Science and Technology for Energy Transition **79**, 14 (2024)
© The Author(s), published by EDP Sciences, 2024
https://doi.org/10.2516/stet/2024012

Available online at:
stet-review.org

Selected Papers from First European Conference on Gas Hydrates (ECGH), 2022
Bertrand Chazallon and Anh Minh Tang (Guest Editors)

REGULAR ARTICLE OPEN ACCESS

Mechanical behaviour and microstructure of methane hydrate-bearing sandy sediment observed at various spatial scales

Thi Xiu Le[1], Michel Bornert[1], Patrick Aimedieu[1], Daniel Broseta[2], Baptiste Chabot[1], Andrew King[3], and Anh Minh Tang[1,*]

[1] Laboratoire Navier, Ecole des Ponts, Univ Gustave Eiffel, CNRS, 6-8 avenue Blaise Pascal, 77455 Marne-la-Vallée, France
[2] Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, LFCR, 64000 Pau, France
[3] Synchrotron SOLEIL, L'Orme des Merisiers Départementale 128, 91190 Saint-Aubin, France

Received: 29 March 2023 / Accepted: 24 January 2024

Abstract. Methane hydrates (MHs) are considered an alternative energy resource but also a potential source of geo-hazards and climate change. The physical/mechanical properties of gas hydrate-bearing sandy sediments are strongly dependent on the distribution of hydrates within the pore space. The purpose of this study is to investigate morphologies and pore-habits of MHs formed in sandy sediments by means of experiments that probe a wide range of scales, from the pore scale – using Synchrotron X-Ray Computed Tomography (SXRCT) and optical microscopy – to the core scale, through mechanical property measurements. The same synthetic sands are used, in which MHs are generated successively under excess gas and excess water conditions. At the macroscopic (core) scale, MH pore habits are inferred by comparing the measured sonic wave velocities to velocities calculated from rock physics models and further assessed via triaxial compression tests. Furthermore, Magnetic Resonance Imaging is used to investigate the kinetics of MH formation and distribution along the core height. The pore habits and MH morphologies are directly visualized at the pore (grain) scale by SXRCT and, with still better spatial and temporal resolution, by transmission optical microscopy, revealing some more complex morphologies than in the hydrate pore habits commonly admitted.

Keywords: Gas hydrates, Sediment, Microstructure, Mechanical properties.

1 Introduction

Gas hydrates are solid ice-like compounds of water and guest molecules, which are either gaseous or liquid at ambient conditions. Methane Hydrates (MHs), natural gas hydrates, form naturally under high pressure and low temperature. They are found worldwide, whether in arctic regions or in shallow marine sediments below the sea bottom (Ruppel, 2007).

Geophysical methods, which involve complex 3D seismic inversion using rock physics and geologic models, are commonly used to estimate the global volume of the MHs located in between the sea bottom and the so-called Bottom Simulating Reflectors (BSRs). MH resource estimates rely on two basic parameters: the porosity and the percentage of the pore volume occupied by MHs, called MH saturation. Cage occupancies and hydration numbers are also important parameters for estimating the natural gas content (Boswell & Collett, 2011). These estimates, ranging over several orders of magnitude (3100 Tm^3 to 7,650,000 Tm^3) (Ruppel, 2007), indicate an enormous potential for MH as a future energy resource. The larger pore size (hundreds of microns) and relatively high permeability of sandy sediments favour the pore-filling habit, in which much of the pore space is occupied by MHs. The high MH saturation in those Methane Hydrate-Bearing Sandy Sediments (MHBSS) is the reason why they are targeted for MH exploration and future methane gas production (Le *et al.*, 2019a).

MH dissociation replaces rigid components with free gas and excess water and causes extraordinary pressure build-ups, which may significantly reduce the geo-mechanical stability of affected sediments. Slope instability and wide-scale gas venting are the two most important geo-hazards associated with MH dissociation. Human activities like drilling and production through Methane Hydrate-Bearing Sediments (MHBS) are considered operational geohazards and cause the same concerns, such as casing collapse, gas leakage outside the conductor casing, and gas blowouts. These geo-hazards provide an additional constraint on exploiting oceanic MHs as a future energy resource (Collett *et al.*, 2014).

* Corresponding author: anh-minh.tang@enpc.fr

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (https://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In addition, methane is an active greenhouse gas that has a global warming potential twenty times greater than an equivalent weight of carbon dioxide when integrated over 100 years. MHs existing in metastable equilibrium can be affected by changes in pressure and temperature that occur mainly with changes in sea level. An instantaneous release of methane gas from onshore or offshore zones could have great impacts on the atmospheric composition and thus on global climate. MH resources prone to natural destabilization on the short-to-medium terms are surface or very shallow burials. For deeply buried deposits, the gas pathway to the overlying ocean or to the atmosphere requires a transfer through the overlying intervals (Boswell *et al.*, 2011). However, detailed knowledge about how the released methane gas reaches the atmosphere needs to be clarified: this is a key issue in understanding the connections between MHs as an energy resource and also a potential player in future climate scenarios.

Natural MHs in sediments can be identified by several methods but using seismic reflection data is the most popular one (Popenoe *et al.*, 1993). Note that the absence of BSR does not imply that there are no MHs within sediments. Logging methods have been widely used for MH exploration because of their accurate parameter determination for MHBS regardless of their high cost (Dallimore *et al.*, 1999). Drilling to get cores is the most effective method for recovering and identifying natural gas hydrates, but it is usually used together with other methods like seismic methods to constrain where the core is taken. ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy used to investigate the molecular structures and physical properties of substances, is one of the most important means for studying MH characteristics in natural MHBS (Davidson *et al.*, 1977). The presence of methane hydrates can also be inferred from the chemistry of the aqueous phase surrounding the sediment (*e.g.* pore-water salinity) following hydrate dissociation (Ruppel and Kessler, 2017). Most of the recovered, *i.e.*, "real" MH samples are obtained during deep coring projects or shallow seabed coring operations, while most of the inferred MH occurrences are from seismic reflection profiles where BSRs have been identified (Collett *et al.*, 2014).

Various studies have been published on the mechanical behaviour of MHBS especially in the scope of methane gas production. Geologic sampling inevitably disturbs natural sediments and the presence of hydrates adds further difficulties to sampling. With new methods like pressure coring, sample disturbances are reduced but still some are not eliminated, such as the loss of effective stress during sampling and shear along the soil-core liner interface (Waite *et al.*, 2009). Therefore, almost all experimental tests, especially those investigating the mechanical behaviour, are conducted in the laboratory using synthetic sandy sediments. Different methods have been proposed and implemented to install MHs in those synthetic sediments, with questions about the particular MH pore habits and morphologies that are generated by the chosen installation process. Until quite recently, the hydrate pore habits or morphologies in the porous space were not observed directly, but inferred from measured mechanical properties such as compressional wave velocities using idealized geometries and simple rock physics models (Choi *et al.*, 2014; Nguyen-Sy *et al.*, 2019).

Reasonable hydrate pore habits, or spatial distributions of the MH within the pore space, have been proposed long ago and first used to predict the elastic properties of MHBSs (Dvorkin *et al.*, 2000). Two pore habits are conventionally expected in MHBSS prepared by the excess gas method, referred to as "cementing grain contacts" and "surrounding and cementing grains": the MH respectively cements adjacent grains at their contact or covers them with a layer (see the idealized geometries D and C in Fig. 1). In MHBSS prepared by the excess water method, two pore-filling habits are hypothesized: one in which the MH floats in the pore fluid, and the other in which it is part of the load-bearing granular frame (A and B in Fig. 1). Measurements of the elastic properties of MHBSS thus provide indirect indications as to how the MH is distributed within the pore space, but direct visualizations of the MH in the pore space by techniques such as Synchrotron X-Ray Computed Tomography (SXRCT) or optical microscopy are still very scarce.

This paper gathers and discusses a set of measurements conducted on the same synthetic sandy sediment of both the mechanical properties at the core scale and MH pore habits and morphologies at the grain scale. Those two sets of properties are indeed closely related: the purpose of this work is to arrive at a coherent picture of MHBSS from pore to core scales. Mechanical properties are investigated via a high-pressure triaxial cell (to perform triaxial compression tests) equipped with ultrasonic sensors for measuring compressional velocities (Le *et al.*, 2019b). Hydrate pore habits and morphologies are visualized by SXRCT and high-resolution optical microscopy (Le *et al.*, 2020a, 2021a,b). Furthermore, the kinetics of MH formation as well as the MH distribution at the sample scale are investigated by using Magnetic Resonance Imaging (MRI) (Le *et al.*, 2020b).

With the exception of the very recent XRCT-based triaxial testing apparatus (Wu *et al.* 2020), whose use is still limited, this investigation is, to the best of the authors' knowledge, the first of its kind that provides a comprehensive picture of MHBSs over such a large range of spatial and temporal scales.

2 Experimental methods

Fontainebleau silica sand (NE34) was used (Fig. 2). It consists of poor-graded sub-rounded grains having diameters ranging from 100 to 300 microns. Tap water was used in the tests. The standard purity of methane gas used was 99.995%.

Figure 1 presents the procedure used to prepare the same MHBSS for the triaxial and MRI experiments in two different MH saturation states: first, excess gas, and then, excess water. This procedure comprises the following steps: (1) Wet sand compaction. Moist sand (having a known moisture content) was compacted by tamping in layers to obtain a void ratio (volume of void divided by

Fig. 1. Preparation of MHBSS. The four conventionally accepted MH pore habits are schematically represented: A – Hydrate floating in the pore fluid; B – Hydrate as part of the load-bearing granular frame; C – Hydrate surrounding and cementing grains; D – Hydrate cementing grain contacts.

Fig. 2. Particle size distribution and scanning electron microscope image of sand (modified from Feia *et al.*, 2014).

volume of sand grains) of 0.63; (2) Consolidation. The specimen was consolidated in drained conditions at a confining pressure of 10 MPa; (3) Methane hydrate formation. The specimen temperature was decreased to 2–5 °C and vacuum was applied to eliminate the pore air. Afterwards, methane gas was injected at 7 MPa during the whole MH formation period. MH formation in these excess-gas conditions was considered complete when the methane gas flow rate became negligible (<0.1 ml/min). This process lasts typically 2–4 days; (4) Water saturation. One end of the specimen was opened to reach the atmospheric pressure during a short period (about 10 s) to let excess methane gas (initially under a pressure of 7 MPa) escape from the sample and then this end was connected to a volume/pressure controller to inject water with a pressure of 7 MPa. This short period (10 s) is long enough to let excess methane gas escape from the specimen (which has hydrate saturation lower than 50%) but short enough to avoid hydrate dissociation, which is confirmed by the measurement of methane gas dissociated at the end of the test. A temperature cycle was finally applied to dissociate and then re-form the MHs in those excess water conditions. It should be noted that, as the specimen was consolidated at 10 MPa in the consolidation step (step 2), the subsequent steps did not induce significant volume change.

Similar pressure (7 MPa) and temperature conditions (3–5 °C) were chosen for the SXRCT experiments. As the sample volume was 3–4 orders of magnitude smaller in the capillaries used for the optical microscopy experiments, ice was first formed by lowering the temperature well below

Fig. 3. Experimental techniques used.

0 °C then increasing it to similar temperatures as the ones used in the SXRCT experiments.

The mechanical behaviour and pore-scale microstructure of MHBSs were observed at various spatial and temporal scales using the four following devices (Fig. 3). Working conditions corresponding to each device are shown in Table 1.

- Triaxial cell: A cylindrical specimen (50 mm in diameter and 100 mm in height) is covered with a neoprene membrane. Confining pressure is applied to the specimen through this membrane. The cell is immersed in a temperature-controlled bath. During the test, the confining pressure, axial stress, pore pressure (gas or water inside the pore space), and cell temperature are controlled. The specimen axial and radial strains can be monitored by displacement transducers. Two ultrasonic sensors are installed at the top and bottom ends of the specimen to measure compressional wave velocity. More details can be found in Le *et al.* (2019b).
- MRI cell: A cylindrical specimen (38 mm in diameter and 76 mm in height) is covered with a neoprene membrane. Confining pressure is applied to the specimen through this membrane. The signal intensity measured through the nuclear magnetic resonance imaging system is proportional to the number of hydrogen atoms of either the liquid (water) or gas (methane) phase – the latter represents a very small amount of hydrogen atoms compared to those of the liquid water. MHs and ice contributions are negligible due to the very short relaxation time of their hydrogen atoms. More details can be found in Le *et al.* (2020b).
- Synchrotron X-ray tomograph (SXRCT): Moist sand is compacted into an aluminium tube (exterior diameter = 6.45 mm; thickness = 0.89 mm). To maintain a low temperature, cooled air is circulated around the aluminium tube. SXRCT scans are performed at the Psiche beamline at the French synchrotron SOLEIL (mean energy: 44 keV). The voxel size is 0.9 µm and the scan time is 12–15 min. More details can be found in Le *et al.* (2021b).
- Optical microscope: Wet sand grains are introduced into a quartz capillary tube closed at one end. The tube has a square cross-section (internal section: 500 microns × 500 microns and 100 microns in thickness). The temperature of the capillary tube is controlled by an annular Peltier element. The whole system is placed horizontally on the table of an inverted microscope (*Nikon*, Ti-Eclipse, ×20 ELWD objective, Hamamatsu Orca 4.0 camera). More details can be found in Le *et al.* (2021a).

3 Results at excess-gas conditions

The results obtained during MH formation in the triaxial cell for samples with different saturation states are shown in Figure 4. Temperature is maintained at 3.6 – 4.4 °C. Methane gas pressure is increased quickly to 7 MPa within one minute and then kept constant at 7 MPa during the test by volume/pressure controller. Figure 4 shows the specimens volumetric strain (ε_v) and compressional wave velocity (V_p) *versus* elapsed time ($t = 0$ corresponds to the moment pore pressure reached 7 MPa). Generally, the specimen volume increases ($\varepsilon_v < 0$) from the beginning to $t = 0.04$ h

Table 1. Working conditions.

	Triaxial cell	MRI	SXRCT	Microscope
Specimen	Cylindrical (50 mm in diameter; 100 mm in height)	Cylindrical (38 mm in diameter; 76 mm in height)	Cylindrical (38 mm in 4.67; 200 mm in height)	Few sand grains
Hydrate formation conditions	Gas pressure: 7 MPa	Gas pressure: 7 MPa	Gas pressure: 7 MPa	Gas pressure: 7 MPa
	Temperature: 3–5 °C	Temperature: 2 °C	Temperature: 1–2 °C	Temperature: 2 °C
Characterisation	Triaxial compression behaviour Compressional wave velocities	MRI signal intensity (total and 1D profile)	3D images of X-ray attenuation	Optical images
Test duration	Several days	Several days	Several days	Several hours

Fig. 4. Results obtained in the triaxial cell during MH formation: volumetric strain (a) and compressional wave velocity (b) *versus* elapsed time. Four different water saturation states S_r (labelled 1, 2, 3 and 4) and different (duplicate) samples (labelled A and B) are considered. The vertical arrow in (b) indicates the induction time when V_p starts to increase.

and then decreases for several hours before reaching a stabilisation. However, the volumetric strain remains negligible (<0.1%) in spite of a 10% volume increase of MHs compared to liquid water. Besides, compressional water velocity (measured by ultrasonic sensors) increases only slightly from the beginning to $t = 0.04$ h and then increases quickly for several hours before reaching a stabilisation.

The compressional wave velocities measured in the stabilisation stage (shown in Fig. 4) are plotted *versus* MH saturation in Figure 5. In order to assess the MH distribution at the grain scale in sandy sediments (pore habit), an assumption is made on the pore habit and the compressional velocities are calculated as a function of MH saturation (Dvorkin *et al.* 2000) and compared to the

Fig. 5. Results obtained by triaxial cell: assessment of hydrate distribution at the grain scale by geophysical model. See the caption of Figure 3 for the meaning of A1–B4. "Contact I" is equivalent to D and "contact II" to C in Figure 2.

experimental data: (i) MHs are located only at the grain contacts (cementing – grain contacts), labelled D in Figure 1; and (ii) MHs evenly envelop the grains (cementing – mineral coating), labelled C in Figure 1. As expected, for equivalent MH saturations model (i) predicts much stiffer MHBSs than model (ii), see Figure 5. More details about the parameters used can be found in Le *et al.* (2019b). The experimental data obtained by Le *et al.* (2019b) have stiffnesses (or compressional velocities) intermediate between those predicted by the two models.

The kinetics of hydrate formation can be equally observed via experiments performed with MRI cells. The cell temperature is maintained at 2 °C. Methane gas pressure in the pore is increased quickly to 7 MPa after three minutes and maintained constant at 7 MPa during the test by means of the volume/pressure controller. Figure 6 shows MH saturations *versus* elapsed time ($t = 0$ corresponds to the moment pore pressure reaches 7 MPa). It can be observed that MH saturation increases from the beginning with a constant rate (time is plotted in logarithmic scale). The rate changes at $t = 1$ h and stabilisation is reached after 50 h. It should be noted that the hydrate saturation is estimated from the MRI signal via preliminary calibration tests, it is agrees with the initial water content (used to prepare the specimen) and the gas amount measured during the dissociation phase at the end of the test (Le *et al.*, 2020b).

Figure 7 presents the signal profile along the specimen. Z represents the position from the specimen bottom, while the MRI signal is proportional to the mass of liquid water in the sample. Profiles taken at various times show that the liquid water content decreases with time during MH formation. The most important information that should be noted from these results is that the liquid water content distribution along the specimen (and thus MH distribution) is homogenous during the whole process (Le *et al.*, 2020b). It should be noted that the effect of gravity on water distribution is negligible, even in the beginning, because soil suction corresponding to this hydric state (25% of water saturation) equals 3–5 kPa (Feia *et al.* 2014), which is much higher than the gravity-induced suction gradient in the specimen (0.76 kPa).

Moving to a smaller (grain) scale, the SXRCT results show the MH growth process over 10 hours, see Figure 8. The grey level obtained from the SXRCT image is converted to a colour scale (shown at the bottom of the image) without adding any segmentation to avoid any potential error related to the segmentation process. In the beginning, liquid water (yellow zones) can be seen located at the contact between sand grains (red zones). Menisci are clearly identified separating methane gas (blue zones) and liquid water. Note that saline water (3.5% of KI) instead of pure water is used in these tests to improve the contrast. It is well known that saline water (compared to pure water) may alter MH equilibrium curve (lower temperature or higher pressure), MH nucleation and formation kinetics (more difficult to form MH), and MH saturation (smaller MH saturation under the same conditions), but it does not significantly alter the MH morphology, which is the most important information provided by SXRCT. Following the application of temperature/pressure conditions (7 MPa of methane gas pressure and 1–2 °C of temperature), MH protuberances and layers can be observed on the sand grain surfaces. The presence of MHs becomes more and more significant over time (Le *et al.*, 2020a).

Observations by optical microscopy (Fig. 9) show that, under excess gas conditions, the hydrate protuberances observed by SXRCT correspond to MH crystals formed on the sand grain surfaces. Optical microscopy reveals morphological features that are apparent but not

Fig. 6. Results obtained in MRI cell during MH formation: MH saturation *versus* elapsed time. Only one out of two similar tests is represented.

Fig. 7. Results obtained in MRI cell during MH formation: signal profiles at various times, starting ($t = 0$) with a water saturation $S_r = 25\%$. T1 and T2 correspond to tests 1 and 2, which are duplicates.

identifiable in the SXRCT images: MH hydrate spikes or filaments growing into the methane phase from the sand grain surfaces or, more precisely, from the hydrate layers (halos) on these surfaces (Le *et al.*, 2021a). These spikes are too thin (a few microns in diameter) to be distinguished by SXRCT.

Figure 10 shows optical microscopy observations showing MH growth on a planar glass substrate. These results evidence the development of a hydrate layer on the substrate and also that of MH spikes (Le *et al.*, 2021a).

4 Results at excess-water conditions

Figure 11 presents the compressional wave velocities measured for various hydrate saturation in the triaxial cell. In order to assess the MH pore habits in excess-water conditions, the four models proposed by Dvorkin *et al.* (2000) and depicted in Figure 11 are considered: in addition to the two cementing models presented above, a model considering MHs as a fluid component (pore-filling) and another considering MHs as sediment frame components (load-bearing) are used. The experimental results agree with the "load-bearing" and "pore filling" models. These results suggest that the presence of water modifies the MH pore habits; MHs located at the grain contacts or/and around grain surfaces (cementing) are progressively converted or/and redistributed into the sediment pore space. Following the temperature cycle, the experimental data correspond to the pore-filling model. In fact, the heating/cooling cycle allows completing the conversion of MH pore habits into non-cementing type, as manifested

Fig. 8. Results obtained by SXRCT: hydrate growth at the grain (or pore) scale. Square dimensions: 540 µm × 540 µm.

Fig. 9. Results obtained by optical microscopy: hydrate crystals (a) and hydrate spikes or filaments (b) observed on sand grain surface.

by the lower stiffnesses observed with temperature cycles (Fig. 11).

Results obtained from triaxial compression tests are shown in Figure 12 where the deviator stress (axial stress minus radial stress) and volumetric strain are plotted *versus* axial strain. The results are then used to perform Rowe's stress dilatancy analysis (Pinkert, 2016) in order to assess the cohesion between sand grains. The results (shown in Fig. 13) suggest that the cohesion is close to zero for all these specimens.

The expectation related to hydrate distribution at the grain scale obtained from triaxial compression tests (*i.e.* in excess-water conditions, hydrates exist as particles in the pore space, there is no cementation between the grains) can be confirmed by the SXRCT observations shown in Figure 14. Actually, in the excess-water zone, hydrate particles can be found floating in the pore space between sand grains.

5 Discussion

In this section, the above results obtained from different techniques are gathered with existing results from the literature to discuss some features of gas hydrates in sand sediments.

5.1 MH nucleation in excess-gas conditions

Gas hydrate formation in bulk water is different from that in sediment matrix due to interactions between the sediment and pore fluid (Abbasi *et al.*, 2022; Everett, 1961). The presence of particles/sediments promotes heterogeneous hydrate nucleation and therefore shortens the induction time (Heeschen *et al.*, 2016). Note that the induction time is the time taken for crystal nuclei to be formed until their occurrence, it is detected via *e.g.* temperature rise (endothermic nature of gas hydrate formation) and/or

Fig. 10. Results obtained by optical observation: MH layer propagation on a planar (glass) surface: (a) $t = 0$ s; (b) $t = 1.3$ s; (c) $t = 2.2$ s; (d) $t = 18$ s.

Fig. 11. Results obtained by triaxial cell: assessment of MH distribution by geophysical model. See the caption of Figure 4 for the meaning of A1-B4.

pressure decrease (gas consumption for gas hydrate formation in a closed system). Increasing the driving force for gas hydrate formation (by applying higher pressure and/or lower temperature) indeed reduces the induction time (Metaxas *et al.*, 2019).

Bagherzadeh *et al.* (2011) used the MRI technique to investigate the formation of MHs in an unconsolidated bed of silica sand and found that MH formation was not uniform and the nucleation of hydrate crystals occurred at different times and different positions inside the sample. In the present work, the induction time in triaxial tests can be defined as the duration before V_P starts to increase (see Fig. 4b). The observed induction time, approximately 0.3 h, is almost independent of the initial water saturation. This agrees with the results of Chong *et al.* (2016) who found an induction time of 0.1–0.8 h for fine sand (0.1–0.5 mm) initially containing a water saturation of 75% at (8 MPa, 4 °C). In the MRI tests of the present

Fig. 12. Results obtained by triaxial cell: mechanical behaviour under triaxial compression. See the caption of Figure 4 for the meaning of A1–B4.

work (at 7 MPa, 2 °C), MH saturation is observed to increase as soon as the MH equilibrium conditions are reached (at 25% of initial water saturation, shown in Fig. 6).

5.2 MH growth in excess-gas conditions

The gas hydrate growth rate following nucleation increases with subcooling, *i.e.*, the distance to equilibrium conditions (Metaxas *et al.*, 2019; Turner *et al.*, 2005). Furthermore, the observations by Bagherzadeh *et al.* (2011) point to a faster MH formation in samples with lower initial water saturation. In this study, MH spikes are observed to grow into the gas phase from grain surfaces and/or methane gas/water interfaces and to become thicker over time (Figs. 8 and 9). MH spike formed under excess-water conditions have been observed by Lei *et al.* (2019), who hypothesized that it is similar to ice spike formation (of the hollow MH tubes serving as water conduits for further MH growth into methane gas space). In the study presented here, the MH

Fig. 13. Results obtained by triaxial cell: assessment of hydrate distribution at pore scale via Rowe's stress-dilatancy analysis. See the caption of Figure 4 for the meaning of A1–B4. φ_{cs} is the critical state friction angle.

Fig. 14. Results obtained by SXRCT: MHs in excess-water conditions.

spikes or filaments are shown to extend in the gas phase from the hydrate films (halos) on grain surfaces or methane gas/water interfaces. Evidence for their hollowness serving as conduits for the water phase is gained from optical microscopy observations: when their extremity in the gas phase encounters a grain surface, then a hydrate halo spreads around the hitting point (Le *et al.*, 2021a). The SXRCT experiments indicate that some of these MH spikes or filaments become crystal-like.

Thanks to the high attenuation coefficient ratio between Xenon hydrate and water, a thin water film between Xenon hydrate and sand surface has been observed by Chaouachi *et al.* (2015) by using SXRCT. Lei *et al.* (2019) observed methane hydrates growing on sand surfaces in both excess-gas and excess-saline-water experiments and suggested that water migration driven via water film between sand grain and MHs facilitates MH growth over sand grains near the original water menisci. Furthermore, MH morphologies evolved after the initial MH formation mainly via diffusion. In the present study, the high temporal resolution of SXRCT allowed the observation of liquid, water moving from grain contacts to form MHs at nearby sand grain surfaces. However, due to the voxel size and scan time limit of SXRCT scans in this study (0.9 microns and a dozen minutes), the presence of water or hydrate films (halos) over the sand substrate could not be confirmed. Those films are however visible by optical microscopy, which also reveals the nature and growth mechanisms of the protuberances apparent in SXRCT scans (Fig. 8).

The mechanism of MH layer formation at grain surfaces can be analysed via optical microscopy. Figure 10 shows the propagation of MH layers on the quartz capillary wall during MH reformation. Halos (MH layers) propagate quickly over quartz under the gas phase, jump over the water droplets they encounter and leave behind an MH crust over those water droplets. Similar phenomena have been observed for cyclopentane hydrates by Martinez de Banos *et al.* (2016). A thin liquid water film is sandwiched between the quarzitic surface and the MH crust, which incorporates the small water droplets present and allows for further MH growth on the solid surface (substrate), a phenomenon analogue to cryogenic suction in frozen soils.

MH growth is affected by macro-scale properties (such as the initial water saturation) and micro-scale properties (the initial water distribution in the pore space) (Zhang *et al.*, 2019). By using first water-saturated sand and then injecting methane gas to displace free water in order to obtain a desired initial water saturation for the MH formation, MHs are observed to be formed heterogeneously in the sample even at low initial water saturation by using MRI (Wang *et al.*, 2018; Zhang *et al.*, 2019) as the initial water distribution was not a homogeneous. Homogeneous MRI profiles obtained in the present work during the MH formation following the excess-gas method (Fig. 7) show a homogeneous MH distribution at the sample scale (initial water saturation: 25%). This agrees with the results by Bagherzadeh *et al.* (2011), who used the same preparation procedure (dry sand mixed with the desired water quantity before compaction, initial water saturation of 25%). However, MHs were found distributed heterogeneously for the samples with high initial water saturation (Bagherzadeh *et al.*, 2011). It should be noted that the samples for triaxial tests were prepared with an initial water saturation in a range of 25–50%. It is then supposed that MHs are distributed homogeneously in these samples.

5.3 MH morphologies and pore habits in excess-gas conditions

The injection of methane gas at a pressure of 7 MPa and a temperature of 3–4 °C induce the transformation of water into MHs (triaxial tests). The results show that this MH formation under excess-gas condition increases V_p (see Fig. 4b), and this increase reaches the stabilization state at the end of the MH formation. Almost the entire quantity of available water is transformed into MHs and the distribution of MHs is similar to that of water prior to their creation. Comparison between the experimental data and Dvorkin's model (Dvorkin *et al.*, 2000) shown in Figure 5 suggests that at a low initial water saturation, MHs are mainly distributed at grain surfaces (cementing – mineral coating), while at a high initial water saturation, the role of MHs at grain contacts is dominant (cementing – grain contacts). These macroscopic results agree with that of Waite *et al.* (2004) by using similar approaches (velocity measurements and Dvorkin's model).

Within the spatial resolution of sub-micron voxel size of SXRCT images in this study, MH morphologies and pore habits are observed directly without the need of segmentation. This is complemented by observations via optical microscopy, which provide further details as to the layer or halos present on the sand grains. This allows to discuss the four types of MH pore habits, proposed by Dvorkin *et al.* (2000): cementing (grain-grain contacts or mineral coating), load-bearing and pore-filling, usually used for predictions of physical/mechanical behaviours of methane hydrate-bearing sandy sediments (Pinkert and Grozic, 2014; Sanchez *et al.*, 2017; Uchida *et al.*, 2012; Waite *et al.*, 2009). It is usually assumed that MHs formed under excess-gas conditions in sandy sediments (following the excess-gas or ice-seeding method) have the shape of pendular water menisci (at grain-grain contacts) or thin uniform methane hydrate layers coating sand surfaces (cementing – mineral coating) (Priest *et al.*, 2005; Waite *et al.*, 2004). The present study and that of Lei *et al.* (2019) showed irregular shapes over sand surfaces, different from the idealised one proposed by Dvorkin *et al.* (2000). Not only MHs pore habits but also MHs morphologies in sandy sediments (which can only be observed at high spatial resolution) are important for determining the physical/mechanical behaviours of MHBSS. At similar MH saturation, different MH morphologies (spikes, "crystals" or layers) at sand grain surfaces (cementing – mineral coating) or at contacts of grains (cementing – grain contacts) can play different roles in the mechanical behaviour of MHBS. We hypothesise here an intermediary model of MHs at the grain scale with complex geometry of MHs that could eventually be porous.

5.4 MH morphologies and pore habits in excess-water conditions

After he formation of MHs under excess-gas conditions, the subsequent water saturation phase significantly decreased V_p during triaxial tests (Figs. 5 and 11). Ebinuma *et al.* (2008) observed a similar decrease in sonic velocities when saturating the gas-saturated MHBSS with water. These results suggest that water saturation modifies the MHs distribution at the grain scale (Ebinuma *et al.*, 2008; Kneafsey, 2011). MHs located at grain contacts and/or at grain surfaces are progressively converted or/and redistributed into the pore space (Choi *et al.*, 2014).

To mimic natural MHBSS, the dissolved gas method is considered as the best method but it is time-consuming especially at high MH saturation due to the low solubility of methane gas in water (Spangenberg *et al.*, 2005). The water-excess method, proposed by Priest *et al.* (2009), is likely to create load-bearing MHs in sandy sediments at MH saturation lower than 40% according to sonic wave velocity measurements. However, MHs are observed to be formed heterogeneously inside their sample via XRCT (Kneafsey, 2011). Kerkar *et al.* (2014) confirmed patchy MHs distribution and heterogeneous MH accumulation with XRCT at higher image spatial resolution. In the work of Lei *et al.* (2019), the effect of water injection on the conversion/redistribution of MHs was confirmed by XRCT scans at high image spatial resolution. Furthermore, the data showed round MHs particles under excess-water conditions. In the present study, MHs are initially formed following the excess-gas method. However, after multiple water migrations, MHs in both excess-gas and excess-water media exist in the sample. MHs in excess-gas media are in cementing forms (mineral coating and/or grain contacts) while round MHs particles mixed with saline water in the pore space under excess-water conditions (Fig. 14). This confirms the pore-filling/load-bearing distribution of MHs in excess-water media (round MH particles floating in saline water in the pore space of porous media). It is supposed that MH distribution at the grain scale of MHBSS after the water saturation at low MHs saturation and after the temperature cycle of triaxial tests is similar to what observed with SXRCT (*i.e.* round MH particles floating in water).

6 Conclusions

MH formation under both excess-gas and excess-water conditions and the effects of formed MHs on the mechanical properties of MHBSS were discussed based on measurements at the macroscopic scale and observations of MH distribution via MRI and SXRCT. It can be seen that:

- MH formation following the excess-gas method can be divided into three steps (MH nucleation, growth and stabilization). MH nucleation in porous media is almost spontaneous as the presence of sediments increases methane gas/water interfaces. MH growth is considered as a stochastic process and depends on driving force for the MH formation. At macroscopic scale, MH saturation seems to increase linearly with the logarithm of time (triaxial and MRI tests) while at microscopic scale, many interesting phenomena have been observed by using SXRCT combined with optical microscopy. At the pore scale, thin water layers at grain surfaces contribute to the formation of MHs in form of spikes which could be prolonged, clogged and become finally crystal-like as long as water is provided. Different MH morphologies and pore habits could co-exist in MHBSS formed following the excess-gas method. MH morphologies and distribution at the grain scale under excess-gas conditions seem to be more complex than described by the both cementing models (mineral coating and grain contacts);
- Water saturation converts (and/or redistributes) MHs in cementing form (grain contacts and/or mineral coating) to the pore space and the temperature cycle allowed for the completion of this conversion (and/or redistribution) for high MH saturation samples. The MH morphologies and distribution at the grain scale of formed MHBSS are supposed to be similar to that of natural MHBSS (pore-filling/ load-bearing habits).

Acknowledgments

This research was funded by the *French National Research Agency* under project ANR-15-CE06-0008, HYDRE: "Mechanical behaviour of gas-hydrate-bearing sediments", and by the *CAPBP* (Communauté d'Agglomération Pau Béarn Pyrénées), project "Laboratoire en capillaire". Use of the Psiché beamline at the Soleil synchrotron was granted under proposal 20181629 "Morphology and evolution of methane hydrates in granular sediment".

References

Abbasi G.R., Arif M., Isah A., Ali M., Mahmoud M., Hoteit H., Keshavarz A., Iglauer S. (2022) Gas hydrate characterization in sediments via X-ray microcomputed tomography, *Earth Sci. Rev.* **234**, 104233.

Bagherzadeh S.A., Moudrakovski I.L., Ripmeester J.A., Englezos P. (2011) Magnetic resonance imaging of gas hydrate formation in a bed of silica sand particles, *Energy & Fuels* **25**, 7, 3083–3092.

Boswell R., Collett T.S. (2011) Current perspectives on gas hydrate resources, *Energy Environ. Sci.* **2011**, 4, 1206–1215.

Boswell R., Moridis G., Reagan M., Collett T.S. (2011) Gas hydrate accumulation types and their application to numerical simulation, *Manuscript* **130**, 17–22.

Chaouachi M., Falenty A., Sell K., Enzmann F., Kersten M., Haberthür D., Kuhs W.F. (2015) Microstructural evolution of gas hydrates in sedimentary matrices observed with synchrotron X-ray computed tomographic microscopy, *Geochem. Geophys. Geosys.* **16**, 6, 1711–1722.

Choi J.-H., Dai S., Cha J.-H., Seol Y. (2014) Laboratory formation of noncementing hydrates in sandy sediments, *Geochem. Geophys. Geosys.* **15**, 4, 1648–1656.

Chong Z.R., Yang M., Khoo B.C., Linga P. (2016) Size effect of porous media on methane hydrate formation and dissociation in an excess gas environment, *Ind. Eng. Chem. Res.* **55**, 29, 7981–7991.

Collett T., Bahk J.-J., Baker R., Boswell R., Divins D., Frye M., Goldberg D., Husebø J., Koh C., Malone M., Morell M., Myers G., Shipp C., Torres M. (2014) Methane hydrates in nature – current knowledge and challenges, *J. Chem. Eng. Data* **60**, 2, 319–329.

Dallimore S., Uchida T., Collett T. (1999) *Scientific results from JAPEX/JNOC/GSC Mallik 2L-38 gas hydrate research well, Mackenzie delta, Northwest Territories, Canada*, Vol. **544**, Geological Survey of Canada Ottawa, Ontario, Canada.

Davidson D., Garg S., Gough S., Hawkins R., Ripmeester J. (1977) Characterization of natural gas hydrates by nuclear magnetic resonance and dielectric relaxation, *Can. J. Chem* **55**, 20, 3641–3650.

Dvorkin J., Helgerud M.B., Waite W.F., Kirby S.H., Nur A. (2000) Introduction to physical properties and elasticity models. Introduction to Physical Properties and Elasticity Models, in *Natural Gas Hydrate. Coastal Systems and Continental Margins*, Vol. **5**, M.D. Max (ed.), Springer, Dordrecht.

Ebinuma T., Suzuki K., Nagao J., Oyama H., Narita H. (2008) Ultrasonic wave velocities associated with formation and dissociation of methane hydrate in artificial sandy sediments, in Offshore Technology Conference, Houston, Texas, May 5–8.

Everett D. (1961) The thermodynamics of frost damage to porous solids, *Trans. Faraday Soc.* **57**, 1541–1551.

Feia S., Ghabezloo S., Bruchon J.F., Sulem J., Canou J., Dupla J.C. (2014) Experimental evaluation of the pore-access size distribution of sands, *Geotech. Test. J.* **37**, 4, 1–8.

Heeschen K.U., Schicks J.M., Oeltzschner G. (2016) The promoting effect of natural sand on methane hydrate formation: Grain sizes and mineral composition, *Fuel* **181**, 139–147.

Kerkar P.B., Horvat K., Jones K.W., Mahajan D. (2014) Imaging methane hydrates growth dynamics in porous media using synchrotron X-ray computed microtomography, *Geochem. Geophys. Geosys.* **15**, 12, 4759–4768.

Kneafsey T.J. (2011) *Examination of hydrate formation methods: trying to create representative samples*, Lawrence Berkeley National Laboratory. Available at https://escholarship.org/uc/item/7v23q5mw.

Le T.X., Tang A.M., Aimedieu P., Bornert M., Chabot B., Rodts S. (2019a) Methane hydrate-bearing sand – an energy resource? in *Proceedings of the 1st Vietnam Symposium on Advances in Offshore Engineering. VSOE 2018. Lecture Notes in Civil Engineering*, vol. **18**, M. Randolph, D. Doan, A. Tang, M. Bui, V. Dinh (eds.), Springer, Singapore, pp. 158–163.

Le T.X., Aimedieu P., Bornert M., Chabot B., Rodts S., Tang A.M. (2019b) Effect of temperature cycle on mechanical properties of methane hydrate-bearing sediment, *Soils Found.* **59**, 4, 814–827. https://doi.org/10.1016/j.sandf.2019.02.008.

Le T.X., Bornert M., Aimedieu P., Chabot B., King A., Tang A.M. (2020a) An experimental investigation on methane hydrate morphologies and pore habits in sandy sediment using synchrotron X-ray computed tomography, *Mar. Pet. Geol.* **122**, 104646. https://doi.org/10.1016/j/marpetgeo.2020.104646.

Le T.X., Rodts S., Hautemayou D., Aimedieu P., Bornert M., Chabot B., Tang A.M. (2020b) Kinetics of methane hydrate formation and dissociation in sand sediment, *Geomech. Energy Environ.* **23**, 100103. https://doi.org/10.1016/j.gete.2018.09.007.

Le T.X., Bornert M., Brown R., Aimedieu P., Broseta D., Chabot B., King A., Tang A.M. (2021a) Combining optical microscopy and X-ray computed tomography reveals novel morphologies and growth processes of methane hydrate in sand pores, *Energies* **14**, 5672. https://doi.org/10.3390/en14185672.

Le T.X., Aimedieu P., Bornert M., Chabot B., King A., Tang A.M. (2021b) New X-ray microtomography setups and optimal scan conditions to investigate methane hydrate-bearing sand microstructure, *Geotech. Test. J.* **44**, 2, 502–519. https://doi.org/10.1520/GTJ20190355.

Lei L., Seol Y., Choi J.-H., Kneafsey T.J. (2019) Pore habit of methane hydrate and its evolution in sediment matrix – laboratory visualization with phase-contrast micro-ct, *Mar. Pet. Geol.* **104**, 451–467.

Martinez de Banos M.L., Hobeika N., Bouriat P., Broseta D., Enciso E., Clément F., Brown R. (2016) How do gas hydrates spread on a substrate? *Cryst. Growth Des.* **16**, 8, 4360–4373.

Metaxas P.J., Lim V.W., Booth C., Zhen J., Stanwix P.L., Johns M.L., Aman Z.M., Haandrikman G., Crosby D., May E.F. (2019) Gas hydrate formation probability distributions: Induction times, rates of nucleation and growth, *Fuel* **252**, 448–457.

Nguyen-Sy T., Tang A.M., To Q.D., Vu M.N. (2019) A model to predict the elastic properties of gas hydrate-bearing sediments, *J. Appl. Geophys.* **169**, 154–164.

Pinkert S. (2016) Rowe's stress-dilatancy theory for hydrate-bearing sand, *Int. J. Geomech.* **17**, 1, 06016008.

Pinkert S., Grozic J. (2014) Prediction of the mechanical response of hydrate-bearing sands, *J. Geophys. Res. Solid Earth* **119**, 6, 4695–4707.

Popenoe P., Schmuck E.A., Dillon W.P. (1993) The cape fear landslide: slope failure associated with salt diapirism and gas hydrate decomposition, in Schwab W.C., Lee H.J., Twichell D.C.(Eds.), *Submarine landslides: selected studies in the US exclusive economic zone*, U.S. Geol. Surv. Bull., pp. 40–53.

Priest J.A., Best A.I., Clayton C.R. (2005) A laboratory investigation into the seismic velocities of methane gas hydrate-bearing sand, *J. Geophys. Res. Solid Earth* **110**, B4, B04202.

Priest J.A., Rees E.V., Clayton C.R. (2009) Influence of gas hydrate morphology on the seismic velocities of sands, *J. Geophys. Res. Solid Earth* **114**, B11, B11205.

Ruppel C. (2007) Tapping methane hydrates for unconventional natural gas, *Elements* **3**, 3, 193–199.

Ruppel C.D., Kessler J.D. (2017) The interaction of climate change and methane hydrates, *Rev. Geophys.* **55**, 1, 126–168.

Sanchez M., Gai X., Santamarina J.C. (2017) A constitutive mechanical model for gas hydrate bearing sediments incorporating inelastic mechanisms, *Comput. Geotech.* **84**, 28–46.

Spangenberg E., Kulenkampff J., Naumann R., Erzinger J. (2005) Pore space hydrate formation in a glass bead sample from methane dissolved in water, *Geophys. Res. Lett.* **32**, 24, L24301.

Turner D., Boxall J., Yang S., Kleehammer D., Koh C., Miller K., Sloan E., Xu Z., Matthews P., Talley L. (2005) Development of a hydrate kinetic model and its incorporation into the OLGA2000-R transient multi-phase flow simulator, in 5th International Conference on Gas Hydrates, Trondheim, Norway, 12–16 June. Available at https://www.osti.gov/etdeweb/biblio/20685609

Uchida S., Soga K., Yamamoto K. (2012) Critical state soil constitutive model for methane hydrate soil, *J. Geophys. Res. Solid Earth* **117**, B3, B03209.

Waite W.F., Winters W.J., Mason D. (2004) Methane hydrate formation in partially water saturated Ottawa sand, *Am. Min.* **89**, 8–9, 1202–1207.

Waite W.F., Santamarina J.C., Cortes D.D., Dugan B., Espinoza D.N., Germaine J., Jang J., Jung J.W., Kneafsey T.J., Shin H., Soga K., Winters W.J., Yun T.S. (2009) Physical properties of hydrate-bearing sediments, *Rev. Geophys.* **47**, 4, RG4003.

Wang S., Wang P., Chen B., Yang M., Li Y. (2018) Velocity mapping of steady water flow through methane hydrate bearing samples, *J. Nat. Gas Sci. Eng.* **53**, 385–393.

Wu P., Li Y., Liu W., Sun X., Kong X., Song Y. (2020) Cementation failure behavior of consolidated gas hydrate-bearing sand, *JGR Solid Earth* **125**, e2019JB18623.

Zhang L., Sun L., Sun M., Lv X., Dong H., Miao Y., Yang L., Song Y., Zhao J. (2019) Analyzing spatially and temporally visualized formation behavior of methane hydrate in unconsolidated porous media, *Magn. Reson. Imaging* **61**, 224–230.