

Webinaire

Journées HYDRATES 2020

22 et 23 Octobre



WELCOME

We are pleased to welcome you for the first “Journées Hydrates” Webinar (and 3rd annual meeting) of the French research consortium GDR2026 Hydrates. This event brings together leading experimental, theoretical, and computational scientists from the community of researchers interested in the various research areas of gas hydrates, fields going from chemical and energy engineering to geosciences and astrophysics through physico-chemistry and thermodynamics.

The scientific program contains 20 oral presentations, including 4 invited keynote lectures, divided into 4 sessions: “Sciences moléculaires et thermodynamique”, “Génie des Procédés”, “Astrophysique et planétologie”, and “Géosciences”.

Organizing and scientific committee

- Christophe Dicharry – LFCR UMR5150 CNRS, Total, Univ. Pau
- Arnaud Desmedt, ISM CNRS - Univ. Bordeaux
- Livio Ruffine - IFREMER, Brest
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- Gabriel Tobie - LPG UMR6112 CNRS, Univ. Nantes
- Anne Siquin - IFPEN

- André Burnol – BRGM, Orléans
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- Christophe Coquelet - CTP, Mines ParisTech
- Anthony Delahaye - Division des Génie des Procédés et Froid, IRSTEA, Antony
- Jean-Michel Herri - LGF, UMR 5703 CNRS, Mines Saint-Etienne
- Sylvain Picaud - UTINAM UMR6213 CNRS, Univ. Franche-Comté
- Anh-Minh Tang - Laboratoire Navier UMR8205 CNRS, Ponts Paristech
- Karine Ndiaye, ISM CNRS - Univ. Bordeaux
- Audrey Bourgeois, ISM CNRS - Univ. Bordeaux

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- [Variability in composition for methane-rich hydrates recovered in a selected site of the Black sea](#)

LIST OF PARTICIPANTS

The webinar is open to all members of the GDR2026 CNRS Hydrates. Below, you will find the list of registered participants to the « Journées Hydrates » originally scheduled at Anglet, France.

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DETAILED PROGRAM

Jeudi 22 Octobre 2020

08h30 Introduction du webinaire Journées Hydrates 2020 par la direction du GDR

08h45-09h25 Plénière AdvaMEG™ - Axens MEG regeneration and reclamation technology, Guillaume Parer, Axens

09h25-10h25 Session 1 : Génie des Procédés (chairmen : J.M. Herri, A. Delahaye)

09h25-09h45 *Modeling of multiphase flow in Rock&Roll Loop*, Madina Naukanova, EMSE

09h45-10h05 *Influence of CH₄ hydrate formation conditions on subsequent exchange kinetic reactions with CO₂ or CO₂-N₂ gas mixtures: application to CO₂ capture*, Claire Pirim, Univ. Lille

10h05-10h25 *Crystallization of mixed clathrate hydrates in presence of salts: an experimental and thermodynamic study for energy capture/storage and water treatment*, Angsar Serikkali, EMSE

10h25-10h40 Discussion ouverte sur la thématique « Génie des procédés »

10h40-11h20 Plénière MD simulation and biogeochemical-experiments of gas-hydrate crystallisation: magneto-chirality, Niall English, University College Dublin, Ireland

11h20-12h20 Session 2 : Sciences Moléculaires et Thermodynamique (chairmen : S. Picaud, C. Dicharry)

11h20-11h40 *Investigation of the acid concentration onto the super-protonic conductivity in mixed THF-strong acid hydrates*, Sophie Espert, Univ. Bordeaux

11h40-12h00 *Modelling of hydrogen hydroquinone clathrate stability conditions and storage capacity*, Christelle Miqueu, Univ. Pau

12h00-12h20 *Calorimetric approach applied to the study of the formation and dissociation of gas hydrate in porous media*, Fatima Benmesbah, Inrae

12h20-12h35 Discussion ouverte sur la thématique « Sciences Moléculaires et Thermodynamique »

12h35-14h00 Pause déjeuner

14h00-14h40 Plénière Clathrate hydrates of planetary volatiles and their fate inside icy worlds, Olivier Bollengier, Univ. Nantes

14h40-15h40 Session 3 : Astrophysique et Planétologie (Chairmen : G. Tobie, B. Chazallon)

14h40-15h00 *Clathrate hydrates FTIR spectroscopy: a key in understanding solar system ices*, Natalia Esteves Lopez, Univ. Bordeaux

15h00-15h20 *A grand canonical Monte Carlo study of the adsorption of N₂ and CO molecules at the surface of clathrates and comparison with ice surfaces*, Antoine Patt, Univ. Franche-Comté

15h20-15h40 *Exploring new phenomena in ice clathrates and filled ices under planetary conditions*, Livia Bove, Univ. Rome

15h40-15h55 Discussion ouverte sur la thématique « Astrophysique et Planétologie »

15h55-16h10 Debriefing – Fin de la première journée

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09h00-9h40 Plénière *Detection and quantification of gas hydrate by using geophysical data and theoretical models : implication to environment and climate*, Umberta Tinivella, Istituto Nazionale di Oceanografia e di Geofisica Sperimentale

09h40-11h50 **Session 4 : Géosciences** (Chairmen : A.M. Tang, A. Burnol)

09h40-10h00 *Natural gas hydrates on continental margins : focus on Black Sea*, Charlène Guimpier, Univ. Bordeaux

10h00-10h20 *Gas selectivity of a thermogenic-like gas hydrate*, Olivia Torres Fandino, Ifremer

10h20-10h40 *Laboratory study of methane hydrate formation in clay-rich matrix: Application to gas hydrate-bearing sediments in the Romanian margin of the Black Sea*, Art-Claire Constant Agnissan, Univ. Bordeaux - Ifremer

10h40-10h50 Pause

10h50-11h10 *« Artificial » sedimentary gas hydrates: influence of nano- to micro- silica beads onto their formation and physical-chemistry properties*, Cyrielle Metais, Institut Laue Langevin

11h10-11h30 *Numerical simulation of CO₂ injection into a depleted reservoir taking into account the Joule-Thomson thermal and the risk of hydrate formation*, Eric Flauraud, IFPEN

11h30-11h50 *Variability in composition for methane-rich hydrates recovered in a selected site of the Black sea*, Bertrand Chazallon, Univ. Lille

11h50-12h05 **Discussion ouverte sur la thématique « Géosciences »**

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13h30-17h30 Comité de Pilotage du GdR

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Conférence plénière

AdvaMEG™ – Axens MEG regeneration and reclamation technology

Guillaume Parer

Axens Solutions, 89 Boulevard Franklin Roosevelt, 92500 Rueil-Malmaison, France

A surge increase in demand for natural gas is leading to an increase in development of deep offshore gas projects under stringent conditions, with the associated risks of hydrate formation, leading to blocked flow lines. Injection of MonoEthylene Glycol (MEG) at the wellhead is an effective way to prevent hydrate formation and guarantee gas flow and continuous production. As a result, the installation of a MEG regeneration and reclamation system is crucial for reduction cost, allowing operators to use less fresh glycol make-up and providing greater protection against hydrate formation and pipeline freeze-up.

Axens' robust and versatile reclamation technology, AdvaMEG™, uses a vacuum distillation and purification system protected by several patents which allows the removal of water from the rich MEG (aqueous MEG stream recovered after gas separation step) but also all types of salts resulting from water formation and from the flow assurance loop. This technology removes glycol contaminants and enables high MEG recovery rate while minimizing waste effluents.

Présentations orales

Modeling of multiphase flow in a rock&roll loop

Madina Naukanova, Jean-Michel Herri, Ana Cameirao, Gianluca Lavalle

Ecole des Mines de Saint-Etienne, France

Entire work is dedicated to the experimental results obtained with the help of in-house made Rock'n'Roll Loop. Rock'n'Roll Loop equipped with an electric motor, a dual-centre drive shaft and torus made of thick wall transparent PVC tube of 0.07 m and 0.04 m diameter and coil diameter of 0.86 m. A dual-centre drive shaft driven by an electric motor leads to a fluid flow in a circle within a torus. Experimental investigations have been carried out to evaluate air and water flow through the torus. As a result of qualitative observations, a flow regime map was produced. Influence of centrifugal force on flow structure, liquid stagnation phenomenon and backward flow were also noticed.

Influence of CH₄ hydrate formation conditions on subsequent exchange kinetic reactions with CO₂ or CO₂-N₂ gas mixtures: application to CO₂ capture

Quang-Du Le, Carla T. Rodriguez, Ludovic Nicolas Legoix, Claire Pirim, Bertrand Chazallon

Université de Lille, CNRS, UMR 8523 – PhLAM – Laboratoire de Physique des Lasers, Atomes et Molécules, CERLA – Centre d'Etudes et de Recherche Lasers et Applications, F-59000, Lille, France

Recovering methane from natural gas hydrate deposits using carbon dioxide injection is currently of great environmental and energetic interest as it shows potential for producing an energy resource while mitigating CO₂ emissions through CO₂ sequestration. This work investigates the exchange kinetic between CH₄ and CO₂ (or CO₂-N₂(v)) in synthetic hydrates, with an emphasis on the impact of CH₄ hydrate formation conditions (e.g. driving force Δp) on the subsequent exchange reactions. Different driving forces Δp are utilized and show that the exchange kinetic is improved by a factor of ~ 3 when the exchange is performed with low Δp CH₄ hydrates, for which there is a higher relative amount of free H₂O(liq) (277 K); the kinetic is further improved when stirring is applied. Isobaric CH₄ hydrates exhibit a fast primary hydrate dissociation and CH₄ release, followed by a slower exchange kinetic, possibly limited by solid-state exchange diffusion or secondary CO₂-rich hydrate formation within the stability field of CH₄ hydrates. Upon exposure to a mixed CO₂-N₂(v) gas stream, secondary hydrate production is governed by the effective Δp remaining after dissolution of the gas mixture, and results in an even slower exchange reaction rate. These results may help optimizing recovery processes in field trial experiments, where both hydrates and liquid water coexist, and aid in predicting the risk of geo-hazards induced by unstable secondary hydrate formation. Furthermore, the exchange kinetic dependencies highlighted here are important as they affect the overall energy efficiency and energy cost of CH₄ recovery processes in gas hydrate field trials.

Crystallization of mixed clathrate hydrates in presence of salts : an experimental and thermodynamic study for energy capture/storage and water treatment

Angsar Serikkali, Ngo Van-Hieu, Baptiste Bouillot, Jean-Michel Herri

Ecole des Mines de Saint-Etienne, France

Fresh-water shortage is viewed as a global grand challenge for the next decades. That requires the advent of seawater desalination and water treatment technology. As a promising novel method, the hydrate-based desalination has been developed and achieved considerable milestones in the past few years. However, the experimental data are still limited in the open literature. Therefore, in this study, thermodynamic equilibrium data of mixed CO₂-Cyclopentane (CP) hydrates in the presence of salts were investigated. In particular, MgCl₂ and CaCl₂, which are dominant cations in water caused hard water. The van de Waals method was employed to describe the equilibrium. By using a set of Kihara parameters for CP, the modeled results indicate the good agreement between the measurement and simulations with the AAD less than 0.5K.

Session 2 : Sciences Moléculaires et Thermodynamique

Conférence plénière

MD simulation and biogeochemical-experiments of gas-hydrate crystallisation: magneto-chirality

Niall English

University College, Dublin, Ireland

Recent studies have shown that proteins and polypeptides produced by micro-organisms can accelerate methane-hydrate formation. However, the role of magnetic fields and chirality in such phenomena is heretofore unclear. Here, we find *prima facie* evidence of differently oriented magnetic fields of varying strength showing intricate control on the hydrate-formation kinetics by R and S versions of a prototypical aromatic peptide derived from a naturally occurring, hydrate-promoting source. We also discuss the wider implications of these results on chirality in the biosphere and hydrates in the environment.

Présentations orales

Investigation of the acid concentration onto the super-protonic conductivity in mixed THF-strong acid hydrates

Sophie Espert^{1,2}, Fabrice Mauvy³, Daniel Sanchez-Portal², Arnaud Desmedt¹

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Ionic clathrate hydrates are particularly interesting in the area of energy for their specific physicochemical properties. The inclusion of ionic guest molecules (such as bases, or acids) leads to form water substructure containing ionic defects. The ionic defects appear as an anionic guest and a hydronium cation participating to the host substructure. A striking property in ionic clathrate hydrates made with strong acids is their protonic conductivity, due to a super-mobility of protons in the host substructure.

By co-including THF (neutral species) and perchloric acid HClO₄ in the hydrate structure, we can tune the acidic species concentration and study its influence on the protonic conductivity. The important role played by this concentration has been investigated by combining Raman imaging and Conductivity measurement. Understanding the mechanisms involve in the conductivity of acid hydrate will help develop their use in energetic issues like a new electrolyte for fuel cells.

Modelling of hydrogen hydroquinone clathrate stability conditions and storage capacity

Christelle Miqueu, Raphael Labeyrie

CNRS/TOTAL/UNIV PAU & PAYS ADOUR, Laboratoire des Fluides Complexes et leurs Réservoirs - IPRA, UMR5150, 64600, Anglet, France

The development of hydrogen as a new energy carrier requires being able to store it under acceptable energy and safety conditions. Recent studies have shown a possible alternative to storage by adsorption in porous materials or absorption in hydrides by considering the trapping of hydrogen within organic clathrates. In particular, Han et al. (Chem.Phys. Lett., 2012) measured satisfactory hydrogen storage capacities at room temperature for hydroquinone (HQ) clathrate due to the multiple occupancy of the cavities by hydrogen molecules, to which are added an extremely rapid capture/release kinetics (a few seconds), a low cost of the material (commercial hydroquinone) and relatively low energies. In this work, the classical van der Waals and Platteeuw theory is modified to consider both the influence of quantum interactions and the possible multiple occupancy of the cavities by hydrogen molecules. The results suggest that the pressures needed to stabilize the HQ-H₂ clathrate is lower than previously expected, and that the quantum effects have a little impact at room temperature. In addition, considering multiple occupations implies a greater hydrogen storage despite fewer occupied cavities.

Calorimetric approach applied to the study of the formation and dissociation of gas hydrate in porous media

Fatima Benmesbah^{1,2}, Livio Ruffine¹, Pascal Clain², Véronique Osswald², Olivia Fandino¹, Laurence Fournaison², Anthony Delahaye²

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Understanding the formation and dissociation mechanisms of gas hydrate in porous media is essential for the development of new technologies like geotechnology and thermal energy storage. In this work, we investigated CO₂ hydrate formation and dissociation in bulk and in two different porous materials: sand and silica gels. A calorimetric approach is used to study the CO₂ hydrate formation process and the amount of hydrate formed according to the porous material. The experimental data are collected using a differential thermal calorimetry device with two identical measuring cells. One cell contains the sample to be studied where hydrate formation and dissociation occur. The other cell contains a reference sample where no phase change occurs. The results show that porous materials like sand and silica gels enhance the amount of hydrate formed compared to the bulk media. In addition, results obtained with nanoporous silica gels showed a higher amount of hydrate formed at the same pressure and temperature conditions. This result may be due to the fact that silica gels provide higher surface area thanks to smaller particle size (20-45µm) compared to sand (80-450µm) and the presence of nanopores which can play the role of nucleation sites.

Session 3 : Astrophysique et planétologie

Conférence plénière

Clathrate hydrates of planetary volatiles and their fate inside icy worlds

Olivier Bollengier

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From the smallest grains of dust to water-rich satellites and exoplanets, icy and aqueous environments rich in other volatiles (e.g. N₂, CH₄, CO₂...) may represent the most widespread chemical setting in our solar system and beyond. Under a wide range of lower temperatures and higher pressures, these chemical systems have been shown to form gas hydrates: solid compounds formed by a lattice of water molecules stabilized by the guest molecules of one or several other volatile species. At relatively low pressures, gas hydrates are found as clathrate structures. Abundant methane clathrate hydrate deposits on Earth offer a prime example of their natural occurrence when the conditions for their stability are met. Beyond Earth, clathrate hydrates have been invoked to explain the plumes of Enceladus or the current atmosphere of Titan, two of Saturn's most intriguing moons.

This planetary context raises the question of the fate of gas hydrates at higher pressures, deeper inside water-rich moons and exoplanets. Laboratory experiments have brought to light common mechanisms for gas hydrates (the results of a delicate thermodynamic balancing act) to adapt to high pressures: the transition from lower-pressure to higher-pressure clathrate hydrates, and the formation of filled ice structures and their dissociation into a mixture of ices at the highest pressures. The same experiments, however, have also revealed that each hydrate-forming system remains unique, both in terms of structures formed and pressures at which the phase transitions occur. The relatively recent exploration at high pressures of the H₂O-CO₂ system will be taken as an example of this complexity. In this system, a well-known clathrate structure transitions directly to a more exotic filled ice structure stable only between 0.7 and 1 GPa. Above this pressure, no H₂O-CO₂ solid compound has been found. However, a change of speciation of CO₂ at higher pressures favors the formation of a crystalline, stoichiometric hydrate of carbonic acid above 4.4 GPa. This example illustrates the complexity brought by pressure into hydrate-forming systems, and the larger diversity of the "gas hydrates" family.

Présentations orales

Clathrate hydrates FTIR spectroscopy: a key in understanding solar system ices

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The formation of clathrate hydrates may play a key role in the stability of gases in many astrophysical bodies, such as comets. They may provide a trapping mechanism responsible for the preservation in the solid state of gaseous species at temperatures higher than expected, thus avoiding their early escape. Observations of comet probe missions suggest that there is a mechanism still unknown which could explain part of the phenomena

linked to cometary activity, such as the remain of these volatile molecules [1]. Gas hydrates form and remain stable only in specific temperature and pressure regimes that depend on the nature of the guest molecules [2]. Theoretical phase diagram of clathrate hydrates show that it could be possible to form CO₂ and CH₄ clathrates at very low pressure (10–10 bar) and temperature (<80 K), but there is a lack of experimental data using these preparation methods [3]. Could clathrate hydrates be formed under such conditions? What if the formation and characterization of these ice-like structures under such conditions could provide precious experimental evidence for understanding the origin and evolution of comets? FTIR spectroscopic identification of carbon dioxide and methane hydrates have been performed at low temperature (10 K) and pressure (base pressure 10–7 mbar) regimes. In an effort to understand the nature of the gas hydrates formed under these conditions, vibrational spectra of distinct gas/ice interactions (clathrate hydrate, gas in/on water ice) were compared. The behaviour of the water crystalline skeleton interactions with the trapped molecules at different temperatures and the influence of various preparation methods will be presented.

[1] *Comets as Tracers of Solar System Formation and Evolutions*. Springer, NY (2017)

[2] Sloan E, *Nature* 426— pp. 353-359 (2003)

[3] Choukroun, M. et al., *The Science of Solar System Ices* — pp. 409-454. Springer, NY (2003).

A Grand Canonical Monte Carlo Study of the Adsorption of N₂ and CO Molecules at the Surface of Clathrates and Comparison with Ice Surfaces

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The Grand Canonical Monte Carlo (GCMC) method is a useful tool to get information on adsorption processes at the molecular scale. This method has thus been used in a large variety of situations, including (recently) the selective incorporation of small molecules in conditions relevant to astrophysics [1-3]. However, because clathrate hydrates are in general in contact with multiple interfaces (gaseous, liquid, and mineral surfaces), the impact of such interfaces on the hydrate properties, has also to be investigated. Therefore, we used GCMC to simulate the adsorption of N₂ and CO molecules at the surface of various structures of solid water as occurring in astrophysical context, including clathrate hydrates, crystalline Ih and low-density amorphous ices. More specially, the selectivity of the surface adsorption process is compared to the one of bulk incorporation when the gas phase contains mixtures of CO and N₂ [4]. In addition, the accuracy of various interaction potential models is evaluated by comparison with available experimental data.

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[2] A. Patt, J.M. Simon, S. Picaud, J.M. Salazar, *J. Phys. Chem. C* 122 (2018) 18432-18444.

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Exploring new phenomena in ice clathrates and filled ices under planetary conditions

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Hydrates are overspread on Earth at depth and in the extra-terrestrial space, both interstellar and on outer planets and moons [1-3]. Under the extreme p-T conditions experienced in these icy bodies hydrates display a rich phase diagram, anomalous dynamical properties, proton conductivity, enhanced quantum effects [4-8].

In this talk I will review our recent experimental results - obtained combining neutron and x-ray diffraction, incoherent inelastic and quasielastic neutron scattering, and Raman spectroscopy under high pressure - on gas (H₂, CH₄) [5-8] filled ices under the extreme conditions experienced in the ice bodies of our solar system.

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[5] U. L. Ranieri et al., *Nature Com.*, 8, 1076 (2017).

[6] S. Schaack et al., *JPC C* 122 11159 (2018).

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[8] S. Schaack et al., *PNAS*, 10.1073/pnas.1904911116 (2019))

Session 4 : Géosciences

Conférence plénière

Detection and quantification of gas hydrate by using geophysical data and theoretical models: implication to environment and climate

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Gas hydrates in marine environment have been mostly detected from analysis of seismic reflection profiles, where they produce remarkable BSRs. Generally, the BSR is a very high-amplitude reflector that is associated with a phase reversal that approximately parallels the seafloor, because the BSR follows a thermobaric surface rather than a structural or stratigraphic interface.

Several studies have revealed a seismic reflector below the BSR that can be associated with the base of the free gas zone, the so-called BGR. The scientific community have been devoted much effort in studying marine sediments to characterize the hydrate reservoir and to quantify the gas trapped within sediments by using geophysical data analysis. To reach this goal advanced techniques have been developed. One approach to estimate hydrate and free gas concentration is based to extract petrophysical parameters through advanced geophysical data analysis and/or modeling, using techniques such as common-image gathers analysis and amplitude versus offset analysis. These results are translated in terms of concentration by using theoretical models, such as modified Biot theory.

The gas hydrate reservoir could be considered a strategic energy reserve, but, on the other hand, the hydrate dissociation due to climate change could be an issue to face. Clearly, the potential gas hydrate reservoir exploitation requires a deep knowledge of the natural and anthropogenic factors that could affect gas hydrate stability. Consequently, more efforts should be devoted to gaining a better understanding of the relationship between the gas hydrate system and complex natural phenomena, such as climate change, slope stability and earthquakes. Here, real cases will be presented in order to consider several aspects of hydrate system around the world.

Présentations orales

Natural gas hydrates on continental margins: focus on Black Sea

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Gas hydrates present a very large gas storage capacity at the origin of a broad research in the energy area (potential energy resource), the sustainability area (huge carbon dioxide-sequestration opportunities) and also in the environmental area such geo-hazards, and potential impact of ocean acidification due to climate change (marine methane injection in the atmosphere) [1,2]. Natural gas hydrates, composed mainly of methane, are found

in marine sediments on continental margins and in the permafrost region. In the context of the study of the Black Sea hydrate deposit, the influence of the complex clay/sand mineral matrix on the methane hydrate formation is studied. Raman spectroscopy is used to characterize the structural properties and composition of gas hydrates to get insights into the formation mechanism of the hydrate deposit of the Black Sea, at the T,p stability conditions mimicking the natural ones.

[1] D. Broseta et al, Wiley-ISTE: London, 2017; Vol. 1

[2] L. Ruffine et al, Wiley-ISTE: London, 2017; Vol. 2

Gas selectivity of a thermogenic-like gas hydrate

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The methane generated during the thermally-activated breakdown of larger organic molecules is named 'thermogenic' methane, and are commonly characterized by a significant portion of non-methane hydrocarbons, as well as, CO₂, N₂ or H₂S. This is typically the case for the gas seeps from the thermogenic hydrates deposit on the Western High at the Sea of Marmara (Turkey). A synthetic multicomponent gas mixture with a composition similar to the Marmara gas sample are used to form complex laboratory hydrates with the aim to investigate the molecular mechanisms that govern their formation processes. Thus, the resulting hydrates were analyzed and compared to the hydrates formed from the Marmara gas sample. High-resolution Raman spectroscopy is employed to disclose information about the type of hydrates structure, composition and occupancy rate. Besides, gas chromatography is used to monitor the concentration changes in the gas phase during hydrates formation.

Laboratory study of methane hydrate formation in clay-rich matrix: Application to gas hydrate-bearing sediments in the Romanian margin of the Black Sea

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Laboratory experiment of hydrate formation in porous media is very challenging, particularly in clay. However, more than 90% of the hydrate deposits are characterized by silty and clayey sediments [1]. The hydrate deposit of the Romanian sector of Black Sea belongs to this category as the sediment contains around ~ 60% of clays [2]. In this work, methane hydrate formation has been investigated in matrices containing clays and sand, with the aim of mimicking the mineralogy of sediments encountered in Black Sea. Experiments were conducted at a given water content for various matrix composition in order to investigate the influence of the mineralogy on hydrate formation kinetics and morphology. In addition, the hydrate-bearing sediments synthesized were analyzed by Raman micro-spectroscopy to gain insights into the relationships between the matrix mineralogy and the cage occupancy at a micrometric scale.

“Artificial” sedimentary gas hydrates: influence of nano- to micro- silica beads onto their formation and physical-chemistry properties

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Gas clathrate hydrates are naturally occurring ice-like materials. They are present on Earth, especially on permafrost regions and ocean floors, where they are mainly formed in sub sediment area. Studying gas clathrate hydrates in presence of sediments is relevant to better understand the influence of these sediments on the clathrate hydrate formation, and to bring new insights about the physico-chemical properties of these ice-like natural materials. In the present study, we propose to mimick natural sediments using mono-dispersed silica beads with sizes ranging from nanometer to micrometer. A particular interest is given to the influence of these sediments' analogues onto the formation kinetics of various gas hydrates (CH₄, CO₂, N₂) by means of in-situ Neutron diffraction. In addition, effects of surrogates onto the molecular selectivity and the gas diffusion have also been investigated by means of Neutron spectroscopy and Raman micro-spectrometry. Important impacts of sediments onto the gas hydrates formation and physical-chemistry properties will be discussed.

Numerical simulation of CO₂ injection into a depleted reservoir taking into account the Joule-Thomson effect and the risk of hydrate formation

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The injection of CO₂ into a depleted hydrocarbon reservoir can lead, under certain conditions, to the formation of hydrates and consequently to a significant loss of injectivity (reduction of permeability due to congestion of the porosity). This phenomenon is partly due to the Joule-Thomson cooling effect accompanying the expansion of the gas injected into the porous medium around the well.

We present here the results of a sensitivity study, carried out with the CorresFlow numerical simulation software, for different injection scenarios and reservoir conditions: the purpose of our analysis is to evaluate the importance of the Joule-Thomson cooling effect on hydrate formation.

Variability of natural gas hydrates composition methane bound in hydrate-bearing sediments in a selected site of the Black sea

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Natural gas Hydrates (NGHs) represent one of the largest methane reservoir on Earth with a total amount of carbon stored higher than all conventional hydrocarbon reserves [1]. The current substantial research efforts to better characterize these deposits [2] is justified by the fact that on one hand enclathrated methane is a potential energy resource that might be extracted and produced in the future to meet the increasing world energy demand. On the

other hand, the temperature-sensitive hydrate deposits can be destabilized due to ocean warming, leading to the release of methane into the water column with potential input into the atmosphere as well as potential destabilization of the seafloor, hastening and perpetuating the cycle of global warming. In the present study, we combined two different techniques (gas chromatography, and micro-Raman spectroscopic imaging) to characterize samples of natural hydrates collected during the Ghass cruise (2015) in the Black Sea onboard the *R/V Pourquoi pas?* This work complements the hydrate-bearing sediments characterization provided in ref [3]. Our molecular scale approach allowed investigating the variability in cage occupancy of the collected samples and the impact of the presence of minor guest component on the overall methane content.

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