the exterior diameter of the PMMA tube ($SOD \geq 20$ mm to maintain a security distance of 8 mm). Dry compressed-air flow was shifted towards the PMMA tube to avoid water condensation during scans (anti-condensation system). Both aluminum and PMMA tubes were rotated together to maintain sample temperature during the scan. The soft tube bringing cooled air from the heat exchanger to the PMMA tube needed to be flexible and long enough to rotate with the PMMA tube.

Twelve tests have been performed with this setup, among which however, only a few gave images exhibiting good enough quality to be used to characterize microstructure (about 40 %). Indeed, it turned out that the cell slightly vibrated during the scans because of the turbulent cooled-air flow. These vibrations induced fluctuations of the CT geometry whose amplitude were too large for an accurate CT reconstruction. The obtained 3D images were thus blurred, with very unsharp edges. An example of an unsuccessful scan is shown in Figure 8. Gray levels within the constitutive phases, including grains, were not homogenous. MH morphology observation was then impossible. An example of a successful scan is shown in Figure 9 (voxel size was 5 μm). The image shows an assembly of sand grains (light gray), the pore space filled with methane gas (black) and methane hydrates (gray). MHs can be observed at grain contacts and also on grain surfaces. The mean gray level of each phase was determined from the gray level profiles (as illustrated in **Erreur ! Source du renvoi introuvable.**10): $G_a = 22500$ (for air, A); $G_q = 33000$ (for

quartz, Q) and $G_{mh} = 26500$ (for methane hydrate, MH). The ratio $R_{mh/q}$ is equal to 0.38, similar to the expected ratio. Furthermore, the standard deviations of the quartz and methane gas phases are close (700). Signal to noise ratio (SNR) was estimated at $(33000 - 22500)/700 = 1/0.067$.

Experimental setup No. 2

In order to improve the image spatial resolution, the setup No. 2 (shown in Figure 11) has been designed. First, to further reduce the SOD, the PMMA tube (used in the setup No. 1) was removed. The nano-focus source was used instead of the micro-focus one, and the aluminum tube was placed closer to it during the scans: SOD was 8 mm instead of 20 mm in the setup No. 1. A Polyvinyl Chloride (PVC) support was fixed to the source and enveloped the aluminum tube. Temperature control was ensured by a circulation of cooled air inside this PVC support, again from the bottom to the top. A thin Kapton film was used to thermally isolate the source (and in particular its thin window) and to protect it from the cooled air. Within this system, only the aluminum tube was rotated during the scans while the PVC support was fixed. A smaller air flow rate (compressed air pressure was about 200 kPa compared to 360 kPa for the setup No. 1) was needed to maintain a similar sample temperature. Actually the heat flux from ambient air through the soft tube walls, between the heat exchanger and the cooled-air inlet, was lower (in particular because of a shorter soft tube length). In addition, the manometer was fixed at the bottom of the cell and the aluminum tube height was reduced to 320 mm (this minimal length being constrained by the diameter of the nano-focus source). These

modifications allowed significantly reducing the amplitude of the vibrations of the aluminum tube during scans.

Methane hydrates were equally formed in sandy sediments in the laboratory then transported to the XRCT room for scans. The PMMA tube (used for setup No. 1) was placed around the aluminum tube to initially form MHs. Compared to the setup No. 1, the installation of the cell in the XRCT room was more complicated as cooled air can only be circulated when the aluminum tube was enveloped by the PVC support. Sample temperature was maintained by a cooling gel wrapped directly around the aluminum tube during its installation. A thermocouple, fixed on the PVC support (see Figure 11), was used to measure the sample temperature close to the scanned zone.

As for the first setup, among the ten scans performed with the second setup, only a few provided images with good quality (about 40 %), again because of cell vibrations. An example of successful result is shown in Figure 12 (voxel size was 3.5 μm). MH was more difficultly distinguished from methane gas even with a better image spatial resolution compared to the setup No. 1 (see Figure 9), because in particular of a poorer signal to noise ratio. $R_{mh/q}$ and SNR were estimated at 1/3 and 1/0.085 respectively (Figure 13).

Another possible reason, to explain the heterogeneity of gray levels in the phases, is related to the heterogeneous and porous structure of the PVC support. Indeed, X-rays passed through a thin PVC layer serving for thermal isolation before being captured by the detector. During the calibration stage of the CT scans, which consists

in recording various radiographs without sample, the PVC layer crossed by X-rays is not exactly at the same position as during the scans with the sample, which induces additional artifacts. For a further development of setup No. 2, another, more homogeneous material (such as PMMA) should be used between aluminum tube and detector. Actually, PVC was chosen in this study because manufacturing the complex-shaped support with PVC was easier (compared to PMMA).

Experimental setup No. 3

Within the two first setups, methane hydrates were first formed outside the tomography room and XRCT scans were performed only when the MH formation was stabilized. During the scans, the cell was closed and the temperature was maintained. Setup No. 3 was primarily developed for SXRCT scans which allow one to continuously follow the formation and evolution of MHs. For this reason, methane gas needs to be supplied and its pressure to be monitored during the scans.

Figure 14 shows the schematic view and a picture of the setup No. 3. A small methane gas bottle (volume of 40 mL) was connected to the methane gas inlet of the cell via a pressure reducer, which reduced the methane gas pressure from 13 MPa inside the bottle to 7 MPa at the gas inlet. This system was used to maintain methane gas pressure in the sample constant at 7 MPa (± 0.1 MPa) during the MH formation and scans.

Cooled air was circulated between the aluminum and a PMMA tube, similar to the one used in the setup No 1 but somewhat smaller and thinner (exterior diameter, $d_{\text{ext}} = 23$ mm; thickness, $t = 2$ mm), for the temperature control. The cooled-air inlet was, in this setup, at the top of the PMMA tube. The PMMA tube was fixed at its top and thus did not rotate during the scans. The compressed air pressure was in the same order as that used for the setup No. 2. In addition, the aluminum tube height was reduced to 180 mm. Two thermocouples, inserted into the PMMA tube to measure the air temperatures close to the air inlet and outlet, showed a rather stable temperature difference of $1.5 - 2.0$ °C during the scans.

Figure 15 shows a preliminary result obtained by XRCT, with a voxel size of $4\text{ }\mu\text{m}$. The micro-focus source was used because the geometry of the tube does not allow high resolution. This 15-hour scan was started 28 hours after the start of the experiment, during which temperature and pressure were controlled, when the formation of MH was considered to be stabilized. MH morphologies (crystals/layers) were clearly observed over grain surfaces. Furthermore, $R_{mh/q}$ and SNR were 0.3 and $1/0.095$ respectively (Figure 16). It can be seen that the $R_{mh/q}$ and SNR were in the same order for the three experimental setups. The difference was that successful scan ratios were lower for the two first setups due to cell vibration while this problem was well resolved by using the third one: all five XRCT tests were successful. The setup No. 3 is however not compatible with higher resolution XRCT imaging because of the large diameter of the PMMA tube.

The setup No. 3 was also successfully used to perform SXRCT scans. An example is shown in Figure 17 (voxel size was $0.9\text{ }\mu\text{m}$). Really small hydrate particles, formed at

the sand grains surface, can be clearly observed. $R_{mh/q}$, $R_{sw/q}$ and SNR were 0.27, 0.73 and 1/0.080, respectively (Figure 18). The ratios ($R_{mh/q}$, $R_{sw/q}$) calculated on the image are close to the theoretical ones. A small increase of salt concentration in the remaining saline water during the MH formation caused a slightly higher $R_{sw/q}$ value.

Furthermore, within the high temporal resolution of SXRCT, the evolution of methane hydrate formation could be followed with time. Figure 19 provides vertical cross-sections through the sample (note that previously shown cross-sections were horizontal) at a same position at various times. Water was initially located at the contacts of sand grains because of the capillary suction (Figure 19a). The air-water interface can be easily identified by the concave meniscus. At 0.8 h from the application of MH formation conditions, these interfaces became irregular and the concave meniscus disappeared. In addition, a thin layer (of water or methane hydrate) appeared on the surface of the grain. As water and methane hydrate have similar gray levels and cannot be distinguished by gray levels, the evolution of their morphology can be used. Actually, irregular interface between the gas phase and water or hydrate phase suggests that this later became a rigid phase (i.e. methane hydrate). Besides, the thin layer appeared on the sand grain surface should correspond to methane hydrate as suggested by Chaouachi et al. (2015). It should be noted that some water was moved out of this area between $t = 0.3 - 0.8$ h. We can then expect that at 0.8 h, methane hydrate was formed at methane gas/water interfaces and at the sand grain surface; MH layers became thicker with time as shown in the Figure 19.

Discussions and recommendations

Three experimental setups were developed for pore-scale morphology and pore-habit investigations of MHs in sandy sediments via XRCT and SXRCT. The image spatial resolution was well improved by using SXRCT instead of XRCT. However, SXRCT scans are costly and access time is very limited. Furthermore, by using saline water, methane hydrates could be well distinguished from the remaining water during the MH formation (Figure 17) while for the case of tap water (e.g. Figure 19), methane hydrates and water could only be distinguished from each other via the kinetics of MH formation (MH crystals or layer were grown over time) or via the interface roughness (smooth interface between liquid and gas due to interfacial tension). However, due to the shift of the phase boundary of methane hydrate formation for saline solution, the sample temperature needed to be maintained at a lower temperature compared to that for water (1-2 °C lower at 7 MPa).

In previous studies where gas hydrate morphology in sediments were investigated, other gas/fluid (THF or Xenon) was used to facilitate the gas hydrate formation because only temperature control (Kerkar et al. 2009) or pressure control (Chen and Espinoza 2018) was required. In the present work, as methane hydrates were investigated, both low temperature and high pressure were required. Furthermore, in order to maintain a low temperature, liquid was usually used in previous studies (Chaouachi et al. 2015; Ta et al. 2015; Zhao et al. 2015; Le et al. 2020). That would avoid the system vibration induced by air flow, as observed in the present work. However, X-ray absorption of water would decrease the image's quality. Furthermore, voxel size in XRCT images, in these studies, was quite large, in a range

of 20 μm to 30 μm due to complex and bulky experimental setups, which were required to control both temperature and pressure (Ta et al. 2015; Yang et al. 2015; Zhao et al. 2015). Within such resolution, small particles of MHs could not be observed. Furthermore, the partial volume effect was important. In the present work, a voxel size of 4 μm was obtained by the setup No. 3 with a very good image's quality, even in a laboratory CT setup, MH morphologies (crystals, layers) were thus clearly observed.

Besides, Lei et al. (2019) used a Peltier plate for temperature control. Yet, a temperature gradient of 4 $^{\circ}\text{C}$ was measured between the top and bottom of the sample (about 54 mm height), *i.e.* 0.08 $^{\circ}\text{C}/\text{mm}$. By using cooled air in this study, the temperature gradient over 150 mm of the tube height was about 2 $^{\circ}\text{C}$, *i.e.* 0.013 $^{\circ}\text{C}/\text{mm}$ which favors the homogeneity of MH formation in the sample. Moreover, by using a small methane gas bottle in this study, associated with a pressure reducer, methane gas pressure was maintained constant during the whole MH formation process.

Among the three experimental setups developed in the present study, the third one was the most optimized. Actually, the aluminum tube height was shortened to minimize the vibration induced by the air flow. The setup No. 2 has the best spatial resolution for XRCT scans (voxel size equals to 3.5 μm) but its experimental procedure is the most delicate. Besides, the setup No. 2 was compatible only with the Nano-focus source while the two others can be used for all types of X-ray source.

Concerning the pressure control system, the sample can be disturbed during the system transportation to the XRCT room in the case of the two firsts setups. However, it avoids occupying the room during a long period. The setup No. 3 (using a small methane gas bottle) is the best choice for SXRCT scans. It however requires a setup compatible with large and heavy samples, as the one available on the Psiche beamline.

Conclusions

The paper describes the scan condition optimizations and the developments of special experimental setups to investigate pore-scale morphologies and pore-habits of MHBS via XRCT and SXRCT.

Based on theoretical attenuation coefficient ratios between phases, XRCT scan conditions were optimized (scan energy, filter thickness and saline water solution). Preliminary XRCT and SXRCT scans performed on compacted sand wetted with pure water or saline water confirmed the theoretical estimations.

Afterward, three experimental setups were developed in the objective of improving the image spatial resolution for pore-scale morphology and pore-habit investigations of MHs in sandy sediments via XRCT and SXRCT. The details of temperature and gas pressure controls were presented. The results obtained for each experimental setup allowed evaluating its performance to observe the morphologies and pore-habits of MHBS. The experimental setup No. 3 seems to be the most appropriate.

527 Sample temperature was controlled by circulating cooled air between the aluminum
528 and the PMMA tube which is fixed at its top. Attention was paid to minimize the cell
529 vibration induced by cooled air flux.

530

531 The choices of temperature and pressure controls presented in the present work can
532 be useful for further studies on MHBS as well as other geo-materials involving a
533 control of temperature and/or gas pressure during XRCT/SXRCT scans.

534

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540 context of proposal 20181629.

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543

544 **Lists of figures**

545

546 Figure 1. Linear attenuation coefficient ratio between phases, and X-Ray

547 transmission through Cu filter, versus photon energy.

548

549 Figure 2. XRCT images of unsaturated sand with (a) pure water; (b) saline water.

551 Figure 3. Gray level profiles along yellow lines in Figure 2: (a) water/quartz; (b) saline
552 water/quartz.

553
554 Figure 4. SXRCT images of unsaturated sand with (a) pure water; (b) saline water.

Figure 5. Gray level profiles along yellow lines in Figure 4: (a) water/quartz; (b) saline water/quartz.

562 Figure 6. Experimental setup principles for XRCT scans of MHBS. SOD: Source

563 Object Distance; SDD: Source Detector Distance.

Figure 8. Example of image of an unsuccessful scan due to the cell vibration,
obtained with the experimental setup No. 1. Voxel size: 5 μ m.

Figure 9. Example of image of MHBS obtained with the setup No. 1. Voxel size: 5 μ m.

Figure 10. Gray level profile along yellow line in Figure 9.

Figure 11. Experimental setup No. 2: (a), (b) Schematic view; (c) picture.

579

580 Figure 12. Example of image of MHBS obtained with the setup No. 2. Voxel size: 3,5

581 µm.

Figure 13. Gray level profile along yellow line in Figure 12.

Figure 14. Experimental setup No. 3: (a) Schematic view; (b) picture.

Figure 15. Example of XRCT image of MHBS obtained with the setup No. 3. Voxel

size: 4 µm.

592

593 Figure 16. Gray level profile along yellow line in Figure 15.

594

595

596

597 Figure 17. Example of SXRCT image of MHBS obtained with the setup No. 3. Voxel
598 size: 0.9 µm.

599

600

601 Figure 18. Gray level profile along yellow line in Figure 17.

(a)

(b)

(c)

(d)

(e)

603 Figure 19. Vertical cross-section showing the MH formation (tap water) at: (a) $t = 0.3$
604 h; (b) $t = 0.8$ h; (c) $t = 2.2$ h; (d) $t = 4.3$ h; (e) $t = 6.0$ h.

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